Research Article

Enhanced Thermal and Electrical Properties of Polystyrene-Graphene Nanofibers via Electrospinning

Yan Li,1,2 Harshit Porwal,1,2 Zhaohui Huang,3 Han Zhang,1,2 Emiliano Bilotti,1,2 and Ton Peijs1,2

1School of Engineering and Materials Science, Queen Mary University of London, London E1 4NS, UK
2Nanoforce Technology Ltd., Joseph Priestley Building, Mile End Road, London E1 4NS, UK
3School of Materials Science and Technology, China University of Geosciences, Beijing, China

Correspondence should be addressed to Emiliano Bilotti; e.bilotti@qmul.ac.uk and Ton Peijs; t.peijs@qmul.ac.uk

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Polystyrene- (PS-) graphene nanoplatelets (GNP) (0.1, 1, and 10 wt.%) nanofibers were successfully produced via electrospinning of dimethyformamide- (DMF-) stabilized GNP and PS solutions. Morphological analysis of the composite nanofibers confirmed uniform fiber formation and good GNP dispersion/distribution within the PS matrix. The good physical properties of GNP produced by liquid exfoliation were transferred to the PS nanofibers. GNP modified PS nanofibers showed a 6-fold increase in the thermal conductivity and an increase of 7-8 orders of magnitude in electrical conductivity of the nanofibers at 10 wt.% GNP loading.

1. Introduction

Electrospinning can produce nanofibers, from a variety of precursor materials, by the application of electrostatic forces to a jetting polymer solution [1–5]. Adding nanofillers into electrospun polymer solution could improve the nanofibers properties for further applications, especially mechanically reinforced composites [6, 7], conductive membranes for fuel cell applications [8] and thin film batteries [9], due to the mats’ high surface area to volume ratio, large porosity, good mechanical properties, and controllable size [9, 10].

Electrospinning has used to produce nanofibers from a variety of natural/synthetic polymers, such as polyacrylonitrile, polyurethane, polycarbonate, polyvinyl alcohol (PVA), phenolic resin, and polystyrene. Graphene's superb properties (theoretical specific area of ca. 2630 m²·g⁻¹, thermal conductivity of ca. 5000 W·m⁻¹·K⁻¹, intrinsic mobility of 2 × 10^5 cm²·s⁻¹·V⁻¹, high Young's modulus of ca. 1.0 TPa, and strength of ~130 GPa [11]) have the potential for replacing other commercial nanofillers like carbon nanotubes [12] as multifunctional filler in electrospun polymer fibers. GNP offers an alternative due to its physical and chemical properties, easy processability, and potential low cost [13]. Few studies have actually examined the possibility of using graphene derivatives as reinforcement in polymer nanofibers. Bao et al. [14] reported poly vinyl acetate-graphene oxide (GO) electrospun nanocomposites where GO was mainly used to improve the optical properties. Das et al. [1] reported electrospun PVA nanofibers loaded with functionalized graphene with increased thermal stability and crystallinity. Kim et al. reported silica/carbon nanofiber (CNF) composites prepared from a graphene/polyacrylonitrile (PAN) solution using electrospinning [2].

Electrospinning of polystyrene nanofiber has been reported before [15–18]. However, defects such as beads or necklace-like fibers were often concomitant with the electrospinning process, which adversely affects the reproducibility of the process and the homogeneity of the resultant nanofiber fabrics. In the present work, GNPs produced from liquid phase exfoliation with controlled size were used to prepare electrospun PS-GNP composite nanofibers. The critical electrospinning parameters which affect the morphology and properties of the PS-GNP composite nanofibers were optimized and thermal and electrical properties measured.
Table 1: Composition of the electrospinning solutions.

<table>
<thead>
<tr>
<th>GNP wt.% in PS</th>
<th>PS (g)</th>
<th>DMF (g)</th>
<th>GNP (g)</th>
<th>Solution A</th>
<th>Solution B</th>
<th>Solution for electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>40</td>
<td>0</td>
<td>PS (10 g) + DMF (40 g)</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>0.1 wt.%</td>
<td>10</td>
<td>40</td>
<td>0.01</td>
<td>PS (10 g) + DMF (30 g)</td>
<td>GNP (0.01 g) + DMF (10 g)</td>
<td>Mix A + B</td>
</tr>
<tr>
<td>1 wt.%</td>
<td>10</td>
<td>40</td>
<td>0.101</td>
<td>PS (10 g) + DMF (30 g)</td>
<td>GNP (0.101 g) + DMF (10 g)</td>
<td>Mix A + B</td>
</tr>
<tr>
<td>10 wt.%</td>
<td>10</td>
<td>40</td>
<td>1.11</td>
<td>PS (10 g) + DMF (30 g)</td>
<td>GNP (1.11 g) + DMF (10 g)</td>
<td>Mix A + B</td>
</tr>
</tbody>
</table>

2. Experimental

Natural graphite (NG) was purchased from Alfa Aesar (product number 43319). N-Methyl-2-pyrrolidone (NMP) (C$_5$H$_9$NO, $M_w$: 99.13 g/mol); dimethylformamide (DMF) (C$_3$H$_7$NO, $M_w$: 73.09 g/mol) solvents and polystyrene (product number 331651, $M_w$: 35,000 g/mol) were purchased from Sigma-Aldrich and used as received. Tetrabutylammonium bromide (TBAB) (C$_{16}$H$_{35}$BrN, $M_w$: 322.37 g/mol) salt was purchased from Bio Basic Inc., which was used to improve the conductivity of the PS/DMF solution in order to improve spinnability.

