Processing of Nano Graphene Plates (NGPs) and NGP Nanocomposite

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY YENA LI ENTITLED Processing of Nano Graphene Plates (NGPs) and NGP Nanocomposite BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering.
ABSTRACT

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In recent years numerous efforts worldwide are addressing all aspects of the rapid developing field of nanocomposites. However, the most important fillers—carbon nanotube and carbon nanofiber—are expensive. In this study, our efforts are aimed at bridging the gap in cost and properties by providing a systematic study of alternative nano materials — nano graphene plate (NGP) and related composites. We fabricated nano graphene plates through the detailed study of raw materials, chemical treatment methods and nano particle dispersion methods. A series of thermal expansion experiments were conducted to investigate the best condition to expand acid treated graphite and expansion ratio of that graphite. Sonication at different levels of energy and ball milling of multiple time durations were used to compare the dispersion efficiency for NGPs. A Particle Size Distribution Analyzer and Scanning Electron Microscope (SEM) were used to study the microstructure and the morphology of the NGP.

NGP related nanocomposites were also produced and investigated. The electrical properties were measured by an in-house designed 4–point electrical
resistivity measurement device, clearly showing a lower percolation threshold when NGP is used as reinforcement. Thermal mechanical properties were examined using Dynamic Mechanical Analysis (DMA). Improved storage modulus, Tg and loss modulus were also found with increasing concentration of NGP.
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Introduction

In recent years, nanocomposites—in an unparalleled fashion—grabbed the attention of both researchers and business leaders within the advanced materials community. According to the National Science Foundation, nanomaterials are materials that have at least one dimension equal to or less than 100 nanometers [1]. Therefore, nanocomposites based on nanomaterials basically consist of matrices with various reinforcements which are less than 100 nm in size. Since 1987, when a research group from Toyota introduced the concept of nanocomposites for the first time, tremendous effort has been focused on carbon nanotubes and carbon nanofiber reinforced composites.

However, nanotubes and nanofibers are still expensive and cannot be mass-produced. More and more research is heading to new nanomaterials, such as nanosilicates [2, 3] and nano graphene plates (NGP) [2, 4 – 8]. These materials are naturally abundant and have good mechanical and electrical properties. The potential commercial markets are broad. They include interior and exterior accessories for automobiles, structural components for electronic devices, films for food packaging, and even some entertainment apparatus like golf balls [9].

In recent years, fuel cell has also become a research topic of increasing importance in the materials science community. Many research groups and companies are competitively searching for new materials to cut the cost. Using NGPs to make bi-polar
plates, which is a critical component in fuel cell in terms of architecture, geometry, volume, mass, mechanical, and electrical properties, undoubtedly is an innovative concept. Thus, these materials really need to be thoroughly studied since they are lower-cost alternatives to carbon nanotubes and carbon nanofibers.

There are few published papers related to NGP, especially on certain important issues like fabrication methods and properties of NGP and NGP composites. Regarding acid-treatment time, no paper clearly explained the exact time duration required for fabrication of expanded graphite. This work studied the impact of varying acid-treatment time on graphite expansion ratio, which is very important for producing NGP. Also, no individual paper comprehensively compares the break-up methods for fabricating NGPs. In this work, several methods of fabricating NGPs were compared for cost-effectiveness. As for dispersing NGP in a resin matrix, very few papers indicate the specific dispersing diluent. An effective diluent was formulated in the course of this study. With the aid of Thermal Mechanical Analysis instruments, Particle Size Distribution machine and Scanning Electron Microscopy (SEM), we studied the thermal properties, mechanical properties, and microstructure of the nano graphene plates. Using a 4-point electrical resistivity measurement device designed in–house, we also investigated the electrical properties of nano graphene plate–based nanocomposites.

The process of mixing NGP with a resin matrix was designed for the purpose of improving the dispersion of NGP in a viscous resin and improving the properties of the
composites. The electrical conductivity measurements show that NGP related vinyl ester nanocomposites have a lower percolation threshold than graphite powder composites. Dynamic thermal mechanical analysis also shows improved integrated stiffness and damping properties.
2.1 Carbon nanotube

When we do a literature search for “carbon nanotube (CNT)” thousands of papers and patents may be found under this active subject. In 1991, Iijima [10 – 12] discovered a new form of carbon — carbon nanotube — in the carbon soot produced by a carbon arc machine. The substance he found was composed of nested cylindrical graphitic layers capped by fullerene-like ends with a hollow internal cavity. Intensive worldwide research efforts have been devoted to the field, including synthesis and purification of high-quality nanotube materials [13], as well as characterization, modification, functionalization, and application of carbon nanotubes.

The reason for such a tremendous focus on carbon nanotubes is obvious. CNT has many unique chemical, mechanical, and electrical properties. Ideally, a carbon nanotube is composed of one or more cylindrical layers of rolled-up graphene sheets, with an interlayer spacing of 0.34 – 0.36 nm that is close to the typical spacing of turbostratic graphite. The length of a nanotube is usually over 1 micrometer, and the diameter ranges from about 1 nm (for single-shelled tubes) to about 30 nm [12, 14]. Both the theoretical model and experimental results [15] show that for the single walled carbon nanotube, Young’s modulus is in the range of 2.8 – 3.6 TPa. For a multi-wall carbon
A compressive strength of 100 – 150 GPa for multi-wall carbon nanotube was reported [16] and a compressive strain of 5% was also obtained. As for electrical properties, CNTs can carry a higher current density than any metal. Its current density is about $10^9 – 10^{10}$ A/cm$^2$, which is over 1000 times that for Copper, before electromigration [17].

Based on those special and excellent special properties, CNTs have many potential applications, such as additives for high-strength polymer composites, efficient field emitters for electron sources, electrode materials for high capacity batteries, and functional components for small-scale electronic devices, sensors, probes, and hydrogen storage tools which is still controversial [18].

Unfortunately, the synthesis and related purification of carbon nanotubes are big hurdles in the way of commercialization of CNTs or CNT-related materials and devices. Currently, the single-wall carbon nanotube can only be produced on a small scale, and the present cost is about $500 per gram. Multi-wall carbon nanotubes have long been scaled up to industrial quantities by Hyperion; a price of about $10 per pound seems achievable over a few years [19]. Also, the shear strength of multi-walled carbon nanotubes was only about 0.08 MPa and 0.3 MPa when measured for shell sliding in two separate multi-wall nanotubes [20]. This weak load transfer was also demonstrated by Cumings and Zettl [21]. Therefore, new materials which are cost-effective and have properties similar to carbon nanotubes are urgently needed.
2.2 Nanocomposites

2.2.1 General properties of nanocomposites

It is reported that the mechanical and thermo-mechanical properties of composites filled with micron-sized filler particles are inferior to those filled with nanoparticles of the same filler [22]. In addition, some unique properties, which conventional micron-sized particles cannot achieve, make nanocomposites stand out and attract great attention.

Basically, nanocomposites are a fascinating class of materials in which at least one filler dimension is in the nanometer range [1]. According to the geometries of fillers, nanocomposites can be classified into three primary categories [5]. Fumed silica dioxide and nanometallic powder are particles, which are characterized by having all three dimensions in the nanometer range [23 – 24]. Carbon nanotube and whisker possess two dimensions in the nanometer range [25]. Mica, clay, and expanded graphite-layered structural fillers have only one dimension in the nanometer range [2 – 4].

