Graphene oxide composite fibres for therapeutic fabrics

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Abstract

Topical administration of various therapeutic factors at different stages of healing has the potential to enhance wound healing rates and reduce pain of chronic wounds. Here, the potential of utilising therapeutic fibres as wound dressings and/or sutures, is demonstrated by wet-spinning graphene oxide (GO) and aspirin adsorbed GO with polyvinyl alcohol, into drug eluting composite fibres. By varying the load of GO in the composite fibres it was possible to tailor strength, stiffness and stretchability. GO loadings of 5 wt.% resulted in fibres five times stronger than polyvinyl alcohol alone. Low loadings of GO 0.2–0.4 wt.% produced super-stretchable fibres. The drug loaded composite fibres exhibited a slow release of aspirin over a period of 3 d which is attributed to the \( \pi-\pi \) interactions between the GO and aspirin. These composite fibres demonstrate promise for incorporating other biological factors using GO as a vector, as well as creating textiles that can deliver therapeutics in a sustained manner, leading to flexible wearable therapeutics and sutures in the future.

1. Introduction

The field of smart textiles and fabrics has experienced significant developments and innovation in recent years [1]. Smart textiles provide intrinsic functionalities and have been developed for a variety of applications including thermal regulation, wound healing, antimicrobial properties, drug delivery, tissue engineering, UV protection, energy storage and more [2–5]. Although pristine graphene has been widely used and incorporated in smart textiles [6], graphene oxide (GO), in parallel, has also established itself in research fields from functional composites [7] and energy storage [8, 9] to drug delivery [10], due to versatile functionalization routes and processability [11–13]. An attractive property of GO for material development and design is its liquid crystalline properties [14–16] which have been utilised to improve mechanical and electrical/thermal properties of materials. GO fibre structures are indeed desirable, and several have been developed, including GO composite fibres by wet-spinning [17, 18]. Polymer free wet-spun fibres from liquid crystalline GO have also been successfully fabricated [19]. Increased elongation of wet-spun GO fibres has also been observed [20, 21]. In addition to these material properties, GO has been shown to have antimicrobial potency [22–24], which supports the potential use of GO in smart wound dressings or sutures to fight against potential infections. GO has also been reported to reduce (i.e. rGO) (and therefore increase in conductivity) in the presence of bacteria [25, 26], which has promise for being incorporated as a trigger in smart wound dressings for detecting the presence of bacteria.

GO is well known to have been utilised for its adsorptive properties to be non-covalently functionalised with polymers, proteins and drugs as potential delivery vectors [10, 27]. These non-covalent functionalisation strategies have been developed due to an abundance of O-containing groups such as C=O, C(O)O, and C–O/O–H, as well as available aromatic regions for \( \pi-\pi \) interactions. Studies have investigated the adsorption of aromatic compounds with GO such as nitro aromatic compounds [28] and salicylic acid (also commonly known as aspirin) [29], which showed that the adsorption was governed by electronic
properties rather than hydrophobic effects. The availability of adsorptive sites on graphene-based materials for aromatic compounds was reported to be regulated by surface properties and defects at the edges and surface of O-abundant GO [28]. Theoretical studies have investigated the adsorption properties of small organic molecules and aromatic molecules with graphene and GO to examine which mechanism (including \( \pi-\pi \), hydrogen bond, vdW, and hydrophobic interactions) governs the adsorption capacity. It was found that adsorption was guided, in the case of aromatic molecules such as salicylic acid, mainly by the ability of the aromatic compounds to \( \pi \)-stack with the GO surface [29, 30]. The analysis also suggested that upon adsorbing aromatics on GO, the translational motion of aromatic compounds in water was supressed; however, the solvent accessible surface area was increased, which could increase the bio-accessibility of aromatic compounds such as aspirin (salicylic acid) [29]. The adsorption of aspirin has also been investigated with carbon nanotubes and activated carbon [31–33]. The successful reversible adsorption of aspirin was observed in activated carbon [31], as well as increased adsorption capacities recorded (e.g. from 41 mg g\(^{-1}\) to 58 mg g\(^{-1}\)) for oxidised multiwalled carbon nanotubes compared to pristine nanotubes [33].

