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Electrical conductivity of ion-doped graphite/polyethersulphone composites

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ABSTRACT

The electrical conductivity of polyethersulphone (PES) insulating polymer was improved by incorporation of electrically conductive graphite and ions. An initial conducting pathway of the PES/graphite composites was formed at lower than 3 wt.% of the filler content. LiCl was found to be an effective dopant for the improvement of the electrical conductivities of the PES/graphite composites. By doping with 0.06 wt.% of LiCl the electrical conductivity was enhanced by two orders of magnitude. The enhancement resulted from intercalation of Li^+ ions into interlayer spaces of the graphite. Upon intercalation, an acceptor GIC, Li-GIC, was consequently formed. The stability of the improved electrical conductivities of the composites contributed with doped-ions was assessed. The electrical conductivity of both un-doped and doped graphite/PES composites slightly increased with increasing temperature and slightly decreased by physical ageing. The enhancement of the electrical conductivities by doping ions was stable at the high temperatures.

1. Introduction

Conductive polymer composites based on insulating polymer matrices and formulated using electrically conductive fillers such as carbon black, carbon fibers, graphite, metal powder and aluminium flakes [1] have been widely investigated in academia and industry because of their outstanding multifunctional properties when compared to the pristine polymer used [2–6]. They have been applied in various fields including light emitting diodes, batteries, electromagnetic shielding, antistatic coating or fibers, gas sensor, corrosion protection and activators [7–9].

Normally, the electrical conductivity of composite materials and as well their mechanical properties are influenced by dispersion, aspect ratio, shape, orientation of conductive fillers in insulating host matrices. In most cases, relatively large quantities of fillers are needed to reach the critical percolation value, as the filler particle size is at micrometer scales. Too high concentration of the conductive filler could lead to materials redundancy and detrimental mechanical properties [10]. The electrical conductivity of composites, filled with micron sized carbon fibers, with the lowest aspect ratio (1 0) loaded as high as 60 wt.% was the similar as compared to 10 wt.% of the one with highest aspect ratio (3 0 0) [2–6]. Graphite is one type of carbon based filler and its electrical conductivity is 10^4 S/cm at ambient temperature as high as carbon fibers [11,12]. Due to being layered structure of graphite, its layers are possibly expanded and exfoliated with treatment to form high aspect ratio graphite with thickness in nano-scale. In case of polymer/graphite composites, a percolation threshold depends on degree of expansion and exfoliation of graphite. The more surface area and the higher aspect ratio of graphite are, the lower amount is needed to form a continuous network. Recently, various useful methods have been applied to achieve these purposes. With thermal shock, expanded graphite can be obtained from the graphite intercalation compound [13,14]. Sonication technique has been applied to this field for exfoliation of graphite [14,15]. Enhancement of interfacial interactions between graphite and polymers has been successfully done through functionalisation of graphite surfaces [16,17]. Introduction of graphite into polymer matrices assisting by these methods induces volume conductivity in the range of 10^{-6}–10^{-4} S/cm at appropriate loading usually above 15–17 wt.% prepared by melt blending processing [18,19]. These improved conductivity properties are due to the synergistic effects of the dispersed graphite in the polymer [20]. Those composites will be a benefit to coatings for electrostatic dissipation applications if its volume electrical conductivity goes up into the range of about 10^{-9}–10^{-5} S/cm or possessing surface conductivity of 10^{-10}–10^{-6} S/cm. However, at these high contents of graphite the optimum mechanical properties of the composites were still unexpected [18,19].

Ion-doping, which is a quite simple method, is often used for preparation of polymer electrolytes [21–23]. This method containing dissolved metal salts has been proposed as an alternative to liquid electrolyte in rechargeable batteries and enhancement of conductivity of polymer electrolyses [21–23]. Recently, only a few of articles were reported that the improvement of electrical conductivity for conductive filler/polymer composites was cooperated with ion-doping method [24,25]. However, there was no any report regarding graphite/polymer systems. In graphite, each

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carbon has four valence electrons. Three of them are each in three sp^2 hybridised orbitals forming σ bond to three nearest neighbour carbon atoms. The remaining electron delocalises in π orbital forming a π bond to a carbon atom in adjacent carbon layer. By bonding with intercalates, the graphite π bonds can gain electrons from or lose electrons to intercalates. In other words, intercalates can act as electron donors or acceptors in doping graphite. [26]. If this method of adding ions takes into account for graphite/polymer systems, it could give rise to decrease in loading of filler and increase significantly the conductivity of the conductive composite. It may also aid in the improvement of the mechanical properties of conductive composites. In this communication we attempted to fabricate a series of electrical conductive graphite/polymer composites by combining doping ions. Polyethersulphone (PES), which is a very attractive engineering plastic polymer because of its superb properties [27], was selected as a model material. The electrical conductivity of PES composites was studied and their conduction mechanism was understood. For practical applications it needs to know whether the improved electrical conductivity of the composites contributed by doped-ions is stable when the materials are processed. So the effects of temperature and physical ageing on the electrical conductivities of the composites were also investigated.

