ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE/GRAPHITIC NANOPLATELET NANOCOMPOSITES FOR ENERGY STORAGE APPLICATIONS

A Thesis by

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ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE/GRAPHITIC NANOPlatelet NANOCOMPOSITE FOR ENERGY STORAGE APPLICATIONS

The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science, with a major in Mechanical Engineering.

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DEDICATION

To my parents (Lal Bihari Prasad Jaiswal and Sakila Kumari Chaudhary Jaiswal), my brother (Amar Jaiswal), and my dear friends
ACKNOWLEDGEMENTS

I am using this opportunity to express my gratitude to everyone who supported me throughout the course of my M.Sc. I shall always remain indebted to my supervisors Assistant Professor Dr. Bin Li and Professor Dr. Hamid Lankarani for having accepted me as a graduate student. I am thankful not only for their aspiring guidance throughout the work but their benign encouragement, positive attitude, invaluably constructive criticism, and friendly advice that helped me keep my spirits high even during difficult times.

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I would also like to express my deep appreciation for the assistance and helpfulness of my fellow research students Zheng Zhuoyuan and Nayan Shrestha for their time and valuable suggestions during the research work.

Lastly, I would like to thank my parents (Mr. Lal Bihari Prasad Jaiswal and Mrs. Shakila Kumari Chaudhary Jaiswal) and my brother (Mr. Amar Jaiswal) for their understanding and blessings.
ABSTRACT

Graphene and graphene based nanomaterials are one of the most intriguing functional materials today because of their exceptional properties including unique electronic properties and high mass to strength ratio, etc. Their unique properties, plus the abundance of naturally existing graphite, the ease of functionalization and synthesis in mass volume; graphene and graphitic nanomaterials have shown great potential in multifunctional polymer nanocomposites. Graphite Nanoplatelets (GNPs) is one of the most desirable graphitic nanomaterials as the reinforcing component for polymer nanocomposites, due to its low cost and higher specific surface area of GNPs compared to other graphitic nanomaterials.

In this study, the heat treated GNPs (ht-GNPs) and surface modified ht-GNP (s-GNP) were used to modify ultrahigh molecular weight polyethylene (UHMWPE). The objective of this study focused on understanding the effects of the GNP loadings, temperature, as well as electric field on energy storage capability of UHMWPE/GNP nanocomposites with and without surface modifications of ht-GNPs. The results suggested that the surface modification could remarkably improve the dispersion of GNPs and the interfacial interactions between GNPs and UHMWPE, both factors have shown the positive impacts on the energy storage performances regardless of testing conditions, compared with ht-GNPs without surface modifications. Meanwhile, at the elevated temperature, for both UHMWPE and nanocomposites, both energy storage capability and efficiency increased, probably due to enhanced dipole switching at high temperature and high electrical field. The results in this research also revealed the sensitivity of the energy storage of UHMWPE/GNPs nanocomposites to various factors, which provides us great opportunities to further optimization of energy storage performances, and eventually leads to high performance energy storage materials based on polymer nanocomposites.
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CHAPTER 1

INTRODUCTION

1.1 ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE)

1.1.1. Polyethylene Materials

Polyethylene (PE) is one of the most common thermoplastic polymers in use today. PE has been the largest volume synthetic polymer and has been used in different forms [1]. The chemical structure of PE in Fig 1 shows it is made with carbon and hydrogen atoms in a long chain [2]; which makes it susceptible to structure alteration to meet the needs and demands of various applications. Some of the properties of PE include excellent wear resistance, good fatigue resistance and outstanding chemical resistance. PE is easily distinguished from other plastics because of its low mass density (~ 0.91–0.97 g/cm³) and good resistance to organic solvents, electrolytic attack and degreasing agents. In general, its melting point ranges from 115-135°C depending upon the molecular weight and branching structures [3].

![Figure 1 Molecular structure of polyethylene](image-url)
Polyethylene is characterized on the basis of its density, structural variations (branching) and molecular weight. In general, PE has been classified as follows: Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), Medium Density Polyethylene, High Density Polyethylene (HDPE) and Ultra High Density Polyethylene (UHMWPE) as shown in Fig 2 [4].

![Schematic molecular structures of different type of PE](image)

**Figure 2 Schematic molecular structures of different type of PE [4]**

High Density Polyethylene (HDPE), shown in Fig 2A, has a linear chain structure with very few branches; thus, it is the densest PE structures giving it very high degree of crystallinity. Density of HDPE falls within the range of 0.94-0.96 g/cm$^3$ [4]. The extremely low number of branches compared to other types of polyethylene and its high density makes HDPE the best choice for heavy duty applications like radiation shielding, self-supporting containers, household and kitchenware products, etc. HDPE is regarded to have higher strength to density ratio (i.e. specific strength), making it more useable in packaging, pipe and petroleum tanks, prosthetic devices (implants), milk and other food bottles, etc. [1, 3-6].

Medium Density Polyethylene (MDPE), as shown in Fig 2B, is the type of polyethylene that has little more branching than HDPE, with lower mass density of 0.926-0.940 g/cm$^3$. Due to
its lower density, MDPE is less ductile and has better stress crack resistance than HDPE [4]. Some applications for MDPE are sacks, gas and pipe fittings, screw closures and carrier bags.

Low-Density Polyethylene (LDPE) is translucent, semi-rigid material with very high branching due to its less compact molecular structure which results in low density 0.910-0.925 g/cm³ [4]. LDPE qualities are low water absorption, flexibility, toughness and resistance to chemicals, organic solvents at room temperature and to corrosion resistance. LDPE offers an advantage of easy extrusion enhancing its manufacturability; hence LDPE are used for chemically resistant fittings, laboratory equipment, gas and water pipes, insulation for wires and cables, liquid packaging and high frequency electrical insulations [3]. However, the numerous branching in LDPE as shown in Fig 2D, results in low density and low crystallinity, and causes LDPE to have low strength, easy flammability, poor UV resistance and susceptible to environmental stress cracking [3, 4, 6], which does somewhat limit its applications.

Linear Low Density Polyethylene (LLDPE) is a type of PE that has a large number of shorter branches compared to LDPE [4]. Since, the branches of LLDPE are shorter, they can easily slide on top of each other while elongating without being tangled as in LDPE. The general schematic of LLDPE is shown in Fig 2C. The LLDPEs degree of branching complexity is lower than that of LDPE and the chemical structure of LLDPE polymers is a compromise between LDPE and HDPE, hence the name LLDPE. Short branches affect the crystallization often increasing the density. The resulting density is higher than LDPE but lower than HDPE. The density range of this polymer is approximately 0.91-0.94 g/cm³ [4, 7]. Some of the basic applications for LLDPE are packaging, lower thickness sheets compared to LDPE, cable covering and containers [1, 4, 6].
In addition to various branching structures, PEs are known as semi-crystalline polymers including both amorphous and crystalline regions within its crystal structures as shown in Fig. 3, the variation of which bring changes to PEs properties [2, 5, 6, 8]. Crystallinity of PE is a very important factor that governs its mechanical properties [8], increase in crystallinity increases hardness, abrasion and wear resistance, modulus strength, creep resistance, barrier properties, density and shrinkage [7, 9, 10]. However, low crystallinity provides economical melt processing, better manufacturability and process ability, good transparency and excellent thermoforming capability [3, 6, 10].

