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Abstract

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High-strength Graphene and Polyacrylonitrile Composite Fiber Enhanced by Surface Coating with Polydopamine

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Abstract

Carbon fibers are well-known reinforcing elements in advanced composites, but these materials remain expensive partly due to the complex processing methods used to form high strength and high modulus fibers. Graphene is seen as an alternative precursor for the formation of high strength carbon-based fibers. Here it is shown that the strength and modulus of graphene-based fibers are enhanced by incorporating a polyacrylonitrile (PAN) binder, surface coating with polydopamine (PDA) and through appropriate pyrolysis heat treatments. Fiber samples were prepared by a wet-spinning method such that the composition of liquid-crystalline graphene oxide (LCGO) and PAN could be varied over the full range. The maximum fiber mechanical strength (220 MPa) and modulus (19 GPa) occurred at a composition of LCGO (80 wt%) and PAN (20 wt%). The mechanical strength was further significantly increased to 526 MPa

through pyrolysis of the LCGO/PAN fiber at 800 °C in a nitrogen atmosphere which caused carbonization of PAN. In addition, surface treatment of the LCGO/PAN fiber with PDA before carbonization improved the mechanical strength by an additional 40%.

Keywords: Graphene oxide, polyacrylonitrile, surface coating, pyrolysis, high strength.

1. Introduction

Carbon based fibers show high specific strengths and specific modulus and have found increasing application for production of high performance carbon composite components, bulletproof vests and other protective garments [1-3]. Polyacrylonitrile (PAN) and its copolymers are the most common precursors for the production of carbon fibers but very high molecular weight with very low defects are required. Moreover, a series of thermal treatments must be carried out to convert the PAN fiber to high tenacity carbon fiber, including thermal stabilization (~300 °C) [4], carbonization (~1000 °C) and graphitization (>2000 °C) [5]. Difficulties in the synthesis of the PAN precursors and the elevated temperatures needed for pyrolysis motivate research into more cost-effective and simpler routes to produce carbon-based fibers.

Recently, carbon nanotube (CNT) and graphene fibers prepared using simple wet-spinning techniques have been developed as high-strength and high-stiffness fibers. The mechanical strength and modulus of wet-spun CNT fibers have been reported at 1.3 GPa and 150 GPa [6], respectively. Zhang *et al.* reported a tensile strength of 850 MPa when the CNT fiber was infiltrated with polyvinyl alcohol. In this case the CNT fiber was fabricated by dry spinning from a multi-walled CNT forest [7]. Although CNT fibers show high mechanical performance, wet spinning is limited by dispersion

stability, and the dry-spinning technique is costly to up-scale [8]. The graphene precursor liquid crystalline graphene oxide (LCGO) can be readily and easily processed into a wide variety of structures including fibers [9-13]. High performance graphene fibers with tensile strength and modulus of 442 MPa and 22.6 GPa, respectively, have been produced using a one-step wet-spinning method [9]. Also, various composite graphene fibers have been prepared using different polymer binders. The reported tensile strengths were in the range of 150 - 450 MPa for PAN binder [14, 15]; ~360 MPa for cellulose binder [16]; and ~178 MPa for a polyetherimide/graphene composite where polydopamine (PDA) was grafted to graphene oxide [17]. Although improvements have been made in the mechanical properties of graphene fiber, the results are still short of commercially available carbon fibers.

Surface treatment has proven to be a reliable method to modify the mechanical performance of fibers [18]. Gao *et al.* [18] showed enhanced mechanical strength of glass fiber by applying a CNT coating on the fiber surface. Such coatings can reduce the incidence of surface defects that reduce fiber strength. Indeed, Ryu *et al.* [19] dramatically improved the tensile strength of CNT yarn from 1004 MPa to 4035 MPa by applying a PDA coating on the CNT surface and through a pyrolysis heat treatment. PDA is known to spontaneously adhere to the surface of various solid materials [20], and has been used to form coatings for various applications such as hydrophilic and biocompatible properties [21], and core/shell nanostructure [22].

