

Research Article

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Mechanochemical Organic Functionalization of Graphite Produces Tunable Coatings of Carbon Fibers by Multilayered Graphite Microparticles

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Abstract

The properties of carbon fiber reinforced composites depend on the adhesion of fibers to the polymer matrix. The improvement of interfacial properties in carbon fiber containing composite materials was extensively studied by introducing water-soluble derivative of graphene, graphene oxide and linkers molecules that were dispersed in the fiber sizing onto the surface of individual carbon fibers. Here we report mechano-chemical synthesis of a series of functionalized multilayer graphite micro particles able to modify carbon fibers simply dipped to their suspensions in various solvents, including water. The known mechanoactivated chemical exfoliation of graphite by maleic anhydride and maleimide was expanded to hexadecylmaleimide and 1,6-dimaleimidohexane. The new materials were characterized by SEM imaging, X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), powder X-Ray Diffractometry (XRD), nitrogen adsorption isotherm surface analysis, and Diffuse Light Scattering (DLS). The coatings produced on both sized and unsized carbon fibers are resistant to ultrasonication. The pH-dependent dispersibility in water and particle size, relatively high surface area, presence of the thiol-reactive maleimide group in the material cross-linked with 1,6-dimaleimidohexane are the welcome properties for drug delivery applications. The facile introduction of various groups to carbon fibers will help tune their properties for industrial applications.

Keywords: Mechanoactivation, Synthesis, Microparticles, Carbon fibers, Graphite

Abbreviations: XPS-X-ray Photoelectron Spectroscopy, FTIR- Fourier Transform Infrared Spectroscopy, XRD-X-Ray Diffractometry, DLS-Diffuse Light Scattering, HDMI-“N-Hexadecylmaleimide”.

Introduction

Four novel functionalized microparticles of graphite have been prepared directly from graphite by the modified approach of mechanoactivated reactive exfoliation or by refunctionalization. Carbon fibers are known to increase strength of polymer composite materials, especially for the applications where high rigidity and low weight are of value. The interface between carbon fibers and the polymer matrix that surrounds those plays an important role in the material properties of the composite material [1,2]. The low affinity of most plastic matrices to the crystalline graphitic domains of carbon fibers is usually remediated by coating the fibers with “sizing”—a polymer with the functional groups improving adhesion.

A better control over the surface of carbon and greater versatility of its properties can be achieved by the direct introduction of functional groups. While covalent modification of low reactive graphitic basal planes is difficult, their ability for π - π stacking can be utilized for direct functionalization. Thus, the pyrene moiety was used as an anchor for introduction of N-hydroxysuccinimide or gold nanoparticles to carbon nanotubes [3,4]. The availability of the graphitic basal planes in the edge-functionalized particles of graphene makes them a promising material for rapid and versatile functionalization of carbon fibers tailored to the polymer matrix in the desired composite. Considering

the known improvement of the mechanical performance of carbon fiber/epoxy composites by grafting graphene oxide into the fibers, development of versatile functionalized graphenes presents a significant practical interest [5].

Besides of a rather expensive synthesis of graphene by the chemical vapor deposition, a variety of top-down methods exist as well. Graphite oxidation and subsequent reduction produce a material called reduced graphene oxide, which is a graphene with more defects [6,7].

In 2013, Baek and coauthors have reported a method that exfoliates graphite into graphene and adds functionalization at the same time due to the Diels-Alder addition of maleic anhydride or maleimide to the diene moieties of the mechanoactivated graphitic layers [7]. While Seo JM, et al., refers to the particles as graphene, their structure seems to better fit the category of micro particles of graphite [7]. This solvent-free mechanochemical procedure produces multilayered graphite microparticles functionalized at the edge of their graphitic planes at the gram scale, and requires inexpensive reagents and a ball mill. However, only two functional groups (anhydride and imido-group) have been introduced to the micro particles.

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Here we report facile preparation of three new types of edge-functionalized graphite micro particles and their adhesion to unsized and sized industrial carbon fibers along with a series of existing carbonaceous materials. The hexadecylimido- and 1,6-hexane-bis-imido-functionalized micro particles of graphite were prepared by the expansion of the mechanoactivated chemical exfoliation of graphite to N-hexadecylimide and 1,6-dimaleimidehexane dienophiles. The (2Z)-4-(6-aminoethyl-1-amino)-4-oxobut-2-enoic acid functional group was introduced to the anhydride-functionalized micro particles of graphite by their reaction with 1, 6-diaminohexane.

Experimental Part

Materials and equipment

1-Hexadecylamine, triethylamine and diisopropyl carbodiimide (DIC) from Alfa Aesar, graphite powder with a diameter of <20 µm - from Sigma-Aldrich, Fmoc-6-aminohexanoic acid (Fmoc-Ahx-OH) - from Chem-Impex International, maleic anhydride, acetic anhydride, nickel (II) acetate, acetic acid, hexane, methanol, N-hydroxybenzotriazole (HOBT), maleimide, N,N-dimethylformamide (DMF), 1,6-diaminohexane and dichloromethane (DCM) - from Oakwood Chemicals. Graphene: Unmodified GraphenX™ graphene was purchased from www.cheaptubes.com and used as-is without further modification. The carbon fibers of the SGL APS type were provided by SGL Corporation. XRD analysis was carried out using a monochro XRD instrument with energy of 40.0 kV by Rigaku Ultima IV. SEM measurements were carried out using InLense and SE2 detector with an energy of 1.50 to 3.00 kV by SIGMA ZEISS. FTIR measurements were carried out from 400 to 4000 cm⁻¹ by Perkin Elmer. The ball millings for graphite functionalization were carried out by Planetary Ball Mill (PBM-04, Micro Nano Tools). XPS measurements were carried out using monochromatic Al Ka x-ray with energy of 1486.6 eV by Thermo Scientific K-alpha⁺ XPS. The hydrodynamic particle sizes have been analyzed by the DLS (Dynamic Light Scattering) method with Zetasizer (model: Malvern Zetasizer Nano Series). Ultrasonication was performed in a Fisher Scientific FS20H ultrasonic bath. UV-vis absorption spectra were measured on Varian Cary 50 UV-Vis spectrophotometer. Braunauer-Emmett-Teller (BET) analysis for the determination of surface area was done by Quantachrome Novawin (version 11.03). ¹H NMR spectra were recorded on a Brucker 400 MHz spectrometer in CDCl₃ and TMS (tetramethylsilane) as an internal standard.