**Figure 3  A. Chain Folded structure in polymer; B. Crystalline structure of PE [10]**

### 1.1.2. Ultra High Molecular Weight Polyethylene (UHMWPE)

UHMWPE is a type of Polyethylene with extremely long chains, giving it higher molecular weight often 1 to 6 million. The major difference between HDPE and UHMWPE is the former has 700-1800 monomer units per molecule while the later has 100,000 to 250,000
monomer units per molecule [11]. This leads to highly entangled polymer chain structures, which are responsible for many unique and superior properties in UHMWPE, compared with conventional PE materials with lower molecular weight. A brief summary of mechanical and physical properties of HDPE and UHMWPE has been shown in Table 1, where UHMWPE over shadows HDPE with its high impact strength and ultimate strength. Based on the data in Table 1 [12], it can be noted UHMWPE has higher wear and abrasion resistance than HDPE. A study conducted to determine the volumetric wear between HDPE and UHMWPE for multidirectional hip simulator showed that HDPE wears 4.3 times faster than the UHMWPE [12].

**Table 1. Summary of physical and mechanical properties of HDPE and UHMWPE [12]**

<table>
<thead>
<tr>
<th>Property</th>
<th>HDPE</th>
<th>UHMWPE</th>
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<tr>
<td>Molecular weight (10^6 g/mole)</td>
<td>0.05 - 0.25</td>
<td>2 - 6</td>
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<tr>
<td>Melting temperature (°C)</td>
<td>130 - 137</td>
<td>125 - 138</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.40</td>
<td>0.46</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.952 - 0.965</td>
<td>0.932 - 0.945</td>
</tr>
<tr>
<td>Tensile modulus of elasticity* (GPa)</td>
<td>0.4 - 4.0</td>
<td>0.8 – 1.6</td>
</tr>
<tr>
<td>Tensile yield strength* (MPa)</td>
<td>26-33</td>
<td>21 – 28</td>
</tr>
<tr>
<td>Tensile ultimate strength* (MPa)</td>
<td>22 – 31</td>
<td>39 – 48</td>
</tr>
<tr>
<td>Tensile ultimate elongation* (%)</td>
<td>10 – 1200</td>
<td>350 – 525</td>
</tr>
<tr>
<td>Impact strength, Izod* (J/m of notch: 3.175 mm thick specimen)</td>
<td>21 – 214</td>
<td>&gt;1070 (No Break)</td>
</tr>
<tr>
<td>Degree of crystallinity (%)</td>
<td>60 – 80</td>
<td>39 - 75</td>
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An important application of UHMWPE is in the form of fibers. Due to its low density (0.97 g/cm³), UHMWPE fibers show excellent specific modulus and specific strength when compared to other reinforcing fibers like Kevlar fiber and glass fiber [13]. Thus, the UHMWPE fibers can be used as light weight reinforcing materials. Composite material made with UHMWPE fibers will retain similar or higher mechanical strength without sacrificing overall weight compared to higher mass of glass fibers, Kevlar and metal fibers [11-15]. This is why,
UHMWPE is one of the most demanded reinforcement material for polymer matrix composites [13, 15].

The extremely high molecular weight of UHMWPE also account for its high melt viscosity compared to HDPE and LDPE. Studies have shown that the increase in molecular weight and its distribution increases its melt viscosity [6, 16] making it more suitable for process-ability.

1.1.3 Electrical and dielectric properties of PE and UHMWPE

Polyethylene materials do not have free electrons; therefore they cannot conduct electricity effectively. Due to the presence of long, essentially straight chains in polyethylene made with methylene groups, where the carbon-carbon and carbon-hydrogen bonds do not show high polar characteristic, PE exhibits a high degree of electrical symmetry, making it completely nonpolar [6]. This excellent electrical property makes PE best suited for insulation of wires and cables including high-frequency circuits in the field of electronics and telecommunication [3-6].

Riande [17] has discussed the electrical properties of various polymers from the standpoint of their electrical insulating behaviors. According to his study, polyethylene- a nonpolar plastic material - was characterized as having the most uniform dielectric properties over all the frequencies and temperatures. Further study of the electrical properties of polyethylene suggests PE does not have sole dependence on one factor, but on several, such as crystallinity, molecular weight, branching and temperature [17-19].

In the recent years, polyethylene-based materials as electrical insulation in power cables instead of traditional oil-paper based systems have been of keen interest. Because of the increasing demands of High Voltage Direct Current (HVDC) transmission systems for power
grid connections, studies for better and more reliable electrical insulating materials have been done [20-23]. The electric permittivity of a material is the measure of its electrical inertness to the applied electric field. Even though HDPE have been used as cable insulation in power cables and high voltage transmission system for its excellent resistance to abrasion and better dielectric properties, its derivative UHMWPE that has extremely high average molecular weight, low dielectric constant around 2.25, high temperature resistance, better abrasion resistance and impact strength; UHMWPE has been a more desirable material for electrical insulation, high voltage applications in the power grid and many other wire and cable coating applications [23-25].

A dielectric material is a substance that does not conduct electricity efficiently but is an efficient supporter of electrostatic fields that is: it can be polarized by applying electric field where its components (atoms or molecules) shift from their original average equilibrium positions and orient themselves towards and away from the field. This effect is called “dielectric polarization”[26]. During dielectric polarization, the positive charges of dielectric material orient towards the field while negative charges shift orient in the opposite direction. Polarization in a dielectric material has been shown in Fig 4. Alignment of internal charges toward the plate creates an internal electric field (i.e. smaller than the original Electric field E) reducing the overall field the dielectric material has to experience. This affects material properties such as energy storage, polarization and so on.
Figure 4 Polarization in dielectric material due to electric field [26]

Polyethylene has semi-crystalline structure which consists of crystalline regions and amorphous regions. Several studies have shown the dependency of dielectric properties in PE with its crystalline regions and the degree of crystallinity [27-29]. Hydrocarbon chains are in order and fold back to form planar crystalline lamellae as shown in Fig 3. These studies also show that the presence of isotropic disordered chain structures in amorphous region can cause cross-linked chains and entanglements which can intrude the efficient transport of charges in different regions of crystalline structure [30]. Research done by Miyanuchi and Yahagi [31] show the dependency of dielectric strength on the degree of crystallinity was changed by varying the annealing process on the same HDPE film. The results as shown in Fig 5 suggest that below 80°C, the electric strength increases with the increase in degree of crystallinity; meanwhile above 80°C the effect is reversed. This could be explained by Frohlich’s amorphous breakdown theory which suggests that the increase in crystal boundaries due to decrease in crystallinity can help trap electrons [31].
Studies have shown that molecular weight, the degree of polymer chain branching, and temperature can play vital role in determining polymers dielectric properties [20-22, 27, 29-32]. Some studies have shown that the increase in molecular weight of polyethylene can increase the electric strength (i.e. for an insulating material, the maximum electrical voltage it can withstand without losing its insulating properties) and the volume resistivity of the polyethylene [20, 32]. M.E. Sepulveda, Martinez and Sanz-Feito [20] studied dielectric strength and space charge accumulation of UHMWPE compared to other similar polymers like LDPE and XLPE. Their results showed that the UHMWPE’s AC breakdown field was lower than that of XLPE and LDPE and, since UHMWPE did not create, higher space charge accumulation (up to 80kV/mm), linear increase of overall space charge profile was obtained. Based on these results shown in Table 2, UHMWPE was considered to be one of the best performing polymer material for High Voltage Direct current (HVDC) applications [24, 25, 33].

