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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 2 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 undoped 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.

Keywords: Polyethersulphone; graphite; doping; ions; electrical conductivity

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 fibres, with the lowest aspect ratio (10) loaded as high as 60 wt% was the similar as compared to 10wt% of the one with highest aspect ratio (300) [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 in to 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 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 mins. 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 4hrs. 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 hrs. After that the solvent was separated by adding methanol into the solution and stirring for 15 mins 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 x 1.9 cm² 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 sec 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 $T_g-3^\circ\text{C}$, $T_g-6^\circ\text{C}$ and $T_g-9^\circ\text{C}$ (T_g is the glass transition temperature of the PES), each for three different aging 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, $\text{k}\Omega$

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 Figure 1.

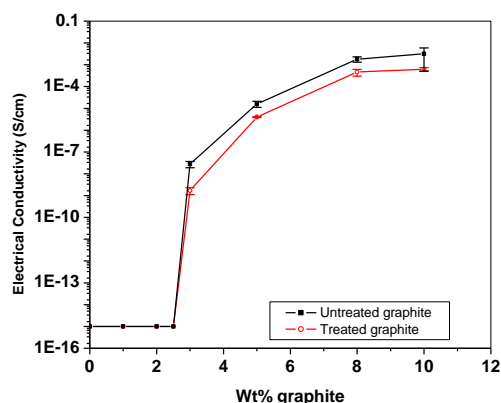


Figure 1: Volume conductivity of PES/graphite (treated or untreated) composites as a function of graphite content

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 amount of each filler. The former exhibited electrical conductivities about one order of magnitude higher than the latter in the filler content ranging 3-10 wt%. The electrical conductivity of the PES/untreated and PES/treated graphite composites at the filler content of 10 wt% are 12 and 11 orders of magnitude higher than that of the pure PES, respectively. PES consists of diphenylene sulphone groups and ether oxygen atoms. Bonds in the PES are strong covalent, its absence of mobile electrons makes it an electrical insulator, in contrast to electrical conductive feature of graphite [31].

The electrical conductivity of a polymer can improve with the addition of graphite. A percolation threshold is able to achieve at lower amount of graphite, when graphite

with high aspect ratio is employed. In this study, the percolation threshold of PES/untreated and PES/treated graphite composites is lower than 3 wt% which is much lower than that of composites prepared with conventional (micro-scale) graphite [10]. The improvement in conductivity of the composites at low loading could be attributed to high aspect ratio of the graphite. The results also indicate that nitric treatment of graphite is not beneficial in electrical conductivity enhancement of the composites since the chemical modification of the graphite surfaces by oxidation leads to a reduction of the aspect ratio of the graphite [6].

3.2. Improvement of electrical conductivity by ion doping

The addition of dilute LiCl content in the PES/treated graphite composites results in great improvement in the electrical conductivity as shown in Figure 2. The electrical conductivity gradually rose to 10^{-5} S/cm and to 10^{-4} S/cm with a LiCl content of 0.04% and 0.06%, respectively, from 10^{-6} S/cm without the dopant. In contrast, the improvement in the electrical conductivity of the PES/untreated graphite composites was insignificant. With increasing LiCl content up to 0.06 wt%, the electrical conductivities were still in the same order of magnitude as the corresponding undoped composite.

Therefore, it is necessary to understand the effect of LiCl-doping on the electrical conductivities of the PES composites. An attempt to further increase the electrical conductivities of the PES/treated graphite composite was done by increasing the amount of LiCl. As expected, the volume conductivities of the composite changes with presence of LiCl. However, it was interesting to find out that the volume conductivity of the composite increased with increasing LiCl content, only when the

content was very low (0.02-0.06 wt%). Beyond these concentrations, the volume conductivities show a downward trend (Figure 3).