When nanoscale fillers are uniformly dispersed in the matrix, the tremendous surface area developed could lead to higher strength, stiffness, and glass transition temperature [26 – 27]. For example, Biercuk’s group [28] obtained encouraging results of
monotonic increase of resistance to indentation (Vickers hardness) by up to 3.5 times on loading using 2% single-wall nanotubes, and a doubling of thermal conductivity using 1% single-wall nanotubes. Also, 1% multi-wall carbon nanotubes-reinforced polystyrene increases the modulus and breaking stress by up to 42% and 25% respectively [29].

Because nanoscale fillers can provide an extraordinarily tortuous, zigzagging path, they improve barrier performance for gas, moisture, and oxygen transmissions. Hence, clay nanocomposites have been used in food packaging [30].

Due to the high aspect ratio and high conductivity of some nanoscale fillers, such as carbon nanotubes, nano graphite plates or nano graphene sheets, nanocomposites containing these fillers can be used in electronic devices. The multi-wall carbon nanotube–filled epoxy resin can achieve percolation at loadings of 0.01% and even 0.004% with careful processing [31]. However, conventional conducting fillers such as carbon black, graphite, and metal fiber or powder, generally require greater than 15% percolation loading in order to achieve percolation [32].
2.2.2 Challenges in the application of nanocomposites

2.2.2.1 Cost

Due to the complicated fabrication process, carbon nanotubes and carbon nanofibres, which are of great scientific interest because of their interesting mechanical, electrical, and thermal properties and therefore potential applications, still cannot be produced in large quantities. In order to reduce the high cost of fabrication [19], numerous efforts are competitively addressing the issue by searching for new nanomaterials and cost-effective fabrication methods.

2.2.2.2. Interfacial issue

It is well known that the high performance characteristics of composite materials depend not only on the physical properties of reinforcement and matrix but also on the interfacial region that exists between these dissimilar components. This interfacial region or interphase that is intermediate between the reinforcement phase and the matrix phase provides an important function in the overall performance of composites, including nanocomposites. Over the past decade, research papers and data on nanocomposites have become more and more available. Unfortunately, some experimental results are inconsistent with theoretical calculations. For example, improvements, insensitivity, or...
even worsening of the mechanical performance of CNTs-based nanocomposites have been reported, even for similar systems tested in different laboratories [26]. For nanocomposites where there are orders of magnitude more interfacial area created by nano particle reinforcement, interfacial issues are especially critical and well worthy studying.

Carbon nanotubes, due to their molecular perfection, are essentially free of defects. However, this kind of perfection hinders the nanotubes’ interaction with other materials. In fact, the majority of research on functionalizing nanotubes lies in the field of improving nanotubes’ interfacial properties. Molecular simulations by Frankland et al. [33] predicted an influence of chemical bonding between the nanotubes and the matrix on interfacial adhesion. If only one percent of the carbon atoms of the nanotubes surface are covalently bonded to the polymer matrix, the interfacial shear strength would be improved by more than an order of magnitude without decreasing the Young’s modulus significantly.

To fully investigate the interface of nanotubes, a more difficult problem deserves consideration. Measurement of the extent and efficiency of stress transfer through the interface between the nanotubes and the matrix currently attracts a great deal of attention. The importance of this parameter rests on the fact that in the nanocomposites of the future, efficient matrix-to-nanotubes stress transfer will be essential to taking advantage of the very high Young’s modulus and strength of the nanotubes.
2.2.2.3. Dispersion

The dispersion of nano-particles in a matrix system is another major problem to be solved for nanocomposites. These nano-scaled particles exhibit an enormous surface area (1000 m$^2$/g and more in some cases), which is several orders of magnitude larger than the surface of the conventional fillers. This surface area acts as an interface for stress transfer, but is also responsible for the strong tendency of the nano-particles to form agglomerates. An efficient exploitation of the nano-particles properties is therefore related to their homogeneous dispersion in the matrix or an exfoliation of the agglomerates.

Various dispersion methods, such as stirring, extrusion, and kneading, for the distribution of nano-particles in solution have been used. A common technique for dispersing nano-particles is the sonication technique [34]. A pulsed ultrasound exfoliates agglomerates and disperses nano-particles in the matrix effectively. However, this method is only manageable for small batches due to the extreme reduction of the vibrational energy with increasing distance from the sonicator tip. Another detrimental effect of this method, due to the local energy input, is the reported rupture of the nanotubes [35] leading to a reduction of nanotubes’ effective length. Another effective and common shear-mixing technique called calander was used to disperse the carbon nanotubes in the
2.3. Nano-graphene plate (NGP)

According to the literature review, generally speaking, the fabrication process of nanographite plates involves 3 forms of graphite. They are natural graphite flakes, intercalated or expandable graphite, and expanded graphite.

2.3.1 Natural graphite

Natural graphite is a lustrous black carbon mineral. In the carbon family, graphite is the representative of sp² bonding structure, where the layers of hexagons of carbon atoms bound using sp² orbitals are stacked in parallel using π electron clouds with a regularity of ABAB... The basic unit of graphite is called graphene, in which a large number of benzene hexagon rings are condensed to form a rigid planar sheet, with a nearest neighbor distance of 1.42 Angstrom. The interplanar distance is about 3.35 Angstrom and the force between the layers are Van der Waals forces [37].
Graphite is the stiffest material found in nature. Its Young’s modulus is about 1060 MPa, which is several times that of clay [27]. Graphite is an excellent electrical conductor with an electrical conductivity of $10^4$ S/cm at room temperature [2, 38]. It is also a good conductor of heat and has a high melting temperature of 3500 °C. Graphite is extremely resistant to acid, chemically inert, highly refractory, and has a low coefficient of friction. Its layered structure also gives a large anisotropy in the properties of graphite.

2.3.2 Intercalated graphite

Graphite can accept various atoms, ions, and even molecules between its interlayer space of hexagonal layers of carbon atoms through certain chemical and physical treatment methods. This phenomenon is called intercalation [39 – 42]. The
charge transfer complex with graphite obtained in the intercalation reactions is called graphite intercalation compound (GIC). One characteristic of intercalated graphite is the charge transfer between intercalates and graphite layers, which is the main source of the different functions of intercalated graphite [43]. According to the type of intercalate, there are two types of intercalated graphite. The donor type is one in which intercalates give electrical charge to graphite layers and become positive ions in the gallery of graphite layers. The acceptor type is one in which intercalates receive electrical charge from graphite layers and become negative ions in the gallery. Alkali metal GICs are the best known donor type GICs. For example, lithium GICs have been the most intensive research topic for battery applications in recent years [44 – 51]. For acceptor type GIC, acid intercalate graphite attracts more attention, since after some acid treatment, the graphite exhibits interesting high expansion properties. Based on these properties, the intercalated graphite (expandable graphite) can be heat–treated at high temperature to produce expanded graphite.