Synthesis of dienophiles

N-hexadecylimide was prepared by a modified known procedure [8]. Briefly, 1-Hexadecylamine (22.99 g, 0.095 mol) and maleic anhydride (10.51 g, 0.107 mol) were refluxed in 150 mL glacial acetic acid until completion (approximately 6 h, monitored by ¹H NMR). The reaction mixture was allowed to cool to room temperature and poured into 2000 mL of cold deionized water with stirring. This mixture was stirred for 6 h and filtered through filter paper. The solid material is dried in air, broken into a powder, washed repeatedly with deionized water to remove residual acetic acid, and dried in a vacuum desiccator. Yield 28.9 g (84.0%). M.p. 45–55°C; lit. M.p. 103–105°C. ¹H NMR (CDCl₃, 400 MHz): δ 6.67 (s, 2H), δ 3.50 (t, 2H, J= 7.2 Hz), δ 1.63 (m, 28H, 7.56), δ 0.87 (t, 3H). By NMR, the purity of the compound is estimated as ~96%. The product was used without further purification [8].

1,6-Bismaleimidohexane was prepared by a modified known procedure. briefly, maleic anhydride (49.0 g, 0.5 mol) was dissolved in 150 mL DMF in a 500 mL round bottom flask at magnetic stirring. Next, 1,6-diaminohexane (29.05 g, 0.25 mol) was added to the flask at stirring. The solution slightly heated up and turned translucent yellow [9].

The temperature was maintained at 90°C for 30 min on a hot plate. Then acetic anhydride (94 mL, 0.99 mol), triethylamine (13.8 mL, 0.099 mol), and nickel (II) acetate tetra hydrate (0.5 g, 0.0028 mol) were added within 5 min. After the temperature was maintained for 30 min, the reaction mixture was allowed to cool to 40°C and was poured to 2L of deionized water in an ice bath. The brown precipitate was filtered, washed with 1L of water in small portions, dried at 80°C in air for 3 days. The solid mass was crushed into a powder, stirred with 2L of water, filtered, and dried at 80°C in air for 4 h. Yield 120.9g (88%). MP. 125–130°C, lit. m.p. 144°C. ¹H NMR (CDCl₃, 400 MHz): δ 6.70 (s, 4H), δ 3.52 (t, 4H, J=7.4 Hz), δ 1.59 (m, 4H), δ 1.32 (m, 4H). By NMR, the purity of the compound is estimated as ~95 % [9].

Preparation of graphite micro particles

In a typical procedure, 3 g of graphite and 6 g of a dienophile (maleic anhydride, maleimide, N-hexadecylimide or 1,6-dimaleimidohexane) were ground in a 50 mL stainless steel jar using a planetary ball mill operating at 500 rpm for 48 h [7]. The reaction mixture was washed with a solvent (hexane for N-hexadecylimide, methanol for maleimide, methanol for Bis-maleimide, methanol for maleic anhydride) on a fritted glass funnel. The graphite micro particles were dried, weighed, and washed again. The washing cycles continued until the constant weight of the product (typically, 3–6 mL of each solvent was used in each of 3 washing cycles). The extent of functionalization was estimated by the gravimetrically measured weight gain [7].

Non-functionalized graphite micro particles: Graphite was processed in the same ball mill under the same conditions but without a dienophiles to produce the control material GC.

Pre-treatment and non-covalent modification of carbon fibers: Unsized carbon fibers were prepared by heating chopped 1-2" bundles of sized fibers (APS) in a nitrogen purged furnace at 500°C for 5 h to remove any surface coating. The fibers to be modified (100 mg) were sonicated in a suspension of 100 mg of graphite micro particles in 10 mL of a solvent for 3 min, filtered and washed with 5 mL of the same solvent.

Preparation of graphene quantum dots

These particles were made using a modified method based on Ye, R et al. Briefly, a 300 mg portion of anthracite coal was ultrasonicated in 60 mL of 96% H₂SO₄ and 20 mL 60% HNO₃ for 6 h, then heated to 100°C for 24 h with continuous stirring. After cooling to room temperature, the solution was poured over 100 g of ice. The pH of the solution was brought to ~7 by a 3M (and at the end – 0.01M) sodium hydroxide solution. The solution was decanted, passed through a 0.45 µm PTFE syringe filter, dialyzed through a 3500 Da membrane against deionized water for 7 days. The solvent was removed in vacuum to produce the material GQD [10].

Preparation of graphite micro particles functionalized with (2Z)-4-(6-aminoethyl-1-amino)-4-oxobut-2-enoic acid (GAM)

A mixture of 3 g of maleic anhydride functionalized graphene (GMA) and 33 g of 1,6-diaminohexane was stirred in 100 ml of DMF at 110°C for 20 min, next at 90°C for 2h. The mixture was cooled to room temperature and centrifuged. The precipitate was washed with DMF (3X13 mL) and dried at room temperature in air, yield 84% (GAM).