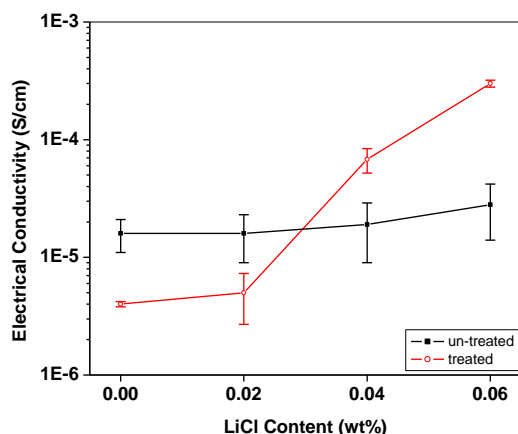


Figure 2: Volume conductivity of PES/UG5% and PES/TG5% with LiCl content

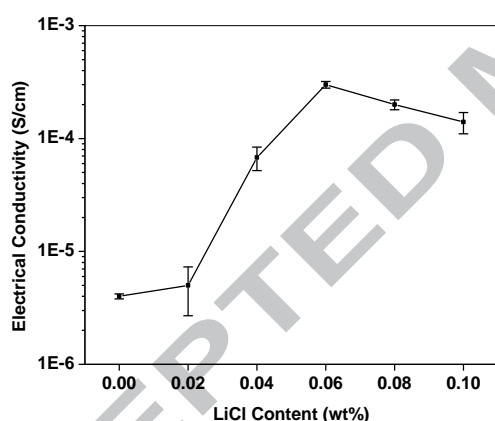


Figure 3: Volume conductivity of LiCl doped PES/TG5% composites

Lithium ions (Li^+) derived from LiCl in DMF solution could diffuse into interlayer spaces of the graphite employed and formed a lithium ion-graphite intercalation compound (Li-GIC) as follows [32]:



It is believed that there is no chloride ions intercalation due to their negative charges. Lithium ions accept π electrons from the graphite, according to the direction of charge transfer, Li-GIC is considered as an acceptor GIC [33, 34]. Upon the intercalation, extra holes are created in π orbitals of carbon atoms in the graphite and Fermi energy

is correspondingly lowered. The density of holes in Li-GIC could be higher than that in the pristine graphite. An electron from adjacent carbon atoms may hop into a hole leaving a new hole behind. Holes are thus mobile. In an electric field, holes are accelerated toward the electric field, which is in the opposite direction to that in which accelerated electrons are moving [33,34]. The force reacting on holes in electric field is equal to eE , where e is the electric charge and E is the electric field. It is the high density and the high mobility of holes that lead to the higher conductivity of the doped composites.

Further increase in the dopant concentration introduces more holes on π orbitals of carbon atoms on graphite layers. Too high a density of holes has been reported to be accompanied by a decrease in their mobility due to a collision broadening [35]. The collision of electrons results in the change of their direction of motion by scattering. Holes thus move more randomly toward the electric field. This suggests the existence of a dilute limit of lithium chloride content which can effectively improve the conductivities of the PES/treated graphite composite.

In order to show that the enhancements of the electrical conductivities of LiCl-doped composites is attributed to charge transfer between intercalate and graphite during intercalation, the effect of the size of intercalates and mixing time on the electrical conductivity were investigated.

Another two kinds of metal chloride, namely, NaCl and KCl were used as dopants for the PES/treated graphite composites. The basic idea is that an intercalation will occur easier for the intercalate having a smaller size, which will contribute to more

charge transfer. The results indicate that the conductivities of each type of doped composites at the same molar content of dopants were in the same order of magnitude. However, the conductivity of the LiCl-doped composites was found to be a little higher than that of the NaCl and KCl -doped composites. The conductivity of the composites containing KCl was found to be the lowest.

Na^+ and K^+ ions which are derived from NaCl and KCl behave as electron acceptors the same way as Li^+ ions do, i.e. they form Na-GIC and K-GIC and accept π electrons from the graphite upon intercalations. The sizes of neutral atoms of Li, Na and K are 0.145, 0.180 and 0.220 nm [36], respectively, and the original interlayer spacing of the graphite obtained from the XRD result is 0.343 nm [16]. There is a difference in the capability of the individual intercalates to diffuse into the original interlayer spaces of the graphite as reflected in the electrical conductivities of each doped composite system. Among the three intercalates, Li^+ ion is the smallest, and Li-doped PES/treated graphite composites correspondingly possesses the highest conductivity.

Mixing time of 0.08% of LiCl and the treated graphite before adding into the PES was varied from 3 hrs to 1, 3 and 7 days. The basic idea is that if intercalation processes occur, then, electrical conductivities of the doped composites will be correspondingly affected by mixing time. On the contrary, if there is no intercalation, the electrical conductivities of the doped composites should be independent on the mixing time employed. The results are presented in Figure 4.