Another characteristic of GICs is the stage structure, which can be in a wide range from 1 to more than 10. The stage number n is the number of graphite layers sandwiched between two intercalate layers. For example, in a stage 1 GIC, every interlayer of graphite is filled by intercalates with the graphite and intercalate layers being stacked alternately along the normal to these layers. This implies one graphite layer between two intercalate layers. If there are two graphite layers between the intercalate
layers, it is a stage 2 GIC. Three graphite layers are stage 3 GIC, and so on [2]. According to the literature, stage 1 to stage 5 are common products.

2.3.3 Expanded graphite and NGP

Expanded graphite is also called exfoliated graphite. When graphite intercalation compound (GIC) is heated, the GIC induces the vaporization of the intercalated species and hence a significant expansion of the material along the crystallographic c-axis occurs, while the in-plane lattice constant remains almost unchanged. Depending on the intercalation methods, the heating rate and the maximum temperature reached, expandable graphite can lead to volumes expansions as high as 300 [52]. After thermal expansion, expandable graphite becomes expanded graphite which is a highly porous worm-like accordion structure material. The size of the pores is in the range of 10nm to 10μm [2]. The expanded graphite also has very low densities within the range of $2 \times 10^{-3} - 10 \times 10^{-3}$ g/cm$^3$ [53] and a high surface area of about $40 - 85$ m$^2$/g [54 – 55].

Expanded graphite possesses high aspect ratios, which is greater than 1000, once intercalated and exfoliated by chemical processes [56]. After various “break-up” methods, such as sonication and ball milling, the expanded graphite “worm” loses the weak connection and becomes single graphite layers or stacks of a few graphite layer sheets—nano graphene plates (NGP), whose thickness is usually 2 – 400 nm [2, 83]. An NGP may
be viewed as a flattened version of a carbon nanotube. (Fig. 2) This nanoscale material not only inherits the natural graphite’s excellent mechanical properties, good thermal and electrical conductivity, but also shows unique nanoscale properties. In addition, the NGP is about 500 times less expensive than carbon nanotubes [6, 28]. Undoubtedly, NGP is a potential alternative to carbon nanotubes with regard to cost and desired properties.

Fig. 2. Conceptual schematics of single wall carbon nanotube and nano graphene plate

In the past 5 years, although more and more attention is being paid to NGP, from patents to research papers, [2, 4 – 8, 27, 69, 83, 84] researchers mainly focus on the fabrication methods of NGP and different properties of NGP nanocomposites, like electrical and mechanical properties. The first patent in the world related to producing NGP using expanded graphite is from Dr. Jang’s research group [84]. Similar fabrication methods were also reported by Dr. Drzal’s research group at Michigan State University [27] and Dr. Chen’s group at Huaqiao University, China [2, 69]. Until now, most papers have focused on stacked nano graphene plates of several layers. Just recently there are have been a few of papers presented by J. Scott Bunch et al. from Cornell University [83]
that fabricate single graphene sheet from peeling process of natural graphite. However, there is still little published information about mass fabrication methods of NGP. And there is no paper that makes comparison of different expanded graphite break-up methods. As for NGP polymer nanocomposites or NGP related expanded graphite nanocomposites, NGP/epoxy nanocomposite [27], NGP/polystyrene nanocomposite [2, 69], NGP/polyacrylonitrile nanocomposite [7], expanded graphite/polyamide–6 nanocomposites [85] have been mainly studied. However, few papers provide the NGP dispersion method. A systematic study of NGP and its related nanocomposites is urgently needed. In my research, I mainly focus on the above issues.
Fabrication Process of Nano Graphene Plates (NGPs)

3.1. Materials and instruments

3.1.1 Raw materials

The raw material used for preparing NGP in this study was natural graphite with purity of 99 wt% and grain size of 100 mesh, which means an average particle diameter of about 150 µm. Industry-grade 98 wt% sulfuric acid H$_2$SO$_4$ ($\rho = 1.84$ g/cm$^3$), 98 wt% nitric acid HNO$_3$ ($\rho = 1.50$ g/cm$^3$), glacial acetic acid CH$_3$COOH ($\rho = 1.049$ g/cm$^3$), and potassium permanganate were used for the graphite intercalation reaction.

3.1.2 Sonication

In our work, for common sonication (low energy sonication) we used a Branson® ultrasonic cleaner. This kind of ultrasonic cleaner is commonly used in chemistry laboratories for deep cleaning purposes, such as removing contaminants, dirt, grease, waxes, and oils from metal, plastic parts, or glass-wear. They are also widely used for mixing chemicals without special power output requirements. All units feature 40 Hz
industrial stacked transducers with a sweep frequency feature to ensure an even vibrational energy throughout the tank.

For high energy sonication, we used a Sonifier® Cell Disrupters S-450D with a 1/8-inch tapered microtip, which was also purchased from Branson Ultrasonics Corporation. Usually, high energy sonication is designed for biological and liquid processing applications where precise control and parameter measurement are required. It is commonly used in the fields of chemistry and biology, such as biological cell disruption, emulsification, dispersion, and acceleration of chemical and biological reactions.

3.1.3 Ball milling

Ball milling is an effective method to reduce the size of particles. High surface areas in the samples after ball milling have been reported [57, 58]. Ball milling technique can be used to prepare a variety of nanostructured materials, such as pure metallic elements, solid solutions and intermetallic compounds [59]. The changes in the crystallinity of graphite during ball milling have also been examined [60 – 63]. The general conclusion is that graphite passes through a nanocrystalline phase prior to amorphization.
Planetary ball milling was chosen since it is capable of reducing the size of the particles to the nanoscale. In this study, a Fritsh Planetary Mono Mill “pulverisette 6” was used. In order to get the smallest particle size, the manufacturer recommended using a tungsten carbide grinding bowl, lid, and balls. Tungsten carbide has a high resistance to abrasion, which would minimize contamination due to wear. A 250 ml tungsten carbide bowl with a matching lid was therefore selected, along with fifty 10 mm tungsten carbide grinding balls.

3.1.3.1 Cleaning the grinding bowl, lid, and balls

In order to minimize contamination due to wear while milling different samples, careful clean work is necessary before each operation. First, each component was carefully wiped with a paper towel. Then the lid and bowl were washed with water until the water was clear. The balls were put in a metal strainer and rinsed with water until the water ran clean.

3.1.3.2 Factors influencing quantities during grinding

Based on the manufacture’s advice and the literature review, the factors which may affect milling quantities are summarized as follows:
(a). Milling time.

(b). Running speed. Generally speaking, a higher speed will reduce the grinding time and increase the fine fraction.

(c). Reversing operation (regular reversal of the direction of rotation). This is useful for mechanical alloying and improves homogenization of materials.

(d). Number and size of the balls. Usually, using many small balls will increase the fine fraction if running time is increased.

(e). Mass of the balls (type of materials). A higher mass or density of the grinding ball will accelerate the grinding.

(f). Milling medium. Due to some special requirements, some gases, like argon, and some liquids, like ethanol, can be added when grinding.

