FRICION AND WEAR BEHAVIOR OF GRAPHENE REINFORCED EPOXY

Thesis

Submitted to

The School of Engineering of the

UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for

The Degree

Master of Science in Materials Engineering

By

Debora Daloia

UNIVERSITY OF DAYTON

Dayton, Ohio

August, 2014
FRICTION AND WEAR BEHAVIOR OF GRAPHENE REINFORCED EPOXY

Name: Daloia, Debora

APPROVED BY:

Khalid Lafdi, Ph.D.  
Advisory Committee Chairman  
Professor  
Department of Materials Engineering

Vinod K. Jain, Ph.D.  
Committee Member  
Professor  
Department of Mechanical & Aerospace Engineering

Donald A. Klosterman, Ph.D.  
Committee Member  
Associate Professor  
Department of Chemical & Materials Engineering

John G. Weber, Ph.D.  
Associate Dean for Graduate Studies  
School of Engineering

Tony E. Saliba, Ph.D.  
Dean, School of Engineering  
& Wilke Distinguished Professor
ABSTRACT

FRICITION AND WEAR BEHAVIOR OF GRAPHENE REINFORCED EPOXY

Name: Daloia, Debora
University of Dayton

Advisor: Dr. Khalid Lafdi
Co-advisor: Dr. Vinod K. Jain

The focus of this study was to investigate the effect of graphene content on physical, mechanical, and tribological behavior of epoxy resin. Four composite samples, consisting of 0, 1%, 5%, and 10wt% graphene were fabricated using a 3 roll mill for dispersion and heat press for curing. Friction and wear tests were conducted on a laboratory scale tribo-test dynamometer, using a ring-on-flat configuration, for one hour duration at an average sliding speed of 0.3 m/s under a variable pressure of 0.26 to 0.39 MPa. Dynamic mechanical analysis (DMA) was used to determine the storage and loss moduli and contact angle measurements were determined to compute the surface energy of worn and unworn composite samples. Scanning electron microscopy and polarized light microscopy was used to study the graphene dispersion in the epoxy and study the wear mechanisms. In addition, electrical conductivity was measured to determine the percolation threshold and as an alternate method to verify the graphene dispersion in the epoxy.
The tests indicate that storage modulus and surface energy increased by 62.5% and 55% respectively with graphene content. The tribological behavior of graphene composites showed that this nanofiller was very effective in stabilizing the coefficient of friction and reducing wear rate as well. Neat epoxy showed a high wear rate and an unstable coefficient of friction. On the other hand, 5wt% of graphene exhibited the highest stable coefficient of friction. The improvement on wear resistance was remarkable, for example, the 10wt% composite resulted in a wear reduction of almost 98% when compared with the neat epoxy. It may be noted that the manufacture of graphene based composites was relatively easy, quick, and inexpensive while the samples exhibited improvements in many relevant properties.
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Khalid Lafdi, for his guidance through the course of this research and for his advices and insights throughout this project. Additionally, I want to thank Dr Vinod K. Jain (co-advisor), who has always been willing to share with me his time and knowledge, for his abundant support, critical comments, and correction of the thesis. I also thank Dr Donald Klosterman who accepted being a member of my thesis committee and for his help in the first stage of my work when I was deciding the polymer that would be used as base of my research.

I would like to thank the faculty and staff of the Chemical Engineering Department, I am most grateful to Mr. Matthew Boehle for his excellent technical assistance in the lab, particularly for his help in building and setting up some key machines, which were essential for my research.

I owe my deepest gratitude to ZF Group – Brazil Division for giving me the opportunity to conduct this research and for providing technical and financial support. I am very grateful to Mr. Paulo Zanotto and Mr. Walter Haertel for all of their support, encouragement and opportunity for professional growth. I would like to thank the Friction Material’s team of Research and Development Group, especially Mr. Ivan Gregori and Graciliano Fernandes, for all the technical discussions. I also thank the
Chemical laboratory team, for their prompt help with tests in laboratory. Finally, I would like to thank my family and friends, in particular my parents and sister, for their unending love and continuous support and encouragement. Then, I want to thank God for wisdom and perseverance that He has bestowed upon me and for all that He helped me to conquer in my life so far.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iv
ACKNOWLEDGEMENTS ................................................................................................................. vi
TABLE OF CONTENTS ................................................................................................................... viii
LIST OF FIGURES ........................................................................................................................ x
LIST OF TABLES ........................................................................................................................ xii
LIST OF ABBREVIATIONS AND NOTATIONS ........................................................................... xiii
CHAPTER
I. INTRODUCTION .......................................................................................................................... 1
   1.1 Background ....................................................................................................................... 1
   1.2 Friction and Wear ............................................................................................... 2
       1.2.1 Friction and Wear Behavior of Reinforced Polymers ...................... 3
   1.3 Graphene ..................................................................................................................... 6
       1.3.1 Atomic Structure ...................................................................................... 6
       1.3.2 Graphene Production ........................................................................ 8
       1.3.3 Production of Graphene Reinforced Composites .......................... 9
       1.3.4 Properties of Graphene Composites ............................................. 11
   1.4 Friction and Wear of Nanocomposites ................................................................. 13
       1.4.1 Effect of Particle Size on Wear of Composites ......................... 14
       1.4.2 Role of Nanofiller Concentration .................................................. 16
       1.4.3 Tribology of CNT and CNF Filled Composites ......................... 17
       1.4.4 Friction and Wear of Graphene Composites ............................. 20
II. EXPERIMENTAL ...................................................................................................................... 23
   2.1 Sample Preparation ................................................................................................. 23
   2.2 Graphene Dispersion ......................................................................................... 30
LIST OF FIGURES