The LiCl-doped composites prepared with 3 hrs and 1 day mixing time have the same level of electrical conductivity which are the two highest value among the four

values. The volume conductivity decreases continuously with the prolonged times. The difference between the lowest conductivity obtained from the doped composites prepared with 7 days mixing time and the highest conductivity values is as large as 3 orders of magnitude. The results imply that only a certain amount of Li^+ ions make the greatest improvement in the electrical conductivities and are consistent with Figure 4 which shows that 0.06 wt% of LiCl is the proper content. The exceeded amounts tend to lower the electrical conductivities of the doped composites. The results also indicate that intercalation occurs.

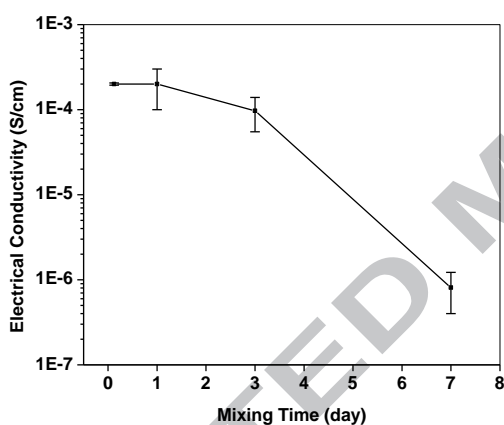


Figure 4: Volume conductivity of PES/TG5%/LiCl0.08% composites at different mixing times

3.3. Stability of Electrical conductivity of doped graphite/PES composites

For material processing it is very important to know whether the electrical conductivities of the PES/graphite composites enhanced by doped ions are stable. The electrical conductivities of the LiCl-doped PES/TG5% composites with LiCl contents of 0.02, 0.06 and 0.1 wt% at room and elevated temperatures were measured and compared with undoped ones. The results are listed in Table 1.

Table 1 Volume conductivity of PES/TG5% and LiCl-doped PES/TG5% composites at various temperatures

Temperature (°C)	Volume conductivity (S/cm)			
	PES/TG5% /LiCl 0.00%	PES/TG5% /LiCl 0.02%	PES/TG5% /LiCl 0.06%	PES/TG5% /LiCl 0.1%
20	4.2×10^{-6}	4.2×10^{-6}	3.1×10^{-4}	1.4×10^{-4}
50	4.3×10^{-6}	8.3×10^{-6}	3.3×10^{-4}	1.4×10^{-4}
75	4.8×10^{-6}	8.3×10^{-6}	3.4×10^{-4}	1.5×10^{-4}
100	5.6×10^{-6}	9.1×10^{-6}	3.6×10^{-4}	1.7×10^{-4}
125	6.7×10^{-6}	1.0×10^{-5}	3.7×10^{-4}	2.2×10^{-4}
150	7.1×10^{-6}	1.0×10^{-5}	4.0×10^{-4}	2.4×10^{-4}
190	7.7×10^{-6}	1.1×10^{-5}	4.3×10^{-4}	2.6×10^{-4}

The electrical conductivity of the doped composites slightly increased with increasing temperature as same as the undoped ones. This means that the electrical conductivity enhanced by the dopant was stable at the high temperatures. The temperature dependence of the electrical conductivity of conducting composites having conductive particles dispersed in insulating matrices is normally expressed as [37]:

$$\sigma(T) = \sigma_0 \exp\left[-\frac{T_0}{T}\right]^z \quad (3)$$

Where:

σ = Conductivity, S/cm or S/m

σ_0 = Proportionality constant

T = Absolute temperature, K

T_0 = a constant

$\chi = \text{a constant}$

From Equation 3, a relationship: $\ln \sigma(T) \propto \left(\frac{1}{T}\right)^\chi$ is obtained. The electrical conductivity data shows a good fit with a value of $\chi = 1/4$ in the plot of $\ln \sigma(T)$ versus $T^{-1/4}$ as shown in Figure 5. A value of $\chi = 1/2$ has been reported for many systems such as polyimide/carbon nanoparticle composite [38] and multi-walled carbon nanotubes/polypyrrole nanocables [38]; whereas $\chi = 1/4$ has been reported for carbon black filled polyimide nanocomposites [39].