Figure 5 Effect of crystallinity on the electric strength of HDPE [31]
Holding electrical charges in dielectric material has been used for energy storage in various electrical devices and electronic applications [24, 25]. With its nonpolar structure, UHMWPE has low dielectric constant (2.25) which can prohibit its electrical application as dielectric material that requires higher permittivity [6, 15]. Studies have shown that UHMWPE when used in fiber form along with specific volume of conductive filler materials such as nanoparticles, metal oxides and ceramics can remarkably increase dielectric permittivity and mechanical strength [20, 34, 35].

Table 2. Dielectric strength of tested polymers [20]

<table>
<thead>
<tr>
<th>Material</th>
<th>α (kV)</th>
<th>β</th>
<th>Thickness (mm)</th>
<th>Eₚ (kV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>10.48</td>
<td>4.452</td>
<td>0.154</td>
<td>68.05</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>5.365</td>
<td>1.046</td>
<td>0.145</td>
<td>37.00</td>
</tr>
<tr>
<td>XLPE</td>
<td>28.36</td>
<td>6.363</td>
<td>0.443</td>
<td>64.02</td>
</tr>
</tbody>
</table>

1.2 GRAPHITIC NANOMATERIALS

1.2.1 Graphene

Graphene is a single layer of sp² carbon-carbon atoms showing a 2D hexagonal structure. Graphene possesses extraordinary mechanical, thermal and electronic properties, and have been widely accepted as one of the most promising materials structures for broad applications. Graphene is considered as one of the strongest material with Young’s modulus of 1 TPa and tensile stress of 130 GPa which is 100 times stronger than that of steel. It has been studied to have theoretical specific surface area close to 2630 m²/g and thermal conductivity of up to 5000
Besides, these graphene is also considered to have very unique electronic property; the monolayer graphene is a semi-conductor at zero distance apart; its linear energy dispersion and the amount of charge it carries could be considered massless. These massless charges travel at a speed of $\sim 10^6$ ms$^{-1}$ [37] and is a unique behavior that has gained popularity in the last decade for quantum electrodynamics [36-38].

![Figure 6 Structures of graphene and graphitic nanomaterials [36]](image_url)

Graphene is also considered as the fundamental structure for other graphitic nanomaterials. Fig 6 shows graphene with monolayer of hexagonal structure followed by different types of graphitic nanomaterial. Graphite, which naturally exists, consists of multiple layers of graphene sheets in crumbly structures that are bonded via Van Der Waals force. By reducing the number of graphene layers in graphite, the graphitic nanoplatelets could be obtained. The graphene sheet can also be “wrapped up” to form 1-D nanostructures (1D), known as Carbon Nanotubes (CNTs). Depending on the numbers of the wrapped up graphene sheets, single-walled CNTs and multi-walled CNTs could be achieved. The 0-D soccer ball shaped
molecules known as Bucky Balls or Fullerene is also an important type of graphitic nanomaterials showing unique properties and functions.

There have been two essential methods in synthesis of graphene:

i) Top-down approach:

In this approach, heavy graphitic materials like 0-D Fullerenes, 1-D carbon nanotubes and 3-D graphite are used as source of carbon for the production of graphene. The top-down approach is one of the most popular method used in the oxidation of exfoliated graphite, through the Staudemaier, Brodie and Hummers method [39]. Prepared graphite oxides are expanded into either single layer or a few layered graphene by exfoliation or heat-treatment to form graphene oxide nanosheets by ultrasonic treatment in aqueous solution [40]. Once the graphene oxides are prepared, they are reduced to graphene by using several methods solvo-thermal reduction [41], radiation-induced reduction, hydrogen plasma treatment [42], thermal annealing [43] and electrochemical reduction [44]. Among all these methods, chemical reduction method using reductants like metal Fe, hydrazine and alcohols is the most common and frequently used method [45].

Even though, the exfoliation of graphite oxide and chemical reduction process seemed to be more feasible in mass-production scale, functionalization and processing of graphene layers, has its own withdraws. The resulted graphene has been reported to have defects in its framework due to the formation of oxygen-containing groups, and while doing the ultrasonic treatment, results in incomplete reduction that eventually deteriorates the electronic and mechanical properties of reduced graphene oxide [40]. Some researchers have claimed to prepare the graphene nanosheets by the same exfoliation method but without using chemical reducing agent, Abdelsayed et al [46] did the synthesis in water without any reductants.
ii) Bottom-up approach:

Contrary to top-down approach where graphene is obtained from larger forms of carbon like graphite, bottom-up approach uses the synthesis of graphene in mass volume using small; organic molecules excluding particles that exclusively have graphene. For instance, decomposition of hydrocarbons into graphitic materials through chemical vapor decomposition (CVD) using metal surfaces [40, 47]. Another method for synthesis of graphene is epitaxial growth of graphene on SiC water surfaces. In this process, SiC is first decomposed then desorption of Si is done [48]. Although this bottom-up approach results in graphene with fewer defects as compared to that of top-down approach, its processing and operating costs are relatively higher than the other approach. Thus, since both of these methods have their own pros and cons, newer improvised methods are still to be approached to achieve better quality graphene nanomaterials.

1.2.2 Graphite Nanoplatelets and Their Applications

Graphite Nanoplatelets (GNPs) are very thin nanoparticles with an average thickness of 3-10 nanometers and are usually comprised of small stacks of platelet-shaped graphene sheets [49-51]. These nanoplatelets have diameter ranging up to 100 micrometers and are comprised of the same material as in carbon nanotubes. Fig 7 shows the morphology of an isolated GNP revealed by scanning electron microscope. Therefore, graphite nanoplatelets have similar properties as those of CNTs but in a plain form [51]. Due to their unique size and morphology [51-57], GNPs have enhanced barrier properties and improved mechanical properties, such as: surface hardness, strength and stiffness. GNPs also have excellent electrical and thermal conductivity due to the presence of pure graphitic composition [51, 55, 58-61].
The unique nanoscale size, shape, structure and material composition of GNP makes it vital particle in enhancing almost all the barrier properties of the composite where it is used [36, 38, 57-60, 62-64]. GNPs can be used to increase electrical and thermal conductivity and reduce component mass while maintaining integrity. It can also be used to increase stiffness and toughness (impact strength) of other matrix materials. Some of the most common and potential applications of GNP include:

i) Ultracapacitor electrodes [52]

ii) Anode materials for lithium-ion batteries and conductive additive for battery electrodes [38]

iii) Electrically conductive inks, thermally conductive films and coatings [40, 65]

iv) Additives for lightweight and metal-matrix composites [40]
v) Radiation and electromagnetic shielding, antistatic, shrinkage and corrosion resistant coatings [66-68]

vi) Barrier material for packaging and films or coatings for EMI shielding [28]

vii) Substrate for chemical and biochemical sensors

Together with other types of graphitic nanomaterials, GNP{s have been used to fabricate high performance and multifunctional polymer nanocomposites. Although CNT’s have been extensively studied as an ideal nanomaterial to improve the mechanical [61, 65], electrical and thermal properties [36, 61, 62] of polymer materials, there are several advantages of using GNP{s instead of CNTs, besides the lower cost of GNP{s. They are:

a) GNP{s can be dispersed more easily than CNTs, which results in even distribution of reinforcement throughout the polymer composite [49, 51, 54, 65].

b) GNP{s have larger surface area compared to CNTs, so a greater area can be covered using GNP{s, enhancing the bonding property where interface can be achieved. This accounts for homogeneous distribution of load and escalation in strength of the composite [63, 65]. To achieve similar results, a higher aspect ratio of CNT would be required than graphene, which negatively affects the mechanical property by increasing the volume concentration of the nanofiller.

c) One of the greatest advantages also results from the 2D graphene layer in GNP{s: better lubrication during any frictional movement causing less wear, debris generation and longer life-time of the material [11, 62, 63, 65].
1.3 UHMWPE NANOCOMPOSITES

1.3.1 Polymer Nanocomposites

Polymeric materials are inexorably limited in applications due to their intrinsic properties, such as their characteristic high electrical resistivity, low thermal conductivity, stability and ductile nature as mechanical properties [69-72]. Despite these properties, polymers have some impressive characteristics such as; they are cheap, easy to process and have higher strength to weight ratios. If nanometric additives are used in polymers, it improves several negatives in its properties and increases it functionality and manufacturability [72].

