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Surface-conductive UHMWPE fibres via in situ reduction and deposition of graphene oxide

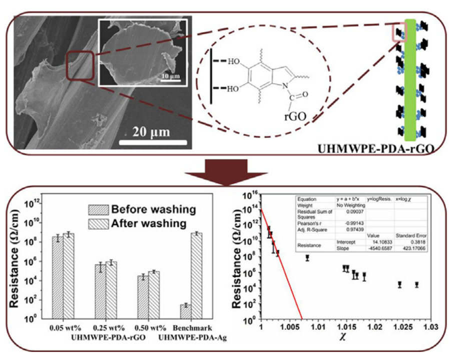
Kui Wang [a,1], Mingqiao Liu [a,1], Changyuan Song [a], Lu Shen [a], Peng Chen [a,b,*], Shian Xu [c]

[a] Ningbo Key Laboratory of Polymer Materials, Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering (NIMTE), CAS, Ningbo 315201, China
[b] Department of Science, Zhijiang College of Zhejiang University of Technology, Keqiao, Shaoxing 312000, China
[c] Ningbo Dacheng Advanced Material Co., Ltd., Cixi 315300, China

HIGHLIGHTS

- Surface-conductive UHMWPE fibres with resistance down to 10^5 Ω/cm were prepared via in situ reduction and deposition of GO.
- The surface conductivity of rGO deposited UHMWPE fibres was much more durable than that of Ag deposited fibres.
- High performance of UHMWPE fibres including low density and ultrahigh tenacity was fairly maintained through rGO deposition.
- GO was partially reduced during the process producing graphene as a conductive composition and GO bonded tightly with fibres.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface-conductive ultra-high molecular weight polyethylene (UHMWPE) fibres were prepared via in situ reduction and deposition of graphene oxide (GO). GO was dispersed in water to form a uniform and stable suspension. Subsequently, GO was chemically reduced into rGO and spontaneously deposited onto gel-spun, ultra-drawn UHMWPE fibres. The UHMWPE was coated with polydopamine (PDA), emulating the surface coating in mussels, prior to the rGO deposition to improve the bonding between rGO and the fibre surface. Characterizations using SEM, EDX, FTIR and XPS confirmed the effectiveness of the PDA coating and rGO deposition and the covalent bonding between PDA and rGO. The electrical resistance of UHMWPE-PDA-rGO decreased monotonically with increasing GO percentage in the suspension and deposition cycle. The UHMWPE-PDA-rGO exhibited an electrical resistance of 10^5 Ω/cm, whereas UHMWPE and UHMWPE-PDA showed a resistivity of $>10^{12}$ Ω/cm. Using Ag deposited UHMWPE-PDA as the benchmark, UHMWPE-PDA-rGO was superior in durability, conductivity and retention of ultrahigh tensile properties. Analysis using the TGA data and linear density confirmed the partial reduction of GO during processing. Furthermore, a plausible log-log linear relationship was revealed between the resistance and the weight ratio of UHMWPE-PDA + G_{TGA} and pure UHMWPE-PDA (χ), which tentatively explained the deposition mechanisms.

* Corresponding author at: Ningbo Key Laboratory of Polymer Materials, Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering (NIMTE), CAS, Ningbo 315201, China.
E-mail address: pchen@nimte.ac.cn. (P. Chen).

[1] The two authors contributed equally to this work and should be considered as co-first authors.

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1. Introduction

Conductive fibres are needed in cases requiring flexibility, electromagnetic shielding, anti-static and/or conductive properties [1,2]. Generally, metal fibres meet these criteria, but they also exhibit shortcomings, such as high density, low strength and susceptibility to corrosion. Polymeric conductive fibres are superior to metal fibres and are developed using unique conductive polymers [3–5] or by blending with conductive additives such as black carbon [6,7]. Unfortunately, the high cost of conductive polymers, the rigorous fabricating process and the diminished mechanical properties limit the utility of polymeric conductive fibres. Electroless plating was recently attempted in our institute with the idea of creating a thin conductive surface while keeping the main body intact. This method was used to fabricate surface-conductive ultrahigh molecular weight polyethylene (UHMWPE) fibres with silver deposition [8]. As a follow-up and a comparative work, we discuss in this paper the surface-conductive UHMWPE fibres, which were developed via in situ reduction and deposition of graphene oxide (GO). These fibres appear to be durable, highly conductive and can keep other valuable properties to a large extent.

The UHMWPE fibres were chosen as the deposition target due to multiple reasons. Firstly, UHMWPE fibres are commercially available and feature ultrahigh mechanical properties, low density and excellent chemical resistance. The UHMWPE fibres exhibit high axial thermal conductivity, 15–30 W m^{-1} K^{-1}, which is comparable or superior to some metallic alloys (e.g. ca. 10 W·m^{-1}·K^{-1} for stainless steel) [9]. On the contrary, the conductivity of UHMWPE fibres is extremely low, typically 10^{-14}–10^{-15} S·m^{-1} [10,11]. Improving the UHMWPE fibres' conductivity while keeping other valuable properties, such as high strength and thermal conductivity, are the ideals of material design and optimisation.

