A multiscale hydrothermal carbon layer modified carbon fiber for composite fabrication†

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A novel multiscale hydrothermal carbon layer (MHTCL) for carbon fiber (CF) surface modification was developed. The MHTCL is a multiscale high-disorder amorphous carbon coating with a colored appearance, abundant functional groups, multiscale roughness, a large specific surface area, a high surface energy, and good wetting ability. The O/C atom ratios of the MHTCL-modified CF were in the range of 0.17–0.23, and the functional groups were mainly C–O and C=O groups. During the low-concentration glucose hydrothermal treatment with the carbon fibers (CFs), the glucose generates furan derivative intermediates, which adsorb on the surface of the CFs and carbonize continuously, finally forming the MHTCL on the CFs. The fracture and rupture of the MHTCL during the forming process produce new nucleation centers on the CF surface, which result in abundant multiscale irregular particles. The MHTCL is a facile method for the modification of CFs. The fabrication of the CF composites demonstrated that the MHTCL obviously increases the interlaminar shear strength of the CF/polyimide composite and the interfacial interaction of the CF and polyetheretherketone.

1. Introduction

Carbon fiber (CF) has received extensive interest due to its outstanding strength-to-weight and stiffness-to-weight ratios. CF composites have been widely used in wind turbine applications, automotive energy systems, catalyst supports, fuel cells, turbo machinery, compressed gas storage and transportation, and antistatic and electromagnetic shielding materials. For CF composites, the properties of the CF/matrix interface play a decisive role in determining their final mechanical properties.2–4

However, CF has very few high energy sites, a few functional groups, and a dense microstructure;7 which lead to poor absorption and a weak interface with the matrix. In general, the CF is sized or coated by a sizing layer on the surface, which facilitates fiber handling and improves the fiber/matrix adhesion. Polymer sizings are focused on polymers that are compatible with the CF and matrix, pre-wet the CF, and improve the interfacial adhesion with the matrix,8,9 such as epoxy for CF/epoxy,10 polyetherimide (PEI) for CF/polyetheretherketone,11 polypropylene-g-maleic anhydride for CF/polypropylene,12 polyethylene-g-maleic anhydride for CF/polyethylene, and polyether sulfone for CF/polyether sulfone.13,14 However, commercial polymer sizings have been shown to decrease the surface tension and quantity of functional groups of the CFs, which may lead to weak CF wettability and poor composite interfacial shear strength.15,16 Our recent research on PEI sizing indicated that dewetting of the PEI particles on the CF substrate occurred at the melting point of the polymer (Fig. S6, ESI†); similar phenomena have been researched for many years in the physics field.17 The dewetting of the polymer on the surface of CFs means poor interfacial adhesion.18 Surface chemical modification of CF is also a typical approach used in this field, such as surface oxidation,19 electrochemical treatment,20 plasma etching,21,22 or high-energy irradiation chemical grafting.23,24 The surface chemical modification increases the number of functional groups on the CF surface but decreases the single fiber tensile strength. Carbon layers on CFs have also been frequently reported for CF composite fabrication. Graphene (GE) coating,25 carbon nanotube (CNT) coating, and situ chemical vapor deposition (CVD) CNT coating have been reported to improve the composite performance26–28 by increasing the surface area and roughness of the CFs. However, these approaches are not efficient for large-scale fabrication.

Hydrothermal carbon (HTC) materials have plentiful surface functional groups and reproducible resources29 and have attracted considerable interest from researchers studying heavy metal absorption,30 catalyst supports,31–33 battery anodes,34–36
sensing, semiconductors, and drug delivery. However, very few papers on materials modified by HTC have been published.

In this study, a multiscale hydrothermal carbon layer (MHTCL) on CFs was fabricated for the first time via simple hydrothermal treatment of unsized CFs in glucose solution. The MHTCL was verified to be a high-disorder amorphous carbon layer with abundant polar organic groups and multiscale roughness. The forming mechanism of the MHTCL is also discussed. The fabrication of the CF composites indicates that coating with MHTCL can be used as an effective modification method for CFs.