Determination of amino-groups on carbon

It was performed by the modified procedure of determination of amino-groups on carbon nanofibers. Specifically; 150 mg of the aminated graphite (GAM), 175 mg (0.5 m mol) of 6-(Fmoc-amino)hexanoic acid (Fmoc-Ahx-OH), and 67.5 mg (0.5 m mol) of N-hydroxybenzotriazole (HOBT) were mixed in a 15 mL vial. Then a solution of 80 µL (0.5 m mol) of diisopropylcarbodiimide (DIC) in 1

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mL of DMF was added. The mixture was magnetically stirred for 12 h and filtered. The solid material on the filter was washed with DMF (3 mL), methanol (3 mL), DCM (3 mL), and dried in air overnight. A 20 mg sample of the dried material was shaken for 45 min with a 20:80 (v/v) mixture of piperidine and DMF and centrifuged at 10,000 rpm for 4 min. The centrifugate was diluted X20 (dilution factor, DF) with 20:80 (v/v) mixture of piperidine and DMF, and the absorbance was measured at 290 nm [11].

The density of amino-groups was calculated using the following equation [11]:

$$\text{Density of NH}_2 \text{ (mmol/g)} = \frac{\text{Absorbance}}{\frac{\text{Mass of the material}^*}{1.75} \times (\text{DF})}$$

DLS measurements: A 5 mg sample of a material was suspended in 10 mL of deionized water by ultra-sonication for 10 min, decanted, and measured on the Zetasizer instrument.

XRD analysis

A 4-6 mg of a sample was placed on the sample holder and measured from 5 to 80 degree with a scan speed of 0.300 deg/min and sample width of 0.0200 degree. The data was processed by PDXL2 software.

SEM imaging

A few drops of a suspension of ~5 mg of a sample in 10 mL of hexane was affixed on a silicon wafer with a carbon double sticky tape and dried on air. The sample was rinsed with hexane and dried on air again.

FTIR analysis

A 3-5 mg of a sample was ground in a mortar with ~50 mg of dry KBr and pressed into transparent KBr pellets. The transmission data in the 400-4000 cm⁻¹ range was processed by Spectrum2 software.

XPS analysis

A 2-5 mg sample was attached to a conductive stage by double-sided carbon tape and held at 5×10^{-8} mbar for 4 h before the experiment. The data were processed by the "Advantage" software package.

Surface analysis

An approximately 0.05 g sample of a material was evacuated and pre-heated at 100°C for 5.5 to 14 h. Next, the sample was cooled by liquid N₂, and the adsorption of N₂ gas was measured at an array of pressures. The surface area was calculated by the Brunauer-Emmett-Teller (BET) analysis, and the Barrett, Joyner and Halenda (BJH) method was used to calculate the average pore size and volume.

Results and Discussion

Functionalized graphite microparticles

Preparation of functionalized graphite microparticles by ball milling with a dienophile: The graphite microparticles functionalized with maleimide (GMI, Figure 1b) were prepared in air with maleimide as the dienophile, which produced 4.5% weight gain. The extent of functionalization depended on the reaction conditions. When the ball milling was performed in air, the weight gain was 4.5%, increased when the reaction was run under nitrogen (16% weight gain) and reached 27% under 74 millitorr vacuum. The SEM analysis did not reveal any substantial influence of the reaction atmosphere on the size and morphology of graphite microparticles. All other functionalized microparticles of graphite have been prepared under vacuum to minimize potential oxidation by the atmospheric and adsorbed air.

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The graphite microparticles functionalized with maleic anhydride (GMA, Figure 1a) were prepared under 80 millitorr vacuum. With maleic anhydride as the dienophile, which produced 7.2% weight gain.

The graphite microparticles functionalized with N-hexadecylmaleimide (GHDMI, Figure 1c) were prepared under 84 millitorr vacuum conditions with N-hexadecylmaleimide as the dienophile, which produced 5.4% weight gain.

The graphite microparticles functionalized with 1,6-dimaleimidohexane (Gbisi, Figure 1d) were prepared under 80 millitorr vacuum (weight gain 6.2%) or under nitrogen (weight gain 13%) with 1,6-dimaleimidohexane as the dienophile. Thus, we optimized the conditions of the mechanochemical synthesis and expanded its applicability to N-substituted maleimide.

Graphite microparticles functionalized with (2Z)-4-(6-aminohexyl-1-amino)-4-oxobut-2-enoic acid (GAM)

This aminated material was prepared by re-functionalization of the maleic anhydride derivative GMA with excess of 1,6-diaminohexane. SEM images of functionalized graphite microparticles prepared by Mechanoactivation (a-d) are presented in Figure 1.

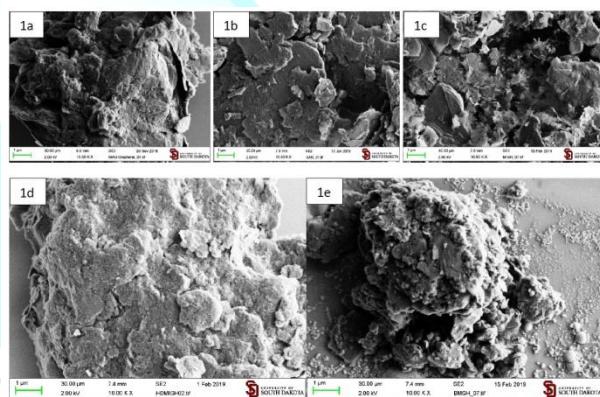


Figure 1: Functionalized graphite microparticles prepared by ball milling. 1a – GMA, 1b – GMI, 1c – GMI, 1d – GHDMI, 1e – Gbisi.

The direct quantitative analysis of amino-groups on carbons is difficult because carbon absorbs and catalyzes degradation of most of the dyes involved in the analysis. Therefore, we employed the Fmoc-based analytical protocol [11] (Figure 2).