2.1. GNP and PS-GNP/DMF Solutions. GNP was manufactured according to the method described in [19] via ultrasonication of natural graphite in NMP using an ultrasonic probe (Model GEX 750, 750 W, 20 kHz, Amplitude at 20%, continuous power). The resultant dispersion was then centrifuged (CF) using a Hettich Mikro 22R centrifuge for 45 min at 500 rpm to remove nonexfoliated graphite from the GNP suspension. The prepared GNP suspension was filtered and redispersed in DMF. It should be noted that NMP was used for exfoliation of GNP, while DMF was used for processing of nanofibers because of the lower boiling point. PS solutions (20% w/w) were prepared by dissolving PS in DMF with and without the addition of salt (tetrabutylammonium bromide (TBAB), 0.02% w/v). PS-GNP (0.1, 1, and 10 wt.%) composite solutions were prepared by mixing PS/DMF solution and GNP/DMF dispersions (see Table 1). A reference sample was prepared by electrospinning PS/DMF solution without GNP.

2.2. Electrospinning. Electrospinning schematic set-up of this work is illustrated in Figure 1. PS/DMF and PS-GNP (0.1, 1, and 10 wt.%)/DMF solutions were placed in a syringe connected with a metal needle that was controlled by a syringe pump (KD Scientific, Model 780200) at a constant flow rate of 1.0 mL/hr, with an injection volume of 100 μL. A high voltage power supply (Gamma High Voltage Supply, Model ES30-0.1P) was used to generate a potential difference of 20 kV between the needle tip and the collector (a static aluminium foil) grounded target placed 15 cm from the tip of the needle. All the experiments (Table 2) were carried out at 25°C and a relative humidity of ca. 40%.

2.3. Characterizations. Scanning electron microscopy (SEM, FEI, Inspector-F) was conducted to assess the morphology of the graphite, exfoliated GNP, and electrospun PS and PS-GNP nanofibers. Transmission Electron Microscopy (TEM, JOEL JEM-2010) was utilized to see the morphology and the dispersion of GNP in the PS-GNP nanofibers. Raman spectroscopy (Nicolet Almega XR) was utilized to characterize natural graphite, exfoliated GNP, and nanofiber. Low
Table 2: GNP concentrations in PS and parameters of electrospinning process.

<table>
<thead>
<tr>
<th>GNP in PS (wt.%)</th>
<th>Voltage (kV)</th>
<th>Tip-target distance (cm)</th>
<th>Flow rate (mL/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10/15/20</td>
<td>10/15/20/30</td>
<td>0.2/0.5/1.0</td>
</tr>
<tr>
<td>Optimized parameters</td>
<td>0.1/1.0/10</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

![SEM images of (a) graphite, (b) GNP, (c) TEM image of exfoliated GNP, and (d) Raman spectra of graphite and GNP.](image)

3. Results and Discussion

Length (l), width (w), and thickness (t) of the natural graphite flakes were approximately 800, 600, and 26 μm, respectively (Figure 2(a)). After exfoliation, the average length and width of the exfoliated GNP were 1.1 ± 0.4 μm (Figure 2(b)), while the thickness was ~2 nm (aspect ratio ~500). The edges of graphene sheets (Figure 2(c)) indicated that single-layer graphene and few-layer graphene were obtained after liquid phase exfoliation. Raman spectra (Figure 2(d)) confirmed the peaks of graphite and exfoliated graphene.

Please refer to Supplementary Material available online at [http://dx.doi.org/10.1155/2016/4624976](http://dx.doi.org/10.1155/2016/4624976) for Raman data on nanofibers, showing typical spectra with D, G, and 2D peaks.

In order to obtain consistent, bead-free nanofibers, electrospinning parameters and solution formulation were optimized. A series of preliminary experiments were performed to study the effect of flow rate, applied voltage, and tip-target distance on fiber formation (Table 2). Finally, bead-free PS-GNP composite fibers were obtained after achieving optimal conditions for the electrospinning process. Bead formation was decreased with increasing flow rate at a fixed voltage of 20 kV. A flow rate of 1.0 mL/hr resulted in good quality nanofibers free of beads defects. In the case of electrospun PS fibers (20 wt.% PS in DMF) without TBAB (Figures 3(a1), 3(a2), and 3(a3)), the average diameter of the fibers was slightly larger because of the relatively higher PS concentration and hence viscosity of the spinning solution but also as a consequence of lower ionic conductivity. The effects of the
Figure 3: SEM images of nanofibers without and with TBAB and statistics of the diameters of nanofibers with TBAB.
viscosity and the ionic conductivity of the spinning solution have been extensively reported in the literature. In terms of viscosity, it has been observed that there is an optimal spinning window, usually between \(\sim 1\) and 200 poises [22]. Beaded PS fiber structures have been observed for lower viscosities, while bead-free PS fibers have been observed for higher viscosities [23]. For even more extreme (low or high) viscosities, spinning of continuous fibers is completely inhibited [16, 24, 25].