3.1.4 Particle size analysis

A Nicomp model 380 Particle Size Analyzer, which is based on dynamic light scattering to obtain a distribution of particle size, was used to measure the sizes of NGPs. Because of the high concentration of NGP, which has high surface energy and tends to agglomerate, the samples must be diluted to get acceptable data. In our work, we had two types of samples: wet samples, which are treated by different sonication methods; and dry
samples, which are ball milled. For wet samples, the sample was simply diluted further using the sonication medium. For dry samples, acetone was used as a diluent. The diluted solution was placed into the Particle Size Analyzer sample container, which was a small two-inch long glass tube. The tube must be filled three quarters full to ensure that the laser passes through the sample.

This Particle Size Analyzer system processes data using Gaussian distribution analysis. It has the useful attribute that the resulting distribution settles quickly to a stable, reproducible result with continuing acquisition of light scattering data. However, the drawback of this system is that it can only measure the overall sample size and cannot give sample size information in a specified direction. Therefore, other methods and instruments are still needed in order to provide a complete characterization of particle size.

3.1.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is a type of electron microscope capable of producing high resolution images of a sample surface. Today it is heavily used in research to study the microstructure of the samples. In our work, a JEOL model JSM – 35 CF SEM was used to characterize the expanded graphite and NGP structure at the
micrometer and nanometer level.

3.1.6 Thermogravimetric Analyzer (TGA)

Thermogravimetric Analyzer (TGA) measures the weight change of a sample as a function of time or temperature. Thermogravimetric analysis involves heating a sample in an inert or oxidizing atmosphere and measuring its weight. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability. It can be used to assess the moisture content in the sample, examine the oxidative stability, and monitor the decomposition kinetically. In this work, TGA measurements were conducted using a TA Instrument TGA Q-500. The main goal for doing TGA experiments is to determine the best temperatures for expanding the intercalated graphite according to the loss of sample weight.
3.2 Experimental procedure

3.2.1 Acid treating graphite

The idea of treating graphite using acid is to produce graphite intercalation compound (GIC), which can give off a great amount of gas after a high temperature treatment. With the aid of this high gaseous pressure produced between graphite layers, the graphene layer, basic unit of natural graphite, separates from each other. The methods that can give natural graphite complete expansion were compared and investigated.

Fig. 3. Acid treatment process set-up.
Based on the literature review, four methods of acid treatments were compared and studied. For each method, the treatment equipment set-up is the same (Fig. 3). However, the chemicals and the concentration of each compound are different.

Method 1 [65, 66]

The graphite and potassium permanganate was measured out into the desired sample size, mixed, and placed in a glass beaker. An ice bath was needed to cool the sample during the exothermic reaction. After the graphite beaker was secured in the ice bath, concentrated nitric acid was measured using a graduated cylinder. The acid was carefully poured into the graphite potassium permanganate mixture while it was being magnetically stirred to keep it uniformly dispersed. Then glacial acetic acid \( \text{CH}_3\text{COOH} \) was slowly added to the mixture. Because of the strong reaction from those strong acids, a pipette was used to slowly introduce acid to prevent overheating. The natural graphite, nitric acid, glacial acetic acid, and potassium permanganate mixed ratio is 1:1:0.8:0.06 by weight. The slurry was allowed to mix in the ice bath for 40 minutes.

After the acid treatment, the mixture was washed to remove any excess acid. Iodized water was slowly added to the graphite – acid mixture to dilute the acid. The washing process was stopped once the pH of the diluted graphite – acid mixture reached pH 5. Then the GIC was placed in an oven to dry at 80 °C.
Method 2 [68]

The procedure for method 2 is the same as for method 1. However, in this process, concentrated nitric acid was replaced by sulfuric acid and the graphite, sulfuric acid, glacial acetic acid, and potassium permanganate mixed ratio by weight is 1: 0.5: 2: 0.07. The reaction time was 2 hours.

Method 3 [64]

Without using potassium permanganate, method 3 used only graphite, sulfuric acid, and nitric acid. The mixed weight ratio of the graphite: sulfuric acid: nitric acid was 1:1:1. The slurry was mixed for 2 hours.

Method 4 [2, 5, 69]

Method 4 is similar to method 3 but does not use potassium permanganate; in method 4 the mixed weight ratio of the graphite: sulfuric acid: nitric acid was 1:10.3:2.1 (H$_2$SO$_4$:HNO$_3$ mixed volume ratio is 4:1). This method was also conducted several times using different mix times. Due to the stronger acid used in methods 3 and 4, more heat was released when preparing the mixture of method 3 and method 4 than that of methods
3.2.2 Expansion

In order to obtain a better expansion ratio, a small amount of GIC was thinly spread over the bottom of the crucible so as to create the most space for complete expansion. Then the crucible was put into the furnace. The expansion temperature and the expansion time were varied to determine the best conditions for GIC expansion. TGA, which is commonly used to test the weight change as a function of time or temperature over a slow increase in temperature range, was used to determine that best condition. In this study, thermal decomposition in TGA was set to increase temperature sharply to 800 °C, 850 °C, 900 °C, and 950 °C respectively, and maintain that temperature for 2 minutes for each run.
3.2.3 Break-up expanded graphite “worm” to form NGPs

There are several methods to break up the expanded graphite “worm”-like structure into a single or a few graphene layers. However, no published paper compared those methods. In this study, three common methods were compared and investigated.

Method 1

Common sonication (low energy sonication) was conducted with a Branson® Ultrasonic Cleaner, which was introduced in 3.1.2. Usually just the desired liquid chemicals are mixed. However, in this study, tiny glass beads with diameter 1 mm and different sonication mediums—deionized water, methanol, and acetone—were used and compared. Expanded graphite worm, beads and one sonication medium were placed into a little bottle and sonicated for 8 hours.

Method 2

High energy sonication must be conducted in an ice bath to prevent overheating. Acetone was chosen as the sonication liquid medium based on break-up method 1. The expanded graphite worm was sonicated for 8 hours with a sonication energy level of 40 – 45 watts.
Method 3

Ball milling was conducted with consideration of the influence of grinding quantity factors, which was previously introduced in 3.1.3.2. The milling time was set to 8 hours, 16 hours, and 40 hours for comparison. In particular, the speed was set to a maximum speed of 600 rotations per minute (rpm) and with the reversing operation mode, which means the rotational direction of the planetary mono mill changes after the chosen running time has elapsed in order to obtain uniform size and smaller particles. A half-hour cool down period closely followed by a milling cycle was used to ensure that the milling balls and bowl would not be damaged by overheating.
The experimental procedure used in the present study may be summarized in the following flow chart:

1. Natural graphite
2. Acid treatment (4 methods)
3. Intercalated graphite
4. Wash with water and dry
5. Expandable graphite
6. Abrupt heating to 800 °C – 950 °C
7. Expanded graphite
8. Break-up expanded graphite worm (Sonication, high energy sonication, or ball milling)
9. Nano graphene plates
3.3. Results and discussion

3.3.1 The impact of acid treatment for expandable graphite on the fabrication of NGPs

As stated in the literature review on the graphite intercalation compound (GIC), there are many materials that can be intercalated into the graphite layers. The purpose of choosing acids to treat natural graphite is to obtain GIC, which can emit more gases after exposure to a heat source to push apart those graphene layers by the gaseous pressure after its decomposition.