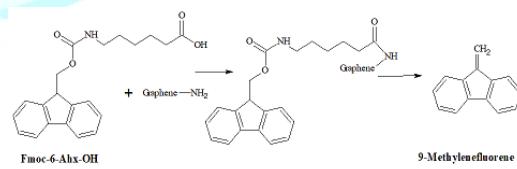


Figure 2: Analysis for the surface amino groups.

First, the amino-groups on the carbon's surface are covalently coupled with a chromophore-containing Fmoc-6-Ahx-OH. Next, after removal of the excess of Fmoc-6-Ahx-OH, cleavage of the Fmoc-moiety with piperidine releases into solution one molecule of 9-methylenefluorene per each surface amino-group, which is determined photo metrically. In the aminated graphite microparticles GAM, the density of amino-groups determined by the Fmoc method was 0.22 m mol/g [11].

FT-IR Spectroscopy

The surface functional groups have been identified by FT-IR spectroscopy. The strong adsorption at $\sim 1700\text{ cm}^{-1}$ is characteristic to the stretching C=O vibration in the material functionalized with imido-groups (GMI), the material functionalized with maleic anhydride (GMA), and its derivative open with a diamine (GAM) (**Figure 3**). For the maleic anhydride derivative (GMA), the C=O vibration occurs below the characteristic for the anhydride 1800 cm^{-1} wavenumber. These points to the hydrolysis of the anhydride ring, which is consistent with the literature [7]. The presence of the absorption band at $\sim 3098\text{ cm}^{-1}$, which is characteristic for C(sp²)-H stretching vibrations indicates that some molecules of maleic anhydride acylated OH-groups available at the oxidized edges of graphene layers. The absence of an unreacted phase of maleic anhydride was confirmed by the powder XRD analysis. No multiple reflections characteristic for maleic anhydride were observed [12]. The materials functionalized with weak acylating agents - maleimide derivatives did not show the C(sp²)-H band. A series of bands at $\sim 1200\text{-}1285\text{ cm}^{-1}$ characteristic for the presence C-O bonds is especially strong for the maleic anhydride derivative. The nitrogen-containing GMI shows a weak shoulder at $\sim 1345\text{ cm}^{-1}$ due to C-N absorption, which is barely visible in GAM. The strong $\sim 1580\text{-}1600\text{ cm}^{-1}$ bands of the stretching vibrations of non-symmetrical C=C in GMA are much weaker in the nitrogen-containing materials GMI and GAM and almost not visible in the materials GHDMI and Gbis (**Figures 3 and 4**).

Introduction of sp³-carbons to the materials in the processes of cycloaddition and a diamine acylation leads to the C-H stretching vibrations at $\sim 2850\text{-}2968\text{ cm}^{-1}$. Broad absorptions at $\sim 3000\text{-}3500\text{ cm}^{-1}$ characteristic for -OH and -NH stretching vibrations are especially strong for the aminated material (GAM) (**Figure 3**).

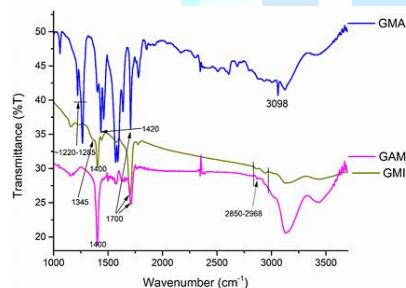


Figure 3: FTIR-spectra of known (GMA, GMI) functionalized graphite microparticles and the aminated material (GAM).

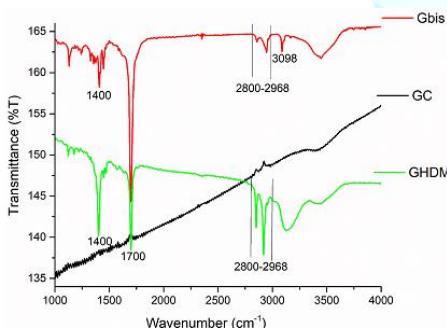


Figure 4: FTIR-spectra of new functionalized graphite microparticles prepared directly by Mechanoactivation (GHDMI, Gbis). The ball milled non-functionalized graphite (GC) is a reference.

The absorption patterns of new functionalized graphite microparticles directly synthesized by ball milling of graphite with long-chain derivatives of maleimide are similar to the materials GMA, GMI and

GAM. Due to the presence of long alkyl chains, the new materials show prominent absorptions at $\sim 2850\text{-}2968\text{ cm}^{-1}$, which is especially strong for the GHDMI derivative, containing hexadecyl groups (**Figure 4**). The material Gbis functionalized with a molecule with two maleimide moieties shows an absorption band at $\sim 3098\text{ cm}^{-1}$, which is characteristic for C(sp²)-H stretching vibrations. These points to the presence of free maleimide groups in the graphite microparticles, which may enable their subsequent cross-linking and re-functionalization.

Powder XRD

According to the XRD diffraction patterns of the functionalized graphite microparticles, the spacing between graphene layers ($\sim 3.5\text{\AA}$, $20=26.4^\circ$) matches the one in the parent graphite, which is consistent with their multilayer morphology. This allowed us to categorize the particles as multilayered particles of graphite. This lack of other reflections confirms that the material does not contain any maleic anhydride impurity, which is known to produce a multitude of reflections scattered all over the spectral range [12,13] (**Figure 5**).

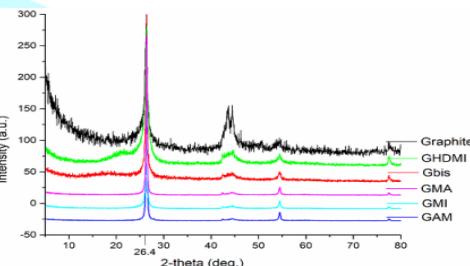


Figure 5: XRD patterns of functionalized multilayered graphene microparticles.

