Polyethersulphone/graphite conductive composites for coatings

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POLYETHERSULPHONE/GRAPHITE
CONDUCTIVE COMPOSITES FOR COATINGS

by

Siriwan Leesirisan

A Doctoral thesis submitted in partial fulfillment of the requirements
for the award of Doctor of Philosophy of
Loughborough University

Supervisor: Dr. Mo Song
Institute of Polymer Technology and Materials Engineering

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ABSTRACT

In this research, the electrical conductivity and thermal properties of polyethersulphone (PES) insulating polymer were improved, at its optimum micromechanical properties, by filling with electrically and thermally conductive graphite, for use in coatings for electrostatic dissipation applications. The graphite employed was a micro-/nano-graphite with aspect ratios in the range 100-600. Two types of the graphite, untreated and treated, were used for PES composites and LiCl-doped PES composite fabrication via a solution method. The treated graphite was surface functionalised by concentrated nitric acid treatment. FT-IR indicated the effectiveness of concentrated nitric acid treatment in introducing additional -COOH groups on the surfaces of the graphite. XRD, SEM and TEM revealed the dispersion of the graphite throughout the PES matrix in both an immiscible and disordered manner, and the existence of aggregates of graphite. Nanoindentation testing showed insignificant decreases in the nanohardness and elastic modulus of the PES/treated graphite composites when the treated graphite content was not more than 5 wt%; whereas, increasing the content of the treated graphite increased the nanoscratch resistance of the composites. Due to the high aspect ratio of the graphite, the electrical conductivities of the PES/untreated and PES/treated graphite composites were enhanced at low loadings. An initial conducting pathway was formed at lower than 3 wt% of the filler. The enhancement by 2 orders of magnitude of the electrical conductivity of a PES/treated graphite composite could be accomplished by doping with 0.06 wt% of LiCl. MDSC showed improvements in the thermal conductivity of the PES matrix by 165 and 91% with the addition of 5 wt% of the untreated and treated graphite, respectively. DSC curves illustrated higher glass transition temperatures of the PES/graphite composites and doped PES/graphite composites, compared to the pure PES. Decreases in relaxation enthalpy with time, due to physical ageing of PES, were smaller when the PES was filled with the graphite or LiCl-doped graphite. The decrease in relaxation enthalpy of the materials was accompanied by increases in glass transition temperature and characteristic length. Physical ageing also led to a decrease in the electrical conductivities of the PES/graphite composites and doped PES/graphite composites.
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CHAPTER 1

INTRODUCTION AND AIMS OF THE PROJECT

1.1 INTRODUCTION

Composites are multi-component materials which comprise multiple different phase domains in which at least one phase domain is a continuous phase [1]. There is a high level of interest in using polymer-based composites for applications ranging from building and construction, transport, furniture and house wares, packaging, handling and storage, and coatings [2-3]. Different properties of materials are required for individual applications, so are their levels of electrical conductivity. While the electrical insulation properties of materials are needed for building and construction, and furniture and house ware applications, coatings for electrostatic dissipation applications must possess relatively low electrical resistivity in order to meet requirements (Figure 1.1).

![Figure 1.1 Classification of materials by surface resistivity (unit Ω/square) [4]](image)

Electrostatic charge is commonly created after the separation of two materials between which electron transfer has occurred during their contact. Electrostatic discharge (ESD) is the transfer of charge between bodies at different electrical potentials [5]. Sudden discharge causes an upset of the normal operation of an electronic system and equipment malfunction or failure. As electronic devices have become smaller, their sensitivity to ESD has increased. The generation of static electricity in the environment can not simply be eliminated. The best way is dissipation of charge in a controlled manner by the use of conductive or dissipative electrostatic control materials.
Among engineering plastics, polyethersulphone (PES) is a very attractive polymer due to its superb properties [6-8]. It has a high resistance to heat, combustibility and many commonly used acids and bases. It is also stable over a wide range of temperatures. It emits little smoke as it burns and it self-extinguishes. PES will be a benefit to coatings for electrostatic dissipation applications if its volume electrical conductivity is developed up to the range of about $10^{-9}$-$10^{-5}$ S/cm, or if it possesses surface conductivity of $10^{-10}$-$10^{-6}$ S. The desired electrical conductivity of polymer composites can be tailored by the loading of electrically conductive fillers into insulating polymer matrices. In addition, polymers filled with some type of electrically-conductive filler also become a thermally-conductive composite.

Common fillers used in ESD protections are carbon powder or carbon black, carbon fibres, metal powder and aluminium flakes [9]. Recently, PES materials filled with carbon fibres which possess volume conductivities in the range of $10^{-6}$-$10^{-4}$ S/cm have been commercially available [10]. Unfortunately, no information relating to the filler and loading level has been provided. However, there has been a report on PES filled with micron sized pitch-based carbon fibres [11]. In order to achieve PES composites with a certain level of electrical conductivity, the pitch-based carbon fibres with the lowest aspect ratio (10) were loaded as high as 30 vol%, compared to 5 vol% of the one with the highest aspect ratio (300). At a high content of the filler, the properties of the composites are sacrificed, and performance/cost becomes ineffective.

Another type of carbon-based filler, namely graphite, is an alternative to carbon fibres and can be used for imparting electrical conducting properties to insulating polymers. The electrical conductivity of graphite is as high as that of carbon fibres ($10^4$ S/cm at ambient temperature) [12-13]. Being a layered structure filler, its layers can be expanded and exfoliated with treatment to form a high aspect ratio graphite with a thickness in the nano-scale. This is advantageous over conventional conductive fillers (micro-scale). In addition, the graphite surfaces can be functionalised to improve their dispersability in, and interactions with, polymer matrices. As a result, conducting polymer composites with low loadings
of the graphite can be achieved and the micromechanical properties of polymer matrices can be retained or improved.

The potential applications for PES composite materials with improved mechanical and thermal properties could be in microelectronics for thermal transfer coatings with low heat build-up characteristics. PES composite materials with improved electrical conductivities and mechanical properties could be used as electromagnetic interference shielding coatings. Another potential application for PES composite materials with these improved properties could be in the military and defence sectors as a multifunctional coating material for surface protection such as for aircraft wings to protect against abrasion, erosion, and scratching caused by wind, sand, snow and other airborne particles.

1.2 AIMS OF THE PROJECT

The aims of the project are to improve the electrical conductivity as well as the thermal properties, at the optimum micromechanical properties, of PES, by addition of graphite for coatings and electrostatic dissipation applications. The research is one of Cytec Engineered Materials' interests, and so far there has been no report on PES/graphite conductive composites. The following aspects were involved in the research.

1) Preparation of micro- and nano-sheets of graphite and chemical modification of the surfaces of the graphite to enhance interfacial interactions between graphite and the PES matrix

2) Fabrication of PES/graphite conductive composites with improved electrical and thermal conductivities, and scratch resistance for coating applications

3) Investigation of the structural and the micromechanical properties of the PES/graphite composites

4) Investigation of the conductive behaviour of the PES/graphite composites, experimentally and theoretically
5) Investigation of the thermal behaviour and the effect of physical ageing on the electrical conductivities of the PES/graphite composites

The scientific goal of this research is to gain a fundamental understanding of the conductive behaviour of the PES/graphite composites. The technical goal of this research is to develop PES hybrid materials with improved electrical and thermal conductivities and good scratch resistance.
CHAPTER 2
LITERATURE REVIEW

2.1 Introduction
The background related to this research and the progress of research on expanded, sonicated graphites and their composites based on polymers are reviewed as follows.

2.2 Electrical Resistivity

2.2.1 Resistance and resistivity

The following definitions of resistance and resistivity are taken from ASTM D1711 [14]

Surface resistance ($R_s$) - "the ratio of the dc voltage applied to two electrodes (on the surface of a specimen) to the current between them" Surface resistance is the reciprocal of surface conductance.

Volume resistance ($R_v$) - "the ratio of the dc voltage applied to two electrodes (on or in a specimen) to the current in the volume of the specimen between the electrodes" Volume resistance is the reciprocal of volume conductance.

Surface resistivity ($\rho_s$) - "the surface resistance multiplied by the ratio of specimen surface dimensions (width of electrodes defining the current path divided by the distance between electrodes)" Surface resistivity is expressed in $\Omega$ or $\Omega$/square unit and it is the reciprocal of surface conductivity.

Volume resistivity ($\rho_v$) - "the volume resistance multiplied by the ratio of specimen volume dimensions (cross-sectional area of the electrodes divided by the distance between electrodes)" Volume resistivity is usually expressed in $\Omega$-cm or in $\Omega$-m and it is the reciprocal of volume conductivity.
Materials may be classified according to their volume resistivity. The volume resistivities of some materials are compared in Figure 2.1. The large difference between the highly conductive materials such as copper and silver and the highly insulating material such as polytetrafluoroethylene is up to 24 orders of magnitude. Materials whose volume resistivities fall in the range $10^0$ to $10^8 \, \Omega \cdot \text{cm}$, in between conductors and insulators, are referred to as semiconductors. It can be seen that polymers are good insulators.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{resistivities.png}
\caption{Comparative electrical resistivity of materials [15-16]}
\end{figure}
2.2.1.2 Factors affecting resistivity

The resistivity is a characteristic of a material which will be constant if the material is not changed in its composition and is not contaminated by moisture and ions. Changes in the formulation or chemical composition lead to significant changes in the resistivity [17]. For example, blending polyamide with an epoxy resin results in decreases in the resistivity of the epoxy when the amount of the polyamide exceeds 30% (Figure 2.2).

*Figure 2.2 Variation of resistivity with change in epoxy/polyamide ratio [17]*

Besides the effect of changes in compositions, minor amounts of impurities such as metal ions also influence resistivity [17]. Ionic impurities in micrograms, especially when moisture coexists, can decrease resistivity as much as 6 to 11 orders of magnitude.
The degree of cure or extent of polymerisation also affects resistivity [17]. The resistivity increases as the cure progresses, and stabilises after the cure is completed. Thus, resistivity can be used as an indication of optimum cure conditions. Figure 2.3 shows isothermal polymerisation of an amine-cured epoxy as a function of volume resistivity.

Figure 2.3 Isothermal polymerisation of an amine-cured epoxy as a function of volume resistivity [17-18]

Resistivity is essentially dependent on temperature, as shown in the following Equation:

\[ \rho = \rho_0 e^{-E_s/RT} \]  

(2.1)

where:
\[ \rho = \text{Resistivity at temperature } T \]
\[ \rho_0 = \text{a constant} \]
\[ k = \text{Boltzmann's constant} \]
\[ E_a = \text{Activation energy} \]
\[ T = \text{Absolute temperature, K} \]

Tremendous decreases in resistivity values can occur at elevated temperatures. Resistivity-temperature curves of some polymers are shown in Figure 2.4. Moreover, resistivity is also dependent on frequency, voltage, pressure, light and the conditioning of the sample [17].

*Figure 2.4 Volume resistivity-temperature curves of some polymers [17]*
Moisture and contaminants have a more severe effect on surface resistivity than on volume resistivity. High humidity or a contaminating environment affects surface resistivity almost immediately but it affects volume resistivity in several days or weeks time. A reduction of 11 orders of magnitude in the surface resistivity of polyethylene that was contaminated with fingerprints and subsequently exposed to 96% relative humidity (Table 2.1) has been reported.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Resistivity, Ω/square</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 50% humidity</td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
</tr>
<tr>
<td>As received</td>
<td>&gt;10^18</td>
</tr>
<tr>
<td>Contaminated with fingerprints</td>
<td>-</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>~10^18</td>
</tr>
<tr>
<td>As received</td>
<td>-</td>
</tr>
<tr>
<td>Contaminated with fingerprints</td>
<td>-</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>~10^18</td>
</tr>
<tr>
<td>As received</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2.2 Conductance and conductivity

The reciprocal of a resistance is the conductance, expressed in units of Ω⁻¹ and the reciprocal of resistivity is the conductivity, expressed as (Ω-cm)⁻¹ or S/cm [14].

2.3 Polyethersulphone (PES)

PES is one of the engineering polymers. It is an aromatic polymer consisting of diphenylene sulphone groups and ether oxygen [19-20]. The structural repeating unit is represented as follows:
PES is usually amorphous with a high glass transition temperature, $T_g$. Due to thermal stability of the sulphone and ether groups, PES has a useful high temperature resistance (up to 400°C) with high rigidity and low creep. It is also transparent, highly resistant to most chemicals and has flame retardant properties. Typical applications include cargo liners, automotive fuses, aircraft interiors, light reflectors, medical equipment, fire barriers, household goods, electrical/electronic components such as heater components, and printed circuit boards [21]. PES may be reinforced with glass fibres and carbon fibres to increase its tensile strength and stiffness [20]. Like most polymers, PES is an electrical insulator with the volume conductivity as low as $10^{-15}$ S/cm. PES will be a benefit to ESD dissipative coating applications if its volume electrical conductivity is developed up to the range of about $10^9$-$10^5$ S/cm. As a coating material, it will also provide superior wear resistance, thermal stability and corrosion resistance [22].

2.4 Applications of Conductive Filled-Polymer Composites

2.4.1 Electrostatic dissipation applications [5]

In daily life, one may have experienced static electricity through touching a metal doorknob after sliding across a car seat or walking across a carpeted room. However, to industry, static electricity has been a serious problem for centuries. Problems associated with static electricity and electrostatic discharge (ESD) become severe, especially to electronic devices, as they have become smaller and more susceptible to ESD. For example, electrostatically charged surfaces can attract and hold contaminants, causing product defects. Characteristics of a semiconductor device can be changed, degraded or even destroyed by ESD. ESD may cause malfunction or failure of the operation of an electronic system. It can be seen that ESD impacts on
yield, quality and reliability of products, cost of manufacturing, repairing, shipping, workforce and also profitability.

Static electricity is defined as “an electrical charge caused by an imbalance of electrons on the surface of a material”. The imbalance of electrons produces an electric field that can affect other objects at a distance. Electrostatic discharge is defined as “the transfer of charge between bodies of different electrical potentials”.

![Diagram of triboelectric charge](image)

**Figure 2.5** Triboelectric charge: (a) contact; (b) separation
Electrostatic charge is commonly created by the contact and separation of two materials, called triboelectric charging. It involves electron transfer between the materials. Materials with no static charge (electrically neutral) will have an equal numbers of positively charged protons (+) and negatively charged electrons (-) in their atoms. When two neutral materials are placed in contact (Figure 2.5 (a)) and then separated (Figure 2.5 (b)), electron(s) are transferred from the surface of one material to another. The material that gains electron(s) becomes negatively charged, while the one that loses electron(s) is positively charged.

Table 2.2 Typical triboelectric series

<table>
<thead>
<tr>
<th>+</th>
<th>Rabbit fur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td>Mica</td>
</tr>
<tr>
<td></td>
<td>Human hair</td>
</tr>
<tr>
<td></td>
<td>Nylon</td>
</tr>
<tr>
<td></td>
<td>Wool</td>
</tr>
<tr>
<td></td>
<td>Fur</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
</tr>
<tr>
<td></td>
<td>Aluminium</td>
</tr>
<tr>
<td></td>
<td>Paper</td>
</tr>
<tr>
<td></td>
<td>Cotton</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
</tr>
<tr>
<td></td>
<td>Amber</td>
</tr>
<tr>
<td></td>
<td>Sealing wax</td>
</tr>
<tr>
<td></td>
<td>Nickel, Copper, Brass, Silver</td>
</tr>
<tr>
<td></td>
<td>Gold, Platinum</td>
</tr>
<tr>
<td></td>
<td>Sulphur</td>
</tr>
<tr>
<td></td>
<td>Acetate rayon</td>
</tr>
<tr>
<td></td>
<td>Polyester</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>-</th>
<th>Celluloid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silicon</td>
</tr>
<tr>
<td></td>
<td>Teflon</td>
</tr>
</tbody>
</table>

The position of a material in the triboelectric series is the factor that indicates the polarity and magnitude of the charge. When two materials contact and separate, the one at the higher position in the table will have positive charge(s). The higher charge will be created if two materials are far apart from each other in the table. Table 2.2
shows a typical triboelectric series. Almost all materials, including water and dirt particles in the air, can be triboelectrically charged.

The charge \( q \) on an object is determined by the capacitance of the object \( C \) and the voltage potential on the object \( V \) as in the following equation:

\[
q = CV
\]  

The amount of charge created by triboelectric charging is also affected by contact area, speed of separation and relative humidity. Table 2.3 shows the variation of voltage levels with relative humidity.

<table>
<thead>
<tr>
<th>Means of Generation</th>
<th>10-25% RH</th>
<th>65-90% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walking across carpet</td>
<td>35,000V</td>
<td>1,500V</td>
</tr>
<tr>
<td>Walking across vinyl tiles</td>
<td>12,000V</td>
<td>250V</td>
</tr>
<tr>
<td>A worker at a bench</td>
<td>6,000V</td>
<td>100V</td>
</tr>
<tr>
<td>A polythene bag picked up from a bench</td>
<td>20,000V</td>
<td>1,200V</td>
</tr>
<tr>
<td>A chair with urethane foam</td>
<td>18,000V</td>
<td>1,500V</td>
</tr>
</tbody>
</table>

If a charge is created and remains on the material, it becomes an electrostatic charge around which an electrostatic field forms. An electrostatic charge may also be created by induction, ion bombardment or contact with another charged material. However, the most common way is triboelectric charging. When a charge is created on the surface of a material, how fast the charge will be transferred is indicated by the electrical characteristics of the material.
**Insulative materials or insulators**

A material of this kind prevents or limits the flow of electrons across its surface or through its volume due to its extremely high surface resistivity (> $1 \times 10^{12} \, \Omega/$square) and volume resistivity (> $1 \times 10^{11} \, \Omega\cdot$cm). If charges are created on the surface of an insulator, both positive and negative charges can reside on an insulative surface at different locations at the same time and may remain in place for a very long time.

**Conductive materials or conductors**

This kind of material has a low surface resistivity (< $1 \times 10^{5} \, \Omega/$square) and volume resistivity (< $1 \times 10^{4} \, \Omega\cdot$cm). A conductive material allows electrons to flow easily across its surface or through its volume. Electrostatic charge can be created triboelectrically on conductors in the same way as it is on insulators. When a conductor becomes charged, the charge (either negative or positive) will be uniformly distributed across the surface. As long as the conductor is isolated from other conductors or the ground, the static charge will remain on it. If the charged conductive material comes into contact with another conductive material, electrons will easily transfer between the materials. The excess charge on a material will be neutralised when electrons flow to ground if the material is attached to an earth grounding point.

**Static dissipative materials**

Static dissipative materials have surface and volume resistivities between insulators and conductors ($1 \times 10^{5} - 1 \times 10^{10} \, \Omega/$square and $1 \times 10^{4} - 1 \times 10^{9} \, \Omega\cdot$cm, respectively). Electrons can flow across or through dissipative materials but the flow is controlled by the surface resistivity or volume resistivity of the materials. Charge can be created triboelectrically on a static dissipative material. Like conductors, the static dissipative material will allow the transfer of charge to other conductive materials or the ground. The transfer of charge from a static dissipative material will take longer time than that from a conductive material of equivalent size.
Direct electrostatic discharge either to or from a device causes ESD damage. How severe the damage is, is determined by the ability of the device to dissipate the energy of the discharge or withstand the voltage levels involved. Many electronic components are sensitive to ESD at relatively low voltage levels. For example, many disk drive components have sensitivities of less than 10 volts. Packed circuitry devices are intensely sensitive to ESD.

Apart from using ESD-protective workstations and personnel static controls such as wrist straps, static control clothing and shoes, the use of conductive and dissipative static control materials is the way to protect ESD sensitive products from electrostatic discharge. The ability of materials to be used for ESD protection is defined by the materials resistivity. Electrostatic shielding is provided by materials having resistivity in the conductive range, while dissipative materials provide charge dissipation. Polymer/carbon black conducting composites have been commercially available to make electronic packages, trays, work surfaces and wrist straps. High-temperature composites made of engineering resins such as polyimide, polyetheretherketone (PEEK) filled with carbon fibres can be used for ESD control in clean rooms where microprocessors are made. [23]

2.4.2 Electromagnetic interference/radio frequency interference shielding applications

Electromagnetic interference (EMI) is defined by NATO as “an electromagnetic disturbance which interrupts, obstructs or otherwise degrades the effective performance of electronic or electrical equipment”. Examples of interference phenomena or disturbance can be seen in daily life: receivers are interfered with by illuminated signs, microcomputers are disturbed by electrical household appliances, electronic telephones pick up radio signals.

For electromagnetic interference to occur, the 3 following conditions must be present: [24]
1) There must be an interference source called an "emitter" of electromagnetic energy. The emitter may propagate electromagnetic energy intentionally such as a two-way radio or unintentionally such as a power transformer.

2) There must be a device that is susceptible to the electromagnetic energy being emitted by the emitter. If the device does not have an ability to reject the energy which it is being exposed to, electromagnetic interference may occur.

3) The two devices must share a common propagated electromagnetic field. The distance between the devices and their orientation with respect to each other may have a significant role in determining whether the devices will react with each other.

Radio frequency interference (RFI) is a special kind of electromagnetic interference in which radio frequency transmissions cause interference problems in equipment operation. Radio frequencies are found in the range 10 kHz to 10 GHz in the electromagnetic spectrum (Figure 2.6).

![Figure 2.6 Classifications and characteristics of electromagnetic radiation [25]](image)
Natural radio noise such as lightning and thunderstorms originates from an atmospheric source, while all electrical or electronic equipment is a man-made source of radio disturbance. Man-made sources of radio emissions or disturbances include two-way radios, pagers, mobile phones, communication systems and radars. Power cables, transformers, medical equipment, fluorescent tubes, personal computers and many other unintentional emitters also produce radio frequency energy [26].

In many cases, EMI is a life threatening problem. It has been reported that medical devices such as pacemakers, blood-gas pumps, hearing aids, wheelchairs and electronic imaging devices are interrupted or interfered with in the presence of mobile phones or radio devices [27]. There has also been an incident in which the low frequency of a radio signal disrupted the avionic systems of a commercial passenger plane. The plane lost electromechanical devices that indicate orientation at cruise altitude as a result of the use of portable radios and laptop computers in the cabin. Such internal sources of EMI are obviously dangerous to the plane because they are so close to the systems they might affect. However, external sources such as radio and radar transmitters on the ground or radar from a passing military aircraft can be even more disruptive due to the high power and frequency of such equipment [28].

Electromagnetic interference shielding is typically used to protect electrical equipment from externally unwanted electromagnetic radiation. EMI protection is particularly important to small, densely packed and sensitive electronic devices operating at high frequencies. EMI shielding reduces unwanted electromagnetic radiation to levels that do not adversely affect equipment by both reflecting and absorbing. The reflection depends on the permeability and the conductivity of a shielding material, also on the frequency and wave impedance of an electromagnetic wave [29]. The remaining radiation is reduced by absorption when it passes through the shielding material. Figure 2.7 shows how an incident electromagnetic wave can be attenuated by a shielding material. Likewise, EMI shielding is also used in the attenuation of EMI/RFI emissions of internal components to acceptable levels.
Figure 2.7 Reflection and absorption of electromagnetic waves by a shielding material [25]

Metal-based materials have been conventionally used as EMI shielding materials [28]. However, metals are not easily mouldable and leaks in the shielding may occur at the seam [30]. Conductive filler filled-polymer composites have gained popularity because of their light weight, corrosion resistance, flexibility and processing advantages [31]. It has been reported that to manufacture polymer-based composites with satisfactory EMI protection, 25-40 wt% of aluminium flakes or carbon fibres, or 5-10 wt% of stainless steel fibres is required [25]. Recently, epoxy filled with 10-15 wt% single-walled carbon nanotubes has been able to meet the shielding effectiveness (SE) demands which are around 20 dB for commercial applications such as mobile phones [31]. 20 dB is equal to or less than 1% transmission of the electromagnetic wave.