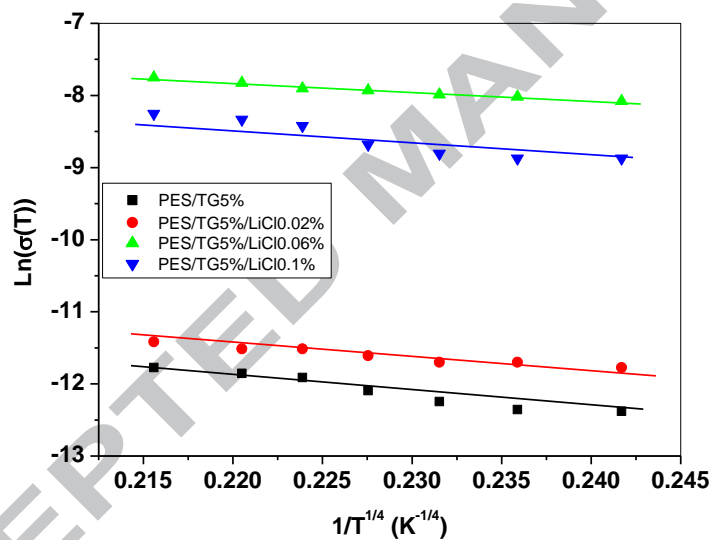


Figure 5 Temperature dependence of electrical conductivity for LiCl-doped PES/treated graphite composites with various contents of LiCl, plotted against $T^{-1/4} \text{ (K}^{-1/4}\text{)}$

The measured electrical conductivity values of composites at elevated temperature are mainly contributed by two factors which are coefficient of thermal expansion (CTE) of polymer matrix and conductive particles, and thermal activation of holes and electrons [40]. The latter is the more prominent factor at elevated temperatures.

The difference between the CTE of the PES polymer matrix and the graphite contributes to a decrease in the electrical conductivity value. The CTE of the PES is $55 \times 10^{-6}/^{\circ}\text{C}$ [41] while that of graphite within the measured temperature range (20-190 $^{\circ}\text{C}$) is about $22 \times 10^{-6}/^{\circ}\text{C}$ in the c-direction but is negative in the ab-direction [11]. The coefficient of thermal expansion of materials is defined as the change in length per unit length for a change in temperature one degree Centigrade. Materials typically have a characteristic of positive expansion coefficient i.e. expand in response to heating but contract in response to cooling. The negative expansion coefficient in the ab-direction of the graphite means that the graphite will contract on heating [11]. With increasing temperature, the PES expands by taking up more space the polymer chains are moving around more vigorously. In the mean time, the graphite sheets will shrink in ab-direction but expand in c-direction. The vigorous movement of the PES polymer chains may end up being a thick barrier in a conductive path or the shrinkage of graphite sheets may make the inter-particle distance wider.

Contrary to the CTE, the thermal activation of holes and electrons contributes to an increase in the electrical conductivities of the composites. With rising temperature, there are more thermally activated holes and electrons acquiring the necessary energy for jumping or hopping across the potential barriers. Generally, barrier heights in conducting particle filled composites can be significantly reduced when the filler loading is sufficiently high [38]. The variation of barrier heights among the different composite systems filled with 5 wt% treated graphite is due to the difference in the effective amounts of Li^+ ions presenting in the gallery of the graphite. With the presence of the guest Li^+ intercalate, a hopping conduction can more easier occur

along c-axis of graphite in which the barrier height has been lowered after the intercalation.

The electrical conductivities of the doped PES/treated graphite composites and undoped PES/treated graphite composites, which were aged at three different temperatures (below 3°C, 6°C or 10°C of T_g.) for different times, were measured and compared with corresponding non-aged samples in Table 2.