Surface analysis

The microparticles of Gbis (more projections are given in **Figure 6a** and **Figure 6b**) preserve the high porosity of the material and their morphology is very similar to that of the control material GC (ball milling without a dienophile) (**Figure 6**).

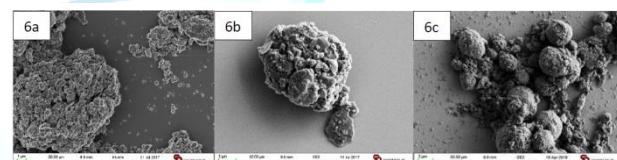


Figure 6: SEM micrographs of a, b Gbis microparticles. c. Control material GC.

This is in contrast with all other low porous functionalized materials (**Figure 1**). The retention of the morphology in Gbis could be attributed to the cross-linking ability of 1,6-dimaleimidohexane. The surface analysis results of the new materials are presented in **Table 1**.

	Surface area (m ² /g)	Average pore radius (Å)	Total pore volume (cc/g)
Graphite	14.1	134.7	0.095
GC	521.4	51.4	1.34
GMA	19.4	102.7	0.1
GMI	9.32	89.7	0.042
GAM	22.3	59.4	0.066
GHDMI	6.2	290.2	0.09
Gbis	27.9	172.1	0.24

Table 1: Surface analysis of functionalized graphite microparticles.

The kinetic energy generated in the mill breaks graphite chunks into small particles, which drastically increases the surface area and the

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total pore volume. However, the resulting GC material is not functionalized, and its pores are significantly shrunk comparing with graphite. The increase of the surface area of graphite upon mechanoactivated functionalization is much less pronounced while functionalization with HDMI (N-Hexadecylmaleimide) even decreases this parameter. Among all functionalized microparticles of graphite, the Gbis material has the highest surface area and total pore volume, perhaps, due to the cross-linking by the bifunctional Bis-maleimide. The drastic increase of solvation of Gbis by water and methanol compared with even more polar GMA and GMI further points at the unique properties of the cross-linked Gbis, which contains both hydrophobic alkyl chains and reactive maleimide-groups while maintaining the pore size of the bulk graphite.

Dispersibility in solvents

The type of the functional group on the graphite microparticles significantly affected their dispersibility in DCM, methanol, and water, which was estimated by sonicating 10 mg of the microparticles in 5 mL of the solvent for 6 min and observing the suspension for 1 week.

The control material GC (ball mill grounded graphite microparticles) was suspended to test their stability in different solvent systems. The suspended GC was mostly stable in water up to 3 days while in hexane it completely precipitated after 40 minutes, and in DCM it took 60 minutes for complete precipitation.

The microparticles MA and MI prepared by the known method, did not form a stable suspension with water, hexane, or DCM. However, relatively stable suspensions (not completely separated after 1 day) were obtained in methanol. The suspension of control GC in methanol was stable up to 3 days [1].

The most hydrophobic GHDMI containing long alkyl chains (16 carbons), expectedly failed to form a suspension in water. It is suspension in methanol was stable for 1 day and completely separated in 1 week. GHDMI was best solvated by DCM, which produced a suspension still stable after 1 week. The least polar hexane, however, did not sustain a stable suspension with neither GHDMI nor any other functionalized microparticles. Therefore, introduction of a long alkyl chain to a maleimide-functionalized microparticle of graphite significantly increased its dispersibility in methanol, and especially – in DCM.

In the material Gbis, the maleimide moieties are cross-linked with a short alkyl chain (6 carbons). The suspension of Gbis in DCM was less stable than that of GHDMI: while persisting for 1 day, it completely separated in 1 week. However, dispersibility of Gbis in methanol noticeably improved compared with GHDMI: the Gbis suspension in methanol still persisted after 1 week. Remarkably, Gbis was the only type of functionalized microparticles that was able to form an aqueous suspension still stable after 1 day. Although the suspension completely separated in 1 week, its stability was sufficient for the industrial modification of carbon fibers using a “green” non-toxic and non-flammable dispersant. The drastic increase of solvation of Gbis by water and methanol compared with even more polar GMA and GMI is consistent with the higher porosity of Gbis and the cross-linking ability of 1,6-dimaleimideohexane.

Due to the presence of acidic groups on the graphitic surface, the stability of the aqueous suspensions was higher at higher pH values, adjusted by aqueous HCl and NaOH. While after 7 h, the aqueous suspension of Gbis at pH = 3 completely separated, the particles mostly remained suspended at pH = 7 to 11.

The observed dispersibility of the materials was consistent with the pH-dependent particle sizes measured by DLS. Thus, changing pH from 7.0 to 5.0 led to the substantial increase of the average particle

size from 367 to 526 nm. This makes the Gbis material a candidate for a pH-controlled drug delivery scaffold (**Table 2**).

PH	4	5	7	8	10
Avr. particle size, nm	526 ± 37.87	566 ± 47.73	356 ± 80.67	365 ± 80.54	367 ± 77.60

Table 2: pH-Effect on the size of Gbis particles determined by DLS.

Modification of carbon fibers with known carbon particles

For comparison, we examined adhesion of four types of carbon particles (graphite, commercial GraphenX, carbon quantum dots GQD, and graphite milled without a dienophile (GC)) to carbon fibers [10] (**Figures 6c and 7**).

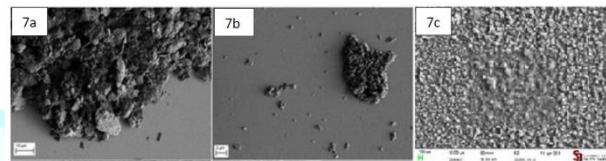


Figure 7: Carbon particles: (a) unmodified graphite, (b) Graphene™, (c) Graphene quantum dots GQD.