In addition to achieving better strength, modulus and toughness in a polymer nanocomposite, it could have excellent electrical and thermal properties to have variety of applications. For example, the graphitic nanomaterials have been frequently used to fabricate polymer nanocomposites with enhanced electrical properties. Meanwhile, polymer nanocomposites have behaved better with thermal properties when used as substrate and packaging material in miniaturization and advancement of electronic industry. With proper control of the network of these nanomaterials in these polymer nanocomposites, they could withstand higher temperature and dissipate thermal energy efficiently without breakage [15, 58, 73, 74].

Regarding dielectric properties of polymer nanocomposites, according to Maxwell-Wagner-Sillars polarization (MWS), higher dielectric constant can be achieved by introducing conductive fillers in to the polymer matrix through interfacial polarization phenomenon. In this study, since GNP s have relatively higher surface area as compared to any other filler materials, these have more interfacial area that can hold larger amount of charges at its interfaces. So, in
general higher dielectric constant can be expected for GNP-filled polymer nanocomposites. In the research done by Fuan He [75], one of the highest dielectric constant has been reported for poly (vinylidene fluoride) with GNP nanocomposites (PVDF/GNP). This nanocomposite was prepared by solution-cast and compression molding method, and recorded dielectric constant was $10^8$ at relatively lower filler loading % (@ 2.34 vol.%) at high frequencies around 1000 Hz and higher. The result from this research has been shown in Fig 8.

![Figure 8 Frequency dependence of dielectric permittivity of PVDF/GNP nanocomposites at room temperature [75]](image)

In addition, the dielectric constant of a material usually follows percolation threshold behavior and can be predicted the power law as shown in Eqn. 1 [76]. Percolation threshold is the fraction of the filler content at which the inclusions form a continuous path instead of electric resistivity. This kind of continuous network (path) often renders the composite an electrical conduction, resulting dielectric breakdown [28].
\[
\varepsilon' \propto (\phi_c - \phi)^{-s}
\]
Equation 1

where \(\phi_c\) is the critical filler volume fraction at which percolation in \(\varepsilon'\) takes place and is called percolation threshold; \(s\) is the critical exponent of \(\varepsilon'\).

A study was done with high density polyethylene-graphite (HDPE-Gr) nanocomposites to determine the variation of dielectric constant as the function of filler loading wt.%. The result as shown in Fig 9 recommended that when the filler concentration is below 0.039 wt.%, dielectric property is less dependent on frequency and showed minimal \(\varepsilon'\).

![Figure 9 Dielectric constant of HDPE-Gr nanocomposite as a function of frequency](image)

This pioneering idea of using nanometric additives into polymers to make composites have also opened multiple ways in advanced technologies including redox capacitors, catalysis, electrochemical displays, printed circuit boards and sensors [72, 77]. Besides, graphene-polymer based nanocomposites could also be used as high temperature conducting materials such as
bipolar plates for polymer electrolyte membrane fuel cells and high temperature conductive adhesives [64, 72, 78, 79]. According to research done by Debelak and Lafdi [72], carbon (graphene) based nanofibers have been anticipated to be used into polymers instead of nanotubes in many applications due to its cheaper price and easier processing techniques.

1.3.2 UHMWPE/Graphitic Nanomaterial Nanocomposites

Since, UHMWPE is a semi crystalline polymer, and its usage in different applications demanded better strength and toughness for better functionality. Delgado and Addiego [80], developed a new processing method to homogeneously disperse graphite nanoplatelets (GNPs) into the UHMWPE matrix. They characterized the prepared nanocomposite to study its microstructural aspects and toughness to make it more suitable for application in electronic devices and equipment. Their results suggest that, when GNPs are blended with UHMWPE to make Nanocomposites, the in situ UHMWPE toughness and impact energy had increased from 17.5 J/cm² to 19.5 J/cm². Thus, Delgado and Addiego proved the addition of graphene nanoplatelets (GNPs) increases the strength and toughness of UHMWPE.

Mujibur Khan and Hassan Mahfuz [34] also conducted a research in reinforcing UHMWPE filaments with 2.wt% of Single-walled carbon nanotube (SWCNTs). According to their results, when the modified UHMWPE-SWCNT Nanocomposites was tested with multiple cycles of loading and unloading, it’s Ultimate Tensile Strength and Young’s modulus had increased by 120 and 463% respectively. In short, the yield strength (0.2%) had increased by 500% with the addition of carbon based nanomaterials to polymer. This suggests that UHMWPE fiber’s mechanical strength and modulus can be increased drastically by using graphene nanoplatelets in controlled manner.
A Bhattacharyya and S. Chen [81] tried to disperse graphene oxide or graphene in UHMWPE using two different methods to prepare unique nanocomposite films. The first method, being the pre-reduction method, graphite oxide (GO) was exfoliated and dispersed into organic solvents and then reduced to graphene before the addition of UHMWPE. In the second method, the reduction of graphene oxide was done after the UHMWPE was added to conduct reduction method. The results were surprising because the nanocomposite that was prepared by the pre-reduction method had higher crystallinity than the in situ method (still comparable to that of pure film). Both of these processes increased the modulus from 864 to 1236 MPa, increased the strength from 12.6 to 22.2 MPa and significantly reduced creep resistance from 50% to 9% when compared to pure film. The results suggest that the pre-reduction method definitely increases the tensile strength and creep resistance of the polymer nanocomposite while in the situ method made the nanocomposite material more ductile thus making suitable for other application where ductility is more important.

1.4 RESEARCH OBJECTIVES AND RATIONALE

This research aims at development of UHMWPE/graphitic nanomaterials nanocomposites for high intensity energy storage applications via understanding the roles of surface modification of nanomaterials as well as the dispersion of nanomaterials in nanocomposites for energy storage applications. In particular, in this study, the dielectric properties at high electrical field will be investigated.

