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Micromechanics of reinforcement of a graphene-based thermoplastic elastomer nanocomposite

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ABSTRACT

In this work, a series of graphene-reinforced thermoplastic elastomers were prepared, with the introduction of graphene nanoplatelets (GNPs) of different particle diameter. Their microstructures were characterised by scanning electron microscopy (SEM) and quantified by polarised Raman spectroscopy. The GNPs were well-dispersed and their orientation across the cross-section of the injection moulded samples was consistent with the shear rate profile of fountain flow mechanism. The mechanical properties of the nanocomposites were evaluated by tensile testing and it was found that the GNPs contributed to significant improvements in both the stiffness and strength. A micromechanical model based on the combination of shear-lag theory and the rule-of-mixtures was introduced to analyse the stiffening mechanisms. The effective aspect ratio of GNPs was in the order of 100 and decreased with increasing filler loading due to agglomeration. Finally, the stress transfer efficiency from the matrix to GNPs was evaluated by observing the Raman band shifts under tension.

1. Introduction

Thermoplastic elastomers (TPEs) based on thermoplastic vulcanizate blends are considered an interesting class of materials since they combine the melt processability of thermoplastics with the properties of conventional thermoset rubbers [1]. The TPEs usually have excellent weatherability, ozone resistance, chemical resistance to oils and abrasion resistance; however, their applications are limited by their relatively poor mechanical properties [2]. In this context, inorganic fillers have been incorporated within the TPEs and enhancements in their mechanical performances have been reported in the literature [3–7]. More recently, since the isolation of monolayer graphene [8] and the discovery of its unique properties, graphene and graphene-related nanomaterials have been employed extensively as reinforcement in elastomers [9].

It has been reported previously that although the intrinsic Young's modulus of monolayer graphene has been found to be very high (~1 TPa) [10,11], it cannot be fully utilized in bulk nanocomposites, especially in soft materials such as elastomers due to inefficient stress transfer from the low modulus matrix to the high modulus filler by shear at the filler/matrix interface [9,12–17]. In addition, we showed recently that classical micromechanics can be applied for the study of the mechanisms of stress transfer in polymeric matrices with varying stiffness and a theory was developed, which can predict the modulus of bulk nanocomposites based on the characteristics of the nanoplatelets [15,17]. The reinforcing mechanism of elastomers reinforced by graphene is different from that of stiff polymers: the normalized modulus of an elastomer/graphene nanocomposite is dependent upon the graphene orientation, the aspect ratio and volume fraction of the filler, while it is independent of the filler modulus [17]. This result suggests that the filler geometry and the processing methods (which in turn affect the nanoscale filler distribution [9,18]) will eventually determine the mechanical properties of the elastomeric nanocomposites.

In the present work, we have undertaken a comprehensive study of the mechanisms of reinforcement of a TPE by GNPs. The composite samples based on a thermoplastic elastomer (Alcryn®) and GNPs with three different flake sizes were prepared by melt mixing. The microstructure of the injection moulded specimens was studied by quantifying the orientation factor of the fillers with polarised Raman spectroscopy. The mechanical properties of the nanocomposites with different filler loadings were evaluated by tensile testing followed by stress transfer measurements by observing the 2D Raman band shifts of the fillers during *in situ* deformation. Moreover, we applied our recently developed theory [17] to the experimental results from tensile testing and correlated the fittings with important geometrical characteristics of the filler, such as the effective aspect ratio. Through the experimental and theoretical analysis, we can conclude that the enhancement of thermoplastic elastomers with graphene nanoplatelets is effective, and gives considerable potential to develop high-performance engineering plastics, with tuned, application-specific properties.

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2. Experimental methods

2.1. Materials and preparation

Graphene nanoplatelets (GNPs) with nominal lateral diameters of 5, 10, 25 μm (dimensions claimed by the supplier) and average thicknesses in the range of 6–8 nm were purchased from XG Sciences, Inc. Lansing, Michigan, USA and used as received. Three grades of xGnP® M5, M15 and M25 were used. The thermoplastic elastomer, Alcryn® 2265 UT (Unfilled Translucent), which is based on a partially cross-linked chlorinated olefin interpolymer alloy, was purchased from A. Schulman, Inc.

The melt mixing of the composites was undertaken in a Thermo Fisher HAAKE Rheomix internal mixer. The mixing took place at 165 °C and 50 rpm for 5 min. The GNP fractions in the nanocomposites were 1%, 5%, 10%, and 20% by weight. The Alcryn nanocomposites in this study are coded based on the type of the matrix, the diameter and weight content of the fillers. For example, the sample code 2265-M15-GNP10, means that the matrix is the Alcryn 2265, the diameter of the GNPs is 15 μm and the weight percentage of the filler is 10 wt%.

The dumbbell-shaped tensile specimens were prepared by injection moulding in a HAAKE Minijet Piston Injection Moulding System. The temperatures of the barrel and the mould were set as 185 °C and 30 °C. The injection pressures were 500 bar, 550 bar, 600 bar, 700 bar and 800 bar for the neat polymer and the nanocomposites filled with 1 wt%, 5 wt%, 10 wt% and 20 wt% of GNPs, respectively. The injection pressure was held for 10 s followed by post-injection pressure of 200 bar, held for 5 s, for all specimens.