2.4.3 Thermal management applications
2.4.3.1 Conductive adhesives [32]

Adhesives are used in the assembling and packaging of electronic devices. Polymer adhesives such as epoxies, silicones, cyanate esters and polyimides have, to a large extent, replaced many traditional interconnect materials such as solder and wires for
commercial and consumer electronics due to their low processing temperature, ease of rework and cost effectiveness. Adhesives may be classified according to the function they are to perform. One main function in which conductive fillers are essentially required is thermal dissipation. Normally, adhesives filled with electrically-conductive material (Electrically-conductive adhesives) have a high level of thermal conductivity, allowing electronic components to dissipate heat through. In case of high risk of electrical shorting, electrically-conductive fillers will be replaced with electrically-resistive but thermally-conductive fillers such as aluminium nitride, boron nitride, alumina or beryllia. Applications of thermally-conductive adhesives include the attachment of power devices, heat sinks, large capacitors and transformers.

2.4.3.2 Thermal greases [33]

Thermal greases are generally made of silicone filled with metal oxides, thermally-conductive fillers. They find applications in reducing thermal contact resistance occurring at the interface of two solid electronic components by filling the voids between the contacting surfaces. Small amounts of grease should be used to avoid voids being created within the grease itself and increases in the thermal resistance across grease thickness. Thermal greases may migrate at high temperatures, evaporate at low pressures or vacuum, and cause contamination.

2.4.3.3 Heat sinks [34-35]

A heat sink is a metal that is brought into contact with the hot surface of an electronic component from which it absorbs and dissipates heat using thermal contact. Heat sinks are widely used in electronics such as microprocessors, servers and power converters. A heat sink usually consists of a base with one or more flat surfaces and an array of comb-like protrusions for increasing the air contact area and the heat dissipation rate. A fan is often attached to a heat sink to provide increased airflow over the heat sink. Thermally-conductive grease may be used to ensure optimal thermal contact between a heat sink and a cooling needed component and thermal
adhesives may be used to hold the heat sink onto the component. Heat sinks are generally made of aluminium or copper or aluminium alloy. However, polymer-based composite heat sinks have the light weight, complex shaped mouldable characteristics which were previously restricted to many metal-based heat sinks. They also have cost advantages. Commercially available composite heat sinks are made of polyphenylene sulphide, polypropylene, polycarbonate, polybutyrene terephthalate or polyamide filled with thermally-conductive fillers. The composites may have thermal conductivity as high as 50-500 times that of the corresponding insulating polymers.

2.5 Conductive Fillers
In order to achieve a composite with the desired conductivity, three basic factors, which are resistivity, loading level and geometry of the filler, must be considered [23]. The resistivity of a composite is closely related to the resistivity of the filler. For example, carbon black whose volume resistivity is about $10^{-1} \ \Omega \cdot \text{cm}$ can be used to make polymer composites with a resistivity of $10^0 \ \Omega \cdot \text{cm}$; whereas, silver powder can produce composites with lower volume resistivity ($10^2 \ \Omega \cdot \text{cm}$). The resistivity of silver is of the order of $10^6 \ \Omega \cdot \text{cm}$.

The effect of filler loading on the composite resistivity follows a universal pattern, regardless of filler type. At low filler loading, the resistivity of the composite remains almost undisturbed. As the filler loading reaches a critical point, there will be a sharp

![Figure 2.8 Simplified view of the percolation transition [23,36]](image-url)
drop in the resistivity. This point is called the percolation threshold when there is enough conductive filler to form a continuous conductive path through the composite (Figure 2.8).

The geometry of the filler determines how much filler volume is needed to reach the percolation threshold. Perfectly spherical fillers require as much as 40 vol% loading to reach the percolation threshold. Low-structured carbon black particles require between 5 to 35 vol% loading. At high loadings of fillers, other characteristics of polymer matrices are altered to some extent [37-38]. Figure 2.9 shows that high-structured (large aspect ratio) carbon black results in a much lower percolation threshold. However, it is difficult to control the level of resistivity in the required range ($1 \times 10^5 - 1 \times 10^9 \ \Omega \cdot \text{cm}$) due to the steepness of the percolation curve.

![Figure 2.9 Resistivity of high- and low-structured carbon black/polymer composites [23,36]](image)

Similarly, the amount of conventional graphite (micro-scale) required to make a polymer composite with a satisfactory conductivity is usually as high as 20 wt% or higher, which will result in a material with poor mechanical properties and high
densities [39-41]. The advanced technique for expansion and exfoliation of graphite is a key to the utilisation of graphite as a nano-conductive filler. When nano-scale graphite is dispersed in a polymer matrix, the particular morphology and structure provides the advantage in forming a conducting network at low loadings [42]. Figure 2.10 (a) and (b) show that at a certain loading level, high aspect ratio sheets lead to a higher conductivity compared to conventional graphite flakes.

![Diagram](a)

![Diagram](b)

*Figure 2.10* Schematic illustrations of the effects of geometry of graphite on the formation of a conductive network: (a) polymer/graphite nanosheets; (b) polymer/conventional graphite flakes [42]

2.6 Graphite

2.6.1 The structure of graphite

Graphite is composed of stacked parallel-layer planes with trigonal sp² bonding. The carbon atom within each layer plane is bonded to three other carbon atoms, forming a series of continuous hexagons, which is considered as a basically infinite two-dimensional molecule. The bond is covalent and has a short bond length (0.1421 nm) and high bond strength (524 kJ/mol) [12]. The fourth valence electron of carbon is paired with another fourth electron of carbon in an adjacent plane by a much weaker Van de Waals bond (7 kJ/mol). The spacing between the layer planes (0.3354 nm) is more than twice the spacing between atoms within the basal plane. The stacking of these layer planes occurs in two ways, —ABABAB— the stacking
sequence of hexagonal graphite, where the carbon atoms in every other layer are superimposed over each other as shown in Figure 2.11, and —ABCABCABC— the stacking sequence of rhombohedral graphite, where the carbon atoms in every third layer are superimposed. Hexagonal structure is the common form of graphite; whereas, rhombohedral structure can be considered as an extended stacking fault of hexagonal graphite.

![Figure 2.11 The atomic structure of graphite [43]](image)

2.6.2 The properties of graphite

The particular crystal structure of graphite results in anisotropy, that is the properties of it may vary considerably when measured within the plane (along the ab-direction) or perpendicular to the planes (the c-direction). The properties of ideal graphite are as follows:

2.6.2.1 The physical properties of graphite

Density

Graphite has a density of about 2-2.25 g/cm³, which is quite low compared to other metal fillers (nickel 8.9 g/cm³ and silver 10.5 g/cm³) [44]. This is an advantageous characteristic especially in aircraft applications.
Melting point

Graphite does not have a normal melting point, which occurs at a pressure of one atmosphere. However, melting of graphite can be observed at a pressure of 100 atm. and a temperature of 4200K.

Heat of vaporisation

The heat of vaporisation of graphite is about 355.8-598.2 kJ/mol, which is higher than that of many metals (silver 250.5 kJ/mol and copper 300.3 kJ/mol) [12,45-46]. The large amount of energy required to vaporise graphite is a benefit for the design of ablative structures such as rocket nozzles and nose cones.

2.6.2.2 The thermal properties of graphite

Thermal conductivity

The thermal conductivity of graphite is high in the ab-direction (390 W/m·K) [12]. However, in the direction perpendicular to the basal plane (the c-direction), it is approximately 200 times lower (2 W/m·K). In the ab-direction, graphite can be considered as a good thermal conductor comparable to high-conductivity metals (silver 420 W/m·K and copper 385 W/m·K) while in the c-direction, it is a good thermal insulator.

Thermal expansion

The thermal expansion of graphite is significantly anisotropic. It is low in the ab-direction but higher by an order of magnitude in the c-direction [12,47-49]. Figure 2.12 shows the thermal expansion of graphite. In the ab-direction, in the temperature range -273 to 400°C the thermal expansion is negative with a minimum at 0°C. However, in the c-direction, it increases with temperature slowly and gradually. The coefficient of thermal expansion is about 25×10⁻⁶/°C at 0°C and reaches 28×10⁻⁶/°C at 400°C [48,50].
Figure 2.12 Thermal expansion of graphite [12,47-49].
2.6.2.3 The electrical properties of graphite

Electrical resistivity

An electrical current is a flow of electrons. In electrical conductors such as metals, the outer electrons can move readily since the attraction between the nucleus of the atom and the outer electrons is weak. In the case of electrical insulators, electrons are not free to move as a result of strong bonding between the electrons and the nucleus [12, 51].

Graphite is considered a semi-metal. In the atomic structure of graphite, the highest valence band overlaps the lowest conduction band and the delocalised fourth valence electrons form a partially-filled conduction band [12,51]. The delocalised electrons on the basal planes move readily in response to an electric field; as a result, the electrical resistivity of graphite parallel to the basal planes (the ab-direction) is low. In the c-direction, the spacing between planes is relatively large and there is no mechanism for the electrons to move from one plane to another. The electrical resistivity of graphite perpendicular to the plane is consequently high. Resistivity values are as low as $2.5 - 5.0 \times 10^{-4} \ \Omega \cdot \text{cm}$ in the ab-direction but they are possibly as high as $3000 \times 10^{-4} \ \Omega \cdot \text{cm}$ in the c-direction [12,51].

The electrical resistivity of graphite in the ab-direction increases with temperature, as a result of a decrease in the electron mean free path. It, however, decreases slightly with increasing temperature in the c-direction since electrons can jump or tunnel from one plane to another.

2.6.2.4 The mechanical properties of graphite

The bond between atoms within the basal plane of a graphite crystal is much stronger than that between the planes. Therefore, the strength in the ab-direction is much higher than that in the c-direction. The Young’s modulus of elasticity of graphite varies by up to two orders of magnitude with the direction. Young’s modulus plotted
against the angle ($\phi$) between the $c$-direction and the direction of measurement is shown in Figure 2.13.

![Graph showing Young's modulus of graphite as a function of the angle ($\phi$) between the test direction and the $c$-axis][12,48]

**Figure 2.13** Young's modulus of graphite as a function of the angle ($\phi$) between the test direction and the $c$-axis [12,48]

### 2.7 Expanded Graphite

#### 2.7.1 Preparation

Carbon atoms within a layer of graphite are bonded by strong covalent bonds; whereas, those between the layers are held together by the weaker bonds, Van der Waals forces. Therefore, it is possible for a wide variety of atoms and molecules such
as alkali metals, alkaline earth metals, rare earth elements, halogens, metal halides, metal oxides and acids, to intercalate the spaces between the layers of graphite with an increase of the layer distance to values \( (d_1) \) that are determined by the size of the guest, from the original distance \( (d_0) \) (Figure 2.14). The guests presented in the interlayer spacing of graphite are called intercalates and the products composed of host graphite and intercalates are called graphite intercalation compounds (GICs). A mixture of concentrated sulphuric acid and concentrated nitric acid in a volume ratio of 4:1 is an example of the chemicals which have been used as intercalating agents. Sulphuric acid serves as an intercalate and nitric acid is an oxidiser. By immersing natural flake graphite into a mixture of those acids, the following reaction occurs:

\[
n(\text{graphite}) + n\text{H}_2\text{SO}_4 + n/2(\text{O}) \rightarrow n(\text{graphite-}\text{H}_2\text{SO}_4) + n/2\text{H}_2\text{O}\\
(O) = \text{Oxidant}\\
(\text{graphite-}\text{H}_2\text{SO}_4) = \text{GIC}
\]

A peculiarity of GICs is their tendency to form stacked compounds in which an intercalate fills only a fraction of the interlayer spacing, which is called the staging phenomenon. Figure 2.14 shows a schematic cross-section of stages 1, 2 and 3 GICs in the Daumas-Herold domain model [54]. Stage number \( n \) indicates the number of graphene layers which are in between sandwiched intercalate layers.

---

**Figure 2.14** Stages 1, 2 and 3 of GICs in the Daumas-Herold domain model

(---) graphene layer (O) intercalated layer [54].

---
Expanded graphite can be formed by the rapid heating of a GIC to a high temperature, typically 900 to 1050°C. The process of preparing expanded graphite is shown in Figure 2.15 [55]. The solid lines shown in the figure represent the graphite sheets when they are viewed in the direction parallel to the sheets.

\[ \text{H}_2\text{SO}_4 \quad \text{HNO}_3 \]
\[ \text{soaping} \quad \rightarrow \quad \text{rapid heating} \]

**Figure 2.15** A schematic diagram showing the formation of expanded graphite from natural flake graphite [55]

### 2.7.2 Structure

Expanded graphite also has a layered structure but its layer spacing is larger than that of natural flake graphite. As a result, expanded graphite possesses a higher expansion ratio in the c-axis. The expansion ratio of expanded graphite is possibly as high as 300. The structures of expanded graphite largely depend on experimental conditions such as temperature, concentration of oxidiser and intercalating time [56]. Figure 2.16 (a)-(b) shows the SEM micrographs of natural flake graphite and expanded graphite. Figure 2.16 (c)-(d) reveal the loose structure of expanded graphite.

Moreover, the TEM micrograph in Figure 2.17 clearly shows that a sheet of expanded graphite is composed of thinner sheets [57]. Figure 2.18 illustrates a model of expanded graphite and graphite nanosheets.
Figure 2.16 SEM micrographs of: (a) natural graphite flakes; (b) expanded graphite; (c)-(d) expanded graphite at higher magnification [56]

Figure 2.17 A TEM micrograph of thinner sheets inside expanded graphite [57]
2.8 The Preparation Method of Polymer/Graphite Nanocomposites

2.8.1 Melt blending

In this method, nanocomposites are prepared by blending a polymer and expanded graphite in molten state using a mixing instrument [58-61]. This method is solvent free.

2.8.2 Solution blending

In this method, a polymer and expanded graphite are mixed in a solvent. It can be produced in one of two ways. Either: (a) expanded graphite is first dispersed in a solvent to prepare a suspending solution. Then, the solution is added into a polymer solution prepared by dissolving the polymer with the same solvent [41], or (b) a polymer is first dissolved with a solvent and is directly mixed with expanded graphite. Mechanical stirring aided by a sonicator may be employed to promote optimal dispersion of expanded graphite in the polymer matrix [40,56]. The polymer is then intercalated into the gallery spaces of the expanded graphite to form polymer nanocomposites after the solvent evaporation.

Figure 2.18 A schematic model of expanded graphite and graphite nanosheets [57]
2.8.3 In situ polymerisation or intercalation polymerisation

This is a conventional method used to synthesise polymer nanocomposites [39,53,55, 57,62-66]. First, the gallery spaces of expanded graphite are intercalated by monomer and catalyst through physical absorption. In situ polymerisation can then be initiated after the intercalation process reaches equilibrium state. Figure 2.19 is a schematic illustration of the exfoliation process of expanded graphite during in situ polymerisation. During polymerisation, monomers in the gallery spaces of expanded graphite are gradually converted to polymer. In the meantime the gallery spaces increase and more monomer molecules can enter the galleries, resulting in further delamination and exfoliation of the graphite sheets [55,67]. Finally, they can be finely dispersed in the polymer matrix.

![Figure 2.19 Exfoliation process of expanded graphite during in situ polymerisation [55]](image)

2.9 The Morphology of Polymer/Graphite Nanocomposites

Expanded graphite maintains its layered structure in polymer matrices in which they are dispersed as evidenced by SEM micrographs. Figure 2.20 (a) shows the microscopic structure of expanded graphite, compared to that of a maleic anhydride grafted polypropylene/expanded graphite (gPP/EG) nanocomposite prepared via the solution intercalation method in Figure 2.20 (b).
TEM technique reveals that graphite nanosheets are randomly dispersed in polymer matrices forming an effective conducting network. A micrograph showing the typical structure of a PMMA/nanographite composite prepared via the in situ polymerisation is presented in Figure 2.21 [39]. The solid lines represent graphite nanosheets viewed from the direction parallel to the plane of the nanographite.

**Figure 2.20** SEM micrographs of: (a) EG; (b) a gPP/EG (1.99 vol%) nanocomposite [41]

**Figure 2.21** A TEM micrograph of a PMMA/sonicated graphite nanocomposite [39]
2.10 The Electrical Conductivity and Thermal Properties of Polymer/Graphite Nanocomposites

2.10.1 Electrical conductivity properties

Expanded and exfoliated or sonicated graphites have shown their abilities as excellent conductive fillers for polymer matrices in many research works [41,55-57].

The percolation threshold of transition in electrical conductivity from an insulator to a semiconductor of polymer/expanded graphite nanocomposites is lower than that of the polymer filled with unexpanded graphite and carbon black [56]. Among the three fillers, expanded graphite possesses the highest aspect ratio and the largest surface area per gram.

It is found that milling of graphite flakes causes a decrease in the aspect ratio of the graphite by pulverising both its thickness and diameter size, which will affect the percolation threshold for electrical conductivity [68]. Epoxy composites reinforced with sonicated graphite by the in situ polymerisation method percolated at lower than 5 wt% of reinforcement while the composites reinforced with sonicated plus milled graphite percolated at a higher wt% of reinforcement (10 wt%). The calculated aspect ratios of the sonicated plus milled graphite (1.1 μm, 20 nm) and the sonicated graphite (13 μm, 30 nm) from their average diameter and thickness were 55 and 433, respectively.

In addition, the methods used in preparing polymer/expanded graphite nanocomposites were found to cause differences in electrical conductivity results, due to the differences in morphology and internal microstructure of the expanded graphite dispersal phase in the nanocomposites [58]. During composite processing by the melt blending method, graphite particles are broken up resulting in graphite with low width-to-thickness ratios. Graphite nanosheets also tend to accumulate with each other during melt blending [53]. Both cases lead to a higher percolation threshold of
conductivity. Therefore, the solution blending and the in situ polymerisation methods are preferable to the melt blending method in nanocomposite compounding.

> Figure 2.22 Relationship between volume resistivity of PS/exfoliated graphite composites prepared by the in situ polymerisation and weight% of exfoliated graphite [59]

> Figure 2.23 Relationship between volume resistivity of PS/exfoliated graphite composites prepared by the melt blending and weight% of exfoliated graphite [59]
A percolation threshold comparison between two composite preparation methods, in situ polymerisation and melt blending, was proposed by Xiao et al. [59]. The percolation threshold in conductivity of in situ polymerised polystyrene/exfoliated-graphite composites is lower than 2.5 wt% (Figure 2.22). The volume resistivity of the melt-blended composites also decreases with increasing amounts of exfoliated graphite; however a sharp decrease in resistivity only appears when the amount of the exfoliated graphite reaches as high as 20 wt% (Figure 2.23).

More recently, a number of studies have been conducted and markedly low fractions of expanded or exfoliated graphite for satisfying the percolation threshold in conductivity of polymer/graphite nanocomposites have been reported. Chen and co-workers [42] found that the percolation threshold of PS/graphite nanosheet composites film prepared via in situ polymerisation of styrene with sonicated graphite in an ultrasonic bath was only about 1 wt%. The authors also reported that the application of sonication during the in situ polymerisation of methyl methacrylate (MMA) with graphite nanosheets resulted in PMMA/graphite nanosheets composites film with a percolation threshold as low as 0.6 wt% [53]. Aspect ratios of graphite nanosheets for using in the preparation of the two composites systems have been reported to be around 100-500. Chen’s co-worker also applied ultrasonic irradiation during in situ polymerisation of nylon 6/foliated graphite nanocomposites [69]. A critical concentration of less than 1.5 wt%, and the filler aspect ratios of 100-300 have been reported.

2.10.2 Thermal properties

There have been a number of reports on the improvement in coefficient of thermal expansion, thermal stability and thermal conductivity of polymer/graphite nanocomposites, compared to the pure polymer [59-60,68,70-73].

It was reported that surface-treated nanographite (acrylamide grafting) lowers the coefficient of thermal expansion (CTE) of epoxy matrix [68]. The CTE values of
epoxy filled with other commercial carbon materials, namely PAN-based carbon fibres, vapour-grown carbon fibres (VGCF) and carbon black are all higher than that of epoxy/treated nanographite as shown in Figure 2.24.

![Graph showing coefficients of thermal expansion](image)

**Figure 2.24** Coefficients of thermal expansion of composites with 3 vol% of reinforcements [68]

A similar result was obtained by Yasmin et al. [70]. The addition of 2.5 wt% of graphite platelets reduced the CTE value of pure epoxy (60×10⁻⁶/°C) to 36-41×10⁻⁶/°C. That is 30-40% lower than that of the epoxy matrix.

Du et al.'s TGA curves of pure polyaniline (PANI) and PANI/graphite nanocomposite in Figure 2.25 are evidence of an enhancement of thermal stability of polymer/graphite nanocomposites. The weight loss curve of the PANI/graphite nanocomposite clearly appears above that of the pure PANI.

The effectiveness of graphite in imparting thermal conductivity to polymers can be clearly seen from the works of two research groups using different thermally-conductive fillers. Aluminium nitride was used by Lee et al. [74] while graphite nanoplatelets were employed by Fukushima et al. [73]. The thermal conductivity of HDPE filled with 20 vol% of aluminium nitride measured by the hot-wire method
(0.6 W/m.K) was found to be much lower than that of HDPE filled with 20 vol% of graphite nanoplatelets (1.1 W/m.K).

Fukushima and co-workers [73] have also studied the thermal conductivity of nylon 6/graphite nanoplatelet composites measured by the halogen flash method. The thermal conductivity was found to increase almost linearly as a function of graphite nanoplatelet loading. The graphite nanoplatelet loading as high as 10 wt% was required to make the composites with thermal conductivities 3 times higher than that of the intrinsic value of nylon 6 matrix (Figure 2.26).

Moreover, it has been found that the addition of graphite affected the crystallisation temperatures ($T_c$) of high-density polyethylene and nylon 6 matrices in the composites. The crystallisation temperatures of the composites increased with increasing graphite loading [61,69]. A more specific view is that, at a given loading of graphite, the composites with smaller particles or disk-shaped graphite had a higher crystallisation temperature than that filled with larger or spherical graphite [61].
Chapter 2

Literature Review

Figure 2.26 An improvement of the thermal conductivity of nylon 6/graphite nanoplatelet composites (thermal conductivity values of all samples are derived from reference 73)

2.11 The Micromechanical Properties of Polymer/Graphite Nanocomposites

Micromechanical properties of a material can be basically obtained by using nanoindentation experiments. There have been numerous studies on micromechanical properties of materials. However, it is rare to find the studies on polymer/graphite composites.

Chasiotis et al. [75] reported that a nanoindentation performed on epoxy composites reinforced with graphite platelets having 15 \( \mu \text{m} \) average size would provide data on the localised micromechanical properties. In contrast, the bulk-level behaviour would be obtained through conducting a nanoindentation on the composites with 1 \( \mu \text{m} \)-sized graphite platelets. Figure 2.27 compares the elastic modulus, measured by the nanoindentation and the tension tests, of the pure epoxy to that of the composites with two different graphite platelet sizes (1 and 15 \( \mu \text{m} \)) and volume \% (0.5 and 3\%). At a
certain graphite platelet size, the elastic modulus slightly increases with increasing graphite content. In addition, the elastic modulus values from the indentations of the pure epoxy and of the 0.5% of 1 μm graphite epoxy composites are quite consistent with the values from the tension tests.

![Figure 2.27](image)

*Figure 2.27* The elastic modulus of epoxy/graphite platelet composites, at various graphite contents, measured by indentation and tension tests [75]

The storage modulus values of graphite nanoplatelet/epoxy composites measured by dynamic mechanical analysis (DMA) and that obtained from the nanoindentation (continuous stiffness measurement mode, CSM) in Odegard et al.’s work [76] have been found to increase with increasing graphite nanoplatelets. This trend is in good agreement with the studies on a HDPE filled with graphite conducted by Thongruang et al. [77]. Another finding was a decrease in storage modulus measured by micromechanical measurements with increasing nanoplatelet diameter.