There have been thousands of experimental studies using various nanomaterials to achieve high performance polymer nanocomposites with increased mechanical, electrical and thermal properties, etc. However, these studies barely reproduce the success of theoretical
predictions of polymer nanocomposites. Among many factors, dispersion of nanomaterials as well as the interface between nanomaterials and polymer matrix is widely considered as the two most challenging structural factors showing remarkable effects on the properties of polymer nanocomposites. The high specific surface areas of nanomaterials lead to their high surface energy. To minimize the high surface energy, nanomaterials tend to aggregate and form large agglomerates. These agglomerates typically act as the structural defects showing negative impacts on the performances of the polymer nanocomposites. Thus, how to individualize the nanomaterial particles and achieve uniform dispersion remains the fundamental issue in polymer nanocomposites. Currently melt compounding, ultrasonication and surface modification of nanomaterials are most commonly used and most effective approaches to achieve uniform dispersion. To Meanwhile, the interfacial structures also play a significant role in polymer nanocomposites. An appropriate interface could not only benefit mechanical properties by effectively enhancing stress transfer, but also benefit various physical properties, such as dielectric properties, in which, the interfacial polarization is essential. Usually, to improve effective interfacial interactions, surfactants, which could interact/react with both nanomaterials and polymers, are applied in polymer nanocomposites.

PE materials have been commercially used in energy storage devices, and their dielectric properties have been frequently studied. However, for UHMWPE, in spite of its extraordinary mechanical and thermal properties, its applications in electronics and energy storage devices are still very limited. Thus, UHMWPE was studied as the matrix material for the composites. Meanwhile, the low cost GNPs were chosen to modify the dielectric properties of the nanocomposites. Besides the excellent mechanical and physical properties, similar to CNTs, the commercial GNP products also possess reactive groups on the particle surface, because of the
oxidation process in GNP manufacturing. These reactive groups, such as hydroxyl and carbonyl groups, could be used to react with surfactants, leading to surface modified GNPs. Thus, the improved dispersion of GNPs and stronger interface would be expected.

As introduced in 1.3.1, in the presence of electric field, the positive and negative charges within the dielectrics are displaced from equilibrium position and each of them faces towards the edges of the capacitor plate. This displacement of charges creates a local electric dipole within the dielectric material; this process is called polarization of dielectrics. Since, the applied electric field still exists, it distorts the aligned charges; this phenomenon is explained by the principle of superposition. According to this principle, the distorted charge distribution is equivalent to the original distribution plus a dipole thus created whose moment is given by Eq. 2 [82].

\[ p = Qd \]  

Equation 2

where \( d \) is the distance vector from \(-Q\) to \(+Q\) of the dipole and \( p \) is the intensity of polarization.

For the dielectric material, the electric flux density \( D \) related to its polarization is given by Eqn 4.

\[ D = \varepsilon_o E + P \]  

Equation 3

where \( D \) is the electric flux Density, \( \varepsilon_o \) is the permittivity of free space \((= 8.854 \times 10^{-12})\) and \( E \) is the applied electric field.

Thus, it is obvious that the dielectric properties and energy storage capability are directly related to the eternal electrical field. The dielectric relaxation behaviors at low electrical field have been extensively studied. However, the understanding on the dielectric relaxation of polymers and polymer composites is still very limited [83]. In particular, for the high density electric charge energy storage applications, the dielectric property at high electric field is of great importance.

In this study, the UHMWPE/GNP nanocomposites were fabricated with and without surfactant. The silane agent was used as the surfactant to modify the surface properties of the
GNPs. The use of this surfactant was not only intended to improve the dispersion quality of GNPs in the UHMWPE matrix, but also to improve the interfacial interactions between GNPs and UHMWPE. The nanocomposites with different loading of GNPs were fabricated using melt compounding method to study the effect of the compositions. At last, since the operation of energy storage devices and electronic frequently deals with elevated temperatures, thus the effect of the temperature on the high field dielectric properties and energy storage capabilities were also investigated.
CHAPTER 2

FABRICATION AND CHARACTERIZATIONS OF UHMWPE/GNP NANOCOMPOSITES

2.1 MATERIALS

The matrix polymer used in this work is the commercial grade UHMWPE powder (GUR, 1020 O) purchased from TICONA. The GNP s with an average thickness of 6nm and an average diameter of 5μm were supplied by XG Science. Octadecyltrimethoxysilane (ODMS) used as surfactant was purchased from Sigma Aldrich. The 95% ethanol purchased from Sigma Aldrich will be used for the surface modification of GNP s.

2.2 MODIFICATION OF GNP s

2.2.1 Heat Treatment

The GNP received from the manufacturer (TICONA) was in powder form. These GNP materials still have some acid molecules within the layers of GNP. If these acid molecules are left as is, they could affect the further processing of GNP nanocomposite and its properties. The received GNP was thermally treated at 800°C in air for 30 seconds to decompose and eliminate the acidic residuals from within the layers of GNP. Afterwards, the GNP was allowed to cool at room temperature before further processing. The heat treated GNP is designated (ht-GNP) and was used to make nanocomposites with different compositions. Due to the expansion of the gaseous product of the acidic residuals, the ht-GNPs were further exfoliated.
2.2.2 Surface Modification of ht-GNPs

The ht-GNPs obtained in 2.2.1, were also used for preparation of surface modification GNP (s-GNP). The chemical modification of ht-GNP has been done using alkoxy-silane coupling agents; that is, ODMS, with two major advantages:

- at one end of the silane structure, they bear alkyl groups that are capable of reacting with non-polar UHMWPE matrix, due to their same chemical structures
- at the other hand, they have functional groups which can establish covalent bonding with the reactive groups on the surface of GNP particles, thus leading to enhanced interfacial interactions [84].

![Scheme 1 Surface modified GNP (s-GNP)](image)

In this study, the ht-GNPs were chemically treated with ODMS in boiling 95% ethanol for 5 hours. The ratio between ht-GNPs and silane agent was fixed 1 gram/4 ml. During this time, the constant turbulence of boiling ethanol ensured even mixture to promote chemical. The ht-GNPs/ethanol suspension was obtained by low intensity sonication in water bath (Branson...
The suspension was then heated to allow ethanol to reflux. Liquid ODMS was slowly added to the boiling ht-GNP/ethanol suspension. The reaction was left to reflux for 5 hours. After cooling to room temperature, the mixture was filtered, and the solutes were thoroughly rinsed using both ethanol and acetone to remove any unreacted ODMS, followed by vacuum drying overnight. The dried black power was designated as s-GNP for fabrication of nanocomposites. The schematic illustration of the s-GNP is given in Scheme 1.

### 2.2.3 Fabrication of UHMWPE/GNP Nanocomposites

Both ht-GNPs and s-GNPs were used to fabricate nanocomposites with UHMWPE. The concentrations of GNPs in the nanocomposites are 0.5wt%, 1.0wt% and 3.0wt % respectively. The UHMWPE power was melted at 180 °C in a Brabender compounder, and then different amount of GNPs were added to the compounder with a rotation speed of 70 rpm. After mixing for 15 mins, the UHMWPE/GNP nanocomposites were obtained. The nanocomposites were then compression molded at 180°C to thin sheets with an average thickness of ~300μm using a Carver hydraulic hot press. It should be noted here, although thin films around 10-20 μm thick are more ideal for high field study, the thin sheets were prepared for characterization, because of the high viscosity of UHMWPE and its nanocomposites. The high viscosity does not favor the fabrication of thin film samples without providing very high pressure. The specimens with a diameter 1 cm were cut off the thin sheet for characterization of high field dielectric properties.
2.3 CHARACTERIZATION of MODIFIED GNPs

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a powerful tool to characterize organic chemical structures. Thus, it was applied to examine if the surface modification in 2.2 was successful. The FTIR analysis was conducted on a Nexus 670 ESP analyzer. To conduct FTIR analysis, 0.2 mg of GNPs were manually ground and mixed with 1 g potassium bromide (KBr) as diluent and background. After the uniform fine power of the mixture of GNPs and KBr were obtained, a hydraulic press was used to press the power into a disk sample for FTIR analysis.