The effects of composite composition, PDA surface treatments and pyrolysis on the mechanical properties of PAN/graphene fibers are reported here. The composite composition was systematically varied to determine the optimum level of graphene reinforcement and then the PDA surface coating / pyrolysis methods were applied to

investigate strength and stiffness enhancement mechanisms.

2. Experimental methods

2.1. Materials

Dispersed liquid crystalline graphene oxide (LCGO) (10 mg/ml) in water was prepared using previously published methods [9, 11, 23], the mean size of GO flakes was 37 ± 23 μm . PAN homopolymer (molecular weight: 200,000) was purchased from Polysciences, Inc. (USA). Dopamine hydrochloride was purchased from Sigma Aldrich (USA).

2.2. Fabrication and pyrolysis of LCGO/PAN/PDA fiber

To prepare composite PAN and LCGO fibers by wet spinning, the as-received aqueous dispersions of LCGO were first converted to a N,N-dimethylformamide (DMF) dispersion. The LCGO was collected by centrifugation of the water dispersion and supernatant water was removed. Next, the graphene was re-dispersed in solvent mixture of equal volumes of water and DMF. The solid was again recovered by centrifugation and the same process was repeated a minimum of six times to remove water. Finally, the collect LCGO flakes were dispersed in DMF (10 wt%) and mixed with a PAN/DMF solution (10 wt%) using a vortex mixer. The proportions of LCGO/DMF and PAN/DMF were varied to control the final composite composition. LCGO/PAN fibers were fabricated by wet spinning by extruding the spinning dispersion through a 22-guage spinneret into a coagulation bath of mixed water/isopropyl alcohol (IPA) (7:3) solution. When preparing the neat LCGO fiber an addition of 1 wt% calcium chloride was added to the coagulation bath. The LCGO/PAN solution injection speed was 5- 20 ml/h and

the coagulation bath was rotation at 20- 30 rpm to form continuous fibers. After spinning, LCGO/PAN fiber was removed from the coagulation bath and completely dried in air atmosphere at 280 °C for 1 h. The PDA coating was applied by immersing the fiber in aqueous dopamine (Tris-HCl buffer, pH 8.5) solution and heating overnight at 60 °C. Polymerization of the dopamine was evident from a change in color of the dopamine solution to brown. Finally, LCGO/PAN/PDA fiber underwent sufficient washing by water to remove non-polymerized DA and pyrolysis was performed at 800 °C in a nitrogen atmosphere.

2.3 Characterization

The thermal stability of the fiber samples was measured using thermogravimetric analysis (TGA, SDT Q600). The temperature was gradually increased from room temperature to 1000 °C at the rate of 5 °C/min in air or in a nitrogen atmosphere. The ratio of the Raman intensity (I_D/I_G) of the D and G peaks was obtained with a dispersive Raman spectrometer (Senterra Raman) using a 633 nm excitation. The mechanical properties were measured using a universal testing machine (Instron 5966) at a loading rate of 1mm/min. The liquid crystal characteristics of the LCGO/PAN dispersions were observed using a 90° polarized transmission optical microscope.

3. Results and Discussion

Large sheets of GO that can form liquid crystalline dispersions are a robust template for matrix-guided molecular level self-assembly of polymers [12, 23, 24]. This process allows for the production of composite materials with enhanced mechanical performance by simple mixing a polymer with LCGO [25, 26]. Inspired by this idea,

LCGO/PAN based composite formulations were produced in a wide range of ratios by combining the LCGO/DMF and PAN/DMF dispersions and subsequent wet-spinning to form composite fibers of controlled composition. The birefringence property of the LCGO/PAN spinning solution is shown in Fig. S1 confirming their liquid crystal character.