2. Experiments
2.1 Pretreatment of CFs

The received T700 CF tows (ZhongFu ShenYing Co., China) were extracted with acetone (Sigma-Aldrich) in a Soxhlet extraction equipment at 358 K for 12 h. The unsized CF tows were stored in a glass desiccator with silica-gel desiccant.

2.2 Hydrothermal treatment of unsized CFs

Glucose (Sigma-Aldrich) was used as the precursor for the MHTCL. The glucose was dissolved in deionized water with a concentration of 2–40 g L\(^{-1}\). The unsized CF tows were placed into glucose solutions in clean glass test tubes and sealed with silicone rubber plugs and then sealed in a 2000 ml stainless steel (AISI 316L) autoclave half-filled with 1000 ml of deionized water. The autoclave was placed into a pre-heated oil bath and heated at 473 K for 4 h. The equipment is shown in Fig. S1.†

After the hydrothermal carbonization, the MHTCL-modified CFs were clipped out of the tubes with tweezers and washed five times in abundant ethyl alcohol (Sigma-Aldrich) and deionized water, sequentially, and then dried at 323 K for 12 h. Some of the MHTCL-modified CFs and sediment samples were heat-treated at 673 K for 4 h in a nitrogen atmosphere tube furnace to decompose the organic groups. The sample codes and concentrations of the glucose solutions used in the experiment are listed in Table 1.

2.3 Fabrication of CF-reinforced polyimide composites

First, 20 g polyimide (PI) powder (Changchun Institute of Applied Chemistry, CAS) was dissolved in 200 g of 1-methyl-2-pyrrolidinone (Sigma-Aldrich) at 353 K. The CF tow fragments (approximately 300 000 fibers per sample) were placed into a Teflon mold, and the hot 1-methyl-2-pyrrolidinone/PI solution was then poured into the mold. The product was then dried at 353 K for 24 h and then at 373 K for 24 h. After removal from the mold, the samples were dipped in the hot PI solution in a vacuum oven for 1 h and in air for 1 h. Then, the samples were dried at 353 K for 24 h, at 373 K for 24 h, at 423 K for 24 h, and then at 473 K for 1 week in drying oven. The composites contained approximately 60 wt% CFs.

2.4 Fabrication of CF-reinforced polyetheretherketone composites

Composite samples were prepared by hot press molding, the strands of unsized CFs and excess polyetheretherketone (PEEK) powder (P450, Victrex Co.) were placed into a stainless mold previously coated with the remolding agent, and then, the mold was placed between two plates of an automatic press vulcanizer that was previously heated to 673 K. The two plates were kept in contact with the mold for 15 min to allow the PEEK to melt uniformly. Then, 6 MPa of pressure was applied for 30 s to allow the PEEK to impregnate the CFs. The samples were air cooled at room temperature.

2.5 Scanning electron microscopy analysis

The samples were examined using scanning electron microscopy (SEM; Hitachi 4800, Japan) at an accelerating voltage of 5–8 kV. To reduce charging during SEM imaging, the samples were
pasted onto aluminum stubs using conductive adhesive tape and sputtered with platinum.

The SEM images of CFs in Fig. 1(c and d) and S3† were obtained using another scanning electron microscope (TM1000, Japan) using an accelerating voltage of 15 kV.

2.6 Raman spectroscopy analysis
Raman spectroscopy measurements were performed using a Renishaw inVia Reflex confocal Raman microscope working at an excitation wavelength of 542 nm. Deconvolution of the spectra was performed by assuming mixed Gaussian/Lorentzian peaks to describe both the main D and G bands. The data treatment was performed using Origin Pro 2015 software.