In fact, until recently, the GIC formed from acid intercalation is still a compound whose composition and structure have not yet been studied in sufficient detail [64]. However, several reaction models were proposed in the literature. For example, in the graphite – sulfuric acid GIC system, the reaction formula can be expressed in the following: [64 – 67]

\[ n \text{ (graphite)} + n \text{ H}_2\text{SO}_4 + \frac{n}{2} [\text{O}] \rightarrow \text{[graphite} \cdot \text{HSO}_4 \cdot \text{H}_2\text{SO}_4] + \frac{n}{2} \text{H}_2\text{O} \]

[O] represents the oxidizer. [graphite \cdot \text{HSO}_4 \cdot \text{H}_2\text{SO}_4] represents H\text{SO}_4 – GICs.

For the graphite – nitric acid GIC system,
\[ n \text{ (graphite)} + n \text{ HNO}_3 + [O] \rightarrow [C^{+}_{24n} \cdot \text{NO}_3^- \cdot 3\text{HNO}_3] + \text{NO}_2 + \text{H}_2\text{O} \]

\[ [C^{+}_{24n} \cdot \text{NO}_3^- \cdot 3\text{HNO}_3] \text{ represents graphite nitrate.} \]

If the oxidizer is H$_2$SO$_4$, then the formation of graphite nitrate– H$_2$SO$_4$ system can be shown by the reaction

\[ 24n \text{ C} + 3 \text{ H}_2\text{SO}_4 + \text{HNO}_3 = C^{+}_{24n} \text{HSO}_4^- \cdot 2\text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O} \]

where \( n \) is the stage index.

In order to get a single nano graphene layer or a stack of a few graphene layers, the stage index of GIC and the expansion ratio are important from the micro level and the macro level. In fact, acid treatment methods 1 and 2 originally came from the best recipe ratio and time in [65, 66, 68] for preparing expanded graphite “worm”. From Table 1, we can roughly see Method 2 can get a better expansion ratio (15.6) than Method 1 (12), although Method 1 has the advantage of not using sulfur containing chemicals and of time efficiency. The reason that Method 2 has a better expansion ratio might be that method 2 used more oxidizer (K$_2$MnO$_4$). However, according to the literature [64], graphite: HNO$_3$ weight ratio 1: 1 and graphite: H$_2$SO$_4$ weight ratio 1: 0.33-0.5 will have a stage 2 structure, which means after high temperature expansion, two graphite layers may still be sticking together.
Table 1. Influence of acid treatment method on the structure of the expanded graphite.

<table>
<thead>
<tr>
<th>Acid treatment methods</th>
<th>Reaction time</th>
<th>Volume per unit mass after high temperature (ml/g)</th>
<th>Expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method 1 (weight ratio)</td>
<td>40 min</td>
<td>24.7</td>
<td>12.0</td>
</tr>
<tr>
<td>C:HNO₃:CH₃COOH:K₂MnO₄=1:1:0.8:0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method 2 (weight ratio)</td>
<td>2 hours</td>
<td>31.6</td>
<td>15.6</td>
</tr>
<tr>
<td>C:H₂SO₄:CH₃COOH:K₂MnO₄=1:0.5:2:0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method 3</td>
<td>2 hours</td>
<td>19.3</td>
<td>9.1</td>
</tr>
<tr>
<td>C:H₂SO₄:HNO₃=1:1:1 (weight ratio)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method 4</td>
<td>2 hours</td>
<td>33.9</td>
<td>16.8</td>
</tr>
<tr>
<td>C:H₂SO₄:HNO₃=1:10.3:2:1 (weight ratio)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H₂SO₄:HNO₃ = 4 : 1 &lt;volume ratio&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Influence of acid treatment method on the structure of the expanded graphite.

In Method 3, the chemical proportion was used for preparing stage 1 GIC [64]. However, speaking from the macro level, the expansion ratio is not very good. Based on published information [2, 5, 69] about producing nano graphene plates, Method 4 (graphite: H₂SO₄ : HNO₃ mixed weight ratio is 1: 10.3 :2.1 – H₂SO₄ : HNO₃ mixed volume ratio is 4: 1) was tried. It can get the best expansion ratio of these 4 methods, using the same reaction time.

However, the literature about Method 4 is not specific. There is no agreement on
the reaction time and ratio of graphite to mixed acids. Actually, the acid treatment time is very important because less time would cause incomplete intercalation while more time may introduce over oxidized graphite compounds. Both cases affect expansion greatly. In our study, we set the ratio of graphite to mixed acids and perform trials different acid treatment times. Table 2 and Fig. 4 clearly show the best acid treatment time is 21 hours.

<table>
<thead>
<tr>
<th>Reaction time (hours)</th>
<th>Volume per unit mass after high temperature (ml/g)</th>
<th>Expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>19.7</td>
<td>9.4</td>
</tr>
<tr>
<td>2</td>
<td>33.9</td>
<td>16.8</td>
</tr>
<tr>
<td>3</td>
<td>49.8</td>
<td>25.2</td>
</tr>
<tr>
<td>4</td>
<td>48.7</td>
<td>24.6</td>
</tr>
<tr>
<td>5</td>
<td>54.1</td>
<td>27.5</td>
</tr>
<tr>
<td>6</td>
<td>57.1</td>
<td>29.1</td>
</tr>
<tr>
<td>16</td>
<td>66.1</td>
<td>33.8</td>
</tr>
<tr>
<td>20</td>
<td>71.3</td>
<td>36.5</td>
</tr>
<tr>
<td>21</td>
<td>82.1</td>
<td>42.2</td>
</tr>
<tr>
<td>22</td>
<td>57.6</td>
<td>29.3</td>
</tr>
<tr>
<td>23</td>
<td>51.6</td>
<td>26.2</td>
</tr>
<tr>
<td>24</td>
<td>41.7</td>
<td>20.9</td>
</tr>
<tr>
<td>28</td>
<td>42.9</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 2. The effect of intercalation time on the graphite expansion ratio in Method 4 (graphite: H₂SO₄: HNO₃ = 1: 10.3: 2.1 (weight ratio)).
Fig. 4. The influence of acid treating time on the GIC expansion ratio in Method 4.
3.3.2 The effect of exfoliation temperature on the GIC expansion

The expansion temperature and expansion time are also important for the fabrication of NGPs. Besides intercalation methods, a proper expansion time and suitable expansion temperature can lead to a fully expanded graphite worm-like or accordion-like structure as shown in the SEM picture. (Fig. 5)

![Fig. 5. Scanning electron microphotographs of expanded graphite.](image)

In order to produce a single graphene layer or a few graphene layers, thorough expansion
of GIC is necessary. We took samples produced using the fourth acid treatment method—which was treated for 2 hours—and conducted a series of experiments. The results are shown in Fig. 6 and Fig. 7.

Fig. 6. Volume per unit mass of expanded graphite after high temperature expansion vs. oven temperature.

Clearly, 900 degree Celsius is the best expansion temperature, which means at that temperature, the gaseous phases are more effective in pushing apart the graphite interlayers.
Fig. 7. Volume per unit mass of expanded graphite after high temperature expansion vs. expansion time in the oven.