2.2. Characterisation of the nanocomposites

The actual loadings of GNPs in the nanocomposites were obtained by thermogravimetric analysis (TGA) using a TA Q500 TGA instrument. The samples were heated from room temperature up to 600 °C under a 50 mL/min flow of N_2 at 10 °C/min. Three samples were tested for each material in order to ensure reproducibility of the results.

The morphologies of the fillers, neat polymer and the microstructure of the nanocomposites were examined using scanning electron microscopy (SEM). The samples (GNP powders and cryo-fractured dumbbells) were placed on conductive carbon tapes, which were stuck on aluminium stubs. Subsequently, the coating process was carried out using Au-Pd alloy in order to provide satisfactory conductivity to the samples. The images were acquired using a high-resolution XL30 Field Emission Gun Scanning Electron Microscope (FEGSEM) at 6 kV.

The XRD diffractograms were obtained from a PANalytical X'Pert3 diffractometer with Cu Kα radiation. The 2-theta angle range was selected from 5° to 90° with a step size of 0.03° and a step time of 180 s operated at 40 kV and 40 mA.

Stress–strain curves were obtained using dumbbell-shaped specimens in an Instron 4301 machine, under a tensile rate of 50 mm·min^{-1} with a load cell of 5 kN.

Raman spectra were obtained using a Renishaw InVia Raman spectrometer with a laser wavelength of 633 nm and an objective of 50×, which produces a spot size of 1–2 μm. The Raman 2D band shift of the injection moulded samples (gauge length ~55 mm) was studied following the application of strain on the nanocomposites with the highest loading of GNPs (20 wt%). The tests were carried out using a mini-tensile rig. The strain was determined by measuring the extension of the two grips with a digital caliper. The Raman laser spot was in the order of 1–2 μm and it was focused on the same point of a single flake on each sample surface. The results were based on 5 composite samples for each type of GNPs, at the highest loading. All the spectra were fitted with a single Lorentzian curve.

The spatial orientation of the GNPs in the composites was determined using the method reported in previous studies from our group [13,14,19]. The equipment employed was a 514 nm Raman spectrometer by Renishaw with 'VV' (vertical-vertical) polarisation, in which the incident and scattered radiation were polarised in the same direction. In the test, the laser was aligned perpendicular to the surface of the materials either along X or Z axis, as shown in Fig. S1-Supplementary Material. The Raman G bands were recorded as a function of rotation angle (Φ_X, Φ_Z) and the rotation angles were used to estimate the orientation distribution function (ODF) [14,19]. Regarding the X-axis tests, the orientation factor may vary throughout different regions, since the samples were injection moulded [20]. Hence, the tests were carried out on a number of regions across the cryo-fractured cross-sections of the samples (red dash lines in Fig. S1) to give the variation of the orientation parameter values.

3. Results

3.1. Characterisation of the filler and matrix

The three types of GNPs were examined by scanning electron microscopy as shown in Fig. S2(a–c). It can be seen that the flake size increases from M5 to M15 to M25. However, the M15 and M25 GNPs batches seem to include a number of smaller flakes, which will decrease the average lateral size quoted by the manufacturer. Another important observation is that folded and looped structures can be found particularly in larger flake samples (Fig. S2(d and e)). Overall, the three types of fillers display the stacked and agglomerated structure of many-layer graphene. The cryo-fractured cross-section of the neat elastomer can be also seen in Fig. S2(f). Two distinct morphologies can be observed, revealing the two components in the matrix and indicating that the polymer blend is not completely miscible, as expected from earlier reports [1].

The Raman spectra of the GNPs are shown in Fig. S3(a). The G (~1580 cm^{-1}) and 2D bands (~2680 cm^{-1}) are well defined for all types of the nanoplatelets, consistent with the signature of graphitic structures. The 2D bands are broad and asymmetric suggesting that the nanoplatelets consist of many layers of graphene [11,21,22]. Moreover, broad and weak D bands can be observed at ~1360 cm^{-1} which is an indication of defects that are present in the structure. The XRD patterns of GNPs are also shown in Fig. S3(b), which display the sharp and strong peaks at $2\theta \approx 26°$ consistent with reflections from the (0 0 2) plane of graphite, while weak peaks can be seen at $2\theta \approx 42.1$, 44.3 and 54.4° corresponding to reflections from (1 0 0), (0 1 0) and (0 0 4) planes, respectively.

3.2. Characterisation of the composites

Thermogravimetric analysis was employed initially to determine the actual volume fractions of the fillers after the preparation procedure. The mass residue and volume fractions of the filler in the prepared composites are given in Table S1. It can be seen that the final mass fractions were very close to the nominal mass fractions of the nanocomposites.

The cross-sectional surfaces of cryo-fractured dumbbell samples were investigated by SEM as shown in Fig. 1. The low magnification images of the composites with highest loading (20 wt%) Fig. 1(a–c) indicate that a uniform distribution of the fillers was achieved even at high filler contents. The observation of different regions of the cross-section reveals a distinct alignment of the fillers, which was induced by the shear rate distribution during the injection moulding procedure, known as the fountain flow mechanism [20,23]. The orientation of nanoplatelets due to the fountain flow mechanism in the case of our samples can be seen in Fig. S4. There are regions within the samples with different degrees of orientation of the fillers, due to the variation of shear rate generated by the combination of the injection pressure and the slightly lower temperature of the mould walls [20,23].

The high magnification SEM images (Fig. 1(d–f)) demonstrate the morphologies of the individual flakes within the matrix. Generally, the