2.7 X-ray photoelectron spectroscopy analysis
The X-ray photoelectron spectroscopy (XPS) measurements were recorded on a AXIS ULTRA X-ray photoelectron spectrometer using a Mg Kα X-ray source (1253.6 eV) operated at 14 kV and 300 W with an emission current of 25 mA. Survey scans were collected from 0 to 1100 eV. Casa XPS instrument software was used for the deconvolution of XPS spectra. For calibration purposes, the C 1s electron binding energy from adsorbed ubiquitous organic material was referenced at 284.6 eV. Different functional groups were assigned using reported C 1s chemical shifts for various organic compounds. The relative amounts of these groups were estimated from respective areas of the assumed Gaussian/Lorentzian curves. The C 1s XPS spectra in Fig. S5† were not calibrated.

2.8 Surface energy analysis
The dispersive component, polar component, and total surface energy of the MHTCL-modified CFs was determined using dynamic contact angle analysis (DCAA) of the MHTCL-modified CFs in the pure liquids using a DCA21 dynamics contact angle analyzer, Data Physics Co. Six fibers with lengths of approximately 5 mm were first bonded to double-sided tape with

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Fig. 1  SEM images of samples (a) CF1, (b) CF2, (c) CF3, (d) CF4, (e) CF5, (f) CF6, (g) CF7 and (h) CF8. Images (i–l) were selected from sample CF4 to highlight the fractures of the MHTCL.
3.2 Raman spectra

Fig. 2 presents Raman spectra of the unsized CFs, MHTCL-modified CFs, and by-product hydrothermal carbon spheres (CSS) in the residues. The samples were characterized by two broad overlapping bands at approximately 1380 cm\(^{-1}\) (D-mode) and 1587 cm\(^{-1}\) (G-mode); the ratio of their intensities, \(I(D)/I(G)\), reveals the disorder of the carbon materials. However, in amorphous carbons, the development of a D peak indicates ordering, exactly the opposite from the case of graphite.\(^{48}\) There is nearly no D peak and a very small D peak in the spectra of CF4 and the by-product CSSs, respectively, which indicates the high disorder of the carbon structure on the sample surfaces. The spectra of the heat-treated samples showed an obvious D peak because of the further aromatization during the heat treatment and increase of the ordering.\(^{41}\)

The D and G bands of the MHTCL-modified CFs were similar to those of the by-product CSSs and had the same peak positions as previously reported hydrothermal CSSs;\(^{45,46}\) the Raman spectra differed greatly from those of the CFs. It was verified that the surfaces of the hydrothermal treated CFs were completely covered by the MHTCL, a highly disordered amorphous carbon layer.
3.3 XPS analysis

The unsized CFs and MHTCL-modified CFs were characterized by XPS. Consistent with previous reports,46,47 the C 1s spectra peak of the MHTCL-modified CFs shifted to higher binding energy (BE) because of the increase of the sp3 carbon atoms in the MHTCL, in contrast with that of the unsized CFs (Fig. S5, ESI†). As observed in Fig. 3, the O/C atomic ratios of the CFs treated in solutions with different glucose concentrations were determined by XPS. The surface O/C atomic ratio of the unsized CFs was 0.09, and that of sample CF2 was 0.17. The O/C atomic ratios gradually increased with increasing glucose solution concentration used in the hydrothermal treatment. From these results, it can be inferred that the surface of the CFs was covered by MHTCL for the 2 g L\(^{-1}\) glucose solution hydrothermal treatment, which is consistent with the SEM images and Raman spectra.

The increase of the glucose concentration led to only a slight increase of the roughness of the MHTCL, as observed in Fig. 1. The O/C ratios of the MHTCL surface did not change with the glucose concentration.48 The increase of roughness led to an increase in the number of oxygen atoms on the top surface of the samples, leading to a gradual increase of the O/C atomic ratio determined by XPS which only detect the surficial atoms. The O/C ratios of the CF surface are consistent with those of previously reported HTC spheres and oxidized CFs.42,48,49 The curve fit of the XPS spectra indicates that the oxygen atoms originate from C–O groups and a small amount of C=O groups (Fig. S4, ESI†), which is in agreement with the widely accepted furan-rich HTC carbon structure.50