With the above in mind, therapeutic fabrics, which can sense infections and treat wounds accordingly could transform the way wounds are treated, as shown in recent work [34]. Dermal injuries can render the human body significantly vulnerable to infections and furthermore, the systematic administration and concentration of drugs at the wound site, be it for pain relief or antimicrobials, is generally lower in concentration than the administered dose due to limited vascularisation [35, 36]. Topical administration of drugs can result in higher concentrations in the wound bed where it is needed. Therefore, in this work, we have developed flexible, high loaded GO composite fibres, also adsorbed with aspirin as a model target therapeutic, which have the potential to be developed into therapeutic fabrics for wound dressings or sutures for open wounds. GO, known to have antimicrobial properties in itself, was wet-spun with polyvinyl alcohol into continuous composite fibres and the fibre mechanical and spectrochemical properties characterised. Aspirin release was subsequently measured from PVA and PVA/GO fibres for drug eluting tests.

### 2. Materials and methods

#### 2.1. Materials

GO powder was purchased from Graphenea and used as-received (characterised by AFM and FE-SEM, figure 1(a)). Hydrolysed polyvinyl alcohol (PVA) (99.1-%) (M\(_w\) 85 000–124 000) and DMSO (\( \geq 99.9\)% ) was purchased from Sigma-Aldrich. Acetone used in the coagulation bath was purchased from VWR chemicals. For the drug loading experiments, aspirin (acetylsalicylic acid) (\( \geq 99.9\)% ) was purchased from Sigma-Aldrich.

#### 2.2. GO spinning dope

For the preparation of a typical GO spinning dope, first, 7 g of PVA was added to 115 ml of DMSO and 35 ml of deionised water. The mixture was stirred (IKA™ C-MAG HS 7 Ceramic Plate Magnetic Stirrer) for 12 h at 95 °C to fully solubilise the PVA. 0.25 g of GO was added to 50 ml of DMSO, and the mixture was sonicated in a bath sonicator (ultrasonic bath, 45 kHz, 80 W) for 30 min. The dispersion of GO was then added to the PVA solution such that samples with GO to PVA weight percentages of 0.2%, 0.4%, 2%, 4% and 5% were produced. A control dope of PVA was also prepared. Each spinning dope was sonicated for 30 min in a bath sonicator before spinning. For the drug eluting fibres, aspirin was dissolved in the PV A/GO-PV A solutions to produced. A control dope of PV A was also prepared. Each spinning dope was sonicated for 30 min in a bath sonicator (ultrasonic bath, 45 kHz, 80 W) for 30 min. The dispersion of GO was then added to the PVA solution such that samples with GO to PVA weight percentages of 0.2%, 0.4%, 2%, 4% and 5% were produced. A control dope of PVA was also prepared. Each spinning dope was sonicated for 30 min in a bath sonicator before spinning. For the drug eluting fibres, aspirin was dissolved in the PVA/GO-PVA solutions to a concentration of 1 mg ml\(^{-1}\). The dispersion was then further mixed and sonicated for 30 min prior to wet spinning (figure 1(b)). Rheology measurements of the spinning dopings were performed on a TA Instruments HR-3 Discovery Hybrid Rheometer, operating in flat plate geometry with Peltier temperature control. The flow sweep of shear rate was measured from 0.1 to 50 s\(^{-1}\) at 21 °C, with a sample gap of 1 mm, and sample volume 1.2 ml.

#### 2.3. Wet-spinning continuous GO composite fibres

The fibres were spun in a wet-spinning rig with a 10 ml syringe (Fisherbrand™ Plastic PP Syringes, Luer Lock), a syringe pump (Cole-Parmer® 78-8110C) set at a rate of 20 \( \mu l \) h\(^{-1}\), a 21-gauge (0.514 mm diameter) spinneret, coagulation bath, roller and motor (PARVALUX SD12M Motor Gearbox, powered by a DC Agilent E3631A power supply (figure 1(c)). The coagulation bath was filled with fresh acetone, and the dopings were sonicated for 30 min before being spun into fibres. Two spools of each fibre were produced (figure 1(d)), to allow an ample length of fibre for testing.