As shown in Fig. 7, an oven time of 2 minutes is the best for an expandable graphite to complete its expansion. Heating the expandable graphite for too long overexpands the worm–like structure, which breaks when the structure is over–strained. The heating may also cause the accordion structure of the expanding graphite worm to disintegrate from oxidation. Both of the above may decrease the volume per unit mass a bit.

TGA was used to check the conclusion drawn from the data as stated above. Fig. 8 is the typical thermal decomposition process of GIC under air flow in a range of room temperature to 1000 °C. Clearly, between 800 °C and 950 °C, there is a great mass drop, which is related to the abrupt release of various gaseous species from expandable graphite interlayers.
In this work, instead of starting measurements from room temperature, the TGA was set to increase temperature sharply to the desired temperature (800 °C, or 850 °C, or 900 °C, or 950 °C, respectively) and keep it at that temperature for 2 minutes in order to simulate high temperature expansion using the commercial oven. The results are shown in Fig. 9.
In this plot, the number under each curve is the slope of that line, which indicates the mass loss percentage per minute. Under 900 °C for 2 minutes, the sample experienced the highest level of mass loss. That means this condition provides the maximum gas species give–off, which implies the graphite layers are pushed apart the most by the gases. The information shown by TGA is consistent with our previous results.
3.3.3 Break–up of expanded graphite “worm”

In order to obtain good quality NGPs, every step should be carefully compared and studied. In nanotechnology research, dispersion of nano particles is one of the most difficult issues. Although breaking up expanded graphite “worm” structure (separating the graphite layers) is not an actual nano-particles dispersion problem, ideas and methods can be borrowed from that research area to study how to get a uniform dispersion of single layers or stacks of several nano graphite layers.

Usually in chemistry or biology labs, common sonication is an easy way to mix or disperse chemicals. Most researchers simply put chemicals together in a container for sonication. However, in our study, small glass beads with a diameter of about 1 mm were used to help break up expanded graphite “worm” structures. For the first break–up method, water was used first as a sonication medium. Fig. 10 and Fig. 11 show the different dispersion results between the case without using tiny glass beads and the case using tiny glass beads. Using tiny glass beads during low energy sonication, the main size domain is about 730 nm compared to 900 nm for the case without using tiny glass beads. The tiny glass beads jump randomly with the sonication wave in the expanded graphite/water solution, which helps destroy the expanded graphite “worm” structure, assisting the formation of nano graphene sheets. Therefore, using tiny glass beads can get better
results.

Fig. 10. NGP size distribution using common sonication (low energy sonication) with deionized water as a sonication medium (without glass beads).

Fig. 11. NGP size distribution using common sonication (low energy sonication) with deionized water as a sonication medium (with glass beads).
Fig. 12. NGP size distribution using common sonication (low energy sonication) with methanol as a sonication medium (with glass beads).

Fig. 13. NGP size distribution using common sonication (low energy sonication) with acetone as a sonication medium (with glass beads).
In the literature, usually the sonication medium is not clearly indicated or only one sonication medium is used. In our study, different sonication mediums were also tested. Fig. 11, Fig. 12, and Fig. 13 show the particle size distribution of NGPs obtained using different sonication mediums.

Fig. 14. Comparison of sonication results using different sonication mediums.

Fig. 14 shows the NGP dispersion in different sonication media after 8 hours of
sonication. Obviously, NGPs are finely dispersed in acetone, whereas in deionized water and methanol, flocks are observed, which demonstrate that using acetone as a sonication medium is better than using water and methanol. The main size domain is about 280 nm for the expanded graphite – acetone solution. This phenomenon might be due to the similar polarity between acetone and NGPs. During the acid intercalation reaction of graphite, some –OH and –COOH groups are attached to the edge of the thin graphene sheets [2, 32, 70, 71], which cause the graphite sheets to be hydrophilic. The affinity between the “polar” graphene sheets and the polar chemicals like acetone drives the liquid molecules to further intercalate into expanded graphite spacing, resulting in more complete break–up of the expanded graphite “worm” structure. In addition, different liquids transfer the sonication wave differently [72]. The NGP’s size distribution after high energy sonication is shown in Fig. 15. There are two main size domains. This can be attributed to the fact that high energy sonication (tip sonication) cannot give a completely uniform energy distribution [34, 35].
Fig. 15. NGP size distribution using the high energy sonication method with acetone as a sonication medium.

Fig. 16, Fig. 17, and Fig. 18 show the NGP’s size distribution after the ball milling. Generally speaking, increasing ball milling time decreases the particle size, which can be seen by comparing these three figures. An interesting observation is that for 40 hours of NGP ball milling, there are two separate main size domains (a bimodal distribution). This could be due to the formation of other forms of graphite induced by ball milling. For example, it is reported that curved- or closed–shell carbon nanostructures appear after ball milling graphite for an extended duration of time [59]. However, ball milling is still the more convenient candidate method for mass fabrication of NGPs over those small batch sonication methods.
Fig. 16. NGP size distribution using the ball milling (8 hours milling time) break–up method.

Fig. 17. NGP size distribution using the ball milling (16 hours milling time) break–up method.
Particle Size Distribution Analysis can only give statistic data of the overall size of the particles. SEM can be used collaboratively to examine the sample visually to find each dimension of the particles. From the SEM observation, most graphite sheets have thicknesses in the magnitude of about 10 to 100 nm, which is similar to the previously reported data [2, 4, 32].
Fig. 19. SEM picture of NGP absorbed on graphene sheet of expanded graphite.
Nano Graphene Plate (NGP) Nanocomposites

4.1 Material and instruments

4.1.1 Materials

Ball milled NGP were used as reinforcement with a thermosetting resin of the vinyl ester family as matrix material. Vinyl esters are methacrylated epoxy difunctional polyesters and as such are often described as a cross between polyester and epoxy resins. In fact, both the mechanical properties and the price of vinyl esters fall between those of polyesters and epoxies, but vinyl esters outperform both polyesters and epoxies in corrosion resistance and toughness (elongation).

There are many agents that can be selected to facilitate the curing of vinyl ester resins, either at room temperature or at elevated temperatures. Vinyl ester resins cure by free radical polymerization. Therefore, an initiator is required to cure the resin. Usually, organic peroxides, for instance, methyl ethyl ketone peroxide and benzoyl peroxide, can be chosen as the initiator. Other peroxy–type compounds, like peroxyesters, and non–peroxide free radical sources, such as azonitrile compounds, may also be selected. Promoters can be used with organic catalysts to speed curing. The most commonly used promoters are cobalt naphthenate and cobalt octoate. In our study, 2–butanone peroxide (Luperox® DHD–9 from Aldrich) was used as the initiator, and cobalt naphthenate 6%
solution (OMG Americas Inc.) was used as the promoter.

However, if only the above mixture is used as the matrix, it is too viscous to mix in the reinforcement sufficiently. Therefore, in order to mix NGP thoroughly later, n–butyl glycidyl ether (BGE) 95% was selected as a diluent to help disperse the NGP in our study. Butyl glycidyl ether is a common diluent with similar oxirane ring-like epoxy resin molecules. It is usually used to dilute epoxy resin, but in our study it is selected based on the fact that it is naturally a short chain epoxy. Generally speaking, vinyl ester can be toughened by epoxy [73]. Therefore, butyl glycidyl ether is a reactive diluent which can also help improve toughness.

