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Reinforcement in melt-processed polymer–graphene composites at extremely low graphene loading level

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ABSTRACT

We have prepared polymer nanocomposites reinforced with exfoliated graphene layers solely via melt blending. For this study polyethylene terephthalate (PET) was chosen as the polymer matrix due to its myriad of current and potential applications. PET and PET/graphene nanocomposites were melt compounded on an internal mixer and the resulting materials were compression molded into films. Transmission electron microscopy and scanning electron microscopy revealed that the graphene flakes were randomly orientated and well dispersed inside the polymer matrix. The PET/graphene nanocomposites were found to be characterized by superior mechanical properties as opposed to the neat PET. Thus, at a nanofiller load as low as 0.07 wt%, the novel materials presented an increase in the elastic modulus higher than 10% and an enhancement in the tensile strength of more than 40% compared to pristine PET. The improvements in the tensile strength were directly correlated to changes in elongation at break and indirectly correlated to the fracture initiation area. The enhancements observed in the mechanical properties of polymer/graphene nanocomposites achieved at low exfoliated graphene loadings and manufactured exclusively via melt mixing may open the door to industrial manufacturing of economical novel materials with superior stiffness, strength and ductility.

1. Introduction

Among its other superlative properties [1–3], graphene is the strongest material known to man [4]. As a result, it has long been known that graphene has the potential to be a superlative filler in reinforced composites. To this end, much work has studied the effect of graphene on the mechanical properties of polymer matrices [5]. Although, such research has progressed in many directions, two of the most common aims are either to produce high-performance composites such as high-strength, polymer–graphene fibers or to achieve modest levels of reinforcement but at very low graphene loading

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levels. The latter goal is important for a number of applications such as in hierarchical composites, where the main reinforcement is due to relatively large fillers such as carbon fibers. However, achieving relatively small increases in stiffness and strength of the matrix by adding a nano-filler can lead to non-trivial increases in the ultimate composite properties. This should be achieved at very low loading levels, both for reasons of cost and to avoid significantly altering other matrix properties.

Typically, polymer/graphene nanocomposites have been manufactured using covalently or non-covalently modified graphene via in situ polymerization, solution blending or melt compounding or by a combination of these manufacturing techniques. This work has been extensively reported in articles and in literature reviews [5–9]. From an industrial point of view, melt blending is the only practical approach as it does not make use of high quantities of solvents nor does it require the development of a dedicated line in a polymer manufacturing facility. However, to date, relatively few papers have been published on polymer/graphene nanocomposites manufactured solely via melt processing, i.e. without a solution-processing step to the composite formation procedure [10–14]. None of these papers have shown significant degrees of reinforcement at very low volume fraction (<0.1%). In this paper, we report the fabrication of polymer/graphene nanocomposites via melt compounding, using pristine graphene layers at weight fractions lower than 0.1 wt%. The polymer matrix used in this study was polyethylene terephthalate (PET), a choice which was made for a number of reasons. Firstly, previous work has shown that graphene can be used to effectively reinforce PET [15]. In addition, PET is widely used in applications where mechanical properties are relevant and so reinforcement of PET could prove highly useful. Also, the structure of PET and previous research on graphene and PET [15] leads us to expect reasonable interactions between the graphene and the polymer matrix, for example between the graphene surface and the aromatic groups present on the PET chains [16]. We find that by dispersing extremely low volume fractions of exfoliated graphene into the polyethylene terephthalate matrix via melt blending, materials with significantly improved mechanical properties are formed. This approach is simple and compatible with industrial processes and paves the way to using exfoliated graphene layers at an industrial scale. Interestingly, the reinforcement mechanism is distinct from that normally found in nanocomposites and is associated with modifications to the fracture process due to the presence of graphene.

2. Methods

Graphite was purchased from Sigma Aldrich Ltd. (product code 332461). The exfoliated graphene layers have been manufactured, in house, using liquid exfoliation in the solvent N-methyl-pyrrolidone (NMP) [17–19]. Basically, powdered graphite was shear mixed in the solvent NMP at an initial concentration of 100 g L^{-1}. The shear mixing was performed on a Silverson Mixer using a 32 mm rotor for 90 min at a speed of 6000 rpm and a batch volume of 2.5 L according to a procedure previously reported in literature [19]. The solvent was removed by filtering the shear mixed dispersion through lab paper using a Buchner funnel. The resulting powder was dried at 60 °C overnight in a vacuum oven.

Polyethylene terephthalate was purchased from Goodfellow Cambridge Ltd. (product code ES306310). PET and PET/graphene nanocomposites with a load varying from 0.01 wt% to 0.1 wt% were prepared by melt compounding, on a Brabender melt mixer, at a temperature of 260 °C. The melt mixing was performed by adding approximately half of the polymer quantity to the mixing bowl. Once the torque started to increase finely grinded graphene powder was added to the mixing bowl. When the polymer melted and the torque started to diminish, the remaining polymer was gradually added to the mixer. For all the materials the melt compounding was performed at an initial screw speed of 50 rpm for 4 min, then the screw speed was increased to 80 rpm within 1 min and the melt mixing was conducted at this speed for another 5 min.

The materials obtained via melt compounding were compression molded at 280 °C on an electrically heated hydraulic press. The samples were then cut into stripes with the following dimensions 50 mm × 10 mm × 0.5 mm (L × w × t). Mechanical characterization was conducted on a Zwick Tensile Tester using a load cell of 2.5 kN, a gauge length of 20 mm and a speed of 5 mm min^{-1}. For all materials, 5 strips were mechanically tested.

Transmission electron microscopy (TEM) was performed on a TECNAI G2 20 Twin electron microscope in bright field mode at 200 kV. The sections were prepared using a Leica EM UC6 ultramicrotome cutter with a cryo-chamber (EM FC6). The cutting was performed at a temperature of −40 °C and a speed of 0.40 mm s^{-1}. The thin sections were placed on 200 mesh copper grids.

Scanning electron microscopy (SEM) was performed on tensile fractured surfaces using a Zeiss Ultra or a Zeiss Supra scanning electron microscope at a voltage of 5.0 kV or 15.0 kV, respectively. Prior to being analyzed the samples were mounted on stubs and their surfaces were platinum coated.

Helium ion microscopy (HeIM) was carried on a Zeiss Orion Plus – helium ion microscope. The tensile fractured surfaces were mounted on stubs. No coating was necessary in this case.

3. Results and discussion

As described in the experimental section, the graphene powder was produced by liquid exfoliation [17–19]. This process is ideal in this case as it is known to produce graphene which is largely defect free [17,20]. TEM analysis (Fig. 1A and B) showed the graphene flakes produced by this method to be of good quality with mean lateral size and thickness of ~500 nm and ~5–6 layers, respectively. We note that we do not achieve very high monolayer content. However, this is not a disadvantage: previous work has shown few-layer graphene to be a more effective reinforcing material than monolayer graphene [21]. To facilitate composite formation by melt processing, the exfoliated graphene was separated from the solvent to give a dry, weakly bound, reaggregated powder. Such powders are known to be very easy to re-exfoliate [22,23].