The treatment of carbon fibers with an aqueous suspension of carbon quantum dots (GQD) led to a flat positioning of the dots over the surface of fibers (Figure 8d), while the commercial graphene (GraphenX) formed clusters just loosely associated with the carbon fiber's surface (Figure 8b). Commercial graphite did not coat carbon fibers from its aqueous suspension at all (Figure 8c). However, it did deposit loosely associated clusters from its suspension in hexane (Figure 8).

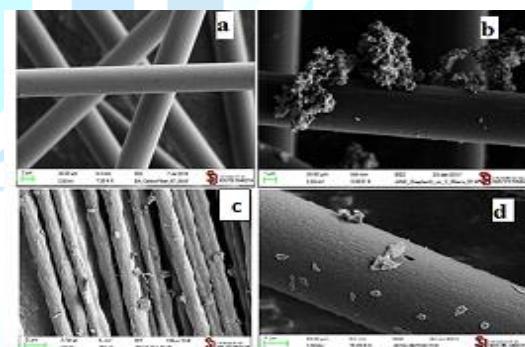


Figure 8: a. untreated carbon fibers. Carbon fibers treated with suspensions of: b. GraphenX in water; c. Graphite in hexane; d. Carbon quantum dots GQD in water.

The deposition of quantum dots on carbon fibers was additionally confirmed by their reduced concentration after exposure to the fibers. An aqueous suspension of carbon quantum dots was divided into two parts. After one part (30 mL) was exposed to carbon fibers (100 mg), concentration of carbon quantum dots was measured in both parts by UV-vis spectroscopy (**Figure 9**).

Concentration of GQD in the stock solution measured by complete evaporation of the solvent was 1.50 g/L. The concentration of GQD in the solution after exposure to carbon fibers was estimated by the Beer-Lambert Law at 260 nm as 1.39 g/L. Therefore, the amount of GQD deposited on 0.1 g of carbon fibers was $(1.50 - 1.39) \text{ g/L} \times 0.030 \text{ L} = 0.0033 \text{ g}$, which 3.3 wt%.

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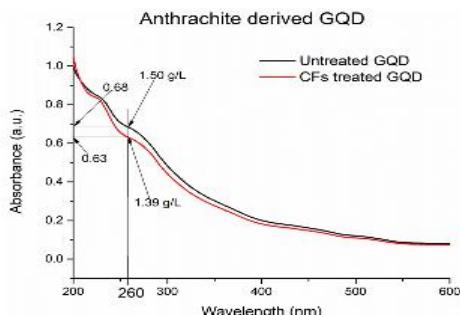


Figure 9: UV-vis-absorption by aqueous suspension of carbon quantum dots. Blue line—before exposure to carbon fibers. Red line—after exposure to carbon fibers.

Modification of carbon fibers with functionalized graphite microparticles

Modification of carbon fibers with graphite microparticles functionalized with maleic anhydride

Maleic anhydride functionalized graphite microparticles (GMA) coat carbon fibers by a simple dipping to their suspension in hexane (Figure 10).

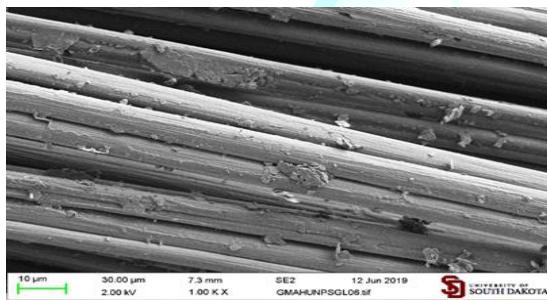


Figure 10: Carbon fibers coated with graphite nanoparticles functionalized with maleic anhydride (GMA) in hexane.

Modification of carbon fibers with graphite microparticles functionalized with maleimide

The coating obtained from the maleimide functionalized graphite microparticles (GMI) seems to be denser and with fewer particles sitting on their edges (Figure 11).

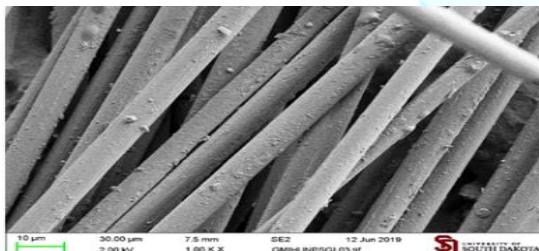


Figure 11: Carbon fibers coated with graphite microparticles functionalized with maleimide (GMI) in hexane.

Modification of carbon fibers with graphite microparticles functionalized with hexadecylmaleimide

The coating by hexadecylmaleimide functionalized graphite microparticles (GHDMI) consists of long flakes almost completely covering the surface of fibers (Figure 12).

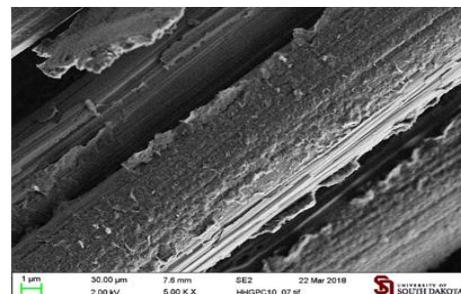


Figure 12: Carbon fibers coated by graphite microparticles functionalized with hexadecylmaleimide (GHDMI) from their hexane suspension.

Introduction of the GHDMI material to the surface of carbon fibers significantly affects its XPS spectrum. The surface elemental analysis of commercial carbon fibers reveals the presence of a noticeable amount of oxygen (C-86.08%, N-3.84%, O-10.08%) due to the plasma treatment routinely used to improve the adherence of fibers to the sizing (coating of carbon fibers before placing them to a composite material). The GHDMI – coated surface contains less oxygen due to the blockage by the long alkyl chains and more carbon because of the high carbon content of alkanes (C-89.98%, N-3.12%, O-6.91%).