2. Experimental

2.1. Materials

Expandable graphite flakes were supplied by Qing Dao Graphite Company (China). Polyethersulphone (PES), molecular weight about 10,000 was obtained from Cytec Engineered Materials Limited (UK). Lithium chloride (LiCl), sodium chloride (NaCl) and potassium chloride (KCl) purchased from Aldrich Company (UK). N,N-dimethylformamide (DMF), nitric acid and sulfuric acid were purchased from Fisher Scientific Company (UK).

2.2. Preparation of nitric treated graphite

First, expanded graphite was prepared by subjecting expandable graphite flake to a preheated furnace at a temperature of 850 °C for 2 min. Then expanded graphite (1 g) was suspended in 40 ml of concentrated nitric acid. The mixture was heated and maintained the temperature at 60 °C using a magnetic stirrer hot plate for 4 h. The resulting material was then filtered and washed with deionised water until pH 7 was reached and dried in a vacuum oven at a temperature of 100 °C for 2 days.

2.3. Preparation of PES/graphite and ion-doped PES/graphite composites

PES/graphite and ion-doped PES/graphite composites were fabricated by solution method. PES and nitric treated or untreated graphite with different weight contents (1, 3, 5, 8 or 10 wt.% related to PES) were dissolved in DMF (80 wt.% related to PES), then, were heated and maintained at a temperature of 50 °C 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, 5 ton) between heated metal plates with lined aluminium foils into sheet form with a thickness of about 0.3 mm. For ion-doped PES/graphite composites with small amount of LiCl (0.02–0.06, 0.08 and 0.1 wt.% related to graphite) in DMF was added into 5 wt.% of untreated or nitric treated graphite before blending with PES polymer. For comparison of conductivity the composites with the (NaCl) and (KCl) were also prepared, respectively. The contents of (NaCl) and (KCl) were the same molar weight as the LiCl.

2.4. Electrical conductivity measurements

Four-Wired Digital Multimeter Model Solartron 7150 was used to measure electrical volume resistances of samples and silver paint as an electrode material. Press moulded samples (240 °C, 5 ton) were cut into 1.9 × 1.9 cm^2 specimens with thickness about 0.3 mm, then, were applied silver paint all over top and bottom of the specimen surfaces and were dried in air. The measurements were conducted at room temperature or at elevated temperatures with 60 s of electrification. The electrical volume resistances of physical aged samples were also measured. The samples were heated to 240 °C to eliminate thermal history, followed by aged at three different temperatures of T_g-3 °C, T_g-6 °C and T_g-9 °C (T_g is the glass transition temperature of the PES), each for three different ageing times of 15, 40 and 60 min, respectively. The volume resistivity, ρ_v, can be derived from the following equation [28]:

$$\rho_v = (A/t)R_v \quad (1)$$

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

The reciprocal of the volume resistivity is the volume conductivity.

3. Results and discussion

3.1. Effect of addition of graphite on electrical conductivity of PES

Volume resistance, R_v, of PES/untreated and PES/treated graphite composites with filler content 1–10 wt.% prepared by the solution method was measured at room temperature by four-wired resistance measurement method. Their volume conductivities, σ_v, are plotted against filler content as shown in Fig. 1.

For very low filler contents (1–2.5 wt.%), the volume conductivity of both systems are close to that of the PES matrix [29,30]. There is a sharp increase in the volume conductivity of PES/untreated graphite composites in the filler content ranging between 2.5–3.0 wt.%. Similarly, a sharp increase occurs at the same range of content for PES/treated graphite composites system. Electrical conductivity of both the PES/untreated and PES/treated graphite composites systems then level off with further increase in the

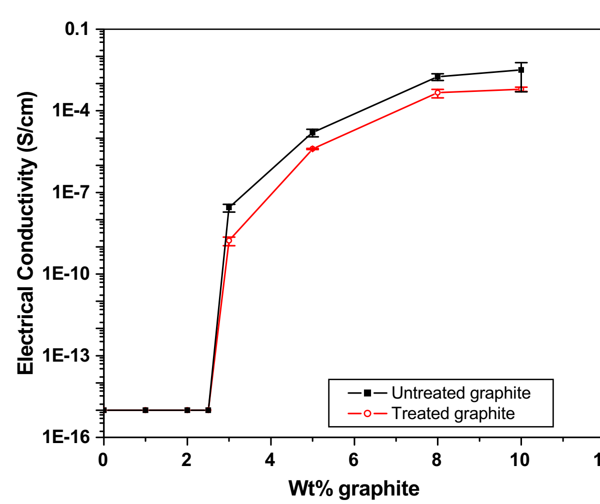

Fig. 1. Volume conductivity of PES/graphite (treated or untreated) composites as a function of graphite content.