2.3.2 Transmission Electron Microscopy (TEM)

TEM has high resolution and magnification, and it has been frequently used to characterize the structures and morphologies of nanomaterials. The GNPs were studied using Transmission Electron Microscopy (TEM, JOEL-EX). To prepare the GNP samples for TEM study, very small amount of GNPs was dispersed in deionized water via low intensity sonication in water bath for 15mins. The resulting suspension of GNPs in deionized water was deposited onto the carbon-coated copper grids by drop-casting, followed by vacuum drying before TEM observation.

2.4 CHARACTERIZATIONS of NANOCOMPOSITES

2.4.1 Scanning Electron Microscopy (SEM)

The dispersion states of GNPs with and without surface modification in the polymer matrix, as well as the interfacial structures were examined using a scanning electron microscopy
(SEM, FEI 200). The nanocomposite thin sheets were immersed in liquid nitrogen for 15 mins before fractured. The thin sheet was completely frozen and became more brittle, thus, during fracture; the morphologies of the nanocomposite would be reserved. The fracture surface of the nanocomposites was sputter coated with gold before SEM observations.

2.4.1 Energy Storage Analysis

For the measurement of energy storage capability, Precision LC II Ferroelectric Tester made by Radiant Technologies Inc. was used. This tester came with Vision Software that could calculate different ferroelectric properties of samples like current-voltage characteristics and ferroelectric hysteresis, which are the interest of this study. The samples were tested in the following steps:

I. The samples were cut into smaller rectangular pieces and cleaned using Acetone to remove any dirt, oil or debris off the samples.

II. The thickness of the sample pieces were measured using ABSOLUTE Digimatic 6” Digital Caliper manufactured by Mitutoyo (Model # 500-196-20).

III. Each piece of sample was then placed one by one in the testing electrode chamber which has two copper electrodes connected to the tester. The sample material was placed in between these electrodes and sealed inside the chamber.

IV. Then, Precision LC II tester was turned on along with Precision 10kV HVI-SC High Voltage Amplifier (made by Radiant Technologies Inc., model no# P-HVi210KSC). The testing frequency was 100 Hz. Besides room temperature (23 °C), the characterization was also conducted at 80°C. To conduct high temperature testing, the sample along with the electrode chamber was placed
inside the temperature chamber (made by Delta Design, model no # 9023). 10 mins after the chamber temperature reached desired temperatures (80°C), Steps V & VI was conducted.
CHAPTER 3

STRUCTURES AND MORPHOLOGIES

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

As a result of the surface modification, the Si-O-C (GNP) covalent bond would be expected to exist in the s-GNP, due to reactions between silane agents and hydroxyl and carbonyl groups on the surface of ht-GNPs. The FTIR spectrum for both ht-GNPs and s-GNP have been shown in Fig 10. The broad peak around 3400 cm$^{-1}$ was assigned to the hydroxyl groups on the surface of GNPs, suggesting that the reactive surface of ht-GNP for further modification.

![FTIR spectra of both ht-GNP and s-GNP](image)

**Figure 10** FTIR spectra of both ht-GNP and s-GNP

The absorption peak at 925 cm$^{-1}$ in s-GNP suggests the successful surface modification of ht-GNP by ODMS. Besides, Si-O-GNP there are few other composition from the result of
reaction with coupling agent such as Si-O-Si and Si-O-CH₃, and the existence of these chemical structures do not have substantial impacts on the improvement of interfaces.

Figure 11 TEM images of (A) ht-GNP and (B) s-GNPs
The TEM morphologies of both ht-GNP and s-GNP in Fig. 11 further proved the success of surface modification. It can be seen in the Fig. 11A that the ht-GNPs are clearer and more transparent compared to s-GNPs. This is because, due to the successful surface modification, the surface of GNP was coated by a layer of ODMS. Meanwhile, since the ODMS is covalently bonded to the surface of GNP, the filtration, rinse as well as sonication could not remove this coating layer from the GNP surfaces.

3.2 MORPHOLOGIES OF FRACTURE SURFACE OF NANOCOMPOSITES

The successful surface modifications could also be proved by the morphologies of the fracture surfaces of the nanocomposites, as shown in Fig 12. In UHMWPE/ht-GNP nanocomposites (Fig. 12A), few agglomerates (encircled regions in image) were found which suggested the dispersion of ht-GNP in UHMWPE still needed further improvement, whereas the dispersion of s-GNP (Fig. 12B) showed more uniform dispersion when viewed at x5,000 magnification. It is easy to understand that for ht-GNPs, due to the incompatibility between ht-GNP and UHMWPE, as well as the very high melt viscosity, the dispersion of ht-GNPs were more difficult. When the images were magnified and viewed at x60,000 magnification (Figs 12a and 12b), the detail interfacial interactions for both nanocomposites were seen. Obviously, s-GNPs led to good interfacial interaction without gaps as observed in UHMWPE/s-GNP compared to UHMWPE/ht-GNP. With proper surface modification by ODMS, the s-GNP could effectively interact with UHMWPE matrix. Thus, despite high viscosity, this interaction could favor the individualization of GNP agglomerates, leading to an enhanced dispersion. This interaction also created stronger interfacial bonding between s-GNPs and the matrix.
Figure 12 SEM images of (A) UHMWPE/ht-GNP composite and (B) UHMWPE/s-GNP composite at x 5000 magnification; SEM images of (a) UHMWPE/ht-GNP composite and (b) UHMWPE/s-GNP composite at x 60,000 magnification
CHAPTER 4

ENERGY STORAGE ANALYSIS

4.1 CURRENT-VOLTAGE CHARACTERISTICS OF NANOCOMPOSITES

The current-voltage characteristics (I-V curves, Fig. 13) of samples were studied between 0 volt and 3500 volts. The reason for studying I-V characteristics of different nanocomposites is to determine the testing voltage/electrical of hysteresis study. It is known that high current leakage is not favorable in energy storage applications, in particular, at high electric field. In this study, the conductive GNPs were used as the nanofiller to modify the properties of UHMWPE, which might lead to high current leakage, particularly, when the loading level of GNPs is high. Except UHMWPE-ht-GNP-3wt% nanocomposites, all other nanocomposites showed the similar I-V characteristic to pure UHMWPE, suggesting their insulating nature and great potential for high density energy storage application. In contrast, the sudden increase of current was found in UHMWPE-htGNP-3wt% nanocomposites starting at 500V. This should be a result of agglomerates and poor interfacial interactions in the nanocomposites observed in the SEM images (Fig. 12). These defects usually lead to large current leakage and consequently reduce their electrical breakdown strengths. The nanocomposites would be shorted at a low voltage, and they are not ideal for high field energy storage applications. In other word, the I-V studies also revealed the positive contribution of surface modification and resulting uniform dispersion of s-GNPs to the dielectric properties. Thus, the analysis at 3500 V in later sections would not include UHMWPE-ht-GNP-3wt% nanocomposites.
4.2 HYSTERESIS BEHAVIORS OF NANOCOMPOSITES

Hysteresis behaviors of both UHMWPE and its nanocomposites were recorded at 1200 V and 3500 V, respectively. The energy storage capability was examined using the Monopolar hysteresis loop obtained from Vision Software. The high field dielectric properties can be studied using hysteresis loop. In this study, four parameters are our research interests:

1) $P_{\text{max}}$----Polarization at highest electric field/voltage
2) Stored Energy---- Area under (A+B) as shown in Fig 14
3) Energy Efficiency---- $A/(A+B)$ as shown in Fig 14
4) Dielectric permittivity ---- Derivative of discharging curve at high electric field/voltage

In which,

$$A = \text{Energy Recovered Integration Area}$$
B = Energy Lost Integration Area

A+B = Energy Stored Integration Area

Energy Efficiency = A / (A+B) = Energy Recovered / (Energy Recovered + Energy Lost)

Figure 14 Illustration of monopolar hysteresis loop for energy storage analysis

For an ideal energy storage application, high values for A and A+B, small value for B would be anticipated.