3.4 Surface energy of MHTCL-modified CFs

The advancing contact angles (CAs) in the deionized water and diiodomethane and surface energies of the samples are summarized in the Table 2. As expected, the MHTCL-modified CFs exhibited decreased CAs in the liquids and increased total surface energies (\(\gamma_T\)) compared with those of the unsized CFs. The polar component (\(\gamma_P\)) of the MHTCL-modified CFs was 6 times larger than that of the unsized CFs as a result of the abundant functional groups of the MHTCL. The dispersive component (\(\gamma_D\)) greatly decreased after the hydrothermal treatment, possibly because the MHTCL increased the roughness and absorbed the air into the micro–nano structure during the wetting process of the CFs. The micro–nano structure may have differed from the classical superhydrophilic rough structure.51

The \(\gamma_P\) and \(\gamma_T\) values of the CFs clearly increased after hydrothermal treatment. Wetting of the fibers by the polymer is a prior condition of good fiber matrix adhesion; these functional groups (C–O; C=O) may play an important role in fiber/matrix adhesion by forming chemical bonding or hydrogen bonding between the fiber and matrix.52 Hydrogen bonding interactions are known to be important for fiber–matrix adhesion, and these interactions can be evaluated by investigating the \(\gamma_P\) of the surfaces.53,54 Therefore, the distinct increase of \(\gamma_P\) and \(\gamma_T\) of the MHTCL-modified CFs may greatly improve the interaction of the CF and matrix.

![Fig. 2](image1) Raman spectra of select samples described in Table 1.

![Fig. 3](image2) O/C atomic ratios on CF surface vs. glucose concentration used in hydrothermal treatment.

**Table 2** Carbon fiber surface energies and contact angles in different liquids\(^a\)

| Samples | Deionized water | Diiodomethane | OWRK surface energy mN m\(^{-1}\) |
|---------|----------------|---------------|-------------------------------|
| CF1     | 83.4(1.8)      | 38.5(0.9)     | 1.89                          |
| CF4     | 60.2(1.7)      | 50.5(1.1)     | 14.48                         |

\(a\) Standard deviations are in parentheses.

**Table 3** Surface area and composite evaluation of unsized CFs and MHTCL-modified CFs

| Sample | BET surface area of the CFs m\(^2\) g\(^{-1}\) | Interlaminate shear strength of the CF/PI composites MPa |
|--------|-----------------------------------------------|--------------------------------------------------------|
| CF1    | 0.44                                          | 67.7                                                   |
| CF4    | 1.03                                          | 92.5                                                   |
3.5 BET analysis of CFs and interfacial interaction evaluation of the their composites

The CF’s BET surface area clearly increased after MHTCL modification, as shown in Table 3. The distinct increase of the toughness, specific surface area, organic functional groups, and surface energy will greatly improve the interfacial interaction. The interlamine shear strength of the MHTCL CF/PI composite dramatically increased compared with that of the unsized CFs, as detected by short beam shear testing in accordance with ASTM D2344. The interfacial interaction was also improved in the CF/PEEK composite fabrication, as shown in Fig. 4. The rupture face of MHTCL CF/PEEK composite is matrix.

Fig. 4  SEM image of the CF/PEEK composite rupture face. Image (a) is the unsized CF (CF1) composite; image (b) is the MHTCL CF (CF4) composite.

Fig. 5  Possible formation mechanism of MHTCL. The images of the HTC sphere and HTC carbon dots were reproduced with permission,53,58 Copyright Year 2012, Elsevier and Copyright Year 2011, Royal Society of Chemistry.
rupture but that of unsized CF interface rupture, which means the MHTCL CF/PEEK composite has better interfacial interaction.\textsuperscript{11}