Modification of carbon fibers with graphite microparticles functionalized with 1,6-dimaleimidohexane.

The treatment of carbon fibers with a hexane suspension of graphite functionalized with 1,6-dimaleimidohexane (Gbis) produced a dense coating of the fibers with the material (Figure 13).

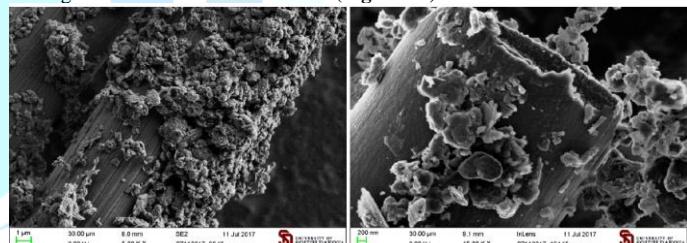


Figure 13: Carbon fibers coated by graphite microparticles functionalized with 1,6-dimaleimidohexane (Gbis) from their hexane suspension.

The strongest effect of Gbis on the elemental composition of the surface is substantial increase of the nitrogen content due to the presence of two atoms of nitrogen in the 1,6-dimaleimidohexane linker (C-85.81%, N-4.92%, O-9.27%). The chemical environment around the atoms of carbon and oxygen on the surface of modified carbon fibers was examined by the deconvolution analysis of the 1s bands with the sp² component fixed at 284.0 eV (Table 3).

The long alkyls chains in GHDMI introduce to the surface more C-C bonds while the highly oxidized C=O groups are blocked by the adsorption of the hydrophobic graphite particles, which is evident from the chemical environment changes around both carbons and oxygens.

This shifts the balance of the oxygen chemical environment from C=O to C-O groups. Similarly to GHDMI, the Gbis particles also introduce the C-C bonds to the surface. However, the graphene surface of the particles is not blocked by hexadecyl chain and introduces its own C=O groups to the surface.

Thus, despite the preferential adsorption of the particles on the C=O groups of the surface of carbon fibers, their contribution to the chemical environment both around carbons and nitrogens does not substantially decrease. The abundance of maleimido- in surface C=O

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groups in Gbis shows in the increased contribution of the sp^2 component.

	C1s (sp^2) (fixed at 284.0 eV)	C1s (C-C)	C1s (C-O-C)	C1s (C=O)	O1s (C-O)	O1s (C=O)
Non-functionalized carbon fibers	3.70%	284.7 (37.4%)	285.3 (45.1%)	288.2 (13.9%)	531.8 (20.9%)	532.8 (79.1%)
Carbon fibers functionalized with GHDMI	3.40%	284.9 (53.7%)	285.7 (35.3%)	288.7 (7.6%)	532.3 (52.0%)	532.5 (48.0%)
Carbon fibers functionalized with Gbis	4.60%	284.6 (52.0%)	285.8 (23.9%)	288.2 (19.4%)	531.9 (22.5%)	532.6 (77.6%)

Table 3: Structural XPS analysis of modified carbon fibers.

Modification of carbon fibers with graphite microparticles functionalized with (2Z)-4-(6-aminohexyl-1-amino)-4-oxobut-2-enic acid

We found that the aminated graphite microparticles efficiently adhere to carbon fibers from their DCM, hexane, or aqueous suspensions. The SEM images on **Figure 14** show that both flat and edge areas of the particles demonstrate substantial affinity to the fibers.

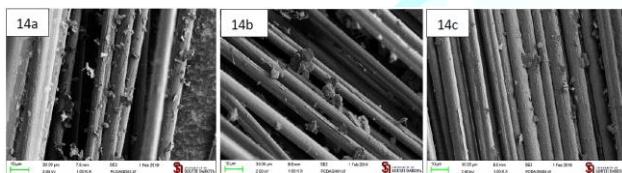


Figure 14: Carbon fibers coated by the aminated graphite microparticles (GAM) suspended in (a) DCM; (b) Hexane; (c) Water.

Modification of sized carbon fibers with functionalized graphite microparticles

Modification of sized carbon fibers with graphite nanoparticles functionalized with hexadecylmaleimide: We found that the adhesive ability of graphite microparticles is not limited to carbon-carbon π -stacking interaction. The hydrophobic interaction seems to play a significant role as well. Thus, graphite microparticles functionalized with N-hexadecylmaleimide (GHDMI) adheres to sized (coated with an organic polymer) carbon fibers upon dipping to their hexane suspension. The subsequent sonication for 10 min knocked off most of loosely attached particles, while the well-adhered particles were retained (**Figure 15**). A similar trend was observed for the suspension of GHDMI in DCM (Fig. 16).

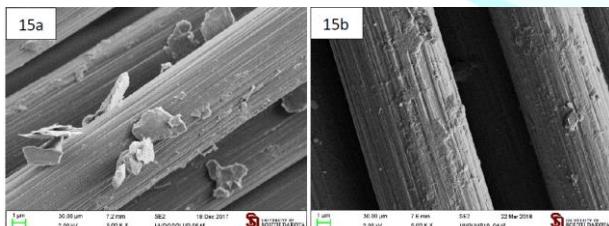


Figure 15: Sized carbon fibers coated by the graphite microparticles functionalized with N-hexadecylmaleimide (GHDMI) suspended in hexane. (a) After regular sonication (3 min); (b) After additional 10 min of sonication.