### 2.12 Problems in This Research Area and Strategy

Three main problems of studies on polymer/expanded or exfoliated graphite nanocomposites and the way in which these problems have been individually tackled are described as follows.
2.12.1 The expansion of graphite

For polymer/graphite composites, a higher aspect ratio and surface area of graphite leads to a lower percolation threshold. The more expansion and exfoliation is achieved the greater the possibility to form a conductive path through the composites at a low loading.

It has been claimed that a mixture of concentrated sulphuric acid and nitric acid in a volume ratio of 4:1 can be used to prepare a graphite intercalation compound (GIC) [78]. By subjecting the GIC to high temperature (900-1050°C), expanded graphite can then be successfully achieved.

Graphite powder with diameter and thickness of the sheets in the range of 5-20 μm and 30-80 nm, respectively, has been obtained by sonication of expanded graphite in alcohol solution in an ultrasonic bath [39]. The aspect ratio (width-to-thickness) of graphite powder is as high as around 100-600.

A mixture of concentrated sulphuric acid and hydrogen peroxide (1:0.08, v/v) can also be used for preparing a GIC [71]. Instead of the high heat treatment, the microwave irradiation was employed for an energy saving approach. Expansion of graphite up to about 200 times along the c-axis was obtained after being irradiated for 10 s.

Moreover, expanded graphite can be prepared via graphite oxide (GO) by oxidisation of natural graphite flakes with KMnO4 in a solution of acetic anhydride and nitric acid at 30°C for 40 minutes, followed by heating the graphite oxide at 600°C under an N2 atmosphere [79]. An expansion ratio of about 30 has been reported.

2.12.2 The dispersion of graphite in polymer matrices

The dispersion of graphite within polymers has a significant influence on the properties of the composites. For electrical properties, it affects variation of the
percolation threshold for conductivity transition. Good dispersion and strong bonding also lead to mechanical property enhancement.

Zheng et al. [40,56] promoted fine dispersion of expanded graphite in a PMMA matrix by using intensive stirring and an ultrasonic bath during the preparation of PMMA/expanded graphite composites by the solution blending method. The sufficient adsorption of the PMMA molecular chains onto various pores of the expanded graphite is also considered as the likely factor contributing to good dispersion. The solution concentration was kept low, as high viscosity may hinder the polymer chains from entering the minor pores of the graphite.

Compatibility between expanded graphite and an epoxy matrix has been successfully improved by pulverising the expanded graphite flakes into nanoplatelets and treating their surfaces [68,80-81]. The expanded graphite flakes can be pulverised by using an ultrasonic processor. Various treatments have been applied to the graphite nanoplatelets including nitric acid treatment, O$_2$ plasma treatment, UV/ozone treatment, amine grafting and acrylamide grafting. Increases in hydroxyl, carbonyl and carboxyl groups on the graphite surfaces have been reported after the nitric acid, O$_2$ plasma and UV/ozone treatment, while acrylamide and amine groups are formed on the surfaces of the graphite nanoplatelets by acrylamide grafting and amine grafting, respectively. Such functional groups can form bonds with the epoxy matrix, resulting in improved compatibility.

2.12.3 The level of electrical conductivity

The conductivity of composites is closely related to the conductivity of the filler. Graphite whose volume conductivity is about $10^4$ S/cm can be used to make polymer composites with conductivities of nearly $10^4$ S/cm. Doping of graphite with metal chloride results in metal chloride intercalated graphite with improved electrical conductivity.
Blazewicz et al. [82] prepared CuCl$_2$ and MnCl$_2$ intercalated fibres by an intercalation process i.e. high heating of the fibres and anhydrous chlorides in a chlorine atmosphere. Resistivities of the fibres are shown in Table 2.4. The lowest resistivity which is almost 20 times lower than the pristine fibres, has been obtained for MnCl$_2$ intercalated P-120 graphite fibres.

**Table 2.4** Comparative resistivities of pristine fibres and metal chloride intercalated fibres [82]

<table>
<thead>
<tr>
<th>Fibres</th>
<th>Resistivity, $\mu\Omega$·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pristine fibres</td>
</tr>
<tr>
<td>P-75</td>
<td>$580 \pm 78$</td>
</tr>
<tr>
<td>P-100</td>
<td>$260 \pm 32$</td>
</tr>
<tr>
<td>P-120</td>
<td>$212 \pm 17$</td>
</tr>
</tbody>
</table>
CHAPTER 3
EXPERIMENTAL

3.1 INTRODUCTION

This research is mainly divided into three parts. The first part is about the filler preparation and its chemical surface treatment. The second part is about the composites and doped composites fabrication. The mechanism of the electrical conductivity enhancement by doping is in the final part. The materials, instrumentations, sample fabrication, experimental procedures and characterisation techniques employed are detailed in the following sections:

3.2 MATERIALS

3.2.1 Graphite

Expandable graphite flakes used for preparing expanded graphite were supplied by Qing Dao Graphite Company (China). The specifications of the expandable graphite are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1 Specifications of the expandable graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Expandable graphite</strong></td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>Expansion volume</td>
</tr>
<tr>
<td>pH value</td>
</tr>
<tr>
<td>Volatiles</td>
</tr>
<tr>
<td>Size</td>
</tr>
<tr>
<td>Sieving residual</td>
</tr>
</tbody>
</table>
3.2.2 Polyethersulphone (PES)

PES, molecular weight about 10,000 was supplied by Cytec Engineered Materials Limited (UK) in the form of pellets and was dried in a vacuum oven at 150°C for 1 day before use.

3.2.3 Lithium chloride (LiCl)

LiCl, purchased from Aldrich Company (UK), was dried at 100°C for 1 day, then, used as a dopant.

3.2.4 Sodium chloride (NaCl)

NaCl was purchased from Aldrich Company (UK) for doping purposes. It was dried at 100°C for 1 day before use.

3.2.5 Potassium chloride (KCl)

KCl, purchased from Aldrich Company (UK), was used to dope PES/treated graphite composites after drying at 100°C for 1 day.

3.2.6 N, N-Dimethylformamide (DMF)

DMF, whose density is 0.944 g/cm³, was purchased from Aldrich Company (UK) and used as supplied as a solvent to prepare PES/graphite composites.

3.2.7 Nitric Acid

Concentrated nitric acid, whose density is 1.42 g/cm³, was purchased from Fisher Scientific Company (UK) and used as supplied to treat the graphite surfaces.

3.2.8 Sulphuric Acid

Concentrated sulphuric acid was purchased from Fisons Scientific Equipment Company (UK) and used as supplied to treat the graphite surfaces.
3.2.9 Ethanol

Absolute ethanol purchased from Fisher Scientific Company (UK) was used as supplied to prepare ethanol solutions for the sonication of graphite.

3.2.10 Methanol

Methanol purchased from Fischer Scientific Company (UK) was used as supplied to precipitate composites from a DMF solution.

3.2.11 Silver Paint

Fast-drying silver paint in methyl isobutyl ketone solvent manufactured by Agar Scientific Limited (UK) was used as an electrode material for volume resistance measurements.

3.3 INSTRUMENTS

3.3.1 Furnace

Carbolite Furnaces Model CSF 1200 was used to prepare expanded graphite from the expandable graphite flakes.

3.3.2 Ultrasonic Dismembrator

Ultrasonic Dismembrator Model 500 and disruptor horn, Fisher Scientific Company (UK) was employed at half of maximum amplitude to prepare graphite nano-sheets (Figure 3.1).

3.3.3 Fourier Transform Infrared Spectrometer (FTIR)

A Unicam FTIR Model Mattson 3000 was used to observe the chemical groups which were introduced on the surfaces of the graphite by acid treatments.

3.3.4 Scanning Electron Microscope (SEM)

SEM Model Cambridge Instrument Stereoscan 360 and Model LEO1530 VP were used to observe the morphologies of graphite, and of the PES and its composites, respectively.
3.3.5 Transmission Electron Microscope (TEM)

TEM Model JEOL JEM 2000 FX was used to visualise the local state of dispersion of graphite in the PES matrix and a Cambridge Huxley ultramicrotome was used to prepare thin samples for TEM observations.

3.3.6 X-Ray Diffractometer (XRD)

X-ray tube Model Hilton Brooks DG3 and X-ray diffractometer Model Philip Type PW 1050 was used to determine gallery spacings of the expandable graphite and sonicated graphite in composites.

3.3.7 X-Ray Photoelectron Spectrometer (XPS)

XPS Model Vg Scientific was employed to analyse the elements on the surfaces of the treated graphite after doping.

3.3.8 Nanoindenter

A Nanoindenter instrument of Micro Materials Limited with a three-sided pyramidal shape (Berkovich) diamond indenter was used to test the nanohardness, reduced modulus, elastic modulus and nanoscratch of the PES and its composites.
3.3.9 Differential Scanning Calorimeter (DSC)

DSC Model 2010 of TA Instruments Inc. was used to determine glass transition temperatures of the pure PES, PES/graphite composites and LiCl-doped PES/graphite composites. DSC was also used to measure enthalpic relaxations and to determine characteristic lengths.

3.3.10 Modulated Differential Scanning Calorimeter (MDSC)

MDSC Model 2920 manufactured by TA Instruments Inc. was used to measure thermal conductivities of the pure PES, PES/untreated and treated graphite composites.

3.3.11 Thermogravimetric Analyser (TGA)

Thermogravimetric Analyser Model Q50 from TA Instruments Inc. was used to measure weight loss % of the PES and PES/treated graphite composites.

3.3.12 Four-Wired Digital Multimeter

Four-Wired Digital Multimeter Model Solartron 7150 (Figure 3.2) was used to measure the electrical volume resistances of samples at room temperature (20°C) and/or at elevated temperatures (50, 75, 100, 125, 150 and 190°C).

Figure 3.2 Four-wired digital multimeter
3.4 THE PREPARATION OF SAMPLES

3.4.1 The preparation of expanded graphite

Expanded graphite was prepared by subjecting the expandable graphite flakes to a preheated furnace at a temperature of 850°C for 2 minutes.

3.4.2 The sonication of expanded graphite

The expanded graphite was immersed in a 50 vol% of an aqueous alcohol solution and sonicated with an ultrasonic dismembrator and a disruptor horn for about 90 minutes at 50% of maximum amplitude. The dispersion was filtered, washed with deionised water and dried at 100°C in a vacuum oven for 2 days. The resulting material (sonicated graphite) is later known as micro-/nano-graphite which will simply be referred to as graphite.

3.4.3 The preparation of surface treated expanded graphite

3.4.3.1 The effect of acid type

40 ml of concentrated nitric acid was added to the expanded graphite (1 g), the mixture was then heated and maintained at 60°C using a magnetic stirrer hot-plate for periods of 0.5, 1 and 2 days. Then the resulting materials were 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. When concentrated sulphuric acid was used as a treating agent, the same procedure was applied.

3.4.3.2 The effect of treatment time

The expanded graphite (1 g) was suspended in 40 ml of concentrated nitric acid. Then the mixture was heated and maintained at 60°C using a magnetic stirrer hot-plate for periods of 2, 4, 12, 24 and 36 hours. The resulting materials were 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.
3.4.3.3 Nitric and sulphuric acid mixture treatment

Treated expanded graphite was prepared by using a mixture of acids and a treatment time as reported in the literature [84]. The expanded graphite (1 g) was suspended in 40 ml of a mixture of concentrated nitric acid and sulphuric acid in a volume ratio of 1:3. Then the whole mixture was heated and maintained at 60°C using a stirrer hot-plate. After 20 minutes of the reaction, the resulting material was then filtered and washed with deionised water until pH 7 was reached and dried in an oven at a temperature of 100°C under vacuum for 2 days.

3.4.4 The preparation of nitric acid-treated graphite

The surfaces of the graphite were treated with concentrated nitric acid by following the procedure in Section 3.4.3.1 using a treatment time of 4 hours.

3.4.5 The preparation of PES/graphite composites

PES/graphite composites were fabricated by the solution blending method. The PES and nitric acid-treated or untreated graphite with different weight contents (1, 3, 5, 8 or 10 wt% related to the PES) were dissolved in DMF (80 wt% related to the PES), then, were heated and maintained at a temperature of 50°C using a stirrer hot-plate for 24 hours. After that the solutions were precipitated by adding methanol and stirring for 15 minutes at room temperature. The resulting materials were dried at room temperature for 14 days and 10 days in a vacuum oven at 155°C. Then, the composites were press moulded (240°C, 5 tons) between heated metal plates with lined aluminium foils into sheet form with a thickness of about 0.3 mm.

3.4.6 The preparation of LiCl-doped PES/graphite composites

LiCl-doped PES/graphite composites were prepared by the solution blending method. 5 wt% of the treated or the untreated graphite and lithium chloride (0.02, 0.04, 0.06, 0.08 or 0.1 wt% related to graphite) in a DMF solution (0.001 g/100 ml) were heated and maintained at a temperature of 50°C using a magnetic stirrer hot-plate. After 3 hours of stirring time, the PES was then added to the solution and maintained at the same temperature for 1 day. After that the solution was
precipitated by adding methanol and stirring for 15 minutes at room temperature. The resulting material was dried at room temperature for 14 days and in a vacuum oven at 155°C for 10 days. Then, the composites were press moulded into a form of sheet with a thickness of about 0.3 mm for the electrical resistance measurements.

3.4.7 The preparation of samples for the study to determine the mechanism of the enhancement of electrical conductivity by doping

3.4.7.1 The effect of the size of intercalate

Another two dopants, sodium chloride (NaCl) and potassium chloride (KCl), were used to dope the PES/graphite composites. 5 wt% of the treated graphite and NaCl or KCl (0.02, 0.04 or 0.06 wt% related to the graphite) in a DMF solution and the PES matrix were blended together using the same procedure as in Section 3.4.6.

3.4.7.2 The effect of intercalation

3.4.7.2.1 Variation of intercalations of the intercalate

A treated graphite content of 5 wt% and 0.08 wt% of LiCl in a DMF solution was heated and maintained at 50°C using a stirrer hot-plate. The stirring time was varied from 3 hours to 1, 3 and 7 days before adding the PES. The rest of the procedure was the same as in Section 3.4.6.

3.4.7.2.2 Minimisation of intercalations of the intercalate

A stirrer hot-plate was employed to heat the PES and 0, 0.06, 0.08 or 0.1 wt% of LiCl in a DMF solution and maintained at 50°C for 1 day. Then, the treated graphite was added and stirred mechanically for 10 minutes before coagulating with methanol. The rest of the procedure was drying and preparing thin films for the electrical resistance measurements, the same as in Section 3.3.5.
3.5 SAMPLE CHARACTERISATIONS [85]

3.5.1 Morphology observations

3.5.1.1 Scanning Electron Microscopy [86]

The morphologies of samples were observed by using SEM. It was conducted in the Secondary Electron Image (SEI) mode at an accelerated voltage of 5-20 kV and several magnifications. In the case of low conductive samples, they were mounted on aluminium stubs and spattered with thin layers of gold on their surfaces before the visualisations.

3.5.1.2 Transmission Electron Microscopy [87]

The local state of dispersion of the graphite in the PES matrix was visualised by using a Transmission Electron Microscopy technique after preparing samples with a Cambridge Huxley ultramicrotome below room temperature to obtain ultra thin specimens. Transmission electron microscopy was performed at an accelerated voltage of 200 kV.

3.5.1.3 X-ray Diffractometry

Gallery spaces of the expandable graphite and sonicated graphite in composites were investigated using an X-ray diffraction technique. X-rays were produced from the X-ray tube with a copper target operated at a voltage of 40 kV and a current of 30 mA. The investigation was conducted on the X-ray diffractometer using Cu Kα radiation (λ = 0.1542 nm). The samples were scanned at a rate of 0.24° min⁻¹ from about 10° to 30° at 29.

Background [88]

X-ray diffractometry is a useful technique to derive information about the structures of semi-crystalline and amorphous materials. When X-rays of one wave length pass through a crystalline material, they will be scattered by all atoms of the crystal lying in the path of the incident beam [89]. The scattered waves are called diffracted beams. Figure 3.3 shows the diffraction of X-rays by a crystal. In diffraction, the angle of incidence (θ), also known as Bragg's angle, is defined as
the angle between the crystal plane and the incident beam. The angle of diffraction is the total deviation of the diffracted beam from the original incident beam, thus, equal to $2\theta$. In order to fulfil Bragg's Law, the difference in the distances travelled by two incident beams A and B must be exactly an integral number ($n$) of wavelength ($\lambda$).

![Figure 3.3 X-ray diffraction by a crystal](image)

From elementary trigonometry:

$$ \sin \theta = \frac{DE}{CE} $$

$$ = \frac{DE}{d'} $$

$$ \therefore DE = d' \sin \theta $$

$$ DE + EF = 2d' \sin \theta $$

$$ n\lambda = 2d' \sin \theta $$

$$ \lambda = 2 \frac{d'}{n} \sin \theta $$

where $\frac{d'}{n}$ is the spacing between adjacent planes, of planes in the form $(nhknl)$, which are parallel to a plane $(hkl)$, and $n$ corresponds to the order of the reflections. The first order of the reflections occurs if $n = 1$ and then a spacing of a plane $(hkl)$ will simply be $d'$. If $n > 1$, the reflections are called higher order. By setting $d = \frac{d'}{n}$, the Equation above can be rewritten as:
\[ \lambda = 2d \sin \theta \]  

Equation 3.1 which is derived from Bragg's law is important in indexing X-ray diffraction patterns and determining distances between layers in a crystal [89].

3.5.2 Functional group determination

3.5.2.1 FT-IR Spectroscopy

Functional groups which were introduced on to the surfaces of the graphite by acid treatment were observed by using a FT-IR spectroscopy technique. Samples and potassium bromide were finely ground before pressing in a die using a pressure of 10 tons to produce a thin transparent disc. FT-IR spectra were recorded at 64 scans and 4 cm\(^{-1}\) resolution over a frequency range of 4000 - 400 cm\(^{-1}\).

**Background** [91]

Infrared spectroscopy is a technique for the measurement of the vibrational frequencies of a sample positioned in the path of an IR beam. It is used to identify the certain functional groups in molecules; a particular bond type has specific frequencies at which it vibrates corresponding to energy levels. It is also used to identify compounds by matching the spectrum of an unknown compound with the reference spectrum (fingerprinting) [92].

Bonds in a molecule can vibrate in six different ways, symmetrical and asymmetrical stretching, scissoring, rocking, wagging and twisting (Figure 3.4). When assigning peaks to specific groups in the IR region, the most useful vibration is stretching.

The region of most interest for chemical analysis is the mid-infrared region (4000 to 400 cm\(^{-1}\)). IR absorption information is generally presented in the form of a spectrum with wave number as the x-axis and absorption intensity or percentage transmittance (% T) as the y-axis. Since absorbance ranges from infinity to zero but transmittance ranges from 0 to 100% T, the transmittance spectra provide
better contrast between intensities of weak and strong bands. The relationship between absorbance and transmittance is as follows:

$$A = \log_{10} \left( \frac{I}{T} \right) = -\log_{10} T = -\log_{10} \frac{I}{I_0}$$  \hspace{1cm} \text{(3.2)}

where:

$$I_0 = \text{the radiant power incident on the sample}$$

$$I = \text{the radiant power transmitted by the sample}$$

\[ \text{Figure 3.4 A variety of vibrations of a molecule [93]} \]

Nowadays, modern infrared spectrometers use a Fourier transform infrared system. A Fourier transform is a mathematical operation used to translate an interferogram into its IR spectrum. Instead of viewing each bond type frequency sequentially as in a basic IR spectrometer, all frequencies are examined simultaneously in an FT-IR spectrometer.
From an IR source in Figure 3.5, light travels to a beam splitter where half of the light is transmitted to a moveable mirror and another half is reflected to a fixed mirror. Light travels back from the two mirrors, then, recombines at the beam splitter before passing through a sample and to a detector. While the light intensity of the recombined beam is being recorded at the detector, in the mean time the moveable mirror is travelling towards the beam splitter. As the moveable mirror is travelling, different frequencies are reflected in different ways, producing constructive and destructive interferences over time (Figure 3.6). Summation of the interferences generates an interferogram from which a Fourier transform is used for calculating a spectrum.

![Figure 3.5 FT-IR spectrometer](image)

**Figure 3.5 FT-IR spectrometer [94]**

![Interferogram and Waveforms](image)

**Figure 3.6 Interferogram [94]**
A brief summary of the reference table of IR data is given in Table 3.2 for some of the main groups. In interpretation of IR spectra, the three significances that need to be considered are intensity (weak, medium or strong), shape (sharp or broad) and position (cm$^{-1}$).

**Table 3.2 Characteristic infrared absorption frequencies [95-96]**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Compound type</th>
<th>Frequency range (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>Alkanes</td>
<td>2960-2850 (s) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1470-1350 (v) bend</td>
</tr>
<tr>
<td>C-H</td>
<td>Alkenes</td>
<td>3080-3020 (m) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000-675 (s) bend</td>
</tr>
<tr>
<td>C-H</td>
<td>Aromatic rings</td>
<td>3100-3000 (m) stretch</td>
</tr>
<tr>
<td>C=C</td>
<td>Alkenes</td>
<td>1680-1640 (m, w) stretch</td>
</tr>
<tr>
<td>C=C</td>
<td>Aromatic Rings</td>
<td>1600, 1500 (w) stretch</td>
</tr>
<tr>
<td>C-O</td>
<td>Alcohols, Ethers, Carboxylic acids, Esters</td>
<td>1260-1000 (s) stretch</td>
</tr>
<tr>
<td>C=O</td>
<td>Aldehydes, Ketones, Carboxylic acids, Esters</td>
<td>1760-1670 (s) stretch</td>
</tr>
<tr>
<td>O-H</td>
<td>Alcohols, Phenols</td>
<td>3670-3580 (s) stretch</td>
</tr>
<tr>
<td></td>
<td>Carboxylic acids</td>
<td>3550-3500 (s) stretch</td>
</tr>
<tr>
<td>O-H</td>
<td>Hydrogen bonded—Alcohols, Phenols</td>
<td>3600-3200 (b) stretch</td>
</tr>
<tr>
<td></td>
<td>— Carboxylic acids</td>
<td>3300-2500 (b) stretch</td>
</tr>
</tbody>
</table>

w = weak, m = medium, s = strong, b = broad, v = variable

### 3.5.2.2 X-Ray Photoelectron Spectroscopy

The elements on the surfaces of the treated graphite after the surface treatments and after doping were analysed by using an XPS technique. X-rays were AlKα radiation which was operated at a voltage of 8 kV and a current of 20 mA.
Background [97-99]

XPS, also known as ESCA (Electron Spectroscopy for Chemical Analysis), is an extremely sensitive technique for analysing the elements presenting on the surfaces with efficiency of filtering out signal from the major elements presenting in the sample.

XPS spectrometer consists of a source of primary radiation, generally AlK\(\alpha\) (energy 1486.6 eV) and an electron energy analyser all contained within an ultra-high vacuum (UHV) chamber. There is a secondary UHV chamber fitted with various sample preparation facilities. A data system is used for data processing. Figure 3.7 shows an XPS spectrometer.

\[E_B = h\nu - E_K - W\]  \hspace{1cm} (3.3)
The kinetic energy of the electron \( (E_k) \) measured by the spectrometer is not an intrinsic property of materials as it is dependent on the photon energy of the X-rays employed. In contrast, the binding energy of the electron \( (E_a) \) derived from Equation 3.3 is the parameter which identifies the electron. The data system will present data as a graph of intensity (usually expressed as counts or counts/s) versus binding energy known as the X-ray induced photoelectron spectrum. The table of binding energies accessible with AlK\( \alpha \) radiation for individual peak identifications of the elements is presented in Appendix 1.