#### 2.4. GO composite fibre characterisation

Fibre cross sections were imaged using a JEOL JSM-6301F FE-SEM with an accelerating voltage of 5.0 kV. ImageJ software was used to measure the cross-sectional areas from the SEM images. Fibre samples were
investigated for birefringence using a polarised optical microscope (DM2500P, Leica Microsystems Ltd, GB) fitted with a DFC295 camera (Leica Application Suite v4.0.0, ©/1.1 HI PLAN 40 ×/0.50). To investigate the distribution of GO through the fibres, Raman spectroscopy was conducted using a Renishaw InVia system, with a 532 nm green edge laser set at 1% power and a 10 s exposure with three accumulations for point spectra. 10 × 10 grid Raman maps were conducted using the 532 nm streamline laser at a laser power of 10%. The Raman map spectra were analysed using the open-source Python Library Hyperspy [37]. They were denoised by performing principal component analysis using singular value decomposition. The first three principal components were used to reconstruct the denoised dataset [38, 39]. The signal range corresponding to the D and G bands (1200–1600 cm⁻¹) were excluded from the background fit. The background (a polynomial of order 6) was fit and subtracted (figure S1 (available online at stacks.iop.org/JPMATER/4/044010/mmedia)). The G-band peak intensity (the summed area of the peak, figure S2) was calculated to analyse the presence and distribution of GO across the PVA-GO composite fibres. FTIR of PVA/GO composite fibres were measured with a Perkin Elmer Frontier instrument, the spectra are the average of three different areas on the fibres. The mechanical properties of the fibres were observed under a tensile load following the standard BS ISO 11566:1996 adapted for use with composite/PVA fibres. Composite fibres were fixed on card frames with a gauge length 15 ± 0.5 mm using an epoxy adhesive (50/50 hardener to resin, Araldite Rapid Adhesive, Huntsman Advanced Materials Ltd, GB). Tensile tests of single composite fibres were carried out on a TST350 tensile stress tester with integrated heating stage (Linkam Scientific Instruments Ltd, GB) with a 20 N load cell operating at 1 mm min⁻¹ crosshead speed at room temperature. The drug loaded fibres, and a control of pure PVA-aspirin were left to elute in water for 1, 3 and 72 h. To confirm drug release, UV spectroscopy was conducted using an Agilent UV/Vis Cary 100.

3. Results and discussion

3.1. GO composite spinning dope and fibre characterisation

The rheology of PVA/GO spinning dopes were measured to ascertain the change in shear stress and viscosity as a function of shear rate (figures 2(a) and (b)). Shear thinning behaviour of polymer nanocomposites is attributed to the alignment of the filler in the inner phase of the polymer matrix which generally occurs at low shear rates [40–42]. A weak shear thinning region at high shear rate, γ, is related to the orientation of PVA chains and the formation of new inter-chain and solute-solvent H-bonding [43]. Dependent on the concentration, the presence of GO alters the suspension rheology in the weak and strong thinning regions. In the high shear rate region, flow curves of the GO suspensions are almost identical to the PVA solution.
Figure 2. Rheology measurements of PVA/PVA/GO spinning dopes (a) shows the shear stress as a function of shear rate and exhibits a non-linear trend at >4 wt.% GO in the spinning dope solutions and (b) shows the viscosity of the spinning dopes as a function of shear rate, where there is a significant difference in viscosity when the spinning dopes contain >4 wt.% GO at low shear rate <1 s$^{-1}$.

There is a threshold at >2 wt.% where the loading of GO in the PVA solution has a significant effect on the viscosity at low shear rate <5 s$^{-1}$, indicating shear thinning behaviour and has been observed in various GO polymer systems in literature [44–46]. For a Newtonian fluid, the shear stress is directly proportional to the shear rate and the coefficient of proportionality being the dynamic viscosity. Spinning dopes of neat PVA and dopes with GO loadings up to 2 wt.% show a linear relationship (figure 2(a)) and act like a Newtonian fluid, however at spinning PVA/GO dopes of >2 wt.% there is a dramatic change in shear stress vs shear rate indicating non-Newtonian fluid shear thinning/pseudoplastic behaviours ($n < 1$).