4.1.2 Experimental instrument

Molds:

Rubber molds were used. Silicone Lubricant (Witco Corporation), which is made for plastic and rubber molds, was used for mold release.

4–point electrical resistivity measurement system:

A self–designed 4–point electrical resistivity measurement device (as shown in Fig. 20) with a HP 3457A multimeter (Hewlett Packard) and current source model 227
from Keithley were cooperatively used to measure the electrical properties of the NGP nanocomposites.

Fig. 20. Self–designed 4–point electrical resistivity measurement.

DMA (or DMTA):

Dynamic mechanical analysis (DMA), or dynamic mechanical thermal analysis (DMTA), is a widely used technique in the polymer research area to measure the stiffness
and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. Damping is expressed in terms of Tan δ and is related to the amount of energy a material can store. When conducting DMA measurement, an oscillating force is applied to a sample of material, and the resulting displacement of the sample is measured. From this, the sample modulus, which shows the stiffness of the sample, can be calculated. By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. In addition, by scanning the temperature during a DMA experiment, the glass transition temperature (Tg), which is a very important parameter indicating the transition between the glassy state (high modulus) and the rubbery state (low modulus), can be observed. The DMA technique can often yield better data than DSC (Differential Scanning Calorimetry) and can also be used to investigate the frequency-dependant nature of the transition. DMA can also resolve beta transitions in many materials that the DSC technique is not sensitive enough to pick up.

In our study DMA of NGP/vinyl ester composite was performed on the Perkin–Elmer DMA 7 series in our study to determine the nanocomposite thermomechanical properties, such as storage modulus, loss modulus, damping factor Tan δ, and glass transition temperature Tg. The experiments were carried out on rectangular–shape samples (9 mm * 4.5 mm * 1.5 mm) using the three–point bending mode. A frequency of 1 Hz with a temperature ramp of 5 °C per minute and a scanning
temperature range from 30 °C to 220 °C were employed.
4.2 Experimental procedure

Vinyl ester was first diluted with BGE. The desired mass ratio of diluent to vinyl ester was 3:20. Then the viscosity of the resin mixture is usable for microtip sonication. The NGPs were carefully weighed and placed in the above resin mixture. High energy sonication was performed to disperse NGP uniformly in the matrix at a 25-watt power level for 20 minutes. Then the initiator and promoter were added at the company’s suggested ratios. A vacuum was applied to remove the bubbles. The mixture was cured at room temperature to create the NGP/vinyl ester nanocomposite. The size of each NGP composite sample was about 45 mm * 4.5 mm * 1.5 mm. Each sample was polished, and silver was painted on the contact areas to ensure good electrical contact between the sample and the 4-point electrical resistivity measurement device.
4.3 Results and discussion

4.3.1 Electrical conductivity

The results are summarized in Fig. 21, Fig. 22, Fig. 23, and Fig. 24. The most common reason for making composites is to improve the properties of pure materials. Like most pure resins, vinyl ester is not electrically conductive, and its room temperature electrical conductivity in the dry state is as low as about $10^{-13} – 10^{-16}$ S/cm.

![Graph of electrical conductivity](image)

Fig. 21. Electrical conductivity of NGP (8 hours milling time)/vinyl ester nanocomposite as a function of NGP content.
Fig. 22. Electrical conductivity of NGP (16 hours milling time)/vinyl ester nanocomposite as a function of NGP content.

Fig. 23. Electrical conductivity of NGP (40 hours milling time)/vinyl ester nanocomposite as a function of NGP content.
However, by adding certain amount of fillers, vinyl ester composite can become a semiconductor. The onset of the pronounced transition from an insulator to a semiconductor, according to theory, is called the percolation threshold, which is an essential property of conductive materials and the basis of comparison between different conductive materials [5].

Literature gives percolation thresholds of \(\sim 5\) wt\% for carbon nanofiber (50 nm to 200 nm) composites [87] and between 0.05 to 10 wt\% using CNT composites [88]. From Figures 21, 22, and 23, the percolation threshold value of the NGP/vinyl ester nanocomposite is approximately 0.5 wt\% of NGP, regardless of whether the NGP is made using the 8 hour-ball milling method, 16-hour ball milling method, or 40-hour ball milling method. This value is much lower than that of conventional conducting composites [2, 74, 75]. And it takes more than 50 wt\% of graphite powder (20 μm diameter) filler to get this high electrical conductivity.

It is well known that graphite has excellent combined mechanical and electrical properties, as stated in Chapter 2. In addition, single crystal graphite has a high aspect ratio (width to thickness) in the range of 100 – 1000 [76]. The theoretical surface area of a graphite sheet is 2630 m\(^2\)/g – 2965 m\(^2\)/g [7, 77, 78]. NGPs not only inherit those conventional merits, but also exhibit those extraordinary and exclusively characteristics of nano materials. The low percolation threshold is attributed to those excellent integrated
properties.

The dispersion of the fillers, the geometry of the fillers, and their size are the three main dominating factors influencing the formation of the conducting network, which are directly reflected by the percolation threshold. In Ko, Frank K’s research paper [86], conductivity increased two orders of magnitude when the fiber diameter decreased from 260 nm to 140 nm. For our NGP/vinyl ester nanocomposites, adding a diluent to the vinyl ester resin and using high energy sonication both contribute to the uniform dispersion of the conducting fillers—NGPs. The sheet–like geometry with a high aspect ratio has unique advantages in forming conducting paths. Therefore, NGP/vinyl ester nanocomposite has better electrical conducting properties than conventional composites.

![Fig. 24. Ball milling time’s effect on electrical conductivity.](image)
Figure 24 shows the impact of ball milling time on the electrical conductivity of NGP/vinyl ester composite. From the chart, we can see that longer ball milling time does not necessarily result in NGPs with good electrical conducting properties. The reason for this may be because of ball milling-induced amorphisation [57, 59, 79].

4.3.2 Dynamic mechanical thermal properties

The DMA data show the mechanical thermal dynamic response of the material as a function of the temperature. As shown in Figure 25 to 31, at 30 °C, all the NGP/vinyl ester nanocomposites show higher storage modulus than the vinyl ester resin. In Fig. 27, the 5 wt% NGP/vinyl ester nanocomposite even shows about a 50 % higher storage modulus than the pure vinyl ester resin. As the temperature increased, both vinyl ester resin and NGP/vinyl ester composite exhibit a sudden drop in the glass-transition region, which corresponds to the material transition from a glassy state to a rubbery state. As a matter of fact, the graphite platelet/epoxy nanocomposites also appear to have a consistently higher storage modulus over pure epoxy [6]. It is obvious that the effect of NGPs is more pronounced on the viscoelastic behavior.
Fig. 25. Storage modulus of NGP (8 hours milling time)/vinyl ester composite with 0.1 wt %, 0.5 wt %, 1 wt% and 5 wt% NGPs.

Fig. 26. Storage modulus of NGP (16 hours milling time)/vinyl ester composite with 0.1 wt %, 0.5 wt %, 1 wt% and 5 wt% NGPs.
Fig. 27. Storage modulus of NGP (40 hours milling time)/vinyl ester composite with 0.1 wt %, 0.5 wt%, 1 wt% and 5 wt% NGPs.