The intensity of a photoelectron peak will usually be taken as the integrated area under the peak following the subtraction of the background. The atomic percentage of the elements concerned is then calculated by dividing the peak area by the sensitivity factor and expressing it as a fraction of the summation of all normalized intensities [97].

\[
A\% = \{ (I_A/F_A)/\Sigma (I/F) \} \times 100\% \tag{3.4}
\]

where:

\[
\begin{align*}
A\% & = \text{Atomic percentage of an element} \\
I & = \text{Intensity taken as the integrated area under the peak} \\
F & = \text{Relative sensitivity factor}
\end{align*}
\]

3.5.3 Micromechanical property testing

3.5.3.1 Nanoindentation

Mechanical property data was obtained by means of a nanoindentation technique using an ideal Berkovich indenter, a three-sided pyramidal shape. The testing condition for the hardness and reduced modulus of the PES and PES/treated graphite composites was set at a maximum load of 5 mN, a loading and unloading rate of 0.5 mN/s and an indentation number of 10. An elastic modulus was, then, able to be calculated using Equation 3.5 and substituting the obtained reduced
modulus value and 0.4 for Poisson's ratio of the indented material [100]. For a
three-sided pyramidal diamond indenter, $E_i = 1140$ GPa and $\nu_i = 0.07$ GPa [101].

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$ (3.5)

where:
- $\nu$ = Poisson's ratio of the indented material
- $\nu_i$ = Poisson's ratio of the indenter
- $E_r$ = Reduced modulus
- $E$ = Elastic modulus of the indented material
- $E_i$ = Modulus of the indenter

**Background**

Nanoindentation is a technique for determining mechanical properties of material
surfaces using either a pyramidal or sphere or conical-shaped diamond indenter. A
material surface which is indented with an indenter loaded with a force results in a
penetration depth ($h$) of the indenter into the material. Load-displacement data is
recorded as a function of time. An indentation experiment consists of a single
loading-unloading cycle (Figure 3.8).

![Figure 3.8 A schematic diagram of a typical indentation load-displacement curve [102]](image)

Figure 3.8 A schematic diagram of a typical indentation load-displacement curve [102]
As the specimen is loaded, the indentation increases and reaches a maximum \((h_{\text{max}})\) at a maximum load \((P_{\text{max}})\). The data obtained from an unloading curve provides information regarding plastic, viscoelastic and elastic behaviour of the tested material [102]. In case of a viscoelastic-plastic material, a loading curve is OB and an unloading curve is BC segment. \(h_r\) is a residual displacement of the indenter after removing the indenter, and contact depth or plastic depth \((h_c)\) is an intercept of a tangent line drawn from the first part of the unloading curve. The area A1 (OBC) corresponds to the plastic work done in the viscoelastic-plastic case; whereas, the elastic work recovered during the unloading segment is represented by the area A2 (CBC'). In the case of a purely plastic material, an unloading curve is a straight line (BC') and \(h_r = h_{\text{max}}\) (A2=0).

**Hardness**

Hardness is proportional to the strength of a material and can be calculated by using the following Equation [103].

\[
H = \frac{P_{\text{max}}}{A} \quad (3.6)
\]

where:

\[
\begin{align*}
H & = \text{Hardness, GPa} \\
P_{\text{max}} & = \text{Maximum load, mN} \\
A & = \text{Projected contact area at the maximum load, nm}^2
\end{align*}
\]

\(A\) is generally expressed in terms of contact depth or plastic depth \((h_c)\), defined in Figure 3.8. For an ideal Berkovich indenter, \(A = 24.5 h_c^2\) [101].

**Reduced modulus of the indentation contact**

The basic idea is that an initial slope of an unloading curve is directly related to a reduced modulus. Thus, a reduced modulus can be analysed from an unloading curve and be calculated by using the following Formula [103].
where:
\( E_r = \frac{\sqrt{\pi} \, S_{\text{max}}}{2\beta \, \sqrt{A}} \)

The nanoscratch test

Nanoscratch tests were performed over the sample surfaces using the same nanoindentation equipment with a Berkovich pyramidal diamond indenter having a tip radius of 50 nm and an included angle of 60°. The normal load applied to the surfaces was ramped up until substantial damage occurred. Three nanoscratches were made for each sample at three different normal loads ranging from 20 to 42 μN.

3.5.4 Glass transition temperature and enthalpic relaxation determination

3.5.4.1 Differential Scanning Calorimetry

A non-isothermal scanning for a glass transition temperature was carried out on a DSC as follows. After drying in an oven at 150°C for 1 day, samples of about 10 mg in a sealed aluminium pan were initially rapidly heated from room temperature to 240°C. After maintaining this temperature for 5 minutes, samples were rapidly cooled to 100°C and were heated from 100 to 240°C at a heating rate of 10°C/min. The whole thermal scanning was conducted under nitrogen atmosphere.

DSC was also used to measure the enthalpic relaxations of the PES, PES/graphite composites and LiCl-doped PES/graphite composites with 0.06 wt% of LiCl. Samples of about 10 mg in a sealed aluminium pan were carried out on the temperature program as follows: rapid heating to 240°C to eliminate thermal
history, followed by aging at \((T_g-3)°C\) for 15, 40 or 60 minutes; rapid cooling to 140°C, followed by a reheating to 240°C at a heating rate of 10°C/min. The whole thermal scanning was conducted under nitrogen atmosphere. The procedure was repeated by changing the annealed temperature from \((T_g-3)°C\) to \((T_g-6)°C\) and \((T_g-9)°C\).

**Background**

Differential Scanning Calorimetry is a thermal analysis technique which has been used for studying thermal transitions in materials. A schematic diagram of a DSC instrument is shown in Figure 3.9.

![Figure 3.9 A schematic diagram of a DSC instrument](image)

There are two holders; one for a sample and another one for a reference, placed in a reservoir of coolant. Each holder base is equipped with a temperature sensor and a micro-furnace with a heater. If the sensors detect a temperature difference between the sample and the reference, energy will be supplied until the difference is typically less than 0.01K [105]. The energy input per unit time (resultant heat flow) is recorded as a function of temperature or time as the sample and the reference are being heated isothermally or in a linearly rising temperature program. Thermodynamic properties of materials, such as heat capacities, glass transition temperatures and melting points are quantified from the measurements. The resultant heat flow is described by Equation 3.8 [105]:

\[ \text{Equation 3.8} \]
\[
\frac{dQ}{dt} = Cb + f(T,t) \tag{3.8}
\]

where:

- \( \frac{dQ}{dt} \) = Resultant heat flow
- \( C \) = Heat capacity of the sample
- \( b \) = Rate of temperature change or \( \frac{dT}{dt} \)
- \( f(T,t) \) = Heat flow from kinetic process

In DSC, the two individual components on the right hand side of Equation 3.8 cannot be distinguished, only the sum of the two components called the total heat flow is determined.

### 3.5.5 Thermal conductivity determination

#### 3.5.5.1 Modulated Differential Scanning Calorimetry

Thermal conductivities were obtained by using an MDSC technique to measure specific heat and apparent heat capacities. Each sample was prepared into a thin specimen (<0.5 mm) and a thick specimen (>3.0 mm). The thin specimens in sealed aluminium pans were carried out on the temperature program under nitrogen atmosphere as follows for a specific heat measurement: rapid cooled to 0°C, followed by a scanning to 75°C at a constant heating rate of 3°C/min with a modulation amplitude of ±1°C over an 80 s period. The specific heat values at 27°C of all samples were recorded. For an apparent heat capacity measurement of the thick specimens in unsealed aluminium pans, an isothermal scanning at 27°C for 40 minutes with a modulation amplitude of ±1°C over an 80 s period were carried out. The apparent heat capacity value of each sample was calculated by multiplying the mean value of its apparent heat capacities per gram, derived in the last ten minutes, to its weight.
3.5.6 Thermal stability analysis

3.5.6.1 Thermogravimetry

Weight loss % of the PES and PES/treated graphite composites were measured by using a thermogravimetry technique upon heating from room temperature to 600°C at a heating rate of 10°C/min under nitrogen atmosphere.

![Thermogravimetry Curve](image)

**Figure 3.10** A schematic two-stage thermogravimetry curve and the corresponding derivative curve [105]

**Background [105]**

Thermogravimetry is a thermal analysis for examining the changes of sample mass as a function of temperature in a scanning mode or as a function of time in an isothermal mode. It is used to characterise the thermal stabilities and the decompositions of materials under the experimental condition employed. Thermogravimetry curves are plotted between mass change ($\Delta m$) expressed as a percentage on the vertical axis and temperature ($T$) or time ($t$) on the horizontal axis. Figure 3.10 shows a schematic two-stage thermogravimetry curve. $T_d$ and $T_f$ are the decomposition and the final temperatures, respectively. A peak in the Derivative Thermogravimetry (DTG) curve shows a maximum change in mass with respect to time of the thermogravimetry curve ($\frac{dm}{dt}$). The DTG curve becomes zero at an interval of a constant mass. The position of a peak may be used as a fingerprint of the presence of a substance in a mixture. The area under
the DTG peak is also proportional to the mass loss. Therefore, the DTG peak area or the peak height is useful in the relative mass loss comparison [106].

3.5.7 Electrical conductivity determination

3.5.7.1 Four-wired resistance measurements

The volume resistances of samples were measured using four-wired resistance measurements with silver paint as an electrode material. Press moulded samples (240°C, 5 tons) were cut into 1.9x1.9 cm² specimens with a thickness of about 0.3 mm, then, silver paint was applied all over the top and bottom of the specimen surfaces and they were dried in air. The measurements were conducted at room temperature or at elevated temperatures with 60 s of electrification. The volume resistivity, $\rho_v$, can be derived from the following Equation [14]:

$$\rho_v = \frac{A}{t} R_v$$  \hspace{1cm} (3.9)

where:

$A$ = The effective area of the measuring electrode, cm²

$t$ = Average thickness of the specimen, cm

$R_v$ = Measured volume resistance, kΩ

Volume conductivity, $\sigma_v$, is thus the reciprocal of the volume resistivity.

Background

Four-wired resistance measurement is a method of measuring the sample resistance excluding the resistance of test leads. A digital multimeter, equipped with a current and a voltage measuring device, is connected across a sample resistance ($R_s$) through two pairs of leads ($R_{lead}$) as shown in Figure 3.11. Current is supplied through the sample from the V+ to V- terminals via the test leads. The sense lines (I+ and I-) are connected to the sample and measure the voltage drop across the sample excluding the voltage across the test leads. Besides, the input impedance of the voltage measuring device is believed to be high enough that no current will flow into it. Therefore the resistance reading is due to the sample as
long as the resistance of the sample is not higher than 1 MΩ [107]. Otherwise, a current leakage to the voltage measuring part may affect the voltage value and consequently affect the resistance reading of the sample.

\[ V = I \times R \]

\[ I_{\text{leak}} = \frac{V_{\text{leak}}}{R_{\text{leak}}} \]

**Figure 3.11** A schematic diagram of the four-wired method [108]
CHAPTER 4

MORPHOLOGICAL AND MICROMECHANICAL PROPERTIES OF PES/GRAPHITE CONDUCTIVE COMPOSITES

4.1 INTRODUCTION

Normally, the shape and the orientation of conductive fillers in insulating host matrices have influences on the electrical conductivity percolation threshold of the composite materials. In the case of polymer/graphite composites, a percolation threshold depends on the degree of the expansion and exfoliation of graphite. The more surface area and the higher the aspect ratio the graphite has, the lower the amount that is needed to form a continuous network. Therefore expandable graphite, a graphite intercalation compound, has been employed. With thermal shock, expanded graphite can be obtained from the graphite intercalation compound. Recently, a sonication technique has been applied to this field for the purpose of exfoliation of expanded graphite. Another important factor which contributes to a low percolation threshold is the dispersion of graphite in polymer matrices. Enhancements of interfacial interactions between graphite and polymers have been successfully done through functionalisations of graphite surfaces.

4.2 THE MORPHOLOGY OF GRAPHITE

Subjecting expandable graphite to a sufficiently high temperature (in this work 850°C for 2 minutes) causes decomposing of an intercalate trapped between graphite layers, which will force the graphite layers apart in the c direction. Figure 4.1 (a) and (b) show SEM images of the expandable graphite flakes, compared to that of expanded graphite in Figure 4.1 (c). It can be seen that the expandable graphite flakes have a dense structure composed of many graphite sub-layers. On the other hand, the expanded graphite is a loose and porous material consisting of pores of various sizes and a sheet thickness in the range of hundreds of nanometres owing to the high volume expansion.
Chapter 4 Morphological and Micromechanical Properties of PES/Graphite Conductive Composites

The expanded graphite is effectively fragmented into sonicated graphite with a thickness of about a hundred nanometres after it is subjected to ultrasonic irradiation in an alcohol solution. The sonicated graphite exhibits a much higher aspect ratio and a larger surface area per gram than the expandable graphite flakes. The high aspect ratio and the large surface area lead to a lower percolation threshold. Figure 4.1 (d) shows an SEM image of the sonicated graphite suggesting a diameter in the range 10-60 μm. Thus, the aspect ratios are as high as around 100-600. It can also be seen that some of the sheets are composed of the

Figure 4.1 SEM photomicrographs of: (a) expandable graphite flakes at low magnification; (b) expandable graphite flakes at higher magnification; (c) expanded graphite; (d) sonicated graphite
thinner sheets. The sonicated graphite is used in PES composite fabrication and is simply called graphite.

4.3 CHARACTERISATION OF TREATED EXPANDED GRAPHITE AND PES/GRAPHITE COMPOSITES

The expandable graphite flakes used in this work are H$_2$SO$_4$-graphite intercalation compound (H$_2$SO$_4$-GIC) resulting from the reaction between natural flake graphite and a mixture of concentrated sulphuric acid and concentrated nitric acid in a volume ratio of 4:1. Sulphuric acid serves as an intercalate; whereas, nitric acid is an oxidiser. Figure 4.2 shows the FT-IR spectrum of the expandable graphite flakes. It can be seen that oxygen containing functional groups such as COOH and C-OH, are originally presented on the surfaces of the expandable graphite flakes [96, 109]. After the heat treatment, the same functional groups remain on the surfaces of the expanded graphite as can be seen from the FT-IR spectrum of the expanded graphite in Figure 4.2. The double peaks at 2361 and 2341 cm$^{-1}$ are due to gaseous CO$_2$ which have originated from the air environment.

![FT-IR spectra of the expandable graphite flakes and expanded graphite (EG)](image)

*Figure 4.2* FT-IR spectra of the expandable graphite flakes and expanded graphite (EG)
Since strong interactions between the filler surfaces and a polymer matrix have a significant influence on a composite performance [109], an attempt was established to increase the quantity of functional groups on the surfaces of the expanded graphite. Types of beneficial functional groups depend on the functional groups available on the PES matrix. PES consists of benzene rings linked by both sulphone (—SO₂—) groups and ether oxygen atoms. The oxygen atoms in the sulphone groups or ether may have strong interactions with the functional groups containing OH such as -COOH groups. Therefore it is of interest to functionalise these groups onto the surfaces of the expanded graphite to enhance the chemical bonding between PES and graphite.

It is well known that a nitric acid oxidation at 115°C has been shown to introduce significant surface acidity to carbon fibres [109-112]. Also sulphuric acid has been used for a liquid chemical oxidation [110]. These considerations lead to an application of nitric acid and sulphuric acid for surface treatments of the expanded graphite.

The FT-IR spectrum of the expanded graphite is compared with that of nitric acid-treated expanded graphite for various treatment times in Figure 4.3. Before the treatment, the stretching vibrations of C=O, C-O and OH deformation of carboxyl groups (-COOH) are observed at 1742, 1261 and 1460 cm⁻¹, respectively [91,96]. The broad peak at 3422 cm⁻¹ can be assigned to the stretching vibration of OH in -COOH groups. After the nitric acid treatment, the % transmittance of the peaks assigned to the C=O stretch and OH deformation of -COOH groups become depleted, compared to the peak at 1636 cm⁻¹ (C=C stretch) indicating an introduction of -COOH groups on the surfaces of the expanded graphite. The assumption is that the intensity of the stretching vibration of C=C remains constant throughout the treatment.

Similar results are obtained from the sulphuric acid treatment (Figure 4.4). However, for the reaction time of 0.5 day the nitric acid treatment caused the most depletion of the % transmittance of the peaks assigned to the C=O stretch and OH deformation than the sulphuric acid treatment. Therefore the nitric acid treatment will be taken into a further consideration.
Figure 4.3 FT-IR spectra of the expanded graphite (EG) and nitric acid-treated expanded graphite for various treatment times.

Figure 4.4 FT-IR spectra of the expanded graphite (EG) and sulphuric acid-treated expanded graphite for various treatment times.
Wu et al. [110] and Pittman et al. [109] reported that the density of functional groups produced from acid treatments was a function of a reaction time. Therefore the nitric acid treatment was performed by varying the treatment times from 2 to 48 hours. Figure 4.5 compares FT-IR spectra of the expanded graphite to nitric-treated expanded graphite for various treatment times. With increasing reaction time, the amount of -COOH groups introduced to the surfaces of the expanded graphite increases. At a reaction time of 4 hours, the amount reaches its maximum and, as observed, results in the most depletion of the % transmittance of the peak corresponding to C=O and OH, compared to the other reaction times.

\[ \text{Figure 4.5 FT-IR spectra of the expanded graphite (EG) and nitric acid-treated expanded graphite for various treatment times} \]

Esumi et al. [83] reported that a mixture of concentrated nitric acid and concentrated sulphuric acid in a volume ratio of 1:3 and a treatment time of 20 minutes could effectively introduce large concentrations of acidic sites on carbon nanotubes. The expanded graphite is, then, treated using the mixture of acids for 20 minutes. It is found that the mixture of acids does not more effectively introduce -COOH groups on the surfaces of the expanded graphite than nitric acid alone as shown in Figure 4.6.
**Figure 4.6** FT-IR spectra of the expanded graphite (EG), nitric acid- and a mixture of acids-treated expanded graphite for different treatment times

**Figure 4.7** FT-IR spectra of the EG, PES/untreated graphite (UG) and PES/treated graphite (TG) composites
Figure 4.7 shows a comparison of the FT-IR spectra of the expanded graphite, pristine PES, PES/untreated and treated graphite composites. Pristine PES has strong triplet peaks of the stretching of \(-O=S=O-\) groups at 1235, 1150 and 1105 cm\(^{-1}\). In the composites filled with the untreated and nitric acid-treated graphite, one peak and two peaks of the sulphone groups, respectively, are shifted. Also their stretching of OH is shifted to a lower wave number, indicating some interactions between the PES matrix and the functional groups on the surfaces of the graphite. Whereas, the triplet peaks of sulphone groups of the composite filled with the mixture of acid-treated graphite appear at the same position as that of the pristine PES. The results suggest the most effective is nitric acid in the surface treatment.

4.4 THE MORPHOLOGY OF PES/GRAPHITE COMPOSITES

4.4.1 XRD

Typical XRD patterns obtained from the expandable graphite and PES/graphite composites prepared by the melt blending and solution blending methods are shown in Figure 4.8. In order to plot them in the same scale, intensity of the expandable graphite was divided by 5.

Sharp diffraction of 002 peaks of XRD patterns of the expandable graphite and graphite in the composites prepared by the melt blending and solution blending methods appeared at the same position of 2\(\theta\) - 26°. Using the Equation derived from Bragg's law, \(\lambda = 2d \sin \theta\), by substituting \(\lambda = 0.1542\) nm. The calculated interlayer spacing (\(d_{002}\)) of all three graphites is found to be 0.343 nm. This suggests the existence of aggregates of the graphite in the composites prepared by both methods. Therefore the distance between organised carbon layers of the graphite structure is retained at 0.343 nm.

It can be seen that the intensity of the peak at 2\(\theta\) - 26° of the graphite in the composite prepared by the solution blending method is lower than that prepared by the melt blending method and their intensities are much lower than that of the expandable graphite. This is evidence of an immiscible structure of the graphite in
the polymer matrix. The result also indicates that the exfoliation occurs in the composite prepared by the solution blending method more than it does in that prepared by the melt blending method. In the former method the high concentration of solvent (80 wt% related to polymer) and magnetic stirring employed, assist PES molecular chains in diffusing into the graphite galleries.

![Figure 4.8 X-ray diffraction of the expandable graphite and PES/treated graphite composites (melt blending and solution blending methods)](image)

The broader width of the 002 peak at the $2\theta \sim 26^\circ$ position of the XRD pattern of the expandable graphite indicates that it contains aggregates of bigger sizes than the graphite in the two types of composites [113]. Another weak peak at about $2\theta = 27.4^\circ$ could be ascribed to weakly-bonded or organic contaminants presenting on the surfaces of the expandable graphite [80]. An amorphous component in both composites, i.e. PES polymer, can easily be noticed as a very broad peak from $2\theta = 12.5$ to $25^\circ$. 
4.4.2 TEM

The more detailed structure of the PES/graphite composites is obtained by a TEM micrograph in Figure 4.9. The solid lines represent the graphite sheets viewed from a direction parallel to the plane of the sheets. The image reveals that the graphite is randomly dispersed in the PES matrix and tends to form a conducting network. It can be obviously seen that there is a coexistence of multi-layers with single layers of the graphite i.e. micro-/nano-graphite. The TEM results coincide perfectly with the prior XRD results.

![TEM micrograph](image)

*Figure 4.9 A TEM photomicrograph of a PES/TG5% composite*

4.4.3 SEM

The morphologies of the fractured surfaces of the pristine PES and PES/graphite composites were examined by SEM. The fractured surfaces of the pristine PES are rather smooth but become rougher with graphite incorporation (Figure 4.10-4.12).

SEM photomicrographs in Figure 4.11 (a) and 4.12 (a) reveal that the graphite is randomly dispersed in both an immiscible and disordered manner throughout the polymer matrix. An immiscible region of the graphite is presented at higher magnification in Figure 4.11 (b) and 4.12 (b). It can be clearly observed at the highest magnification that in an immiscible region the PES do not fill in the pores between the galleries of the graphite and that some of the sheets consisted of thin graphite sheets (Figure 4.12 (c)).
Figure 4.10 A SEM photomicrograph of the pristine PES

Figure 4.11 SEM photomicrographs of a PES/TG5% composite at:
(a) low; (b) higher magnification
Figure 4.12 SEM photomicrographs of a PES/UG5% composite at:
(a) low; (b) higher; (c) highest magnification
4.5 THE MICROMECHANICAL PROPERTIES OF PES/GRAPHITE COMPOSITES

4.5.1 Nanohardness and elastic modulus

A nanoindentation technique was employed in order to achieve the load-depth relationship of the pristine PES and PES/treated graphite composites. Figure 4.13-4.18 show typical loading-unloading curves of the pristine PES, 1-8 wt% TG/PES composites, respectively.

**Figure 4.13** Load-depth data of the pristine PES

**Figure 4.14** Load-depth data of a PES/TG1% composite
Chapter 4 Morphological and Micromechanical Properties of PES/Graphite Conductive Composites

Figure 4.15 Load-depth data of a PES/TG3% composite

Figure 4.16 Load-depth data of a PES/TG5% composite

Figure 4.17 Load-depth data of a PES/TG8% composite
Upon loading, the depth increases as the force is increasing to a maximum load ($P_{\text{max}}$) at a constant rate of 0.5 mN/s. The end of a loading segment is followed by a holding period at which the force is kept constant at a maximum load of 5 mN. During the holding period, a creep is observed and a maximum depth ($h_{\text{max}}$) is determined. The average maximum depth of the composites is higher with treated graphite incorporation. This is an indication of a softer material surface. Next, is an unloading segment in which the force is reduced at the same rate as the prior loading. According to Equation 3.7 and 3.5, the slope ($S$) at the initial of an unloading curve and the elastic modulus of the material ($E$) correspond; a higher slope leads to a higher elastic modulus. The plastic depth ($h_p$) is determined when the slope line intercepts the depth axis. The end of an unloading segment is known as the residual displacement ($h_r$). The discontinuity in the unloading curve of the pristine PES and the composites which is observed at an approximate load of 0.5 mN indicates a recovery of material surfaces.