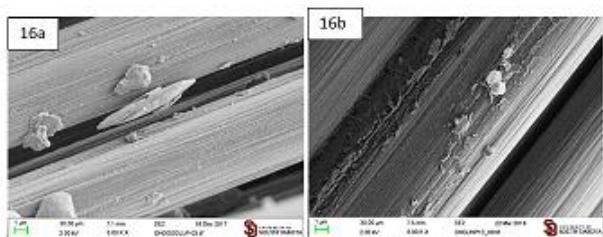


Figure 16: Sized carbon fibers coated by the graphite microparticles functionalized with N-hexadecylmaleimide (GHDMI) suspended in DCM. (a) After regular sonication (3 min); (b) After additional 10 min of sonication.

Modification of sized carbon fibers with graphite microparticles functionalized with 1,6-dimaleimidohexane: Graphite microparticles functionalized with 1,6-dimaleimidohexane (Gbis) adheres to sized carbon fibers from its hexane and DCM suspensions. This produces a denser, more evenly distributed and more resistant to sonication coating than GHDMI (**Figures 17 and 18**).

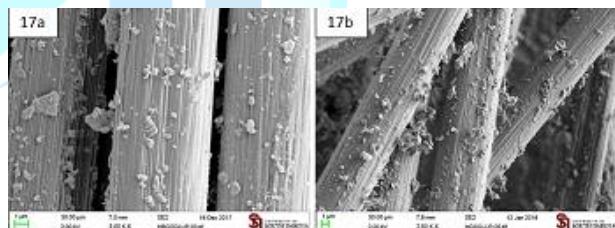


Figure 17: Sized carbon fibers coated by the graphite microparticles functionalized with N-hexadecylmaleimide (Gbis) suspended in hexane. (a) After regular sonication (3 min); (b) After additional 10 min of sonication.

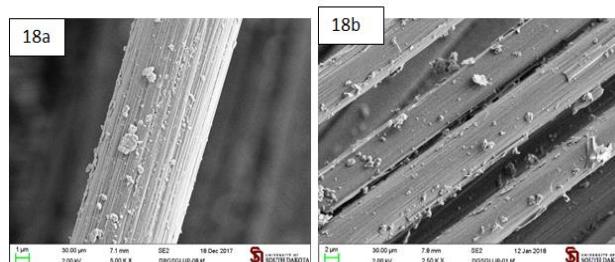


Figure 18: Sized carbon fibers coated by the graphite microparticles functionalized with N-hexadecylmaleimide (Gbis) suspended in DCM. a. After regular sonication (3 min); b. After additional 10 min of sonication.

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The high Dispersibility of **Gbis** particles in water allowed for modification of carbon fibers directly by their aqueous suspension. This produces a less dense coating than suspensions in hexane and DCM, which is however resistant to sonication (**Figure 19**).

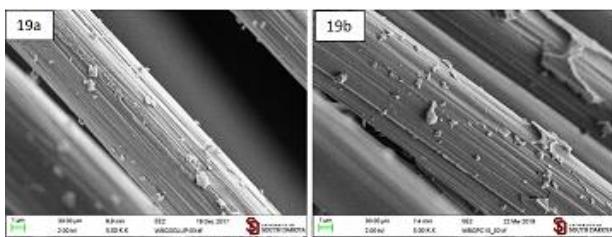


Figure 19: Sized carbon fibers coated by the graphite microparticles functionalized with N-hexadecylmaleimide (Gbis) suspended in water. a. After regular sonication (3 min); b. After additional 10 min of sonication.

Modification of sized carbon fibers with aminated graphite microparticles: The aminated graphite microparticles also retained their affinity to sized carbon fibers. The particles are loosely associating with the fibers mostly by the edges of particles (**Figure 20**).

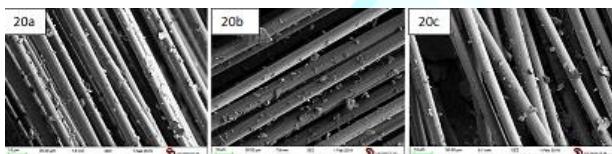


Figure 20: Sized carbon fibers coated by the aminated graphite microparticles (GAM) suspended in (a) DCM; (b) Hexane; (c) Water.

The unmodified graphite particles (GC) obtained by simple ball milling of graphite can evenly coat both carbon fibers and sized carbon fibers by their aqueous suspension as well as the modified Gbis material. That coating, however, is lacking the functional groups introduced by functionalized graphite microparticles (**Figure 21**).

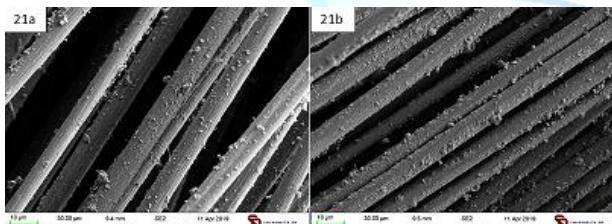


Figure 21: Coating produced by an aqueous suspension of unmodified graphite microparticles (GC) on a. Carbon fibers; b. Sized carbon fibers.

Thus, the affinity of functionalized graphite microparticles to carbon fibers is comparable with the affinity of less available graphene. Further, functionalization of the particles allows for the fine tuning of their affinity and other properties, which make them a viable alternative of graphene for many applications, such as composite films, wound healing, hair dyes, catalysts for green synthesis, and antioxidants [14-18].

Conclusions

Functionalized multi-layer graphite microparticles are able to coat both sized and unsized carbon fibers by simple dipping to their suspensions in various solvents including water. The produced coatings are resistant to ultrasonication. The ability to coat carbon fibers depends on both the

type of functionalized particles and on the suspension solvent. Dispersibility of the Gbis material (which contains both hydrophobic alkyl groups and reactive maleimido-groups) in water and the particle sizes substantially changes between the pH values 7 and 5, which is promising in terms of the drug delivery applications. The results of this work will help efficiently incorporate carbon materials into the composite materials with a diverse range of applications.

The raw and processed data required to reproduce these findings are available to download from
<https://data.mendeley.com/datasets/y5hkynw6v/1>

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