3.6 Possible formation mechanism of MHTCL on CFs

The possible MHTCL formation mechanism is depicted in Fig. 5. The hydrothermal carbonization mechanism was illustrated by Sevilla, Titirici, and Xue et al.\textsuperscript{42,50,53} During hydrothermal treatment at 473 K, the glucose transforms into a series of water-soluble substances (WSS) and partly water-soluble substances (PWSS), mainly furan derivatives, which undergo complex chemical reactions and form polyfuranic intermediates.\textsuperscript{28,42,50,54} TEM and SEM research on HTC spheres has shown that the nano-size spheres spread all over the surface of the HTC spheres,\textsuperscript{51,53} and it has been inferred that the nano-size primary polyfuranic particle is the intermediate.\textsuperscript{53} Considering that the nano-size primary polyfuranic particle is derived from WSS or PWSS in water solution, abundant hydrophilic groups must be reserved on the surface to maintain the low interfacial tension in the solution, similar to water-soluble Nano carbon dots prepared under the same experimental condition. However, in the hydrothermal reaction, the hydrophilicity of the groups is weakened because of the breakage of the hydrogen bonding between the oxygen in the groups and water at high temperature.\textsuperscript{56} Therefore, the plentiful hydrophilic groups cannot stabilize the primary particles well in the high-temperature hydrothermal solution above the critical concentration, and the ripening, aggregation, and crosslinking of the primary nanoparticles finally form the HTC spheres. As a result, the hydrothermal nanocarbon dots can be separated from the hydrothermal solutions with a low yield, as not all of the primary particles transform into microspheres.\textsuperscript{57} If the KH\textsubscript{2}PO\textsubscript{3} is added to the glucose solution to stabilize the nanoparticles, the yield of the nano-carbon dots increases markedly.\textsuperscript{58}

In this study, there was no precipitate or dispersion in the solutions for the glucose concentrations below 15 g L\textsuperscript{-1}. The concentrations of the primary particles may have been below the critical concentration for precipitate growth in the clean glass tubes, which have a very low interface tension with the solution. With the addition of the CFs, the PWSS were absorbed on the CFs to decrease the interfacial tension of the CFs in the solution. In a similar manner, the CFs play the role of nucleation centers, and the unstable primary particles assemble on the CF surfaces. The intermediate substances are absorbed, assemble and carbonize on the CFs, form the MHTCL in a very low concentration glucose solution, in which the HTC cannot be prepared without CFs. The MHTCL thickness does not noticeably increase with increasing glucose solution concentration because of the fracture and rupture of the MHTCL, as previously discussed. The fractures of the MHTCL also produce nanoparticles as new nucleation centers on the CFs or in the glucose solution, which forms the particles on the CFs or the carbon spheres in the solution, respectively. The latter forms the cloudy dispersion liquid or sediments in the test tubes (Fig. S1b, ESI†). The rupture of the MHTCL and the recovery of the HTC continue throughout the hydrothermal treatment, which leads to multiscale irregular particles on the MHTCL.

4. Conclusions

This study introduced hydrothermal carbonization as a novel carbon fiber surface modification method. The MHTCLs were synthesized on unsized CFs in glucose solution at a very low concentration. The MHTCL was verified to be a highly disordered amorphous carbon layer with abundant polar organic groups and multiscale roughness. The formation mechanism of the MHTCL was discussed. The CF plays the role of a nucleation center in the hydrothermal process, which leads to the formation of the MHTCL. The fracture and rupture of the MHTCL lead to multiscale roughness of the MHTCL. The nano-thickness continuous part and nanoparticles of the MHTCL provide evidence confirming that the widely accepted polyfuranic intermediate is a nano-size particle in the hydrothermal process. The intermediate may be a bridge between the HTC carbon dots and HTC carbon spheres in the formation mechanism. The distinct increase of the surface energy, specific surface area, toughness, and organic functional groups of the MHTCL-modified CFs improved the wetting ability of the CFs and noticeably increased the interfacial interaction of the CF and matrix in the CF/composite fabrication. The \textit{in situ} MHTCL preparation on the CFs is a convenient method to improve the interfacial interaction of the CF composites.

Conflicts of interest

The authors have declared no conflicts of interest.

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