By using the obtained data, the nanohardness and reduced modulus values were computed, then, the elastic modulus was calculated by using Equation 3.5. The average nanohardness and elastic modulus of all the samples are plotted against treated graphite content in Figure 4.19 and 4.20, respectively, and are summarized in Table 4.1.
It can be seen that the average nanohardness of the composites at low contents of the treated graphite is close to that of the neat PES. However, the differences between the nanohardness of unfilled and filled system become larger at the

Figure 4.19 Nanohardness of the PES/TG composites at various TG contents

Figure 4.20 Elastic modulus of the PES/TG composites at various TG contents
higher amounts of the filler. The computed nanohardness results coincide with the maximum depth observations as discussed earlier that the composites become softer with the treated graphite incorporation. This can be explained by considering the structure of the PES/treated graphite composites obtained from the SEM photomicrographs which have revealed that the treated graphite dispersed throughout the PES matrix in both an immiscible and disordered manner. In the immiscible regions, the polymer is unable to intercalate in between the galleries of graphite. Therefore the hardness of the composites in such regions is mainly contributed by that of the graphite.

Table 4.1 The mechanical properties of the PES/TG composites at various TG contents

<table>
<thead>
<tr>
<th>TG Content (wt%)</th>
<th>Nanohardness (GPa)</th>
<th>Reduced Modulus (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.42 ± 0.03</td>
<td>4.99 ± 0.18</td>
<td>4.21</td>
</tr>
<tr>
<td>1</td>
<td>0.38 ± 0.02</td>
<td>4.66 ± 0.27</td>
<td>3.93</td>
</tr>
<tr>
<td>3</td>
<td>0.37 ± 0.03</td>
<td>4.57 ± 0.36</td>
<td>3.85</td>
</tr>
<tr>
<td>5</td>
<td>0.36 ± 0.04</td>
<td>4.66 ± 0.18</td>
<td>3.93</td>
</tr>
<tr>
<td>8</td>
<td>0.31 ± 0.04</td>
<td>3.94 ± 0.34</td>
<td>3.32</td>
</tr>
<tr>
<td>10</td>
<td>0.27 ± 0.08</td>
<td>4.10 ± 0.70</td>
<td>3.46</td>
</tr>
</tbody>
</table>

As mentioned earlier, bonds between carbon atoms within graphite planes are much stronger than weak forces that hold the graphite sheets together. Because of the anisotropy characteristics of graphite, it is hard and stiff in the direction parallel to the basal plane. On the other hand, it is bendable in the direction perpendicular to the graphite sheets [114]. The graphite employed retains the anisotropy characteristics of ordinary graphite. Any indentation tests performing on the composites except in the directions parallel to the basal plane direction of the graphite will not achieve the improved hardness.
It should be noted that nanoindentation data, unlike bulk measurement results such as tensile test data, represent the localised behaviour on the micrometer scale of materials [76]. At low amounts of the treated graphite the probability of indenting on the pure polymer phase is high. On the contrary, the chance of indenting on the graphite increases with increasing amount of the filler.

Similar to the hardness results, the elastic modulus of the composites does not differ much from that of the neat polymer at low contents of the treated graphite but the differences become obvious beyond 5 wt% of the filler. The results suggest that the indentations on the composites with higher filler contents were mainly performed on the regions without interfacial interactions between the polymer matrix and the treated graphite, i.e. the immiscible regions. The localised elastic modulus of the composites then solely associates with the graphite characteristics. A nanoindentation experiment which was conducted by Richter et al. [115] has confirmed a complete elastic behaviour in the c-direction of highly oriented pyrolytic graphite (HOPG). There has also been a report on a decrease in the elastic modulus of a composite filled with an elastic material [44].

The load-depth curves also provide another three values relating to the viscoelastoplastic behaviour of materials, elastic recovery parameter, plastic work and reverse plasticity. The elastic recovery parameter is denoted by a ratio of elastic depth \((h_{\text{max}} - h_c)\) to plastic depth \(h_c\). It should be noted that for a pure plastic material, \(h_c = h_{\text{max}}\) then, the elastic recovery parameter is 0. The plastic work is the area enclosed by a loading and an unloading curve. It is equivalent to the energy absorbed due to the loading [116]. It can be seen that the plastic work is inversely related to the elastic recovery parameter. As the plastic work increases slightly with addition of the treated graphite, the elastic recovery decreases slightly (Table 4.2). Besides a creep (an increase in depth with time) at the maximum load during the holding period, a reverse plasticity (a decrease in depth with time) can be observed on the unloading curves at an approximate load of 0.5 mN. The area which is surrounded by a resume unloading curve, a reverse plasticity and an extended part of the original unloading curve corresponds to the energy released by the polymer when it recovers to its equilibrium depth [116].
Table 4.2 Elastic recovery parameter and plastic work of the PES/TG composites

<table>
<thead>
<tr>
<th>TG Content (wt%)</th>
<th>Elastic Recovery Parameter</th>
<th>Plastic Work (nJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.277 ± 0.016</td>
<td>1.03 ± 0.07</td>
</tr>
<tr>
<td>1</td>
<td>0.269 ± 0.010</td>
<td>1.12 ± 0.08</td>
</tr>
<tr>
<td>3</td>
<td>0.267 ± 0.018</td>
<td>1.17 ± 0.07</td>
</tr>
<tr>
<td>5</td>
<td>0.255 ± 0.029</td>
<td>1.19 ± 0.10</td>
</tr>
<tr>
<td>8</td>
<td>0.258 ± 0.036</td>
<td>1.25 ± 0.17</td>
</tr>
<tr>
<td>10</td>
<td>0.214 ± 0.034</td>
<td>1.46 ± 0.33</td>
</tr>
</tbody>
</table>

The plastic index ($\psi$) as proposed by Greenwood and Williamson [117] can be used to describe the extent of plastic deformation for a tribocontact system:

$$\psi = \frac{E}{H} \left( \frac{r^*}{r} \right)^{v_2}$$  \hspace{1cm} (4.1)

In this Equation, $E$ is the composite elastic modulus for two contacting surfaces; $H$ is the hardness of a softer surface and $\left( \frac{r^*}{r} \right)^{v_2}$ is a geometry factor (a constant). When a contact load and contact geometry are determined, a value of $E/H$ will be a key factor in determining the nature of the deformation. For a material with a lower $E/H$ ratio, the contact is more likely to be the elastic than the plastic contact [118] and thus a plastic-deformation-dominated wear mechanism is less likely to occur. The $E/H$ results indicate the deformation mechanism nearly the same below 8 wt% of the graphite (Figure 4.21).
Figure 4.21 E/H vs. content of the treated graphite, which can be used to describe the extent of the plastic deformation for a tribocontact system

4.5.2 Nanoscratch resistance

The mechanism of wear is very complex. It should be understood that the real area of contact between two solid surfaces, compared to the apparent area of contact, is invariably very small, being limited to points of contact between surface asperities. A load applied to the surfaces will be transferred through these points of contact and the localised forces can be very large. The material intrinsic surface properties such as hardness, strength, ductility, work hardening etc. are very important factors for wear resistance, but other factors like surface finish, lubrication, load, speed, corrosion, temperature and properties of the opposing surface etc. are equally important.

Figure 4.22 shows the schematic diagrams of abrasive wear mechanisms. Two body abrasive wear occurs when one surface (usually harder than the second) cuts materials away from the second, although this mechanism very often changes to three body abrasion as the wear debris then acts as an abrasive between the two surfaces. Abrasives can act as in grinding where the abrasive is fixed relative to
one surface or as in lapping where the abrasive tumbles producing a series of indentations as opposed to a scratch.

Figure 4.22 Schematic diagrams of the mechanisms of abrasive wear [119]

Figure 4.23 shows the schematic diagram of adhesive wear produced by the formation and subsequent shearing of welded junctions between two sliding surfaces. For adhesive wear to occur it is necessary for the surfaces to be in intimate contact with each other. Surfaces which are held apart by lubricating films, oxide films etc. reduce the tendency for adhesion to occur.

In order to assess the wear resistance of the PES/treated graphite composite films, nanoscratch tests were performed over the sample surfaces. The normal load applied to the surfaces was ramped up until substantial damage occurred. Three nanoscratches were made for each sample at three different normal loads ranging from 20 to 42 μN. Figures 4.24 show the effect of treated graphite loadings on the scratch depth. It is clear with addition of the treated graphite, the wear resistance
increases. However, the improvement of the nanoscratch resistance is little when the treated graphite content is over 5 wt%.

![Image of schematic diagram of adhesive wear mechanism]

**Figure 4.23** A schematic diagram of the mechanism of adhesive wear [119]

The reason of the improvement of the nanoscratch resistance could be as follows. For the PES, the lack of grain boundaries can not arrest the radial cracks and deviate these crack propagation paths, making the straight forward propagation of these cracks much easier. However, for the PES/treated graphite composites, the micro or nano-sized graphite particles are hard enough to greatly blunt the crack tip, and hence reduce the microcrack propagation rate or stop the cracking growth, as schematically represented in Figure 4.25.

The scratch of an indenter during a scratch test is similar to the abrasion of a hard particle on the material surface during normal abrasive wear. Both are dominated by the mechanisms of microploughing and microcutting. Therefore it is generally accepted that the scratch resistance and the abrasive wear resistance are closely related; that is, materials with the high scratch resistance will have the high abrasive wear resistance. Accordingly, it is expected that the PES/treated graphite composites have improved the wear resistance because the scratch resistance is increased.
Figure 4.24 Scratch depth vs. content of the treated graphite at:
(a) 20 μN; (b) 32 μN; (c) 42 μN
**Figure 4.25** Schematic drawings illustrating the microcrack propagation paths during a nanoindentation pressing.
5.1 INTRODUCTION

Most polymeric materials are electrical insulators; their electrical resistivity values commonly lie in the range of $10^{15}$-$10^{19} \ \Omega \cdot \text{cm}$ [19], which is a beneficial characteristic to many applications. However, materials with a higher electrical conductivity feature ($10^{-9}$-$10^{-5} \ \text{S/cm}$) are advantageous for electrostatic dissipation applications. When an electrostatic charge is created on electronic components, it may either leak away slowly or is suddenly discharged. If a large sudden discharge occurs in an electronic component, which is rare today, it will cause overheating or a breakdown in the component. On the other hand, the charge may leak away slowly through an electrostatic dissipative material and leave no damage to the electronic circuit. In the same way, if a charge builds up on an electrostatic dissipative material, it will be discharged in a controllable manner. Polymeric materials can be tailored to meet the level of electrical conductivity requirements for the electrostatic dissipation applications by an incorporation of electrically-conductive fillers.

5.2 THE PERCOLATION THRESHOLD

Consider a polymer filled with a particle conductive filler, as shown in Figure 5.1. At very low filler loadings, the mean distance between the conductive particles is large. The resistivity of the composites is thus close to that of the polymer host matrix, as seen in an initial plateau. As the amount of the filler increases, the particles get closer. When the amount of the filler reaches a critical content called the percolation threshold, an initial conducting path through the material is formed, resulting in a drastic drop in the resistivity of the composites [120]. In this range, the resistivity is sensitive to a small increase in the filler content. At higher filler loadings, the conducting path forms a three dimensional network and the resistivity is no longer sensitive to a small change in the filler content.
5.3 THE ELECTRICAL CONDUCTIVITY OF PES/GRAPHITE COMPOSITES

Like most polymers, PES is not electrically conductive and its volume conductivity at room temperature is as low as about $10^{-15}$ S/cm [121]. Its electrical conductivity in the presence of graphite will be investigated in this work in the hope of finding a transition to conductive composites. Comparisons will be made between untreated and treated graphite composite systems. Other parameters affecting the electrical conductivity of the composites such as content of the filler and temperature will also be studied. A further increase in the electrical conductivity of the composites at a fixed filler content is to be attempted by a doping method. Also its mechanism was tried to explain.

5.3.1 The effect of the addition of graphite on the electrical conductivity of PES

The volume resistances, $R_v$, of PES/untreated and PES/treated graphite composites with a filler content of 1-10 wt% prepared by the solution blending method were measured at room temperature by the four-wired resistance
measurement method. Their volume resistivities, $\rho_v$, were calculated by using Equation 3.9. The reciprocal of the volume resistivities, which are the volume conductivities, $\sigma_v$, are plotted against filler content in Figure 5.2.

![Graph showing volume conductivities of PES/UG5% and PES/TG5% composites as a function of filler content](image)

**Figure 5.2** Volume conductivities of PES/UG5% and PES/TG5% composites as a function of filler content

Figure 5.2 shows a variation of the electrical conductivities of the PES/untreated and PES/treated graphite composites. For very low filler content (1-2.5 wt%), the volume conductivities of both systems are close to that of the PES matrix [120,122]. There is a sharp increase in the volume conductivities of the PES/untreated graphite composites in a filler content ranging between 2.5-3.0 wt%. Similarly, a sharp increase occurs at the same range of the treated graphite content for the PES/treated graphite composite system. Electrical conductivities of both the PES/untreated and PES/treated graphite composite systems then level off with further increases in the amount of each filler. The former exhibit electrical conductivities about one order of magnitude higher than the latter in a filler content ranging between 3-10 wt%. The electrical conductivities 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.
As mentioned earlier, the PES consists of diphenylene sulphone groups and ether oxygen atoms. Bonds in the PES are strongly covalent, its absence of mobile electrons makes it an electrical insulator, in contrast to the electrical conductive feature of graphite [19].

The electrical conductivity of a polymer can improve with an addition of graphite. A percolation threshold is able to be achieved at a lower amount of graphite, when graphite with a higher aspect ratio is employed. In this study, the percolation threshold of the 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. Loadings of conventional graphite as high as 15-20 wt% or higher are usually needed to obtain a satisfactory conductivity [57]. The improvement in electrical conductivities of the composites at low loadings could be attributed to the high aspect ratio of the graphite. The results also indicate that the nitric treatment of the graphite is not beneficial in the 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 [123].

The relationship between the composite conductivity and the concentration of a conductive filler has been expressed in the form of the following expression [124]:

\[
\sigma = C(\phi - \phi_c)^t
\]  

(5.1)

where:

- \(\sigma\) = Conductivity of the composite
- \(\phi\) = Volume fraction of the conductive filler
- \(\phi_c\) = Volume fraction of the conductive filler at the percolation threshold
- \(C\) = a constant
- \(t\) = the critical exponent of conductivity

Equation 5.1 is valid at filler concentrations above the percolation threshold \((\phi > \phi_c)\) but not far from the percolation threshold (where \(\phi - \phi_c\) is small). The
electrical conductivity results of the PES/UG and PES/TG composites in Figure 5.2 are used in plotting $\log\sigma_m$ versus $\log(\phi - \phi_c)$ in Figure 5.3 (a) and (b), respectively. The critical exponent, $t$, can then be determined from the slope of the plots. Using linear fitting, it is found that both composite systems have an equal $t$ value of 3.76 ± 0.36.

The universal $t$ value usually lies between 1.65 and 2.0 for lattices in three dimensions. Chen et al. has reported an experimental $t$ value of 1.82 ± 0.06, which is in agreement with the percolation theory, for PMMA/conventional graphite composites [53]. A higher value of $t$ is obtained if extreme geometry conductive particles or the tunnelling conduction is present in a conducting composite system. SEM results in Chapter 4 have revealed that the graphite employed in the composites fabricated throughout this study is micro-/nano-graphite possessing the high aspect ratio of 100-600. Clearly, the micro-/nano-graphite can be referred to as an extreme geometry conductive filler when it is compared to conventional graphite which usually possesses aspect ratios around 5-10.

In addition, the tunnelling process is known as a conduction mechanism in conducting composite materials. The mechanism is based on the electron tunnelling when the inter-particle distance is sufficiently small [125]. This means that the actual physical contact of neighbouring graphite sheets may not be present in the network of conductive paths but they should be in the vicinity of each others for electrons to tunnel. This can be confirmed by a TEM result showing the fragmentation of the network of graphite sheets in the PES/treated graphite conducting composite in Chapter 4. Beyond the percolation threshold, an increase in the dimension of graphite conductive paths and a decrease in the inter-particle distance assist the tunnelling of electrons.
Figure 5.3 Linear fits of the electrical conductivity data in Figure 5.2 with Equation 5.1: (a) the PES/untreated graphite composites; (b) the PES/treated graphite composites
In this study, the filler loading was limited to 5 wt% with regard to the micromechanical properties of the composites. An alternative way to improve the electrical conductivities of the composites was attempted by a doping method.

5.3.2 The effect of LiCl-doping on the electrical conductivity of PES/graphite composites

5.3.2.1 Doping

In graphite, each carbon has four valence electrons. Three of them are each in three \( sp^2 \) hybridised orbitals forming three \( \sigma \) bonds to the three nearest neighbour carbon atoms. The remaining electron delocalises in \( \pi \) orbital forming a \( \pi \) bond to a carbon atom in adjacent carbon layers. The electronic energy band structure per unit cell (4 carbon atoms) of graphite is then composed of 16 energy bands which are 12 \( \sigma \) bands and 4 \( \pi \) bands. In the 12 \( \sigma \) bands, half of them are at a low energy (bonding) and another half are at a higher energy (anti-bonding). The two groups are separated by about 5 eV. The 4 \( \pi \) bands; 2 bonding and 2 anti-bonding energy levels, lie between these two groups of \( \sigma \) bands. Since there are 16 electrons per unit cell, 8 energy bands are filled. The Fermi energy \( (E_F) \) of graphite thus lies in the middle of the 4 \( \pi \) bands. The Fermi energy is referred to as the highest occupied energy level in the band.

![Figure 5.4 The one-dimensional energy band of graphite (Dotted area and shaded area are the conduction and the valence band, respectively)](image)

The peculiarity of the band structure of graphite is that the highest valence band (\( \pi \) bonding) overlaps with the lowest conduction band (\( \pi \) anti-bonding) along
the zone edge of about 0.03 eV, making graphite a semi-metal (Figure 5.4) [126]. The Fermi energy \( E_F \) of graphite still lies in the middle of the overlap region, resulting in pockets of electrons and holes (free carriers). It should be noted that a metal has a partially filled energy band in which electrons are allowed to move.

Bonds in graphite are strong within the basal plane but weak between carbon layers. Such a high anisotropy of bonds allows intercalates to occupy the interlayer spaces of the graphite crystal without disrupting the carbon layers. By bonding with intercalates, the graphite \( \pi \) bonds can gain electrons from, or lose electrons to, the intercalates. In other words, the intercalates can act as electron donors or acceptors in doping graphite. The products are then classified as a donor graphite intercalation compound (donor GIC) and an acceptor GIC, respectively. This process is accompanied by a shift of the position of the Fermi energy of graphite to higher or lower depending on the type of intercalates. A donor-type intercalate involving an electron doping causes a shifting of the Fermi energy to a higher energy level, while an acceptor-type intercalate involving a hole doping causes a lowering of the Fermi energy [127].

### 5.3.2.2 The improvement in the electrical conductivity by LiCl doping

Small amounts of LiCl (0.02-0.06 wt% related to graphite) in DMF were added into 5 wt% of the untreated or nitric-treated graphite before blending with the PES polymer. The addition of the dilute LiCl content in the PES/treated graphite composite results in great improvements in the electrical conductivities as shown in Figure 5.5. The electrical conductivities 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 improvements in the electrical conductivities of the PES/untreated graphite composite are insignificant. With increasing LiCl content up to 0.06 wt%, the electrical conductivities are 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.
Chapter 5  The Electrical Conductivity of PES/Graphite Conductive Composites

Figure 5.5 Volume conductivities of PES/UG5% and PES/TG5% with LiCl content.

Figure 5.6 Volume conductivities of LiCl-doped PES/TG5% 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 the presence of LiCl. It is interesting to find out that the volume conductivities of the composite increases with increasing LiCl content, only when the content is very low (0.02-0.06 wt%). Beyond these concentrations, the volume conductivities show a downward trend (Figure 5.6).

Lithium ions (Li⁺), derived from LiCl in DMF solution, were diffused into the interlayer spaces of the graphite employed and formed a lithium ion-graphite intercalation compound (Li-GIC) as follows [128]:

\[
C_x + Li^+ \leftrightarrow C_x^+ \cdot Li
\]  

(5.2)

It is believed that there are no chloride ion intercalations due to their negative charges. The lithium ions accept π electrons from the graphite, according to the direction of the charge transfer, Li-GIC is considered an acceptor GIC [54, 129]. Upon the intercalations, extra holes are created in π orbitals of carbon atoms in the graphite and the Fermi energy is correspondingly lowered. The density of holes in Li-GIC is 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 [130]. The force reacting on holes in an 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 leads to a higher conductivity of the doped composites.

Further increases in the dopant concentrations introduce more holes in 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 [131]. 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 dilution limit of lithium chloride content which can effectively improve the electrical conductivities of the PES/treated graphite composite.

5.3.3 The electrical conductivity of PES/graphite composites in temperature fields

Electrical conductivities of the LiCl-doped PES/TG5% composites with an LiCl content of 0.02, 0.06 and 0.1 wt% at room and elevated temperature were calculated and are compared with that of the undoped PES/TG5% composite in Table 5.1.

**Table 5.1 Volume conductivities of the PES/TG5% and LiCl-doped PES/TG5% composites at various temperatures**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PES/TG5% /LiCl 0.00%</th>
<th>PES/TG5% /LiCl 0.02%</th>
<th>PES/TG5% /LiCl 0.06%</th>
<th>PES/TG5% /LiCl 0.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.2 x 10^-6</td>
<td>7.7 x 10^-6</td>
<td>3.1 x 10^-4</td>
<td>1.4 x 10^-4</td>
</tr>
<tr>
<td>50</td>
<td>4.3 x 10^-6</td>
<td>8.3 x 10^-6</td>
<td>3.3 x 10^-4</td>
<td>1.4 x 10^-4</td>
</tr>
<tr>
<td>75</td>
<td>4.8 x 10^-6</td>
<td>8.3 x 10^-6</td>
<td>3.4 x 10^-4</td>
<td>1.5 x 10^-4</td>
</tr>
<tr>
<td>100</td>
<td>5.6 x 10^-6</td>
<td>9.1 x 10^-6</td>
<td>3.6 x 10^-4</td>
<td>1.7 x 10^-4</td>
</tr>
<tr>
<td>125</td>
<td>6.7 x 10^-6</td>
<td>1.0 x 10^-5</td>
<td>3.7 x 10^-4</td>
<td>2.2 x 10^-4</td>
</tr>
<tr>
<td>150</td>
<td>7.1 x 10^-6</td>
<td>1.0 x 10^-5</td>
<td>4.0 x 10^-4</td>
<td>2.4 x 10^-4</td>
</tr>
<tr>
<td>190</td>
<td>7.7 x 10^-6</td>
<td>1.1 x 10^-5</td>
<td>4.3 x 10^-4</td>
<td>2.6 x 10^-4</td>
</tr>
</tbody>
</table>

The temperature dependence of the electrical conductivity of conducting composites having conductive particles dispersed in insulating matrices is normally expressed as [132]:

---

103
\[ \sigma(T) = \sigma_0 \exp\left[\left(\frac{T_0}{T}\right)^x\right] \]  
\hspace{1cm} (5.2)

where:
\[ \begin{align*}
\sigma &= \text{Conductivity} \\
\sigma_0 &= \text{Proportionality constant} \\
T &= \text{Absolute temperature, K} \\
T_0 &= \text{a constant} \\
x &= \text{a constant}
\end{align*} \]

From Equation 5.2, a relationship: \( \ln \sigma(T) \propto \left(\frac{1}{T}\right)^x \) is obtained. The electrical conductivity data shows a good fit with a value of \( x = 1/4 \) in the plot of \( \ln \sigma(T) \) versus \( T^{-1/4} \) as shown in Figure 5.7. A value of \( x = 1/2 \) has been reported for many systems such as polyimide/carbon nanoparticle composites [132] and multi-walled carbon nanotubes/polypyrrole nanocables [133] whereas \( x = 1/4 \) has been reported for carbon black filled polyimide nanocomposites [134].