Producing conductive UHMWPE fibres is full of challenges. Damages or defects must be avoided to keep the intrinsically ultrahigh properties of UHMWPE fibres. This condition is in contrast with the addition of conductive additives during the fibres' fabrication. Moulton et al. [12] prepared conductive UHMWPE blend fibres with a tenacity of <1/3 of the normal UHMWPE fibres. The creation of a thin conductive surface on the UHMWPE fibres (i.e. deposition) suffered from the fibres' inert and smooth surface. Various surface modification methods have been proposed and used [13–15], among which the mussel-inspired surface chemistry was especially attractive [16–20]. This method consisted of dip-coating in a slightly alkaline aqueous dopamine solution and the self-polymerization of the dopamine, yielding polydopamine (PDA) layers with active amino and hydroxyl groups [19]. Both steps were viable under mild temperature, time and pH, providing a simple, universal and non-destructive process [21].

PDA and its derivatives significantly affected surface modification and especially improved the adhesion effects for many polymers, including UHMWPE fibres. Du et al. [22] developed a facile approach to functionalize various substrates with dopamine methacrylamide (DMA) to provide a versatile and general platform for subsequent surface modification. DMA is a molecule with adhesive properties that mimic those of mussels. Yang et al. [23] synthesized poly(dopamine methacrylamide-*co*-methoxyethyl acrylate) (PDMA-*co*-PMEA) with good adhesion properties through the free radical polymerization of DMA and MEA. Han et al. [24] used a two-step method to fabricate a tough and adhesive polydopamine-clay-polyacrylamide (PDA-clay-PAM) hydrogel. PDA was also used to improve the surface adhesion and other properties of UHMWPE fibres. In our institute, conductive UHMWPE fibres were prepared via electroless silver plating with the fibre surface modified by using PDA [8]. Sa et al. [20] prepared epoxy functionalized UHMWPE fibres by combining of PDA deposition and epoxy grafting, and the modified fibres exhibited excellent adhesion properties and fatigue resistance.

Graphene has been chosen as a novel conductive agent for polymeric fibres [25–29]. Xiang et al. [25] fabricated carbon nanotube and graphene nanoribbon-coated Kevlar fibres with high conductivity of 20 S/cm using a layer-by-layer spray coating method. Molina et al. [26] fabricated graphene-coated polyester (PES) fabrics with low resistance values of 23.15 Ω/cm^2 through the chemical reduction of graphene oxide (rGO) onto the fabric surface. Ha et al. [27] obtained GO coated fibres via electrostatic deposition of GO on polyester/cotton fibres. The GO samples were then chemically reduced. The results showed that the resistance of the fibres decreased rapidly by four orders at the first minute of the reduction. Vinod et al. [28] developed a self-assembly strategy of producing rGO coated electrospun polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) fibres that exhibited unique electrical conductivity and optical transparency.

Graphene oxide was used as the precursor to obtain a uniform layer as it is capable of being well-dispersed in polar liquids (e.g. water). Moreover, GO is readily adsorbed on the fibre surface by the aid of attractive forces between polar groups. However, there are no polar groups on virgin UHMWPE fibres. To the best of our knowledge, graphene or GO deposition has not yet been reported in UHMWPE fibres. We combined the mussel-inspired surface coating, in situ reduction and GO deposition in UHMWPE fibres under a series of conditions. The aim was two-fold: firstly, to fabricate surface-conductive UHMWPE fibres without sacrificing the other properties, and secondly, to tentatively explore the mechanisms of the in situ reduction and deposition process.

2. Experimental section

2.1. Materials

Gel-spun, ultra-drawn UHMWPE fibres consisting of 240 monofilaments (denoted as UHMWPE) and multilayer (ca. 3–5 layers) graphene oxide (denoted as GO) were supplied by Ningbo Dacheng Advanced Material Co., Ltd., China and Ningbo Morsh Co., Ltd., China, respectively. Dopamine hydrochloride ($C_8H_{11}NO_2 \cdot HCl$, AR) and tris (hydroxymethyl) aminomethane ($C_4H_{11}NO_3$, AR) were purchased from Aladdin Reagent Co., Ltd., China. Sulfuric acid, potassium nitrate, potassium permanganate, hydrogen peroxide, hydrochloric acid, hydrazine hydrate ammonia and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were used as received.

2.2. Sample preparation

The sample preparation route is schematically illustrated in Fig. 1.

Firstly, polydopamine (PDA) coated UHMWPE, denoted as UHMWPE-PDA, was prepared as follows. Dopamine solution (0.01 M) was prepared by dissolving dopamine hydrochloride in tris (hydroxymethyl) aminomethane buffer solution (0.1 M, pH = 8.5). A bundle of UHMWPE, wound around a rectangular stainless steel frame and knotted tightly at the ends, was ultrasonically cleaned in acetone for 30 min and vacuum dried at 60 °C for 2 h. The cleaned and dried UHMWPE bundle was immersed into a freshly prepared dopamine solution for 24 h at room temperature, followed by rinsing with deionised water and vacuum drying at 60 °C for 2 h to obtain UHMWPE-PDA.

Secondly, reduced graphene oxide (rGO) coated UHMWPE-PDA, denoted as UHMWPE-PDA-rGO, was prepared following the in situ GO reduction and deposition procedure. The GO was dispersed in deionised water at room temperature and ultrasonically agitated for 1 h to obtain a uniform suspension. The percentage of GO in the suspension were 0.05, 0.25 and 0.50 wt%. The UHMWPE-PDA was immersed into a freshly prepared GO suspension. Subsequently, a mixture of ammonia and hydrazine hydrate (10/1, v/v), serving as the reduction agent, was added dropwise. To obtain the UHMWPE-PDA-rGO, we heated the suspension to 95 °C for 2 h at a rate of 10 °C/min with magnetic stirring, during which the in situ reduction and deposition of GO occurred. This step was then repeated for several cycles. Fresh GO suspension was used for each cycle to prepare a series of samples.