Fig. 1 shows the fabrication process of high tenacity graphene based PAN composite fiber by the wet-spinning method. A typical wet-spinning experiment involves injecting of the LCGO/PAN composite formulation into a rotating coagulation bath to produce the gel-state LCGO/PAN fiber (Fig. 1a). Controlling the injection speed and rotation of the coagulation bath ensures a uniform diameter in the formed gel-state LCGO/PAN fibers. Fiber stretching also occurs during fiber formation and the molecular orientation likely enhances the final fiber mechanical properties. The gel state LCGO/PAN fibers were carefully removed from the coagulation bath and then fixed and dried at room temperature, followed by heating at 280 °C for thermal stabilization in an oxygen rich atmosphere (Fig. 1b). These thermally stabilized fibers were next dipped into dopamine aqueous solution of tris buffer (pH 8.5) and heated at 60 °C. The dopamine adsorbs to the exterior of the LCGO/PAN fiber and self-polymerizes on the surface [27] (Fig. 1c). Finally, the pyrolysis of the fibers was carried out at 800 °C, in nitrogen, to carbonize the PAN - PDA fibers. The pyrolysis process results in the carbonization of the composite fibers (Fig. 1d).

The tensile strength and modulus of the composite fibers as a function of PAN concentration are shown in Fig 2a, and stress-strain curves are represented in Fig S2. As the concentration of LCGO in the composite fibers was increased, the tensile strength also increased until a peak of 220.1 ± 28.2 MPa was achieved at 80 wt% LCGO.

Samples prepared at 90 wt% and 100 wt% LCGO showed lower tensile strengths. The elastic modulus of the fibers showed a similar trend as it increased by increasing the LCGO concentration of up to 90 wt% and then decreased for the neat 100 wt% LCGO fiber. The measured densities of the 100 wt% LCGO fiber (1.1 g/cm^3) and 80wt% LCGO fiber (1.51 g/cm^3) suggested that the PAN polymer occupied much of the vacant space between the large GO sheets. The reduction in void space with PAN increases the modulus, as expected from the rule-of-mixtures model where the composite modulus is a weighted average of the moduli of the two components. The increase in modulus also leads to an increase in tensile strength since the strain at failure remains relatively unchanged for all composites and the pure LCGO fibers [28]. In contrast, the strain at failure of the neat PAN fiber was considerably higher than the composites. The presence of stress concentrations, such as void space or imperfections at the LCGO flake/PAN interface, will induce brittleness and reduce the strain at failure. At high LCGO loadings, the amount of PAN binder becomes insufficient to completely fill the void space and strength and modulus are then reduced.

PDA coating and pyrolysis were performed on the LCGO/PAN fiber containing 80 wt% of LCGO. An ordered inner structure of aligned LCGO flakes was observed in the as-spun gel-state LCGO/PAN fiber using the polarized optical microscopy, (Fig. 2b). Drying reduced the diameter of the LCGO/PAN fiber by a factor of 10 from $248 \pm 0.2 \text{ }\mu\text{m}$ to $25 \pm 0.1 \text{ }\mu\text{m}$. The large volume decrease also generated a wrinkled surface (Fig. 2b, ii) on the LCGO/PAN fiber. The cross section of the LCGO/PAN fiber with 80wt% LCGO had a compact structure, as shown in Fig. 2c. Topographical features on the fiber cross-section are consistent with stacked GO flakes aligned along the fiber axis [9].

The effects of processing conditions on the mechanical properties of the

LCGO/PAN fibers were investigated. Fig. S3 show the stress-strain curves for fibers prepared by controlling the speed of the solution injection, and the rotating speed of the coagulation bath. Varying the solution pumping rate from 5 to 20 ml/h at the same bath rotation speed (20 rpm) had only a small effect on the tensile strength (150 – 175 MPa) and modulus (15 -16 GPa). However, increasing rotation speed of the coagulation bath to 30 rpm, with a pumping rate of 5 ml/h, generated a significant increase in the tensile strength (220.1 MPa) and modulus (19.7 GPa). The combination of the slow pumping rate and high coagulation bath rotation speed induced the highest stretch and the best mechanical performance, suggesting better alignment of the GO flakes.