\( \begin{align*}
-13 &< \ln(\sigma(T)) < -7 \\
0.215 &< 1/T^{1/4} (K^{-1/4}) < 0.240
\end{align*} \)

*Figure 5.7* The temperature dependence of electrical conductivity for the LiCl-doped PES/treated graphite composites with various contents of LiCl, plotted against \( T^{-1/4} (K^{-1/4}) \).
The measured electrical conductivity values of composites at elevated temperature is mainly contributed to by two factors which are the coefficient of thermal expansion (CTE) of the polymer matrix and conductive particles, and the thermal activation of holes and electrons [135]. 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 values. The CTE of the PES is $55 \times 10^{-6}/^\circ C$ [100] while that of the graphite within the measured temperature range (20-190°C) is about $22 \times 10^{-6}/^\circ C$ in the c-direction but is negative in the ab-direction [12]. The coefficient of thermal expansion of materials is defined as the change in length per unit length for a change in temperature of one degree Centigrade. Materials typically have a characteristic of a 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 [136]. With increasing temperatures, the PES expands by taking up more space as the polymer chains are moving around more vigorously. In the mean time, graphite sheets will shrink in the ab-direction but expand in the 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 increases 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 [133]. Variations of the barrier heights among the different doped composite systems filled with 5 wt% treated graphite is due to the difference in the effective amounts of Li$^+$ ions presenting in the galleries of the graphite. With the presence of the guest Li$^+$ intercalate, a
hopping conduction can more easily occur along the c-axis of the graphite in which the barrier height has been lowered after the intercalation.

5.4 THE ENHANCEMENT OF THE ELECTRICAL CONDUCTIVITY BY DOPING

5.4.1 Experimental evidence of the intercalation

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

5.4.1.1 The effect of size of the intercalate

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 more easily for the intercalate having a smaller size, which will contribute to more charge transfer. Figure 5.8 compares the electrical conductivities of the LiCl-doped PES/treated graphite composites previously obtained, to that of another two doped composite systems.

It can be seen that the conductivities of each type of the doped composites at the same content of dopants are in the same order of magnitude. However, the conductivities of the LiCl-doped PES/treated graphite composites are found to be a little higher than that of the NaCl-doped PES/treated graphite composites and that of the composites containing KCl are found to be the lowest.

Na⁺ and K⁺ ions which are derived from NaCl and KCl behave as electron acceptors in 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 the neutral atoms of Li, Na and K are 0.145, 0.180 and 0.220 nm [138], respectively, and the original interlayer spacing of the graphite obtained from the XRD result is 0.343 nm. It can be clearly seen that 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$^+$ ions are the smallest, and LiCl-doped PES/treated graphite composites correspondingly possess the highest conductivity. It should be noted that the graphite used in this study has both unexpanded and expanded layers after the heat treatment. When the sizes of the three intercalates are compared to the spacing of graphite layers that have been expanded, the capability of each species to intercalate the expanded interlayer spaces of the graphite will be insignificantly different. From the SEM results in Chapter 4, it can be seen that the interlayer spacings of the heat treated graphite can be as large as a micron level.

![Graph showing electrical conductivity vs. dopant content](image)

**Figure 5.8** Volume conductivities of metal chloride-doped PES/TG5% composites

5.4.1.2 The effect of mixing time

The mixing time of 0.08% of LiCl and the treated graphite before adding into the PES was varied from 3 hours to 1, 3 and 7 days. The basic idea was that if intercalation processes occur, then, the electrical conductivities of the doped composites will be correspondingly affected by the mixing time. On the contrary,
if there is no intercalation, the electrical conductivities of the doped composites should be independent of the mixing time employed. The results are presented in Figure 5.9.

The LiCl-doped composites prepared with 3 hours and 1 day mixing time have the same level of electrical conductivities which are the two highest values among the four values. The volume conductivity decreases continuously with 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 5.6 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 5.9 Volume conductivities of PES/TG5%/LiCl0.08% composites for different mixing times](image)

*Figure 5.9* Volume conductivities of PES/TG5%/LiCl0.08% composites for different mixing times
5.4.2 The effect of preparation methods on the intercalation of Li$^+$ ions

In order to confirm that the intercalations of intercalates into the graphite interlayer spacings is the mechanism mainly contributing to the enhancements of the electrical conductivities of the doped composites, not their dispersion in the polymer matrix, a new experimental procedure was designated in the way that the Li$^+$ ion intercalations were minimised by allowing a short time (10 minutes) for the dispersion of the treated graphite in the system. However, the period of time for LiCl to disperse in the PES matrix was maintained at 1 day. The previous and the new procedures are called procedure 1 and 2, respectively. A reference sample was also prepared by following procedure 2, but in the absence of an incorporation of the treated graphite. The volume conductivity calculation results from all samples prepared by both procedures, and that of the controlled sample, are shown in Table 5.2 for a comparison.

Table 5.2 Volume conductivities of LiCl-doped PES/TG5% composites prepared by two different procedures

<table>
<thead>
<tr>
<th>Description</th>
<th>Volume conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiCl 0.00%</td>
</tr>
<tr>
<td><strong>Procedure 1</strong></td>
<td></td>
</tr>
<tr>
<td>TG5% + LiCl% 3 hrs + PES 1 day</td>
<td>4.0x10$^6$ ± 0.2x10$^6$</td>
</tr>
<tr>
<td><strong>Procedure 2</strong></td>
<td></td>
</tr>
<tr>
<td>PES + LiCl% 1 day + TG5% 10 mins.</td>
<td>1.1x10$^7$ ± 0.1x10$^7$</td>
</tr>
<tr>
<td>PES + LiCl% 1 day</td>
<td>-</td>
</tr>
</tbody>
</table>
The electrical conductivities of the doped composites with various LiCl contents, prepared using procedure 2, were found to be an order of magnitude lower than that of the corresponding composites prepared in accordance with procedure 1. The electrical conductivity of the controlled sample was much lower than that of all the other samples.

LiCl in both procedures was given the same length of time (1 day) to disperse in the PES matrix. In procedure 1, Li⁺ ions have enough time to intercalate the galleries between graphite sheets. In contrast to procedure 1, the short mixing time for the mixture of the PES and LiCl with the treated graphite would minimise Li⁺ ion intercalations into the graphite galleries, causing the electronic conduction mechanism to take place mainly on the edges of the graphite planes. The results suggest that the intercalations of Li⁺ ions that occurred in procedure 1 contributed to the improvements in the electrical conductivities.

The far lower conductivity of the controlled sample, compared to the two samples with the same content of LiCl, confirms that the graphite is essentially required for the electrical conductivity improvement and that the doping mechanism occurs through the graphite not the polymer matrix. LiCl alone can not make the polymer a semiconductor.

5.4.3 Evidence of the Li⁺ ion intercalations from XPS

The surfaces of 0.02% and 0.04% LiCl-doped treated graphite were investigated by an XPS technique for the Li element. The results of the treated graphite with doping are shown in Figure 5.10 (b) –(c) compared to that of the treated graphite in Figure 5.10 (a).

It can be seen that the XPS spectra of both the 0.02% and the 0.04% LiCl-doped treated graphite have main peaks at 284 and 532 eV which correspond to C(1s) and O(1s), respectively, the same as that of the treated graphite. Li(1s) peak at 55 eV is not detected in both spectra of the doped systems. The absence of an Li(1s) peak may be due to the low concentrations of the dopant incorporation.
Figure 5.10 XPS spectra of: (a) the treated graphite (TG); (b) 0.02% LiCl-doped treated graphite; (c) 0.04% LiCl-doped treated graphite
Nevertheless, all the spectra can confirm the presence of oxygen containing functional groups on the surfaces of the graphite as observed by the peak for O(1s) at 532 eV.

5.5 THE MECHANISM OF ELECTRON TRANSPORT IN PES/GRAPHITE COMPOSITES

5.5.1 A theoretical consideration of electron transport in PES/graphite composites

5.5.1.1 Introduction

Graphite has been widely used to improve the electrical conductivities of polymer composites. However, there is still a challenge to understand and predict the electron transport behaviour in polymer/graphite composites. The conductivity calculated by the conventional method for fibres reinforcing composites does not have a good fit to the experimental results [139]. The electron transport behaviour in the composites is still not clear. In this chapter, quantum theory is used for understanding the electron transport behaviour in polymer/graphite composites.

5.5.1.2 Model development

Generally, polymers are known as insulators. A polymeric solid consists of very long molecular chains. The molecules are formed by bonding a large number of units together repeatedly. Series of extended electronic states can be generated by the overlap of the molecular orbitals. The valence and conduction bands of a polymer are induced by bonding and anti-bonding molecular orbitals. A very high energy is required to activate electrons to the conduction band in polymers. A current in polymers is caused by the movement of charge carriers along the external electrical field. Impurities and defects in polymers introduce a backward scattering of an electron’s wave. The electrical conductivity of a polymer could be described by using the Fermi gas model. The expression of the conductivity of a polymer is as follows.

\[ \sigma = Ae^{\frac{W}{2kT}} \]  

(5.3)
where $\sigma$ is electrical conductivity, $k$ is the Boltzmann's constant, $T$ is temperature and $W$ is the energy difference between the stationary states and the Fermi energy. For polymers, there is a big energy gap between the stationary states and the Fermi level. When electrons move in a polymeric solid, they are attracted into the stationary states and fill the hole left by activated electrons. The effective potential in the polymeric solid is proportional to $e^{-\frac{W}{2kT}}$.

Graphite sheets are assumed to be well dispersed and tightly bound in the PES matrix. The transport behaviour in a graphite sheet-PES-graphite sheet junction (G-PES-G), in which the PES is the part of the insulation, is considered. The thickness of the PES layer is given as $a$.

The effective potential of the perfect polymeric solid is used for describing the potential field in the PES. Since the electrons in graphite sheets can be simply considered as free particles, the potential in the graphite sheets is nearly zero. The PES layer in the G-PES-G junction can be considered as a rectangular potential barrier, namely:

$$U(x) = \begin{cases} 
E_F & \text{if } x < 0, \\
V_0 & \text{if } 0 < x < a, \\
E_F & \text{if } x > a. 
\end{cases} \tag{5.4}$$

where $V_0$ is the effective potential energy of the PES. The electrical field is along the x-axis and only one-dimensional transport along the x-axis was considered.

**Numerical prediction**

The free particle Schrödinger Equation in graphite sheets is as follows [140]:

$$\frac{d^2\psi(r,t)}{dr^2} + \frac{2m\varepsilon}{h^2}\psi(r,t) = 0 \tag{5.5}$$
where $\epsilon$ is the energy of electrons, $m$ is the mass of electrons and $\psi(r,t)$ is the wave function of electrons. Here, electrons are considered in the stationary states, therefore the wave function can be written as follows:

$$\psi(r) = e^{i\frac{p_r}{\hbar}}$$ (5.6)

where $p = -eE$. Here, the Schrödinger Equation is solved in one dimension. The wave function of electrons consists of an incident wave and a reflected wave in the region $x < 0$. In the region $0 < x < a$, the wave function of electrons only consists of a transmitted wave. Thus, the solution to Equation 5.5 is as follows:

$$\psi(x) = \begin{cases} e^{ix} + Re^{-ix} & x < 0 \\ S e^{ix} & 0 < x < a \end{cases}$$ (5.7)

where $R$ is the reflection amplitude and $S$ is the transmission amplitude. The incident current density can be calculated as follows [140]:

$$j(x) = \frac{1}{2m} \left( \psi^*(x) \hat{p} \psi(x) - \psi(x) \hat{p} \psi^*(x) \right)$$ (5.8)

In the PES layer, the Schrödinger function will be as follows:

$$\frac{d^2\psi(x)}{dx^2} - \frac{2m}{\hbar^2} (V_0 - \epsilon) \psi(x) = 0$$ (5.9)

The general solution to Equation 5.9 is as follows:

$$\psi(x) = Ae^{\kappa x} + Be^{-\kappa x} \quad 0 < x < a$$ (5.10)

where $\kappa = \sqrt{2m(V_0 - \epsilon)/\hbar}$. 
By using the continuous conditions at $x = 0$, the following Equations will be held:

\[
\begin{align*}
A &= \frac{1}{2} \left[ 1 + \frac{ip}{\hbar \kappa} \right] + R \left[ 1 - \frac{ip}{\hbar \kappa} \right], \\
B &= \frac{1}{2} \left[ 1 - \frac{ip}{\hbar \kappa} \right] + R \left[ 1 + \frac{ip}{\hbar \kappa} \right],
\end{align*}
\]  
(5.11)

By using the continuous conditions at $x = a$, the following Equations will be held:

\[
\begin{align*}
A &= \frac{S}{2} \left[ 1 + \frac{ip}{\hbar \kappa} \right] \cdot e^{i(p\alpha / \hbar) - \alpha a}, \\
B &= \frac{S}{2} \left[ 1 - \frac{ip}{\hbar \kappa} \right] \cdot e^{i(p\alpha / \hbar) + \alpha a},
\end{align*}
\]  
(5.12)

Then, the reflection coefficient, $H$, and the transmission coefficient, $T'$, can be obtained as follows, respectively:

\[
H = |R|^2 = \frac{(p^2 + \hbar^2 \kappa^2)^2 \sinh^2(\alpha a)}{(p^2 + \hbar^2 \kappa^2)^2 \sinh^2(\alpha a) + 4 p^2 \kappa^2}
\]  
(5.13)

\[
T' = |S|^2 = \left[ 1 + \frac{1}{4 \varepsilon \left( \frac{\varepsilon - 1}{\varepsilon} \right)} \sinh^2(\alpha a) \right]^{-1}
\]  
(5.14)

The wave function of electrons in the PES layer can be rewritten as follows:

\[
\psi(x) = \frac{-2 ip / \hbar}{[1 - (p / \hbar \kappa)^2] \sinh^2(\alpha a) - 2i P / \kappa \cosh(\alpha a)} e^{\alpha x} + \frac{\sqrt{(p^2 + \kappa^2 \hbar^2) \sinh^2(\alpha a) + 4 \kappa^2 \hbar^2}}{\sqrt{(p^2 + \kappa^2 \hbar^2) \sinh^2(\alpha a) + 4 \kappa^2 \hbar^2}} e^{-\alpha x}
\]  
(5.15)
Consider the hole transport in the PES layer, the transmission coefficient, $T$, can also be obtained as follows:

$$
T = |S|^2 = \left[ 1 + \frac{1}{4T'} \left( \frac{1 - \frac{\varepsilon}{V_0}}{\sinh^2(\beta \alpha)} \right) \right]^{-1}
$$

(5.16)

where $\beta = \sqrt{2m(-V_0 + \varepsilon)}/h$.

The conductance of the G-PES-G junction can be expressed in term of $T$ and $T'$ as follows [141]:

$$
G \approx G_0(1 - T' + T)
$$

(5.17)

where $G_0$ is the conductance of a graphite sheet.

Equations 5.14 and 5.16 represent the key results in the research. It was found that these transmission coefficients are trigonometric functions of the Schottky energy barrier, $U(x)$, and distance, $a$, between graphite sheets. Simply, the graphite-PES-graphite junction can be considered as a model for the prediction of the transport behaviour of the PES/graphite composites. By substituting 2 and 10 eV values for $\varepsilon$ and $V_0$, respectively, in Equation 5.17, the conductances of the G-PES-G at various thicknesses of the PES layer can be calculated and shown in Figure 5.11. It can be seen that when the distance between graphite sheets is down to 1.2 nm, $G/G_0$ is found to be 70% at which point the composite is believed to become a conducting material. This means that when the distance between graphite sheets is close to 1.2 nm, a conducting pathway is formed in the composites, resulting in a strong tunnelling current. In micro- and nano-scales, the electrical conductance shows both Ohm’s Law and tunnelling behaviours.
Figure 5.11 An estimation of conductances of G-PES-G as a function of distance between graphite sheets.
CHAPTER 6

THE THERMAL CONDUCTIVITY OF PES/GRAPHITE CONDUCTIVE COMPOSITES

6.1 INTRODUCTION
Since electronic components can produce heat during operation, encapsulating materials are expected to possess high heat dissipation capabilities. As the size of electronic components becomes smaller and smaller, thermal management become increasingly important. An incomplete heat dissipation of such tiny components may result in a failure of the device. A parameter which is used for determining the ease with which heat is transmitted through a material is its thermal conductivity. High thermal conductivity materials such as metals have thermal conductivity values in the range of 10-400 W/m.°C while thermal insulators such as polymers, glasses and ceramics have values between 0.1-2 W/m.°C [142]. However, thermal conductivities of polymer materials can be improved with thermally-conductive filler incorporation [74,123,143-144].

6.2 THE THERMAL CONDUCTIVITY OF GRAPHITE
Graphite is one of the thermally-conductive fillers. It is well-known that the thermal conductivity of graphite is determined by phonon transports (transport of a quantum of thermal energy through the lattice) and is represented by the Debye Equation [12].

\[ K = b C_p v L \]  
(6.1)

where:

- \( K \) = Thermal conductivity
- \( b \) = a constant
- \( C_p \) = Specific heat
- \( v \) = Velocity of the phonon
- \( L \) = Mean free path of the phonon (the average distance a phonon travels between collisions with other phonons)
From Equation 6.1, at a constant temperature, $C_p$ and $v$ are constant: in the basal plane of a perfect or near-perfect crystalline structure of graphite, the mean free path is high and so is the thermal conductivity. In the c-direction, graphite is a good thermal insulator. The thermal conductivity of graphite decreases with increasing temperature since the mean free path is lower at a higher temperature. Despite the offsetting effect of the specific heat, the effect of the mean free path is dominant above room temperature. In addition, phonons are scattered by crystallite boundaries, lattice defects and other phonons.

### 6.3 THE PRINCIPLE OF THE MEASUREMENT OF THERMAL CONDUCTIVITY BY MEANS OF MDSC

MDSC or Modulated DSC is developed to overcome the limitations of a typical DSC. MDSC uses a superimposed sinusoidal oscillation on a constant linear heating (Figure 6.1). As a result of the temperature modulation, a heating rate is not constant, but varies in a periodical way. An average heating rate, called the underlying heating rate, corresponds to a rate for a typical DSC experiment. A modulated heating rate periodically varies between a minimum and a maximum value, which are determined by the value of the underlying heating rate, a period (frequency) and an amplitude of the superimposed sinusoidal temperature (Figure 6.2).

MDSC not only provides the total heat flow but also the two individual components in the general Equation (Equation 3.8). The first component is a heat capacity component ($C_b$) or reversing heat flow and the second one is a kinetic component ($f(T,t)$) or non-reversing heat flow. The total heat flow in MDSC is calculated from an average of the modulated heat flow, which corresponds to the total heat flow in a conventional DSC at the same underlying heating rate. Figure 6.3 shows the modulated heating rate and modulated heat flow for an MDSC experiment on a quenched polyethylene terephthalate (PET).
Figure 6.1 Temperatures as a function of time for a MDSC and a typical DSC [145]

Figure 6.2 Heating rates as a function of time for a MDSC and a typical DSC [145]
Furthermore, a heat capacity \( (C) \) can be determined in a single experiment of MDSC due to the periodical variation in heating rate by the Fourier transformation of the ratio of modulated heat flow amplitude to a modulated heating rate amplitude. This is of interest in this study because there is a relationship between the heat capacity and the thermal conductivity of a material.

Thermal conductivity determinations by MDSC is based on specific heat and apparent heat capacity measurements on a thin specimen (<0.5 mm) and a thick specimen (>3.0 mm), respectively. The MDSC apparatus employed is calibrated using sapphire as a reference material while a polystyrene (PS) sample is used as a reference material for a thermal conductivity calibration. This method is less laborious and more accurate compared to other conventional techniques such as a direct heating technique [146-147]. However, it is suitable for materials with thermal conductivities in the range of 0.1 to 1.5 W/m.\( ^{\circ}\)C [142]. In this study, thermal conductivities were evaluated at 27°C.
6.3.1 The specific heat measurement

Specific heat, the simplified term of specific heat capacity, is the amount of heat required to raise the temperature of 1 g of a material one degree Celsius or Kelvin. Experimental conditions for specific heat measurements are selected to obtain maximum temperature uniformity across test specimens. Small and thin specimens encapsulated in aluminium pans and with a long modulation period are preferred for the best result. By performing a measurement on sapphire, a correction factor \( \overline{C} \) can be obtained by using the following Equation. Then it is used in corrections of the specific heat values of all samples.

\[
\overline{C} = \frac{C_p(\text{literature})}{C_p(\text{measured})} \tag{6.2}
\]

where:

- \( \overline{C} \) = Correction factor
- \( C_p(\text{literature}) \) = The specific heat of sapphire from the literature, J/g.°C
- \( C_p(\text{measured}) \) = The measured specific heat of sapphire, J/g.°C

6.3.2 The apparent heat capacity measurement

Heat capacity is the amount of heat required to raise the temperature of a material one degree Celsius or Kelvin. Thick, cylinder shaped specimens with parallel end face, placed in opened aluminium pans, give the best thermal conductivity results. Silicon oil is applied inside the pans to ensure a good contact between the specimens and the pans. The assumption is that if a temperature modulation is applied on only one face of a specimen, heat flow through the opposite face is zero and there is no heat flow through the sides of the specimen.

6.3.3 Thermal conductivity calculation

When the corrected specific heat and the apparent heat capacity of a sample are obtained, then, a thermal conductivity value can be calculated using the following Equation [142]:
\[ K = \frac{(2\pi \times C^2)}{C_p \times \rho \times A^2 \times P} \]  
(6.3)

where:

- \( K \) = Thermal conductivity, W/cm\(^\circ\)C
- \( C \) = Apparent heat capacity, J/\(^\circ\)C
- \( C_p \) = Specific heat, J/g\(^\circ\)C
- \( \rho \) = Density of the sample, g/cm\(^3\)
- \( A \) = Cross sectional area of the sample, cm\(^2\)

For a circular cylinder sample, \( \rho = M / AL \) and \( A = \pi d^2 / 4 \), the above Equation becomes:

\[ K = \frac{8L \times C^2}{C_p \times M \times d^2 \times P} \]  
(6.4)

where:

- \( K \) = Thermal conductivity, W/m\(^\circ\)C
- \( C \) = Apparent heat capacity, J/\(^\circ\)C
- \( C_p \) = Specific heat, J/g\(^\circ\)C
- \( L \) = Height of the specimen, m
- \( d \) = Diameter of the specimen, m
- \( M \) = Mass of the specimen, g
- \( P \) = Period, s

A thermal conductivity value (\( K \)) is then calculated using Equation 6.4 by substituting the measured and experimental parameters, and the dimension of a specimen. The obtained value will now be called an observed thermal conductivity (\( K_o \)).