Composite fibres were continuously wet-spun from the prepared spinning dopes, drawn, and collected on a reel (figure 1(c)). The resulting composite fibres were found to have predominately cylindrical or ribbon-like profiles via scanning electron microscopy with a large cross-sectional size distribution across the fibres (figures 3(a)–(e)) which has also been observed previously [47]. As the loading of GO increased to 5 wt.% the fibres were predominantly ribbons rather than cylindrical in shape (figures 3(a)–(e)). All the GO fibres were flexible, including at the highest GO loading of 5 wt.% where it was possible to manipulate the fibres into knots (figure 3(f)). A high level of birefringence was observed for all fibres by polarised optical microscopy (POM) (figure 3(g)), qualitatively indicative of well dispersed nano-reinforcement of the GO and alignment within the microstructure. The POM showed that, at all GO loadings, the mixtures remain isotropic without any mesophase formation, similar to the PVA control (100 wt.% PVA). However, there are potentially some birefringent domains at higher GO loading (>4 wt.%) indicating a two-phase composition of anisotropic, liquid crystal-like character, and GO domains coexisting with isotropic regions, which is also supported by the rheology data of the spinning dopes (figure 3(g), 4 wt.% and 5 wt.% GO).

The FTIR of GO, PVA and the GO/PVA composite fibres show several characteristic peaks (figure 4(a)). The pure GO FTIR spectra have various functionalities including C–O stretching bands (1050 cm$^{-1}$), C–OH (1262 cm$^{-1}$), and C=O stretch (1726 cm$^{-1}$). In the spectrum of pure PVA fibres, bands at 1000–1200 cm$^{-1}$...
Figure 3. Cross-section and fibre FE-SEM images with increasing loading (a) 0.2 wt.%, (b) 0.4 wt.% (c) 2 wt.%, (d) 4 wt.%, (e) 5 wt.% and (f) knotted 5 wt.% GO composite fibre demonstrates the flexibility of the composite fibres at high loadings of GO, (mag 500–1000 x) (g) cross-polarized optical microscope images of birefringent polyvinyl alcohol fibres (control) and GO composite fibres at increasing loadings 0–5 wt.%. Scale bar 100 µm for all POM images.

Figure 4. Characterisation of PVA fibres, PVA/GO fibre/aspirin fibres and as-received GO (a) FTIR showing the sharp decrease in the PVA spectra with increasing GO content, (b) point Raman spectra shows the decrease in intensity of the PVA peak at ca. 2918 cm$^{-1}$ with increasing GO in the fibres and (c) three 10 × 10 grid Raman map spectra with increasing GO content (0 (PVA), 0.2 wt.% and 5 wt.%) and subsequent peak intensity in the G-band, with zero intensity in the PVA fibres as expected, colour band = intensity (a.u.) (maps for all samples shown in figure S2).

are attributed to the stretching vibration of C–O. There are significant decreases in the peak intensities of –OH stretching and C–O stretching (at ca. 1091 cm$^{-1}$) of the PVA fibres with increasing GO content in the fibres. The peaks at 2800–3000 cm$^{-1}$ in the PVA fibres are due to –CH$_2$, the intensity of these peaks also reduce with increasing content of GO and have much lower intensity at >4 wt.% GO. The broad and strong absorption at 3000–3700 cm$^{-1}$ is attributed to the symmetrical stretching vibration of hydroxyl groups in
PVA, and the intensity of this absorption reduces with increasing GO content in the fibres. Similar findings of the FTIR spectra on the interaction between PVA and GO/rGO composites supports the present findings [48–50].