The thermal behavior of the LCGO/PAN/PDA fiber was investigated by TGA. Fig. 3a (inset) shows the TGA curve of the LCGO/PAN fiber in air. The LCGO/PAN fiber showed significant weight decrease of ~25% between 180 °C and 300 °C. As reported previously, thermal treatment of PAN between 200 °C and 300 °C in an oxygen rich condition causes the nitrile groups to form an aromatic ladder structure [4, 5]. This aromatization facilitates the further annealing of PAN at high temperature to increase the yield of carbonization [5]. The weight loss during the pyrolysis stage of heat treatment is also shown in Fig. 3a for the LCGO/PAN fiber coated with PDA. Heating to 800 °C in nitrogen causes a weight loss of ~20% because of the carbonization process. A similar weight loss during pyrolysis was observed for the LCGO/PAN fibers without the PDA coating. The Raman spectrum in Fig. 3b shows typical D band and G bands, which indicate sp^3 and sp^2 bonds at 1350 and 1580 cm^{-1} , respectively. The intensity ratio of D peak and G peaks (I_D/I_G) gives an estimate of the amount of defects in the graphene structure [27]. The pyrolysed LCGO/PAN/PDA had a smaller peak intensity ratio of 1.3 in comparison to the non-pyrolysed LCGO/PAN/PDA (1.6). The smaller

intensity ratio of I_D/I_G indicates a conversion of sp^3 to sp^2 bonds due to pyrolysis. Carbonization is known to remove oxygen-containing functional groups, such as epoxy and carboxyl groups, from the surface of the LCGO and hydrogen bonding with PAN [29]. In addition, the diameter of the fibers decreased from $\sim 25 \pm 0.1 \mu\text{m}$ (Fig. 2b) to $\sim 19 \pm 0.1 \mu\text{m}$ (Fig. 4a, b) during pyrolysis giving a more compact structure in the pyrolysed LCGO/PAN/PDA fiber (Fig. 3c) in comparison with the LCGO/PAN fiber (Fig. 2c). Fig. 4c, d shows magnified images of surface morphologies of the py-LCGO/PAN, and py-LCGO/PAN/PDA fiber. The py-LCGO/PAN has a wrinkled structure, while a smoother surface was observed on the py-LCGO/PAN/PDA.

The mechanical strength and elastic moduli of the fibers were affected by four factors. Firstly, the well-aligned inner structure of the large size GO sheets produces effective mechanical reinforcement in comparison with smaller size of GO. Secondly, as the PAN matrix binder filled many of the microvoids in the LCGO fiber, the mechanical strength and stiffness was improved. Density is further increased through the pyrolysis, so the py-LCGO/PAN fiber is more compact by carbonization of PAN and reducing GO. The reduction in oxide defects allows for a more compact structure and resulting in the tensile strength and modulus of LCGO/PAN fiber increasing from $220.1 \pm 28.2 \text{ MPa}$ to $526.2 \pm 28.7 \text{ MPa}$ and from $19 \pm 1.9 \text{ GPa}$ to $72.6 \pm 10.1 \text{ GPa}$, respectively (Fig. 5). Finally, the PDA coating induced higher tensile strength as PDA covered the surface defects of the LCGO/PAN fiber. The surface defects act as stress concentrations and induce fracture by cracking at low stress [18]. Hence, the tensile strength of py-LCGO/PAN increased 40% and reached $738.5 \pm 25.3 \text{ MPa}$. The modulus of $73.2 \pm 13.7 \text{ GPa}$ obtained for PDA coated fibers was unchanged from the uncoated fibers. The LCGO/PAN fiber enhanced by PDA coating has a higher tensile strength than most

previously reported graphene oxide based materials (Table 1). Composite fiber and films formed from graphene oxide have been reported with tensile strengths in the range 148 MPa to 652 MPa [16,17,30-32] The tensile strength and modulus of the py-LCGO/PAN/PDA fiber is also comparable to thermally annealed at 800 - 1050 °C GO fibers [33-35], and the graphene based fibers [36-41].

