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Enhancing the electrical conductivity of polymer composites

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ABSTRACT

An effective approach to reduce inter-particle gaps by nanofillers for making highly conductive polymer composites was reported based on the conductive tunnelling mechanism. A low percentage of nanosized conductive carbon filler (carbon black and graphite) or ions (Li^+, Na^+ and K^+) was filled into the tunnelling phase of expanded graphite (EG) sheets, by which electron transport was enhanced across the junctions of EG sheets and a significant increase in the electrical conductivity of the composites was achieved. In this report, polyethylene (PE) and polyethersulphone (PES) were selected as model materials. The results indicated that for the EG/PE composite the conductive peculation threshold was less than 2 wt% and its conductivity increased three orders of magnitude with the addition of only 1 wt% nanofiller compared with the EG/PE composite. By introducing a very small amount of Li^+ or Na^+ (0.06 wt% related to EG) the electrical conductivity was further enhanced by two orders of magnitude compared to the EG/PES composite. Experimental results were well understood by the theoretical study of the electron transport behaviour in the EG/polymer composites. The gaps between graphite sheets in the matrix must be no larger than 10 nm if the EG/PE composite is to become electrically conductive.

1. Introduction

Electrically conductive polymer composites have been widely applied in anti-static materials [1], electromagnetic interference (EMI) shielding [2], chemical sensor [3], bipolar plates for fuel cells [4], etc. Conventionally, the conductive composites are fabricated by blending micro-sized conductive fillers with polymers. According to the literature [5], anti-static and EMI shielding applications generally require electrical conductivity of at least 10^{-7} S/m and 10^{1} S/m, respectively. Bipolar plate application demands an even higher electrical conductivity of up to 10^4 S/m [6]. The conductive behaviour of the composites can be understood by the percolation theory, which states that the insulating-to-conductive transition of such composites results from the formation of conductive pathways by the conductive fillers. The critical amount of fillers required for such transition is defined as the percolation threshold. Adding more filler is the standard method of achieving desirable electrical conductivity. It was reported that 75 vol% of micro-sized graphite was needed to produce the epoxy-based electrical conductive composite with a conductivity of 10^4 S/m for bipolar plate application [7]. However, high loading of the fillers has seriously negative impact on manufacturability, mechanical integrity and costs of the conductive composites. It has been found that the flexural strength of the epoxy-based conductive composites decreased by ~50% when the loading of graphite increased from 60 vol% to 75 vol% and that when the loading exceeded 75 vol% it was difficult for the epoxy resin to hold up the graphite [7]. According to the percolation theory [8], the loading of the fillers can be lowered by using fillers with high aspect ratio and intrinsic conductivity. It is therefore strongly expected that 1D and 2D nanosized fillers can do a better job than micro-sized fillers as carbon nanotubes (CNTs) and graphene are well-known super conductors with high aspect ratio. With proper dispersion, the percolation threshold for CNT or graphene-based nanocomposites has been reported to be as low as less than 1 wt% [9–11].