To ascertain the distribution of GO in the composite fibres, Raman point and mapping spectra were recorded for all fibres (figures 4(b), (c) and figure S2). The extended Raman point spectra of PVA, exhibits two main peaks at ca. 1435 cm$^{-1}$ and 2912 cm$^{-1}$ which are attributed to stretching vibrations of –CH and –CH$_2$ in PVA, respectively. GO exhibits the familiar D and G bands at 1358 cm$^{-1}$ and 1594 cm$^{-1}$. On increasing the amount of GO in the PVA spinning dope, there is a clear correlation between the intensity of the PVA Raman peaks and the presence of GO. As the wt.% of GO in the fibres increase, the PVA peak intensity decreases up to 2 wt.% where the PVA peak is no longer detectable due to the stronger peaks/presence of GO. This finding has also been shown previously with rGO/PVA hydrogels [51] and GO/PVA hydrogels [52]. Between 2 wt.% and 4 wt.% GO, the PVA bands are shrouded by the presence of GO and the higher intensity recorded at increased loadings of GO. The presence of aspirin in the fibres does not appear in the (FTIR or Raman) spectra, indicating the bands of aspirin are shrouded by the PVA and GO signals and/or the concentration of the aspirin in the fibres is too low to be detected. Furthermore, to demonstrate the even distribution of GO throughout the fibres, Raman maps were recorded for all fibres (including PVA) in 10 × 10 grids. The maps clearly showed the presence of GO evenly distributed in all the GO fibres, the intensity of the D and G bands after background subtraction (figure S1) in the 0.2 wt.% was reduced compared to all other GO/PVA composite fibres (figures 4(c) and S2). As there was no GO present in the control PVA fibre the peak intensity of the ‘G’ band is zero.

### 3.2. Tensile properties of GO composite fibres

Following the collection of the continuously spun composite fibres on a red, (figure 1(d)), the fibres were sectioned into 20–25 mm fibres, mounted, and tested for their mechanical properties. Representative stress–strain curves of wet-spun GO composite fibres at increasing GO loading, exhibit an increase in ultimate strength and Young’s modulus from ca. 20–100 MPa (figures 5(a)–(c)). At low loading (0.2 wt.% GO), there is little improvement in the ultimate strength compared to the PVA control, however, the strain to failure increased from 100% to 150%. For 0.4 wt.% GO-PVA fibres the ultimate strength increased with the presence of GO and exhibited an even larger elongation before failure of 190% which is almost double that of the PVA fibre control (figures 5(a) and (b)). This elongation compared to the neat PVA fibres can be explained by the sliding of GO sheets and the interaction between the PVA and GO sheets and the GO sheets which enables a slight increase in mechanical strength with highly stretchable fibres, which has also been reported previously [52]. GO-PVA fibres with 2 wt.% GO improve in ultimate strength but the strain to failure is similar to the PVA control (figure 5(a)). Interestingly, in line with the rheology and Raman data, there appears to be a transition of the fibre mechanical properties above 2 wt.%, as the strength of the 4 wt.% and 5 wt.% GO-PVA fibres increases substantially compared to the PVA fibres (from 20 MPa to up to 100 MPa) alone. However, the fibres become significantly more brittle with a strain to failure of ca. 1%–2% (figure 5(a)). This increase in strength is explained by the interactions between the GO sheets themselves within the matrix of PVA where the hydroxyl and carboxyl functional groups on the basal planes of GO form strong interactions with the hydroxyl groups of the PVA. Similar mechanical property findings have been discussed in the investigation of GO PVA composite films where they investigated the crystallinity of the films XRD [53, 54]. The Young’s modulus of the higher loading GO fibres saw an increase compared to PVA alone, from ca. 1 GPa to 9 GPa. As stress is proportional to strain following Hooke’s law (within elastic limits), where stress is the restoring force per unit area, and strain is the relative change in the length, the Young’s modulus is the stress equal to the Young’s (elastic) modulus (constant) with strain. Therefore, the Young’s modulus increases with increasing GO content as the relative change in length (strain) reduces and as stress is proportional to strain the Young’s modulus increases in the elastic region. The effect of adsorbing aspirin onto GO and spinning into fibres made a significant difference to the fibre mechanical properties (figure 5(b)), anticipated by the rheological changes observed with the incorporation of aspirin (figure 2(b)). Although still flexible at loadings of GO >4 wt.% (see figure 3(f)), at 5 wt.% GO adsorbed with aspirin, the fibres exhibited an ultimate strength drop from ca. 100 MPa to ca. 45 MPa and a Young’s modulus drop from ca. 9 GPa to 3.5 GPa (figure 5(c)). It is likely that the liquid crystalline properties and therefore strengthening alignment of the GO in the PVA is disrupted by the presence of aspirin due to the π-π stacking between aspirin and GO. Post-processing of the GO fibres, such post-drawing and heating would dramatically increase the mechanical properties as shown previously [51, 55, 56], where PVA-rGO fibres exhibited strengths of ca. 2 GPa and graphene nanoplatelets with PVA fibres, showed strengths of 500–1000 MPa with post-drawing and heating. Post-processing methods could affect the flexibility (of the suture and/or wound dressing) and effectiveness of the loaded therapeutic (i.e. degrading aspirin [57]).
3.3. GO composite fibre aspirin release