The observed thermal conductivity (\( K_o \)) needs to be corrected due to the loss of thermal energy through the sides of the specimen. Thus, a thermal conductivity
calibration constant \( (D) \) is created using Equation 6.5, using polystyrene as a calibration material.

\[
D = (K_o \times K_r)^{0.5} - K_r \hspace{10cm} (6.5)
\]

where:

- \( D \) = The thermal conductivity calibration constant
- \( K_o \) = The observed thermal conductivity of polystyrene, W/m.\( ^\circ \)C
- \( K_r \) = The true thermal conductivity of polystyrene, 0.14 W/m.\( ^\circ \)C at 27°C [142]

A corrected thermal conductivity of the sample can be calculated by substituting the \( D \) value and the observed thermal conductivity of the sample \( (K_o) \) in Equation 6.6.

\[
K = \frac{[K_o - 2D + (K_o^2 - 4DK_o)^{0.5}]}{2} \hspace{10cm} (6.6)
\]

6.4 THE THERMAL CONDUCTIVITY OF PES/GRAPHITE COMPOSITES

Thermal conductivities of the PES/untreated and PES/treated graphite composites were calculated using the experimental data provided by the MDSC technique as outlined in Section 6.3.

6.4.1 The specific heat measurement

Specific heat \( (C_p) \) was obtained by performing a heating run from 0-75°C at a heating rate of 3°C/min with a modulation amplitude of ±1°C over an 80 s period. The MDSC signals of the PES, PES/untreated and PES/treated graphite composites, polystyrene (PS) and a sapphire reference are shown in Figure 6.4.
The specific heat of sapphire from the literature (0.780 J/g.°C) is found to be lower than the measured value (0.805 J/g.°C). By using Equation 6.2, a correction factor is equal to 0.97. After multiplying the correction factor by the measured specific heat values of all samples, the corrected specific heat values are obtained and are compared in Table 6.1.

6.4.2 The apparent heat capacity measurement

Apparent heat capacities (C) were obtained by carrying out an isothermal scanning at 27°C for 40 minutes with a modulation amplitude of ±1°C over an 80 s period. The MDSC signals of the PES, PES/untreated and PES/treated graphite composites and PS are shown in Figure 6.5. The heights, diameters and mass of the specimens were also measured (Table 6.2). Specific heat capacities of samples for the last ten minutes were averaged and used in apparent heat capacity calculations by multiplying the averaged value by the weight of the sample. The results are shown in Table 6.3.

*Figure 6.4 MDSC signals from thin specimens*
Table 6.1 Specific heat measured on thin specimens

<table>
<thead>
<tr>
<th>Description</th>
<th>Measured specific heat J/g.°C</th>
<th>Corrected specific heat J/g.°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>0.962</td>
<td>0.933</td>
</tr>
<tr>
<td>PES/UG1%</td>
<td>1.228</td>
<td>1.191</td>
</tr>
<tr>
<td>PES/UG3%</td>
<td>1.081</td>
<td>1.048</td>
</tr>
<tr>
<td>PES/UG5%</td>
<td>0.958</td>
<td>0.929</td>
</tr>
<tr>
<td>PES/TG1%</td>
<td>1.292</td>
<td>1.253</td>
</tr>
<tr>
<td>PES/TG3%</td>
<td>1.434</td>
<td>1.390</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>1.336</td>
<td>1.295</td>
</tr>
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<td>1.155</td>
<td>1.120</td>
</tr>
<tr>
<td>Sapphire</td>
<td>0.805</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Table 6.2 Dimensions and mass of thick specimens

<table>
<thead>
<tr>
<th>Description</th>
<th>Average Height (L) cm</th>
<th>Average Diameter (d) cm</th>
<th>Mass (M) mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>0.25</td>
<td>0.54</td>
<td>67.363</td>
</tr>
<tr>
<td>PES/UG1%</td>
<td>0.30</td>
<td>0.54</td>
<td>73.472</td>
</tr>
<tr>
<td>PES/UG3%</td>
<td>0.27</td>
<td>0.53</td>
<td>54.839</td>
</tr>
<tr>
<td>PES/UG5%</td>
<td>0.25</td>
<td>0.54</td>
<td>51.273</td>
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<tr>
<td>PES/TG1%</td>
<td>0.25</td>
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<td>74.909</td>
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<tr>
<td>PES/TG3%</td>
<td>0.29</td>
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<tr>
<td>PES/TG5%</td>
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<td>59.868</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.32</td>
<td>0.51</td>
<td>53.472</td>
</tr>
</tbody>
</table>
The Thermal Conductivity of PES/Graphite Conductive Composites

Figure 6.5 MDSC signals from thick specimens

Table 6.3 Apparent heat capacity measured on thick specimens

<table>
<thead>
<tr>
<th>Description</th>
<th>Average specific heat capacity J/g°C</th>
<th>Apparent heat capacity J°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>0.6374</td>
<td>0.0429</td>
</tr>
<tr>
<td>PES/UG1%</td>
<td>0.8329</td>
<td>0.0612</td>
</tr>
<tr>
<td>PES/UG3%</td>
<td>0.9856</td>
<td>0.0540</td>
</tr>
<tr>
<td>PES/UG5%</td>
<td>1.0740</td>
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<tr>
<td>PES/TG1%</td>
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<td>0.0553</td>
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<td>PES/TG3%</td>
<td>0.8972</td>
<td>0.0580</td>
</tr>
<tr>
<td>PES/TG5%</td>
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<td>0.0567</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.6004</td>
<td>0.0321</td>
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</tbody>
</table>
Chapter 6

The Thermal Conductivity of PES/Graphite Conductive Composites

Table 6.4 Observed and corrected thermal conductivities

<table>
<thead>
<tr>
<th>Description</th>
<th>Observed $K_o$ W/m.°C</th>
<th>Corrected $K$ W/m.°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>0.2510</td>
<td>0.181</td>
</tr>
<tr>
<td>PES/UG1%</td>
<td>0.4403</td>
<td>0.374</td>
</tr>
<tr>
<td>PES/UG3%</td>
<td>0.4876</td>
<td>0.421</td>
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<tr>
<td>PES/UG5%</td>
<td>0.5464</td>
<td>0.480</td>
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<tr>
<td>PES/TG1%</td>
<td>0.2597</td>
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</tr>
<tr>
<td>PES/TG3%</td>
<td>0.3721</td>
<td>0.305</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>0.4133</td>
<td>0.346</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.2116</td>
<td>0.14</td>
</tr>
</tbody>
</table>

6.4.3 Thermal conductivity calculation

The observed thermal conductivities ($K_o$) were calculated using Equation 6.4. The corrected thermal conductivities ($K$) were obtained by substituting $D = 0.03$, derived from Equation 6.5, and $K_o$ in Equation 6.6. The results are shown in Table 6.4 and are plotted against filler content in Figure 6.6. With the calibration constant ($D$), the variation between the thermal conductivity value of the pristine PES measured by the MDSC technique (0.18 W/m.°C) and that from literature 0.18 W/m.°C is 0%.

6.5 THE EFFECT OF THE ADDITION OF GRAPHITE ON THE THERMAL CONDUCTIVITY OF PES

As expected, the addition of highly thermally-conductive fillers improves heat transport within the test specimens. It appears that the thermal conductivities at 27°C of both the PES/untreated and PES/treated graphite composites slightly increase with increasing filler content. At a given filler loading, the thermal conductivity of the composite containing untreated graphite is higher than that of the composite containing treated graphite. For example, at a filler content of 5 wt%, the thermal conductivities of the PES/untreated and PES/treated graphite
composites are 165 and 91%, respectively, higher than that of the pure PES matrix (0.181 W/m.°C).

![Graph showing thermal conductivity vs. filler content]

**Figure 6.6** Thermal conductivities of the PES/untreated and PES/treated graphite composites as a function of filler content

A thermal conductivity is determined predominantly by phonon transports. The graphite exhibits a significantly higher thermal conductivity than the PES matrix due to a higher number of phonon vibrational modes and a longer mean free path in the crystalline lattice structure of the graphite, compared to the amorphous structure of the PES. The phonon transports in the composites are then assumed to occur, preferably through the graphite.

As mentioned in Section 6.2, phonon transports in graphite are dominated by crystallite boundary scatterings, defect scatterings and phonon-phonon scatterings. In polymer/graphite composite systems, a crystallite boundary scattering is more precisely considered to be an interfacial boundary scattering occurring at the interfaces between the graphite and the polymer matrix. This means the treated graphite which provides larger interfacial boundaries and/or has higher defects is a poorer thermally-conductive filler.
Interfacial boundary scattering effects are so prominent in nano-scale fillers that the influence of aspect ratios of the fillers on their efficiencies as thermally-conductive fillers is of minor importance [123]. Nano-scale fillers possess tremendous surface area, resulting in tremendous interfacial boundaries at the interfaces in composites. Although the untreated and treated graphite employed in this research possess a large surface area, there exist immiscible regions where graphite layers are not bounded by the PES matrix, as evidenced from the SEM results in Chapter 4. Those layers of the graphite enable phonon conductions with minimised interfacial boundary scatterings [123].

Aspect ratios will be crucial for conventional fillers (micro-scale fillers) in which the interfacial area is reduced. High aspect ratio fillers allow phonon conductions to occur over a long distance, hence, the mean free path is high. Research on the thermal conductivities of polymer composites filled with a conventional thermally-conductive filler (aluminium nitride) reached the conclusion that for a given filler loading, a larger particle size filler leads to a composite with a more enhanced thermal conductivity than the smaller one, by providing a larger mean free path, which helps minimise interfacial phonon scatterings [74].

The effect of phonon-phonon scatterings below room temperature is minimal, as phonons have only a few scatterings. However, phonon-phonon scatterings become more effective as the temperature increases. At elevated temperatures, higher energy phonons are thermally populated, causing rapid decreases in the mean free path [148].

In addition, phonon conductions are affected by interfacial adhesions between fillers and polymer matrices [123]. A damping of phonon vibrational amplitude at the interfaces is more pronounced in a stronger than a weaker interfacial adhesion.

Vovchenko et al. [144] found that thermal conductivities of composites are affected by the densities of binders used for modifications of a filler. Polymer composites filled with high-density binder modified thermo-exfoliated graphite were found to have lower values of thermal conductivities at a given filler content.
than the composites containing low-density binder modified thermo-exfoliated graphite. It was noted that the intrinsic thermal conductivities of the binder are almost 4 times less than that of the pristine thermo-exfoliated graphite.

It is also found that the thermal and electrical conductivities of the PES/graphite composites correlate. As the electrical conductivities of the composites increase with increasing graphite content, their thermal conductivities increase (Figure 6.7). Unlike the electrical conduction in the composites which are assisted by the tunnelling and the percolation mechanism, the heat conduction in the composites are dominated only by phonon transports. Thus, the thermal conductivities of both composites are less enhanced compared to their electrical conductivities which are enhanced by several orders of magnitude at and beyond the percolation threshold. It can be seen that the untreated graphite, compared to the treated graphite, leads to a composite with a higher thermal conductivity below the percolation threshold (less than 3 wt%). Beyond the percolation threshold, untreated graphite leads to a composite with both higher thermal and electrical conductivities.

![Figure 6.7 A correlation between electrical and thermal conductivities of the PES/untreated and PES/treated graphite composites with various contents of fillers](image-url)
7.1 INTRODUCTION

Products made of polymer materials are widely used nowadays. If a service temperature is closed to its glass-rubber transition region, the physical and mechanical properties of the product which are temperature dependent will be affected. With a few change in temperature, the characteristic properties of a rigid glass will transform to that of a rubber. In the case of a continuous exposure the material at the temperature close to but below the glass transition temperature, a phenomenon called enthalpic relaxation or physical ageing will occur in addition to the glass transition. It is universally recognised that as an enthalpic relaxation proceeds the material properties such as yield stress, tensile and flexural modulus increase but fracture toughness, impact strength and creep compliance decrease continuously [149-150]. Also the transport property, for example, decreases in gas diffusion through a polymer membrane [105]. Nevertheless, these effects are totally reversible on a thermal cycling [105]. Clearly, an enthalpic relaxation is commercially importance for variability of the material properties. The thermal stability is another necessary value in determining the suitable processing condition of a material.

This study will investigate whether physical ageing affects the electrical conductivities of the PES/graphite composites, apart from the glass transition temperature and thermal stability investigations of the composites.

7.2 THE GLASS TRANSITION TEMPERATURE

A glass transition temperature \((T_g)\) is exhibited by amorphous polymers or amorphous regions in polymers when a hard, glass-like state is transformed into a viscous, rubber-like state and is observed as a baseline deviation toward the
endothermic direction on a typical DSC curve [151]. Expansions will increase markedly above glass transition temperatures. It corresponds to a change in slope at \( T_g \) in the specific volume versus temperature plot, as illustrated schematically in Figure 7.1. Thus a glass transition temperature can be defined in terms of a kinetic process involving volume contractions. High \( T_g \) provides polymers with greater dimensional stabilities [152].

\[ T_g \]

\[ T_m \]

**Figure 7.1 Free volume in a polymer [153]**

\( T_g \) can be conveniently determined by means of a DSC technique. Thermal history and experimental conditions are the factors that markedly affect \( T_g \) values. Hence, a determination should begin with an elimination of the previous thermal history through a heating up and keeping for 10 minutes at 30°C above the end of the transition temperature, followed by a rapid cooling (quench) to a temperature at least 50°C below the expected \( T_g \) value. During a reheating scan, a deviation of baseline can be observed at the glass transition temperature as a result of a change in specific heat \( (C_p) \). The specific heat of amorphous materials in the liquid state
is higher than that in the solid state [154]. Slower cooling and heating rate result in a lower $T_g$ value [155]. In order to avoid oxidation of a sample, experiments should be performed under nitrogen atmosphere with a continuous flow rate of 10-50 ml/min. Methods of determining $T_g$ from DSC curves are shown in Figure 7.2 (a) and (b).

Figure 7.2 Glass transition temperature determinations: (a) baseline deviation at the transition; (b) baseline deviation at the transition with a small peak [154]

$T_{ig}$, the extrapolated onset temperature, is the temperature at which the extrapolated baseline before the transition intersects the tangent drawn through the highest slope of the transition. Similarly, $T_{eg}$, the extrapolated end temperature, is the temperature at which the extrapolated baseline after the transition intersects the tangent drawn through highest slope of the transition. $T_{mg}$, the mid-point glass transition temperature, is the temperature at the middle of the transition (Figure 7.2 (a)). In the case of a presence of a small endothermic peak at the transition, $T_{eg}$ is considered to be the temperature at the intersection of the extrapolated
baseline after the transition with the tangent drawn through the highest slope of the peak edge (Figure 7.2 (b)).

7.3 THE EFFECT OF THE ADDITION OF GRAPHITE ON THE GLASS TRANSITION TEMPERATURE OF PES

Heat flow of the PES and its composites with the untreated or treated graphite was recorded during a reheating scan at a heating rate of 10°C/min from 120-230°C. Comparisons of heat flow against temperature of the two composite systems are made in Figure 7.3 and 7.4, respectively. The scales of heat flow are for the PES (depicted as UG 0% or TG 0%), and the other curves are vertically shifted.

Figure 7.3 DSC curves of the PES and PES/untreated graphite composites
A glass transition temperature is taken as the extrapolated onset temperature and the reproducibility of peak temperature is ±1°C. The amorphous PES shows a glass transition temperature at about 195°C. In the composites filled with the untreated graphite, the addition of 1 wt% of the untreated graphite filler increases $T_g$ by about 7°C. It can be seen that further increases in the filler content have insignificant effects on $T_g$. The $T_g$ measurements for the composites filled with the treated graphite provide the same tendency as that filled with the untreated graphite. $T_g$s of the PES/untreated graphite composite system are about 201-203°C, while that of the PES/treated graphite composite system are in the range of 201-204 °C.

![Figure 7.4 DSC curves of the PES and PES/treated graphite composites](image)

When the PES is initially heated to 230°C, it becomes soft. Quenching the softened polymer to a certain temperature, i.e. glass transition temperature, transforms it into the glassy state associated with a lowering in coefficient of
expansion, coefficient of diffusion and specific heat. In the glassy state, PES molecular chains can only oscillate about their equilibrium positions [155]. As the glassy PES is being reheated, rotatability of bonds in the main chains increases. At \( T_g \), the rotatability is very large. Above \( T_g \), polymer chains can glide past each other and reach their equilibrium positions.

In the PES composites, there are interactions between the PES matrix and the fillers at the interfaces, in addition to interactions between the PES molecules themselves. With the interactions, as the composites are reheated, the rotation of PES chains is hindered. Some of the interactions still remain even at \( T_g \) of the PES polymer but will be totally destroyed at a higher temperature. The higher the interactions are, the higher the glass transition temperature is. With an increasing amount of each filler (> 1 wt%), the filler-filler interactions become so prominent that the filler will aggregate together; as a consequence, there are no significant increases in the PES-filler interactions at the interfaces. Therefore, the increased amounts of each filler do not have much influence on the rotation of PES main chains and there are no contributions to the glass transition temperatures of the composites.

Glass transition temperatures of the LiCl-doped PES/graphite composites with 5 wt% of the untreated or treated graphite were also measured and are compared in Figure 7.5 and 7.6, respectively. The scales of heat flow are for the undoped PES composite curve (depicted as LiCl 0%), and the other curves are vertically shifted. With Li\(^+\) and Cl\(^-\) ion incorporation, insignificant changes in \( T_g \) of the doped composites are observed.

From Chapter 5, it is known that Li\(^+\) ions are diffused into the galleries of graphite; whereas, Cl\(^-\) ions are dispersed in the PES matrix. Due to being a larger atom compared to sulphur, oxygen, carbon and hydrogen atoms in the PES molecules [138], Cl\(^-\) ions may cause a restriction of the segmental motion of PES main chains if they are present in a high amount in the systems, which then contribute to a higher glass transition temperature of the composites.
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Figure 7.5 DSC curves of the LiCl-doped PES/UG5% composites

Figure 7.6 DSC curves of the LiCl-doped PES/TG5% composites
7.4 THE EFFECT OF THE ADDITION OF GRAPHITE ON THE THERMAL STABILITY OF PES

While the thermal stabilities of the physical structures of polymeric materials are characterised by glass transition temperatures or melting temperatures, thermal stabilities related to the chemical structure of materials can be determined by the mass loss at a particular temperature by a thermogravimetry technique, since polymers are degraded by thermal oxidation reactions.

The thermal stability behaviours of the pure PES and PES/treated graphite composites with various treated graphite contents were studied by means of a thermogravimetric analyser. In the obtained thermogram, temperature is plotted against weight% on the left-handed axis and against the derivative of the former curve with respect to temperature on the right-handed axis (Figure 7.7-7.11). A weight loss curve appears as a steep step and a peak of the corresponding derivative curve appears where the weight loss rate is the fastest.

![Figure 7.7 Thermogravimetric and derivative curves of the PES](image-url)
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Figure 7.8 Thermogravimetric and derivative curves of a PES/TG3% composite

Figure 7.9 Thermogravimetric and derivative curves of a PES/TG5% composite
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Figure 7.10 Thermogravimetric and derivative curves of a PES/TG8% composite

Figure 7.11 Thermogravimetric and derivative curves of a PES/TG10% composite

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It can be seen that a one-stage degradation process of the pure PES and PES/treated graphite composites starts at about 400°C. The weight of the materials is lost due to one volatile material as observed by a single peak on each derivative curve. The volatile material is believed to be sulphur dioxide (SO₂) vapour from PES polymer chains [156]. Non-volatile materials which remain at 600°C are denoted as char. The char residue of the composites tends to increase with increasing amounts of the treated graphite (Table 7.1). The temperature at the maximum weight loss rate of the composites is higher than that of the pure PES, indicating a thermal stability improvement for the composites to some extent. The reproducibility of peak temperature is ±1°C.

**Table 7.1** Char residue of the PES and its composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Char Residue (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>47 ± 0.5</td>
</tr>
<tr>
<td>PES/TG3%</td>
<td>46 ± 0.5</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>50 ± 0.5</td>
</tr>
<tr>
<td>PES/TG8%</td>
<td>49 ± 0.5</td>
</tr>
<tr>
<td>PES/TG10%</td>
<td>51 ± 0.5</td>
</tr>
</tbody>
</table>

Comparisons of the weight loss curves and the corresponding derivative curves of the materials are shown in Figures 7.12 and 7.13, respectively. It can be seen that the weight loss curves of the composites appear above that of the pure PES. Also the height of the derivative peaks of the composites is found to decrease with increasing treated graphite content. It is well known that the area under the derivative peaks or the peak height is proportional to the weight loss [106]. These suggest the improved thermal stabilities of the composites. The improvement is attributed to hindrance diffusion of the volatile decomposition products out of the materials containing graphite sheets [157].
Figure 7.12 The thermogravimetric curves of the PES/TG composites at various TG contents

Figure 7.13 The derivative curves of the PES/TG composites at various TG contents
7.5 THE ENTHALPIC RELAXATION

If a polymer is quenched to, and aged at, a temperature range well below \( T_g \), the polymer chains will not be in their equilibrium conformations and will slowly relax from the non-equilibrium towards the equilibrium with time accompanied by decreases in free volume and enthalpy [158]. This phenomenon is called enthalpic relaxation or physical ageing. The decrease in enthalpy will be recovered during reheating above the \( T_g \) region. The recovery is monitored as a change in heat flow or an endothermic peak superimposed on the \( T_g \) region on a DSC reheating curve [159].

7.5.1 The enthalpic relaxation in PES/graphite composites

In this work, enthalpic relaxation or the physical ageing process was studied at three different ageing temperatures, for three different ageing times, in the glassy state. DSC curves showing relaxation enthalpy peaks of the neat PES polymer, its composites with 5 wt% of the untreated or treated graphite and the 0.06 wt% of LiCl-doped composites aged at \((T_g-3)\)°C, \((T_g-6)\)°C and \((T_g-9)\)°C for 15, 40 and 60 minutes at each ageing temperature, are presented in Figures 7.14-7.18. In all the thermograms, endothermic signals are downward pointing. The scales of heat flow are for non-aged sample curves (depicted as 0 mins.), and aged sample curves are vertically shifted for a comparison.

It can be seen that endothermic peaks, whose magnitudes provide a quantitative value of the decreased enthalpy during ageing, appear at the edge of the \( T_g \) region. The relaxation enthalpy is measured by integration of the area under an endothermic peak of an aged material (equal to \( H_i \)) subtracted by that of the same material without ageing (equal to \( H_0 \)). The start and end point of the baseline for the enthalpy calculation are selected by referring to the corresponding derivative peak with respect to time (Figure 7.19).
The Thermal Behaviour of PES/Graphite Conductive Composites and the Effect of Physical Ageing on Electrical Conductivity

Figure 7.14 DSC curves of the PES aged for different times at:
(a) \( (T_g-3) \)\(^\circ\)C; (b) \( (T_g-6) \)\(^\circ\)C; (c) \( (T_g-9) \)\(^\circ\)C
Figure 7.15 DSC curves of a PES/UG5% composite aged at:
(a) \((T_g-3) \degree C\); (b) \((T_g-6) \degree C\); (c) \((T_g-9) \degree C\)
Figure 7.16 DSC curves of a PES/TG5% composite aged at:
(a) \( (T_g - 3) \) °C; (b) \( (T_g - 6) \) °C; (c) \( (T_g - 9) \) °C
Figure 7.17 DSC curves of a PES/UG5%/LiCl0.06% composite aged at:
(a) \(T_g-3\)°C; (b) \(T_g-6\)°C; (c) \(T_g-9\)°C
Figure 7.18 DSC curves of a PES/TG5%/LiCl0.06% composite aged at:
(a) \(T_g-3\)°C; (b) \(T_g-6\)°C; (c) \(T_g-9\)°C
Figure 7.19 Illustration of a peak area calculation from a heat flow signal

The change in relaxation enthalpy ($\Delta H_r$) during ageing of the materials, which is equal to $H_r - H_0$, is plotted against ageing time ($t$) at the same ageing temperature ($T$), in Figures 7.20-7.22. The results show that at a given ageing temperature the decreases in enthalpy of each material become gradually more pronounced with ageing time. It can be seen that the decreased enthalpy of the PES/untreated and PES/treated graphite composites and that of the pure PES at a given ageing temperature and time, is insignificantly different. However, the changes in enthalpy are found to be smaller for the two doped composite systems compared to that of the corresponding undoped systems. It is also found that at a certain ageing time, the enthalpy is more decreased at a higher ageing temperature.
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Figure 7.20 Variation of relaxation enthalpy with ageing time for samples aged at \((T_g-3) ^\circ C\)

Figure 7.21 Variation of relaxation enthalpy with ageing time for samples aged at \((T_g-6) ^\circ C\)
When the PES is quenched to, and aged at, a temperature just below \( T_g \), the polymer chains relax from higher energy conformations to lower energy ones with time. Thus, the enthalpic relaxation endotherm at a given ageing temperature of the PES, increases in magnitude with increasing ageing time. Due to higher localised molecular motions of polymer chains at higher ageing temperatures, the magnitude of the enthalpic relaxation is accordingly larger at the same ageing time. Incorporation of graphite into the PES polymer causes less freedom of localised rotational movement of PES polymer chains. Between the two composite systems, the decreased enthalpy at the same ageing temperature and time differ insignificantly.