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However, the challenge in the field of electrical conductive composites goes beyond lowering the percolation threshold. It has been found that following percolation conductivity generally remains constant despite further increases in the loading of the fillers, whether in the case of micro- or nano-filled conductive composites. For instance, the maximum conductivity of MWCNT/polyethylene nanocomposites remained at the level of 10^1 S/m as the CNT loading increased beyond 10 wt%. High-level loading of MWCNT also resulted in substantial sacrifice in the mechanical integrity of the polyethylene matrix: its ultimate stress and elongation was decreased by ~40% and ~75%, respectively, as 10 wt% MWCNT was loaded [12]. It is believed that an alternative way should be explored to increase the maximum conductivity of the conductive composites. Generally, the published results have indicated that the maximum achieved conductivity of the conductive composites are commonly 2–4 orders of magnitude lower than the intrinsic conductivity of the nanofillers [13]. According to our previous theoretical investigation, this significant loss is attributable to the contact resistance between fillers and tunnelling resistance resulting from the settlement of polymer chains between the junctions of the conductive network [14]. It follows that effective reduction of these resistances seems to be the way to make the conductive fillers work more efficiently. Practically, it is a promising way to reduce the loading of the fillers. In this communication, we report on a simple strategy to reduce the contact and tunnelling resistances by using hybrid fillers. The results point to a promising application of the strategy in the manufacturing of electrical conductive composites.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE, BS 2581) was supplied by Borealis, Austria. Polyethersulphone (PES), molecular weight about 10,000 was obtained from Cytec Engineered Materials Limited (UK). Expandable graphite (particle size: ~300 μm) was supplied by Qing Dao Graphite Company (China). Expanded graphite (EG) was prepared by subjecting expandable graphite flakes to a preheated furnace at a temperature of 850 °C for 2 min. Ultrafine grinding graphite (UF_4) (particle size: 4–7 μm) was received from Graphite Kropfmühl AG, Germany. Carbon black powder (CB1) with particle size about 50 μm (SEM result) (considered as non-nanofiller) was purchase from Sigma Aldrich, UK. Ultrafine carbon black powder (CB2) with particle size about 26 nm (SEM result) (considered as nanofiller) was supplied by Cobalt, Belgium. Lithium chloride (LiCl), sodium chloride (NaCl) and potassium chloride (KCl) were purchased from Sigma Aldrich Company (UK). N,N-dimethylformamide (DMF), were purchased from Fisher Scientific Company (UK).

2.2. Preparation of expanded graphite/polyethylene or carbon-based hybrid filler/polyethylene composites

Expanded graphite (EG)/polyethylene (PE) composites were prepared by melt the compounding method. The EG filler was mixed with high density PE (HDPE) using Kaake (Pheomix 600, Germany) with a screw speed of 600 rpm at a temperature of 180 °C for 10 min. Then the specimens were prepared by compression moulding at 180 °C.

2.3. Preparation of expanded graphite/polyethersulphone and expanded graphite/ion/polyethersulphone composites

EG/PES and EG/ion/polyethersulphone (PES) composites were fabricated by solution method. PES, EG with 5 wt% (related to PES) and a small amount of LiCl were dissolved in DMF (80 wt% related to PES), and then were heated and maintained at a temperature of 50 °C with stirring using a stirrer hot plate for 24 h. After that the solvent was separated by adding methanol into the solution and stirring for 15 min at room temperature. The resulting materials were dried in a vacuum oven at 155 °C. Then, the composites were press moulded (240 °C, 0.25 MPa) between heated metal plates with lined aluminium foils into sheet form with a thickness of about 0.3 mm. For comparison of conductivity composites with (NaCl) and (KCl), respectively, were also prepared.

2.4. Characterization

Four-Wired Digital Multimeter Model Solartron 7150 was used to measure electrical volume resistances of samples and silver paint as an electrode material. The measurements were conducted at room temperature. The volume resistivity, ρ_v, can be derived from the following equation [15]:

$$\rho_v = (A/t)R_v \tag{1}$$

where A is the effective area of the measuring electrode, cm^2; t the average thickness of the specimen, cm; and R_v is the measured volume resistance, kΩ.

The reciprocal of the volume resistivity is the volume conductivity.

The morphology and the dispersion of filler in the matrix was observed on a field emission gun scanning electron microscopy (FEGSEM) LEO 1530VP instrument (LEO Electron Microscopy Ltd., Oberkochen, Germany), at an accelerated voltage of 5 kV. The samples were freeze fractured in liquid nitrogen; the fracture surfaces were coated with a thin platinum layer; the samples were mounted on aluminium holder with the fracture surface on the top.

3. Results and discussion

Graphite has been widely used to improve the electrical conductivity of polymer composites. In order for PE composites with an insulating matrix to be electrically conductive, a percolation threshold has to be achieved at a lower amount of graphite when graphite with a high aspect ratio is employed. Table 1 shows the variation of volume electrical conductive behaviour of EG/PE and UF_4/PE composites, as measured at room temperature by the four-wired resistance measurement method. It can be seen that electrical percolation threshold is the critical loading of the filler leading to the conductive network formed in the