4. Conclusion

In conclusion, we demonstrated an enhancement in the strength and modulus of LCGO/PAN composite fiber through surface coating with PDA and pyrolysis. The fibers were prepared from a simple wet spinning method using mixed dispersions of LCGO and PAN to control the final fiber composition. The highest tensile strength for non-coated and non-pyrolised LCGO/PAN fibers (220.1 MPa) was observed for 80 wt% of LCGO and 20 wt% of PAN fiber due to the large aligned surface of GO and high GO loading. In addition, after the surface treatment of PDA and pyrolysis, a dramatic improvement of mechanical strength and modulus was observed, 738.5 ± 25.3 MPa and 73.2 ± 13.7 GPa, respectively. As a result, the high mechanical strength of py-LCGO/PAN/PDA fiber has the potential to act as a reinforcing agent for increasing mechanical properties of composite materials.

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Figure and captions

Fig. 1. Schematic diagrams illustrating **a)** wet spinning process of the LCGO/PAN fiber, **b)** thermally stabilized LCGO/PAN fiber immersed in DA solution, **c)** the polydopamine (PDA) self-polymerization on the surface of the LCGO/PAN fiber, and **d)** pyrolysis of LCGO/PAN/PDA fiber at 800 °C in N₂ atmosphere.

Fig. 2. **a)** Tensile strength and modulus of the composite fiber versus LCGO concentration. **b)** **i)** Polarized optical microscopy image of gel-state LCGO/PAN fiber showing LC domains (arrows show the polarizer directions) (scale bar: 200μm). **ii)** SEM image of the surface of dried LCGO/PAN fiber (scale bar: 25μm). **c)** SEM image of the cross section of the LCGO/PAN fiber (scale bar: 500 nm).

Fig. 3. **a)** TGA curves of the thermally stabilized LCGO/PAN/PDA fiber in N_2 atmosphere. Inset is TGA curves of the LCGO/PAN fiber in air condition. **b)** Raman spectroscopy of the LCGO/PAN/PDA (dashed line), and py-LCGO/PAN/PDA (solid line). **c)** Cross section of py-LCGO/PAN/PDA (Scale bar: 500 nm).

Fig. 4. SEM images of the surface of **a)** py-LCGO/PAN, and **b)** py-LCGO/PAN/PDA fiber (scale bar: 25 μm). Magnified surface of **c)** py-LCGO/PAN, and **d)** py-LCGO/PAN/PDA fiber (scale bar: 1 μm).

Fig. 5. Stress-strain curves of the LCGO/PAN fiber (solid line), py-LCGO/PAN (dashed line), and py-LCGO/PAN/PDA (dotted line).

Table. 1. Tensile strength and Young's modulus of GO based fibers prepared in this study and previous reports.

Reference	Species	Method	Tensile strength [MPa]	Modulus [GPa]
This work	Py-LCGO/PAN/PDA	Wet spinning	738	73.2
[17]	PAN grafted GO	Wet spinning	452	8.3
[36]	Glycidyl methacrylate grafted GO	Wet spinning	500	
[31]	Hyperbranched polyglycerol GO	Wet spinning	652	20.9
[32]	Cellulose/GO	Wet spinning	442	34.1
[37]	Ag-doped GO	Wet spinning	300	9.5
[38]	Reduced GO	Wet spinning	360	12.8
[9]	GO coagulated by CaCl ₂	Wet spinning	412	20.1
[39]	Reduced GO/Poly(vinyl alcohol)	Wet spinning	162	10.4
[2]	Reduced GO/CNT/Poly(vinyl alcohol)	Wet spinning	570	
[33]	800 °C thermally treated GO	Wet spinning	420	
[34]	1000 °C thermally treated GO	Wet spinning	214	47
[35]	1050 °C thermally treated GO	Wet spinning	378	36.2
[28]	1800 °C thermally treated GO	Wet spinning	1080	
[40]	GO fiber from film	Twisting	85	1.6
[41]	GO coagulated by CaCl ₂	Dry-jet wet spinning	136	7.9