The presence of \( \text{Cl}^- \) ions causes a restriction of packing of PES polymer chains, resulting in suppression of the relaxation process in the doped composites. As a consequence the change in relaxation enthalpy of the doped composite systems

*Figure 7.22 Variation of relaxation enthalpy with ageing time for samples aged at \( (T_g-9)\degree\text{C} \)*
occurs at a slower rate than that of the undoped composite systems at a certain ageing temperature and time.

The enthalpic relaxation process is normally accompanied by a shift in the glass transition temperature to a higher temperature [160-162]. Figures 7.23-7.25 show glass transition temperatures of the samples aged at $(T_g-3)$, $(T_g-6)$ and $(T_g-9)^\circ$C, respectively. It can be seen that at a given ageing temperature $T_g$ of each material significantly increases with increasing ageing time. Similarly, it is also found that at a given ageing time, $T_g$ of materials aged at a higher ageing temperature are insignificantly higher than that of materials aged at a lower ageing temperature.

![Figure 7.23 Dependence of $T_g$ on ageing time for samples aged at $(T_g-3)^\circ$C](image-url)
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Figure 7.24 Dependence of $T_g$ on ageing time for samples aged at $(T_g-6)\degree C$

Figure 7.25 Dependence of $T_g$ on ageing time for samples aged at $(T_g-9)\degree C$
As enthalpic relaxation or physical ageing proceeds, the PES polymer gradually approaches the characteristics of an equilibrium glass state. Normally, the equilibrium glass state can only be obtained when a polymer is quenched to an ageing temperature at an infinitely slow cooling rate [163]. The longer the material is aged, the nearer it becomes to an equilibrium glass. Similarly, the higher the temperature the material is aged at, the faster it becomes an equilibrium glass. Reheating the longer-aged material or the higher temperature-aged material, from a temperature far below ageing temperature will result in a higher glass transition temperature due to less free volume in the material.

7.6 THE CHARACTERISTIC LENGTH OF GLASS TRANSITION

The characteristic length ($\xi_a$) which corresponds to the size of cooperatively rearranging regions (CRR) is defined by Adam and Gibbs [164] as “the smallest region that can undergo a transition to a new configuration without a requisite simultaneous configurational change on and outside its boundary”. Characteristic length is normally calculated by using Donth's formula [165].

$$\xi_a^2 = \frac{k_B T^2 \Delta(1/c_v)}{\rho \delta T^2} \approx \frac{k_B T^2 \Delta c_p}{\bar{c}_p \rho \delta T^2}$$  \hspace{1cm} (7.3)

where:

- $\xi_a$ = The characteristic length of glass transition
- $k_B$ = Boltzmann’s constant
- $\Delta(1/c_v)$ = Step height of the reciprocal specific heat at constant volume $\approx \Delta c_p / \bar{c}_p^2$
- $\Delta c_p$ = Step height of the specific heat at constant pressure (the specific heat difference between flow and glass zone at $T_g$)
- $\bar{c}_p$ = The mean value of specific heat at $T_g$
- $T$ = Temperature (i.e. $T_g$)
- $\rho$ = The mass density of polymer
\[ \delta T = \text{The mean temperature fluctuation of the subsystem of size } V_a \]

\[ \delta T^2 = (\delta T')^2 \]

In this study, the characteristic length of glass transition of each sample is judged by examining information from the enthalpic relaxation results shown in section 7.5. Each parameter for the characteristic length calculation in Equation 7.3 will be considered. Figure 7.26 shows how \( \delta T \) can be determined from a DSC heating curve. By performing a baseline subtraction and fitting with a Gaussian curve, the dispersion (width) of the Gaussian peak will be equal to \( 2\delta T \) [166].

![Figure 7.26 DSC determination of a value of \( \delta T \) (here, \( 2\delta T = 4.07 \pm 0.02 \))](image)

Table 7.2-7.4 shows \( \delta T \) values of aged samples at three ageing temperatures and at three different ageing times compared to the corresponding non-aged samples (depicted as 0 min.). It can be seen that at a given ageing temperature, the temperature fluctuation (\( \delta T' \)) of each sample decreases with increasing ageing time.
Table 7.2 Dependence of \( \delta T \) on ageing time for samples aged at \((T_g-3)\)°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \delta T ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>PES</td>
<td>2.50 ± 0.03</td>
</tr>
<tr>
<td>PES/UG5%</td>
<td>2.11 ± 0.03</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>2.15 ± 0.02</td>
</tr>
<tr>
<td>PES/UG5%/LiCl0.006%</td>
<td>2.40 ± 0.02</td>
</tr>
<tr>
<td>PES/TG5%/LiCl0.006%</td>
<td>2.24 ± 0.03</td>
</tr>
</tbody>
</table>

Table 7.3 Dependence of \( \delta T \) on ageing time for samples aged at \((T_g-6)\)°C

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<tr>
<td>PES</td>
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</tr>
<tr>
<td>PES/UG5%</td>
<td>2.11 ± 0.03</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>2.15 ± 0.02</td>
</tr>
<tr>
<td>PES/UG5%/LiCl0.006%</td>
<td>2.40 ± 0.02</td>
</tr>
<tr>
<td>PES/TG5%/LiCl0.006%</td>
<td>2.24 ± 0.03</td>
</tr>
</tbody>
</table>

Table 7.4 Dependence of \( \delta T \) on ageing time for samples aged at \((T_g-9)\)°C

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<tr>
<td>PES</td>
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</tr>
<tr>
<td>PES/UG5%</td>
<td>2.11 ± 0.03</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td>2.15 ± 0.02</td>
</tr>
<tr>
<td>PES/UG5%/LiCl0.006%</td>
<td>2.40 ± 0.02</td>
</tr>
<tr>
<td>PES/TG5%/LiCl0.006%</td>
<td>2.24 ± 0.03</td>
</tr>
</tbody>
</table>

At a given ageing temperature \( \Delta C_p \) also increases with increasing ageing time due to the lowering of \( C_p \) of the glassy state caused by densification (decrease in...
Chapter 7

The Thermal Behaviour of PES/Graphite Conductive Composites and the Effect of Physical Ageing on Electrical Conductivity

free volume). The mean value of specific heat \( (\overline{c_p}) \) between the glass and the flow zone at the glass transition consequently decreases. Another two parameters \( (k_b \) and \( \rho \) ) are constant values. These examinations indicate that characteristic length \( (\xi) \) of each sample at a certain ageing temperature will increase with increasing ageing time.

Polymers at a temperature above \( T_g \) have a substantial proportion of free volume (unoccupied volume) which can be present either as holes of molecular size or small voids of packing irregularity [167]. When the temperature gradually falls, the molecular adjustment takes place accompanied by a collapse of the free volume. The adjustments are slower with lower temperature, and finally reach the temperature where the collapse can no longer occur. The residual contraction is then of a solid-like character.

Rapidly lowering the temperature of the soft material through \( T_g \) causes the free volume to freeze. The frozen regions act as molecular boundaries. With the presence of the free volume, the characteristic length is short. However, the free volume will be gradually lost from the material with elapsed time, during ageing at a temperature well below \( T_g \), associated with localised rotational movement. The annihilation of the free volume results in a longer characteristic length [168].

7.7 THE EFFECT OF PHYSICAL AGEING ON THE ELECTRICAL CONDUCTIVITY OF PES/GRAPHITE COMPOSITES

The electrical conductivities of the PES/untreated and PES/treated graphite composites and doped composites aged at three different temperatures, each for three different ageing times, were calculated and compared with the corresponding non-aged samples in Table 7.5-7.7.
Chapter 7  The Thermal Behaviour of PES/Graphite Conductive Composites  
and the Effect of Physical Ageing on Electrical Conductivity

Table 7.5 Variations of the electrical conductivities on ageing time for samples aged at \((T_g-4)°C\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical Conductivity (S/cm)</th>
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<th>1 hr</th>
<th>5 hrs</th>
<th>24 hrs</th>
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<tbody>
<tr>
<td>PES/UG5%</td>
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<td>3.9\times10^{-7}</td>
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<td>2.4\times10^{-7}</td>
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<tr>
<td>PES/TG5%</td>
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<td>8.4\times10^{-8}</td>
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<td>1.8\times10^{-8}</td>
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</tr>
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<td>PES/UG5%/LiCl0.006%</td>
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<td>7.6\times10^{-7}</td>
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<td>1.8\times10^{-7}</td>
<td>1.4\times10^{-7}</td>
</tr>
<tr>
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<td>1.3\times10^{-6}</td>
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Table 7.6 Variations of the electrical conductivities on ageing time for samples aged at \((T_g-7)°C\)

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<th>Electrical Conductivity (S/cm)</th>
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<th>1 hr</th>
<th>5 hrs</th>
<th>24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/UG5%</td>
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<td>3.9\times10^{-7}</td>
<td>2.8\times10^{-7}</td>
<td>3.7\times10^{-7}</td>
<td>3.8\times10^{-7}</td>
</tr>
<tr>
<td>PES/TG5%</td>
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<td>8.4\times10^{-8}</td>
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<tr>
<td>PES/UG5%/LiCl0.006%</td>
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<td>7.6\times10^{-7}</td>
<td>2.0\times10^{-7}</td>
<td>1.7\times10^{-7}</td>
<td>1.6\times10^{-7}</td>
</tr>
<tr>
<td>PES/TG5%/LiCl0.006%</td>
<td></td>
<td>5.6\times10^{-6}</td>
<td>1.2\times10^{-6}</td>
<td>1.3\times10^{-6}</td>
<td>1.2\times10^{-6}</td>
</tr>
</tbody>
</table>

Table 7.7 Variations of the electrical conductivities on ageing time for samples aged at \((T_g-10)°C\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical Conductivity (S/cm)</th>
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<th>1 hr</th>
<th>5 hrs</th>
<th>24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/UG5%</td>
<td></td>
<td>3.9\times10^{-7}</td>
<td>2.7\times10^{-7}</td>
<td>2.8\times10^{-7}</td>
<td>3.7\times10^{-7}</td>
</tr>
<tr>
<td>PES/TG5%</td>
<td></td>
<td>8.4\times10^{-8}</td>
<td>2.9\times10^{-8}</td>
<td>3.6\times10^{-8}</td>
<td>4.2\times10^{-8}</td>
</tr>
<tr>
<td>PES/UG5%/LiCl0.006%</td>
<td></td>
<td>7.6\times10^{-7}</td>
<td>2.0\times10^{-7}</td>
<td>1.9\times10^{-7}</td>
<td>2.0\times10^{-7}</td>
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<td>PES/TG5%/LiCl0.006%</td>
<td></td>
<td>5.6\times10^{-6}</td>
<td>1.0\times10^{-6}</td>
<td>1.0\times10^{-6}</td>
<td>1.0\times10^{-6}</td>
</tr>
</tbody>
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It can be seen that at a certain ageing temperature, the electrical conductivity of each aged sample is lower than that of the corresponding non-aged sample. Data shown in Table 7.5 were used in plotting a relationship between the electrical
conductivities of the samples with ageing ($\sigma$) and that of the corresponding samples without ageing ($\sigma_0$) against ageing time in Figure 7.27. Decreases in electrical conductivities with increasing ageing time are then clearly observed. In the PES/untreated graphite system, the decrease is smaller compared to that of the other three systems, and each system has small variations in electrical conductivities with different ageing times.

As mentioned earlier, quenching a soft material through $T_g$ causes the free volume to freeze. 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 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 composites.

Figure 7.27 Decreases in the electrical conductivities of samples caused by physical ageing
During the densification, graphite sheets are probably forced further apart, in other words, are interrupted by barriers, either spaces or the 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 [137]. If graphite sheets, on the other hand, are too far from the neighbouring graphite sheets, the electrical conductivities of the composites will be dramatically decreased due to the absence of the tunnelling process. Nonetheless, the probability of a tunnelling may be enhanced due to the presence of intermediate states such as impurities or dispersed defects [137]. 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⁺ and Cl⁻ ions, respectively, within the barrier.

Since there are fewer interactions between the PES polymer and the untreated graphite, the localised movement of the PES polymer chains has less influence on the movement of untreated graphite sheets. The electrical conductivities of the aged PES/untreated graphite composites are correspondingly less affected when compared to that of the aged PES/treated graphite composites. With passing ageing time, PES polymer chains acquire more equilibrium conformations. Therefore, localised movement of the polymer chains and also the variation of the electrical conductivities of each aged sample becomes less with prolonged ageing time. In addition, the inter-particle distance between treated graphite sheets in the PES/treated graphite composites is originally longer than that between untreated graphite sheets in the PES/untreated graphite composites due to the presence of oxidised-surface functional groups. Therefore, just a little increase in the inter-particle distance during physical ageing can result in a striking change in the electrical conductivities of the PES/treated graphite composite system.

In the doped PES/graphite composite systems, Li⁺ and Cl⁻ 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 a very small amount in the doped composite system and are randomly dispersed in the
graphite galleries or the polymer matrix which may or may not be in the vicinity of the network of conductive paths.

In addition, a lower ageing temperature results in a slowing of the localised rotational movement of the PES polymer chains [167]. The overall effect of physical ageing on the electrical conductivities of the composites aged at a lower ageing temperatures can be discussed in the same way as those aged at higher ageing temperatures.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

8.1 INTRODUCTION
This research involves improving the electrical conductivity and the thermal properties, at the optimum micromechanical properties of PES, by addition of the graphite for coating and electrostatic dissipation applications. Expandable graphite flakes were used for preparing expanded graphite. Sonication of expanded graphite by ultrasonic dismembrator was performed to yield a micro-/nano-graphite which was simply called graphite. The graphite surfaces were functionalised with concentrated nitric acid treatment. The treated and untreated graphite were used for PES composites and LiCl-doped PES composites fabrication via the solution method. Many techniques were employed to characterise the two composite systems to provide the morphological, micromechanical, electrical and thermal properties of the samples. The mechanism of the electrical conductivity enhancement by doping was also studied. Conclusions can be drawn as follows based on the experimental results obtained.

8.2 CONCLUSIONS
Morphological and Micromechanical Properties
Micro-/nano-graphite prepared by sonication of the expanded graphite possessed aspect ratios in the range 100-600. FT-IR results showed that treatment by concentrated nitric acid was found to be the most effective in introducing additional -COOH functional groups onto the surfaces of the expanded graphite, compared to concentrated sulphuric acid and a mixture of the two acids. The optimum length of treatment time was found to be 4 hours for nitric acid treatment.

XRD studies revealed that the graphite was dispersed throughout the PES matrix in both an immiscible and disordered manner and that there was the existence of
aggregates of the graphite, which were in good agreement with the SEM and TEM results. The distance between the organised carbon layers in aggregates of the graphite was retained at 0.343 nm. XRD also indicated that solution blending was more effective than melt blending as a method to prepare graphite composites with high exfoliation of graphite layers. Formation of a graphite conducting pathway in the PES matrix was observable in a TEM micrograph.

Nanoindentation indicated that the incorporation of the treated graphite in the PES polymer matrix resulted in decreases in the nanohardness and elastic modulus of the PES/treated graphite composites. However, both the nanohardness and elastic modulus of the composites were still close to that of the pure PES up to 5 wt% loading of the treated graphite. E/H ratio indicated that the deformation mechanism of the composites containing up to 8 wt% of the treated graphite could still be considered as elastic deformation. Nanoscratch testing showed that the nanoscratch resistance of the composites increased with the addition of the treated graphite. However, the improvement of the nanoscratch resistance was small when the treated graphite content over 5 wt% was filled in the matrix.

**Electrical Conductivity Property**

Electrical conductivities were calculated from resistance measurements. With the addition of the graphite, the electrical conductivity of the PES polymer was improved. Percolation thresholds of the PES/untreated and PES/treated graphite composites were lower than 3 wt% of the filler. The improvement in electrical conductivities of the composites at low loadings could be attributed to the high aspect ratio of the graphite. It was found that nitric treatment of the graphite was not beneficial in the electrical conductivity enhancement of the composites, since surface functionalisation by the oxidation reaction lead to a lower aspect ratio of the graphite. The electrical conductivities of the PES/untreated and PES/treated graphite composites with 8 wt% of the filler were $1.8 \times 10^{-3}$ S/cm and $4.6 \times 10^{-4}$ S/cm, respectively.

Electrical conduction in the composites could be explained using both the percolation theory and a tunnelling mechanism. According to the percolation
theory, drastically increased electrical conductivity of the composites occurred when the amount of the filler reached a critical content called the percolation threshold, causing an initial conducting path through the material. However, below the percolation threshold, a conducting pathway was possible and occurred due to a tunnelling mechanism when the inter-particle distance of graphite sheets was sufficiently small (close to 1.2 nm). Beyond the percolation threshold, the tunnelling mechanism was assisted by an increase in the dimension of graphite conductive paths and a decrease in the inter-particle distance.

LiCl was found to be an effective dopant for the improvement of the electrical conductivities of the PES/treated graphite composites. However, there existed a dilution limit of LiCl of 0.6 wt%, beyond which its doping ability was impaired. The electrical conductivity of the 5 wt% treated graphite/PES composite with the presence of a LiCl content of 0.06 wt%, was $3.0 \times 10^{-4} \text{ S/cm}$, which was 2 orders of magnitude higher than that of the undoped composite and was at the same order of magnitude as that of the PES filled with 8 wt% of the treated graphite. The enhancement of electrical conductivities of the doped composites was shown to result from intercalations of Li$^+$ ions into interlayer spaces of the graphite. Upon intercalation, an acceptor GIC, Li-GIC, was consequently formed.

The conduction mechanism in the doped composites related the density and the mobility of extra holes, creating $\pi$ orbitals of carbon atoms in graphite. Too high concentrations of the Li$^+$ ions presenting in the graphite galleries lead to too high density of holes, resulting in a collision broadening. The collision affected the mobility of holes, causing a lowering of the electrical conductivities of the doped composites. In addition, the electrical conductivities of both the undoped and doped PES/treated graphite composites were found to increase with increasing temperature, resulting from increased thermally activated holes and electrons.

**Thermal Conductivity Property**

MDSC indicated that the thermal conductivity of the PES could be improved by addition of the graphite. Thermal conductivities in the PES/graphite composites were determined by phonon transport through the graphite. At a filler content of 5
Conclusions and Future Work

wt%, the thermal conductivities of the PES/untreated and PES/treated graphite composites were 165 and 91%, respectively, higher than that of the pure PES matrix. The difference in thermal conductivity improvement was due to the different types of graphite. The lower aspect ratio of the treated graphite leads to higher interfacial boundary scattering of phonons.

**Thermal properties**

Due to interfacial interactions between the PES matrix and the graphite, both the PES/untreated and PES/treated graphite composites containing 1 wt% of the filler exhibited about 7°C higher glass transition temperatures than the pure PES as evidenced by the DSC curves. With higher amounts of the filler, filler-filler interactions became prominent. Accordingly, the glass transition temperatures of both composites containing 3, 5, 8, and 10 wt% of filler were found to be nearly the same as that of the composites containing 1 wt% of filler. TGA found that the addition of the graphite also improved the thermal stabilities of the PES/treated graphite composites. The improvement was attributed to the behaviour of graphite sheets as hindrance diffusion of the volatile decomposition products out of the materials containing graphite sheets.

The addition of the graphite caused a suppression of the enthalpic relaxation processes of PES polymer undergoing physical ageing. The suppression was promoted when dopant was contained in the aged composites as observed by the smaller changes in relaxation enthalpy at the same ageing temperature and time. In the doped composite system, not only the graphite but also CI ions were responsible for less freedom of the localised rotational movement of the PES polymer chains during the relaxation. Also, the glass transition temperatures and characteristic lengths (ξ) of the aged PES, PES/graphite composites and doped PES/graphite composites were influenced by physical ageing. The aged materials attained more equilibrium glass characteristic with time, i.e. having less free volume. The annihilation of the free volume subsequently resulted in a longer characteristic length and a higher glass transition temperature.
Physical ageing leads to decreases in the electrical conductivities of the PES/graphite composites and doped PES/graphite composites. It was a gap creation process at the interfaces between the PES polymer and graphite sheets, which accompanied the free volume annihilation and the densification of polymer during the physical ageing that contributed to the decreases in the electrical conductivities. Due to fewer interactions between the PES polymer and untreated graphite and its closer particle-particle distance, compared to the treated graphite, the electrical conductivities of the aged PES/untreated graphite composites were less affected by physical ageing.

8.3 SUGGESTIONS FOR FUTURE WORK

In this research, the nanoscratch resistance, electrical conductivity and thermal conductivity of the PES were improved by the addition of the graphite. However, for the material to be utilised in industrial applications, it is still in need of further development. The following aspects should be included:

1) Attempts to prepare nano-scale graphite with a high aspect ratio and to improve its dispersion in the polymer matrix.

2) Developments in the electrical conductivity of the composites up to $10^{-2}$ S/cm with the newly developed graphite for use in EMI/RFI shielding applications. Attempts to lower the percolation threshold at even lower graphite loading should be made.

3) Developments in the thermal conductivity of the composites up to 0.6 W/m.°C for thermal management applications. Phonon scattering at the interfaces should be reduced.

4) Micro-wear studies of coatings should be made to provide properties such as abrasive wear.
REFERENCES


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95) [http://science.csustan.edu/tutorial/ir/index.htm](http://science.csustan.edu/tutorial/ir/index.htm) on 06 December 2005.


138) [http://www.webelements.com](http://www.webelements.com) on 06 December 2006.


References


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### Appendix

**Appendix**
|   | 3p_x | 3p_y | 3p_z | 3d_x | 3d_y | 3d_z | 4p_x | 4p_y | 4p_z | 4d_x | 4d_y | 4d_z | 5p_x | 5p_y | 5p_z | 5d_x | 5d_y | 5d_z | 6p_x | 6p_y | 6p_z | 6d_x | 6d_y | 6d_z | 7p_x | 7p_y | 7p_z | 7d_x | 7d_y | 7d_z | 8p_x | 8p_y | 8p_z | 8d_x | 8d_y | 8d_z | 9p_x | 9p_y | 9p_z | 9d_x | 9d_y | 9d_z |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 4s | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  |
| 4p | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  |
| 4d | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  |
| 4f | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  | 2l  |

The most intense lines are marked with an asterisk. Thus for elements Hf to Mg the 3s orbital is usually studied. For Al to As the 3p, and so on.