To assess the potential therapeutic properties of aspirin adsorbed GO-PVA fibres for therapeutic fabrics, drug elution was monitored over a period of 1 h, 2 h, 3 h and 72 h by UV–Vis GO/PVA fibres (see figure S3 for aspirin release from PVA fibres). The 72 h test was conducted for a low and high loading of GO (0.4 wt.% and 5 wt.% GO respectively). At 1 h and 3 h, aspirin release was detected for all GO fibres with the largest release from the lower GO loadings (figures 6(a) and (b)), which could be explained by the reduced number of π–π interactions between the aspirin and GO. A slower release of aspirin was observed for the higher loadings (5 wt.% GO, 1 mg ml⁻¹ aspirin) in the aspirin-adsorbed GO fibres at 1 h and 3 h. Following this observation, the 0.2 wt.% and 5 wt.% aspirin adsorbed GO fibres were left to elute over 72 h to further ascertain drug release capabilities. After 72 h, aspirin elution was still detected in both cases low and high GO loading fibres (figure 6(c)). This slow-release characteristic of the aspirin over a period of 3 d for adsorbed low loading and high loading GO fibres is encouraging as it demonstrates the potential to produce therapeutic fibres/fabric that can sustain drug delivery over several days with reduced so-called ballistic release (i.e. after 1–3 h) with...
tailorable mechanical properties. The slow release is attributed to the increased numbers of $\pi-\pi$ interactions between aspirin and GO due to the higher loading of GO present in the fibre. Similar slow release findings were recently observed in aspirin-loaded PLA/GO biomimetic scaffolds (with GO loading 2%) \cite{58} where a sustained release of 160 h was recorded and in a Ti/GO aspirin adsorbed system, where they recorded an aspirin elution over a 72 h period due to the $\pi-\pi$ interactions between the GO and aspirin \cite{59}. There is now potential to extend drug molecule types utilising GO as a vector for sustained drug delivery, as demonstrated in a recent work where doxorubicin was adsorbed onto GO as a carrier for cancer treatment \cite{60}.

4. Conclusion

Polyvinyl alcohol with increasing loading of GO, and aspirin adsorbed GO were wet-spun into continuous composite fibres and investigated for their mechanical and drug eluting properties for the potential development of smart textiles for wound dressings and wound sutures. The rheological and spectroscopical properties of the spinning dopes and fibres exhibited a significant change at GO loadings of $>$2 wt.%. With increasing GO loadings, the ultimate strength of the fibres increased by up to five times compared to the polyvinyl alcohol control fibres. At low loadings of GO, the elongation before break of the fibres was almost double. The aspirin adsorbed GO fibres exhibited increased strength compared to polyvinyl alcohol fibres, however the presence of aspirin weakened the fibre. Elution of aspirin from the GO-PVA fibres was sustained for a period of 3 d which demonstrates the potential for these fibres to be further developed into sustained-slow-release fibres for wound dressing fabrics or sutures. The future development of multifunctional smart textiles based on GO is encouraging, as alongside GO’s antimicrobial properties, the possibility of successfully adsorbing therapeutics to the surface and processing into continuous fibres for sustained release, is possible, as demonstrated in this work.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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