A comparison of Figures 28 to 31 shows a much higher improvement in the storage modulus at high NGPs loading, especially for the NGPs that are manufactured using 40 hours ball milling time. NGPs produced using 8 hours ball milling and 16 hours ball milling appear to show a similar storage modulus trend.
storage modulus of 0.1% NGP/vinyl ester composite with NGP produced using different milling time

Fig. 28. Comparison of storage modulus of 0.1 wt% NGP/vinyl ester nanocomposite with NGP produced using 8 hours, 16 hours, and 40 hours ball milling time.

storage modulus of 0.5% NGP/vinyl ester composite with NGP produced at different milling time

Fig. 29. Comparison of storage modulus of 0.5 wt% NGP/vinyl ester nanocomposite with NGP produced using 8 hours, 16 hours, and 40 hours ball milling time.
storage modulus of 1% NGP/vinyl ester composite with NGP produced at different milling time

Fig. 30. Comparison of storage modulus of 1 wt% NGP/vinyl ester nanocomposite with NGP produced using 8 hours, 16 hours, and 40 hours ball milling time.

storage modulus of 5% NGP/vinyl ester composite with NGP produced at different milling time

Fig. 31. Comparison of storage modulus of 5 wt% NGP/vinyl ester nanocomposite with NGP produced using 8 hours, 16 hours, and 40 hours ball milling time.
Fig. 32. Comparison of tan δ between vinyl ester resin and NGP (produced by 8 hours ball milling)/vinyl ester nanocomposite.

Fig. 33. Comparison of tan δ between vinyl ester resin and NGP (produced by 16 hours ball milling)/vinyl ester nanocomposite.
Fig. 34. Comparison of tan δ between vinyl ester resin and NGP (produced by 40 hours ball milling)/vinyl ester nanocomposite.

The tan δ plot more clearly shows the change of composite Tg than storage modulus plot. The tan δ of NGP/vinyl nanocomposite as shown in Figures 32 to 34 indicates a shift of Tg to higher values by as much as 10 °C in comparison with pure vinyl ester resin. In fact, pure vinyl ester resin only has as low as 20 °C to 60 °C Tg temperature if cured at room temperature [80]. However, adding NGPs is useful to improve the thermal properties of the material. In addition, the improvement of Tg is generally attributed to good adhesion between the polymer and the reinforced particles so that the nanometer size particles can restrict the segmental motion of cross–links under loading [81, 82]. Through the acid treatment of natural graphite, oxygen-containing
functional groups, which are useful to both physical and chemical interaction between graphite and polymer, are generated [5, 32].

Fig. 35. Comparison of loss modulus between vinyl ester and 0.1 wt% NGP/vinyl ester nanocomposite.
loss modulus of 0.5% NGP/vinyl ester composite with NGP produced at different milling time

![Graph showing loss modulus comparison between vinyl ester and 0.5 wt% NGP/vinyl ester nanocomposite.](image)

Fig. 36. Comparison of loss modulus between vinyl ester and 0.5 wt% NGP/vinyl ester nanocomposite.

loss modulus of 1% NGP/vinyl ester composite with NGP produced at different milling time

![Graph showing loss modulus comparison between vinyl ester and 1 wt% NGP/vinyl ester nanocomposite.](image)

Fig. 37. Comparison of loss modulus between vinyl ester and 1 wt% NGP/vinyl ester nanocomposite.
Fig. 38. Comparison of loss modulus between vinyl ester and 5 wt% NGP/vinyl ester nanocomposite.

The DMA data in Figures 35 to 38 compare the loss modulus between vinyl ester and NGP/vinyl ester nanocomposite. At low concentrations of NGP (0.1 wt% and 0.5 wt %), the loss modulus does not change much. However, with increasing NGP content, there is an obvious increase of NGP composite compared to that of pure vinyl ester. This indicates that the energy dissipation from viscoelastic deformation of NGP/vinyl ester nanocomposite is also improved upon the addition of NGP. Similar results are also reported by Zheng, W. et al for PMMA/expanded graphite nanocomposites [5].
Fig. 39. Comparison of coefficient of thermal expansion between vinyl ester and NGP/vinyl ester nanocomposite with different NGP content.

Using Perkin–Elmer DMA 7 series under constant force mode, the position of the tip was also recorded. From the calculation of the tip position change, the coefficient of thermal expansion (CTE) was briefly estimated. The results are shown in Fig. 39. With increasing concentration of NGP, the CTE of the nanocomposite decreases, indicating good bonding between the nanoreinforcements and the matrix.
Conclusions

The combination of low density and mechanical, thermal, and electrical properties of graphite has attracted more and more attention to the investigation of multifunctional polymer-based nanocomposites in recent years. Based on our experiments and data analysis, the following conclusions are obtained:

1. The acid mixing ratio and intercalation reaction time greatly affect the graphite expansion ratio. This directly influenced the number of nano graphene layers in each stack. In our work, for the fourth acid treatment method (graphite: H$_2$SO$_4$ :HNO$_3$ mixed weight ratio is 1:10.3:2.1 — H$_2$SO$_4$;HNO$_3$ mixed volume ratio is 4:1), reaction time of 21 hours was found to be the best, which was not previously described in the literature. And with the aid of TGA to check the results, 900 °C with 2 minutes oven time is the best expansion condition for acid intercalated graphite.

2. Comprehensively comparing the available nano material production and processing methods—varying energy levels of sonication with different sonication medium and ball milling—acetone was found to be a good sonication medium for breaking up expanded graphite worm-like structures. Ball milling is still the most convenient method for mass fabrication of NGP.

3. 4–point electrical resistivity measurement data of NGP/vinyl ester nanocomposite clearly show a much lower percolation threshold with the addition of NGP vs.
graphite powder. And 16 hours ball milling time is found to be a suitable duration for producing NGPs, reflected by the electrical conductivity of the composites produced using the NGP samples.

4. With increasing NGP concentration, the storage modulus, Tg, and loss modulus of NGP/vinyl ester nanocomposite all improved. Because the intrinsic mechanical properties of natural graphite make NGP a good reinforcement material, composite using NGPs would have improved stiffness and damping properties.

5. The thermal expansion coefficient of NGP/vinyl ester nanocomposite appears to decrease with the addition of NGPs. This could be due to the bonding between NGP and the resin. The low thermal expansion coefficient of NGPs restricts the expansion of resin, which would otherwise have a higher thermal expansion coefficient.
Suggestions for Future Work

The work in this thesis is just a small corner of the iceberg for nano graphene plate (NGP). This new nanoscale material, which has excellent integrated thermal, mechanical, and electrical properties, is beginning to draw more and more attention. It has properties similar to carbon nano tubes (CNT) but with much lower production costs. Research similar to that in the CNT field should also be conducted for NGPs, especially concerning the issues of dispersion and functionalization.

Nanocomposite of NGPs with different polymers and chemicals combinations, such as nano graphene fabric, are also promising. Hopefully, the thin and lightweight characteristics of NGP can bring about amazing electrical devices.
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