In Fig. 15, the representative monopolar hysteresis loops of UHMWPE and UHMWPE/s-GNP-3.0wt% nanocomposites are given. Both pure polymer and nanocomposites showed near linear behaviors, which mean low energy loss, suggesting good potential for energy storage applications. Since the hysteresis loops of other nanocomposites at both testing temperatures are much alike, and they are not shown here. The hysteresis loops were analyzed using four parameters introduced above.
Figure 15 Monopolar hysteresis loops at 100 Hz for UHMWPE and UHMWPE/s-GNP-3.0wt% at room temperature
4.3 EFFECTS OF COMPOSITIONS OF NANOCOMPOSITES

4.3.1 Effects of Compositions on Polarization ($P_{\text{max}}$)

The properties of polymer nanocomposites always show distinct dependence on the compositions of nanocomposites, thus, it is critical to understand the effects of compositions on energy storage capabilities of resulting nanocomposites. In this study, the composition include both concentration of GNPs as well as the surface modification. Dielectric polarization is the fundamental mechanism, and a good energy storage capability requires high polarization of materials. The comparison chart of $P_{\text{max}}$ at 1200 V has been shown below in Fig 16.

![Comparison Chart of $P_{\text{max}}$ at 1200 V](image)

**Figure 16** Effects of concentrations on $P_{\text{max}}$ for both ht-GNP and s-GNP reinforced nanocomposites at 1200 V

According to the I-V curves (Fig.14), it was found that the UHMWPE/ht-GNP-3.0wt% nanocomposite has the highest current leakage at the lowest testing voltage (500V). This suggests that the high loading of ht-GNP might not be suitable for the energy storage
applications. The fact is the UHMWPE/ht-GNP-3.0wt% nanocomposite thin sheet was shorted when the testing voltage was up to 3500V. Thus, to understand the effects of compositions, a lower testing voltage (1200 V) was applied to the nanocomposite samples. It is obvious that the lowest $P_{\text{max}}$ was also found in UHMWPE/ht-GNP-3.0wt% nanocomposites. This result further suggests the non-uniform dispersion of ht-GNPs in the polymer matrix and poor interfacial interaction could sacrifice the polarization phenomenon.

The addition of ht-GNP slightly lowered the polarization, however, the surface modification via ODMS seemed to be able to amend the polarization. In particular, the $P_{\text{max}}$ for UHMWPE/s-GNP-1.0wt% nanocomposite is even slightly higher than the pure polymer, suggesting the contributions of uniform dispersion and stronger interfacial interactions to the polarization in the nanocomposite.

### 4.3.2 Effect of Compositions on Energy Storage Capability

Based on the discussion in 4.1 and 4.3.1, we could conclude that with addition of 3.0wt% ht-GNPs, the nanocomposite has the lowest energy storage capability, thus, the further discussion on the energy storage capability will exclude this nanocomposite, and the energy storage capability will be discussed at a higher voltage (3500 V), at which the UHMWPE/ht-GNP nanocomposite was shorted.

Obviously, the surface modification once again showed positive contributions to the energy storage capabilities of the nanocomposites, due to the enhanced dispersion as well as stronger interface. In particular, the UHMWPE/s-GNP-3.0wt% nanocomposite showed the highest energy storage capability, in contrast to the UHMWPE/ht-GNP-3.0wt% nanocomposite which was easily shorted at this voltage level. Meanwhile, it could be observed that for the ht-
GNP reinforced nanocomposite, a larger deviation among different testing samples is obvious. This might also prove that without proper surface modification, the quality of UHMWPE/ht-GNP nanocomposites was not very consistent, due to the existence of agglomerates as well as the poor interfaces.

![Figure 17 Effects of compositions on energy storage capability of ht-GNP and s-GNP reinforced nanocomposites samples at 3500 V](image)

**Figure 17** Effects of compositions on energy storage capability of ht-GNP and s-GNP reinforced nanocomposites samples at 3500 V

### 4.3.3 Effects of Compositions on Energy Efficiency

In high efficiency energy applications, the energy efficiency is as important as energy storage. High energy efficiency indicates more energy could be released during discharging process, leading to low energy loss. For pure UHMWPE, it shows a high energy efficiency around 90%. The addition of both ht-GNP and s-GNP could further improve the energy efficiency close to 100%. It seems that the dispersion quality as well as interface between GNPs and UHMWPE did not exert greater effects to the energy release of the nanocomposites during
discharging processing. However, combined the results on both energy storage and energy efficiency, the s-GNPs proved to a more effective additive to improve comprehensive energy storage properties at room temperature.

![Figure 18 Effect of compositions on energy efficiency of ht-GNP and s-GNP reinforced nanocomposites at 3500V](image)

**Figure 18 Effect of compositions on energy efficiency of ht-GNP and s-GNP reinforced nanocomposites at 3500V**

### 4.4 EFFECTS OF TEMPERATURE

#### 4.4.1 Effects of Temperature on Polarization ($P_{\text{max}}$)

The operation of energy storage devices and electronic devices frequently faces the elevated temperature, thus it is also important to understand the energy storage performances at elevated temperature. In this study, since PE materials typically start to slowly melt around 100 °C, thus the high temperature performance was evaluated at 80 °C. Effects of temperature on
polarization has been shown in Fig 19. Since 1.0wt% nanocomposites showed the highest polarization at room temperature, thus, only 1.0wt% nanocomposites are discussed here.

**Figure 19 Effect of temperature on polarization of for both ht-GNP and s-GNP reinforced nanocomposites**

Obviously, the increase of the temperature leads to weakened polarization in pure UHMWPE, probably due to the thermal motions of the polymer structures at elevated temperature. It is worthy to note that the addition of ht-GNPs and s-GNPs could enhance the polarization at higher temperature, in contrast to pure UHMWPE material. This should be resulted from the hindered thermal motions because of the interactions between GNPs and polymer matrix as well enhanced interfacial polarization mechanisms. Furthermore, the UHMWPE/s-GNP-1.0wt% showed the highest polarization, which is 50% higher than pure
UHMWPE at 80 °C. Once again, this suggests the positivity of using ODMS to improve the dispersion and interfacial interaction for energy storage applications.

At higher electrical field, the higher field strength seem to be able to conquer the random thermal motion, and led to the higher energy storage capability. Similar increased energy storage capability was also found in the nanocomposites. However, the increase was not as significant as that in pure UHMWPE materials. The different between 1200 V and 3500 V suggests the effects of the testing voltages on the energy storage capability. Obviously, the effects of surface modification on the temperature dependence of energy storage were more significant at 1200V. The simultaneous high voltage (3500 V) and high temperature might have new mechanisms on the energy storage performances of the nanocomposites. Since the understanding of dielectric relaxation at higher field is still very limited, future studies will be needed to gain better insights.