Table 2 The effect of aging time on electrical conductivity of PES/graphite composites aged at three different temperatures

Aging temperature °C	Sample	Electrical Conductivity (S/cm)			
		0 hr	1 hr	5 hrs	24 hrs
T _g -3	PES/TG5%	8.4×10^{-8}	2.6×10^{-8}	1.8×10^{-8}	2.3×10^{-8}
	PES/TG/LiCl 0.006%	5.6×10^{-6}	1.4×10^{-6}	1.3×10^{-6}	1.2×10^{-6}
T _g -6	PES/TG5%	8.4×10^{-8}	2.1×10^{-8}	2.9×10^{-8}	3.0×10^{-8}
	PES/TG5%/LiCl 0.006%	5.6×10^{-6}	1.2×10^{-6}	1.3×10^{-6}	1.2×10^{-6}
T _g -10	PES/TG5%	8.4×10^{-8}	2.9×10^{-8}	3.6×10^{-8}	4.2×10^{-8}
	PES/TG5%/LiCl 0.006%	5.6×10^{-6}	1.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}

It can be seen that at a certain ageing temperature, the electrical conductivity of each aged doped composite sample only slightly decreased compared with that of the corresponding non-aged sample and their changes were similarly as the un-doped composites. It indicates that the electrical conductivities of the PES/treated graphite composites contributed by doping ions were not affected by the physical ageing.

As known, quenching a soften material through T_g causes free volume to freeze in. The free volume will be gradually lost from the material during ageing at a temperature well below T_g by rotational movement of the PES polymer side chains. Disappearance of the free volume causes densification of the polymer which may correspondingly result in the creation of gaps at the interfaces between the PES polymer and graphite sheets. This process will make a contribution to a decrease in the electrical conductivities of the composite.

During the densification, graphite sheets are probably forced further apart, in other words, are interrupted by barriers, whether space or PES matrix. If graphite sheets are still close to the nearest neighbouring graphite sheets or are interrupted by just thin barriers, a tunnelling process can occur directly between graphite sheets [42]. If graphite sheets, on the other hand, are too far from the neighbouring graphite sheets, the electrical conductivities of composites will be dramatically decreased due to the absence of tunnelling process. Nonetheless, probability of tunnelling may be enhanced due to the presence of intermediate states such as impurities or dispersed defects [42]. In the doped composite systems, electrons or holes from a graphite sheet may cross a thick barrier to another graphite sheet via one or several intermediate states i.e. Li^+ ions within the barrier. With passing ageing time, PES polymer side chains acquire more equilibrium conformation. Therefore, localised movement of the polymer side chains and also the variation of electrical conductivity of each aged samples become less with prolonged ageing time.

In doped PES/graphite composite systems, Li^+ ions can assist tunnelling across the insulating polymer if they are present at the vicinity of the graphite conductive paths.

However, the ions are actually incorporated at very small amount in the doped composite system and are randomly dispersed in the graphite gallery or the polymer matrix which may or may not in the vicinity of the network of conductive paths.

In addition, a lower ageing temperature could result in a slower of the localised rotational movement of PES polymer side chains [43]. The overall effect of physical ageing on electrical conductivity of the composites aged at lower ageing temperatures can be discussed in the same way as those aged at higher ageing temperatures.

4. Conclusions

The electrical conductivity of PES polymer was improved by addition of graphite and doped-ions. Percolation threshold of PES/untreated and PES/treated graphite composites was lower than 3 wt% of the filler. It was found that nitric treatment of graphite was not beneficial in electrical conductivity enhancement of the composites since surface functionalisation by oxidation reaction led to a lower aspect ratio of graphite. LiCl was found to be an effective dopant for the improvement of the electrical conductivity of PES/treated graphite composites. Electrical conductivity of 5 wt% treated graphite/PES composite with the presence of a LiCl content of 0.06 wt% was 3.0×10^{-4} S/cm, which was 2 orders of magnitude higher than that of the undoped composite and was in the same order of magnitude as that of PES filled with 8 wt% of treated graphite. The enhancement of electrical conductivity of the doped composites was resulted from intercalation of Li^+ ions into interlayer spaces of graphite. Upon intercalation, an acceptor GIC, Li-GIC, was consequently formed.

The electrical conductivity of both undoped and doped PES/treated graphite composites slightly increased with increasing temperature and slightly decreased by physical ageing. The increase conductivity resulted from increased thermally activated of holes and electrons. Physical ageing led to gap creation process at the interfaces between PES polymer and graphite sheets which accompanied free volume annihilation and densification of the polymer. In comparison between undoped and doped PES/graphite composite systems, it is believed that the improved electrical conductivities contributed by doping ions were stable at high temperatures.

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