The increase in the solution ionic conductivity usually results in improvement in electrospinning production with bead-free, uniform, and thinner fibers, caused effectively by a stronger elongation force and higher draw-down due to the increased charge density of the ejected jet [18, 26, 27]. Conductivity of solution mainly depends on polymer type, solvent used, and the availability of ionisable additives like salts. Low conductivity of the solution will result in elongation of the jet insufficient to produce uniform fiber under electrostatic forces; in this case, beads may also be observed. However, too high conductivities are extremely unstable in presence of strong electric fields resulting in a dramatic bending instability as well as a broad diameter distribution [28]. Slight changes in solution conductivity can result in significant morphological variations in electrospun fibers [27] as also noticed in our study (Figures 3(b1), 3(b2), and 3(b3)).

The addition of TBAB to the PS solution significantly improved the electrospinning process, changing the morphology from bead on-string structure to continuous and homogeneous fiber structure and leading to a smaller fiber diameter and narrower fiber diameter distribution [26, 27]. This is in agreement with previous published papers [27, 29, 30]. Uyar and Besenbacher [27] produced uniform PS fibers from DMF solutions with the addition of TBAB salt and revealed that bead-free fibers were obtained when the conductivity of PS solution is 150–180 \(\mu S/cm\). Nitanan et al. [26] revealed that an excessively high amount of TBAB (0.5 and 1.0% w/v) could result in the clogging of PS solution at capillary tip.

PS-GNP (10 wt.%) without TBAB also resulted in good quality nanofiber without bead formation (Figure 3(a3)). The diameter of the nanofibers decreased with addition of GNP (Figure 3(c); please refer to Supplementary Material for more SEM images about nanofibers). The average diameters of PS and PS-GNP nanofibers (0.1, 1, and 10 wt.%) with TBAB was 680 ± 220, 620 ± 190, 580 ± 180, and 500 ± 150 nm, respectively. The textural morphology of the GNP-loaded fibers was different from that of the neat PS fibers (i.e., rougher and uneven surface) (Figures 3(c1) and 3(c2)). The addition of an appropriate amount of GNPs can be beneficial to shifting the electrical conductivity and the viscosity of the spinning solution toward the respective optimal windows (i.e., optimal conductivity of PS solution \(\leq 550 \mu S/cm\) [26]) and viscosity between \(\sim 1\) to 200 poises [22].

Also, TEM analysis showed similar results. The diameter of the PS/GNP nanofibers was smaller compared to the neat PS nanofibers (Figure 4). The surface roughness of the nanofibers increased with addition of GNP, although GNP was well dispersed and distributed in the PS matrix without aggregation. The surface morphology of the nanofibers changed from relatively smooth to mostly rough. Some nanofiber surfaces showed graphene layers (inset in Figure 4(b3)).

It is noted that the total amount of the solvent used throughout the present work was the same, regardless of the addition of GNPs. With the addition of GNPs, the effective concentration of PS is slightly reduced and the conductivity of PS-GNP/DMF increased [26]. This might explain the reduction of the fiber diameter with addition of GNP. This is in agreement with a previous publication [31].

Once the electrospinning process has been optimized, the effect of GNP in the thermal and electrical conductivity of PS nanofibers is studied. Figure 5(a) compares the thermal conductivity of PS-GNP nanofibers with other electrospun mats.
containing carbonaceous fillers and other similar systems [32–34]. Thermal conductivity substantially increased upon the addition of GNP, up to a 630% increase corresponding to 10 wt.% GNP loading, in line with best results published in the scientific literature (Figure 5(a)).

Figure 5(b) compares the electrical conductivity values of PS-GNP nanofibers with other electrospun mats containing carbonaceous fillers [31, 34–42]. The electrical conductivity of PS/GNP nanofibers increased suddenly corresponding to a GNP content below 1 wt.% reaching 1.4±0.6 S/m for 10 wt.% GNP loading. This is an electrical conductivity of 7-8 orders of magnitude higher than pure PS nanofiber mats.

GNP has proven to be an excellent choice as multifunctional nanofiller, showing great promise in improving both electrical and thermal properties. Hence, the produced ultrafine GNP nanofibers mats could be promising materials for applications in electrodes, conductive wires, and smart fabrics.

4. Conclusions

GNPs were produced using liquid phase exfoliation method and PS-GNP composite nanofibers (0.1, 1, and 10.0 wt.%) were produced via electrospinning of DMF solutions. After optimization of processing parameters, GNP was successfully and homogeneously incorporated within the PS nanofibers. It was found that the addition of GNP leads to a decrease in fiber diameter and increased surface roughness of the nanofibers. Significant improvements in both thermal (6-fold increase) and electrical conductivities (7-8 orders of magnitude) were achieved with the incorporation of up to 10 wt.% GNP.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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