![Graph of Energy Storage vs Temperature](image)

**Figure 20** Effect of temperature on polarization of for both ht-GNP and s-GNP reinforced nanocomposites at 3500V
4.4.3 Effects of Temperature on Energy Efficiency of GNPs

Effect of Temperature on energy efficiency was studied (Fig 21), which suggests increase in energy efficiency for both UHMWPE and nanocomposites when the temperature increased to 80 °C. Similar to the results of polarization and energy storage, the efficiency further increased to close to 1, due to enhanced thermal motion of dielectric dipoles. This linear charging-discharging behavior of UHMWPE and its nanocomposites makes them ideal energy storage materials at high temperature, showing very low energy loss.

According to the results on the effects of temperature, it is obvious that the increase of temperature have positive impacts on the energy storage capability of UHMWPE and its GNP nanocomposites. However, at higher temperature, the effects of surface modification of GNPs on energy storage were not obvious at higher electrical field.

Figure 21 Effect of temperature on polarization of for both ht-GNP and s-GNP reinforced nanocomposites at 3500V
4.5 DIELECTRIC PERMITTIVITY OF NANOCOMPOSITES

Due to the difficulty in dipole switching at high frequency at high electrical field, the hysteresis testing is a more commonly used approach to analyze the dielectric relaxation phenomenon at high fields, instead of conventional dielectric spectroscopy. Dielectric permittivity has been frequently used to analyze the low field (< 5 V) dielectric relaxation properties. In this research, although our primary focus was on the hysteresis behaviors of the nanocomposites, the high field dielectric permittivity of the nanocomposites was investigated at frequency range no higher than 1000 Hz. The high field dielectric permittivity was determined by derivatives of discharging curve on P-E hysteresis loops. As can be seen in Fig 22, for both UHMWPE and nanocomposites, as the frequency increases there is an increase in the dielectric permittivity at 1200V up until 100 Hz and after that frequency, the dielectric constant drops significantly. The same frequency frequency of pure polymer and nanocomposites suggest the dominant roles of the polymer matrix in high field dielectric relaxation. Meanwhile, the highest dielectric permittivity at 100 Hz indicates the frequency vicinity of dipole switching at this electrical field. Compared with both types of UHMWPE/3.0wt% GNP nanocomposites, the pure polymer UHMWPE shows the higher dielectric permittivity. The addition of 3.0wt% ht-GNPs could remarkably reduce the dielectric permittivity, while the surface modification could greatly amend this reduction. However, the dielectric permittivity of UHMWPE/s-GNP-3.0wt% nanocomposites is still lower than that of the pure polymer. Also, the surface modification did not affect the frequency dependence of the dielectric permittivity. The results in Fig. 22 also reveal the different dielectric relaxation at high electrical field. Normally, the addition of conductive fillers in polymer matrix could lead to high dielectric permittivity at low electrical field, such as the results in Figs.8 and 9, when the loading level is reaching a threshold.
Figure 22 Dielectric permittivity of UHMWPE and UHMWPE/GNP-3.0wt% nanocomposites at 1200 V at room temperature

Figure 23 Dielectric permittivity of UHMWPE and UHMWPE/GNP-3.0wt% nanocomposites at 3500 V at room temperature
Furthermore, UHMWPE with s-GNP showed some higher dielectric constant compared to ht-GNP this suggested that the surfactant modified GNP had better interfacial polarization, due to the uniform dispersion as well as better interfacial interactions. The increase of the testing voltage up to 3500V (Fig.23) did not affect the dielectric permittivity very much. The dielectric permittivity still shows the same frequency dependence, and the value of dielectric permittivity is at the same level as that at 1200 V. It is also noticed that, the fast drop of dielectric permittivity when the frequency increased to 1000 Hz, led to very low dielectric permittivity. Even negative value was observed. This result further suggests the limitation of investigating dielectric permittivity at high field and high frequency. This is also why 100 Hz was chosen for studying hysteresis behaviors of the nanocomposites.
CHAPTER 5

CONCLUSIONS AND FUTURE PLANS

On the basis of literature review and results gathered during this research study, it can be noted that metals are quite scarce and hence are polymers to manufacture due to their own morphology and properties. However, the advancing demands advancement in various regions including electronic devices, mechanical appliances, data storage and communications and biomedical. This urge for reliable, low cost and advanced mechanics of dielectric materials for different applications have given rise to the interest in manufacturing composite materials including two or more types of materials that could meet or even surpass these expectations. In this pursuance, polymer based nanocomposites have better advantages over costly and less process ability materials like metals and ceramics owing to the properties of both polymer and filler materials for nanocomposite.

In sum, this study suggested that the successful surface modification of GNPs could lead to uniform dispersion of s-GNPs and good interfacial interactions with UHMWPE as shown in SEM images, which substantially affect the energy storage capability of the resulting nanocomposites. Also, the results showed the addition of conductive GNPs did not lead to dramatic current leakage at high field when proper surface modification was applied, suggesting the potential for energy storage of UHMWPE/GNP nanocomposites.

The agglomerates and poor interface in ht-GNP nanocomposites resulted in high current leakage and lower breakdown strength, which was seen in the results of ht-GNPs at lower voltage when the samples short-circuited. Moreover, the results showed the addition of GNPs and surface modification impacted on energy storage properties at higher temperature. Even at
High operation temperature, the UHMWPE/s-GNP nanocomposites still showed satisfactory energy storage capability. However, the increase in temperature did not reduce the polarization intensity in nanocomposites, while the energy efficiency was further improved to near 100%, unlike other reported polymers and polymer nanocomposites for energy storage applications. The surface modified GNP with UHMWPE polymer at 1 wt.% showed best feature as expected compared to heat-treated GNP with same polymer at same loading and higher loadings included. The elevation of temperature further improved the energy storage as well as energy efficiency for the nanocomposites. These positive effects of temperature should be a result of the enhanced dipole switching at elevated temperature.

Although the addition of GNPs as well as surface modification showed significant impacts on the energy storage performances of the UHMWPE nanocomposites, the results are still below the expectation. To achieve better energy storage performances, following tasks will be conducted:

- **Nanocomposite Processing Optimization**: UHMWPE gained its reputation for its very high melt viscosity. Furthermore, the addition of nanomaterials further increases the melt viscosity. This lead to great difficulty in nanocomposite processing, which also affect the structures of properties of resulting nanocomposites. In the future, the processing temperature, compounding time as well as various dispersion technologies will be investigated to find out the optimal processing conditions. Meanwhile: to deepen the understanding of the roles of interfaces, different surfactants will be applied in surface modification process to adjust the interfacial structures and properties in nanocomposites.

- **Comprehensive Structure Analysis**: UHMWPE is a semicrystalline polymer, and it is believed that the crystal structures will also remarkably impact the energy storage
properties, besides the dispersion and interfaces. The nanomaterials have also proven their capability of changing the crystal structures of the polymer matrix, thus, the crystal structures and morphologies will be thoroughly studied. In addition, thermal analysis will be conducted to study the glass transition of the polymer matrix, which could affect the dielectric relaxation phenomenon.

- Other graphitic nanomaterials will be incorporated into UHMWPE to fabricate nanocomposites with different nanostructures, and the effects of different graphitic architectures on energy storage applications will be studied.
REFERENCES
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