1.1 Layered structure of graphite showing the sp² hybridized carbon atoms tightly bonded in hexagonal rings ................................................................. 7
1.2 Comparison of thermal conductivity of graphene, CNT and graphite .................. 7
2.1 Molecular formulas of (a) Epoxy, Epon 862 and (b) curing agent, Epikure W... 24
2.2 (a) Lehman Mills three roll mixer, (b) schematic of the rolls ............................ 29
2.3 Two-piece mold, window frame and baseplate .................................................. 29
2.4 Three-point bending test configuration ............................................................ 33
2.5 Definition of contact angle .............................................................................. 36
2.6 Measurement of the contact angle between the water drop and composite plate ..36
2.7 Test dynamometer (a) spindle (b) metallic counterface ring (c) sample holder .. 40
2.8 Typical profile of a wear scar ........................................................................... 40
3.1 Optical micrographs of graphene filled epoxy. Arrows indicate the graphene locations. Graphene concentration (a) 1wt%, (b) 5wt% and (c) 10 wt% .. ............ 43
3.2 Overview nanocomposite fracture surfaces showing the graphene dispersion, with graphene content of (a) 1wt%, (b) 5wt%, and (c) 10wt%... ................................. 44
3.3 Enlarged view of nanocomposite fracture surfaces showing graphene morphology, with graphene content of (a) 1wt%, (b) 5wt%, and (c) 10wt%... .......................... 45
3.4 Average values of electrical conductivity for 5wt.% of and 10wt.% of graphene 48
3.5 Storage modulus of the graphene nanocomposites ............................................. 52
3.6 Estimated and experimental storage modulus of graphene nanocomposites based on the Rule of Mixtures ................................................................. 52
3.7 Comparison of estimated Halpin-Tsai model and experimental storage modulii of graphene nanocomposites ................................................................. 53
3.8 Tan$\delta$ of the graphene nanocomposites as a function of temperature .......... 55
3.9 Peak factor for graphene compounds ............................................................... 57
3.10 Contact angle for graphene nanocomposites .................................................. 60
3.11 Surface energy for graphene nanocomposites ............................................... 60
3.12 Coefficient of friction of neat epoxy ............................................................... 64
3.13 Picture of the neat epoxy wear track showing the presence of blackened areas... 64
3.14 Variation of coefficient of friction as a function of time (a) epoxy, 1wt.%graphene and 10wt.%graphene and (b) 5wt.%graphene and 10wt.%graphene ......... 65
3.15 Variation of coefficient of friction with graphene concentration ................. 66
3.16 Variation of depth of wear scar ..................................................................... 68
3.17 Wear track (a) pure epoxy (b) 1wt% of graphene composite (c) 5wt% of graphene composite (d) 10wt% of graphene composite ........................................... 72
3.18 SEM Analysis of wear debris (a) neat epoxy (b) 1wt% of graphene composites (c)5wt% of graphene composites (d) 10wt%of graphene composites............. 74
LIST OF TABLES

2.1 Feed roller speed................................................................. 27
LIST OF ABBREVIATIONS AND NOTATIONS

A_o  Area of contact
Ag  Silver
Al  Aluminum
Al_2O_3  Aluminum Oxide
BSCCO  Bismuth Strontium Calcium Copper Oxide
c  Composite
CaSiO_3  Wollastonite
CNF  Carbon Nanofiber
CNT  Carbon Nanotubes
COF  Coefficient of Friction
CVD  Chemical Vapor Deposition
DETDA  Diethyl Toluenediamine
DMA  Dynamic Mechanical Analysis
DSA  Drop Shape Analysis System
E  Young’s Modulus
E’  Modulus of Elasticity
$E_{\text{adh}}$  Total Energy per Surface Area

$E_c$  Storage Modulus

$E_g$  Storage Modulus of the Nanofiller

$E_m$  Storage Modulus of the Polymer Matrix

Epon 862  Diglycidyl Ether of Bisphenol F

F  Friction Force

f  Filler

hBN  Hexagonal Boron Nitride

H/W  Height-Width method

L  Normal Force

LDH  Layered Double Hydroxyl

LDPE  Low Density Polyethylene

$l_g$  Length

m  Matrix

MoS$_2$  Molybdenum Disulphide

MWCNT  Multi-Walled Carbon Nanotubes

Ni  Nickel

NiS  Nickel Sulfide

PbSe  Lead Selenide

PEEK  Polyether ether ketone

PET  Poly(ethylene terephthalate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phr</td>
<td>Per Hundred of Resin</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl Methacrylate</td>
</tr>
<tr>
<td>PPDT</td>
<td>Poly-p-penyleneeterephthalamide</td>
</tr>
<tr>
<td>PPS</td>
<td>Polyphenylene Sulfide</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>r</td>
<td>Average Radius of the Ring</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Surface Roughness</td>
</tr>
<tr>
<td>SCF</td>
<td>Short Carbon Fibers</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>Silicon Nitride</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Oxidized Silicon</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>T</td>
<td>Torque</td>
</tr>
<tr>
<td>$\tan\delta$</td>
<td>Loss Factor</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>$t_g$</td>
<td>Thickness</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra-High Molecular Weight Polyethylene</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume Fraction</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Volume Fraction of nanofiller in the nanocomposite</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>Zirconium Oxide</td>
</tr>
<tr>
<td>$\alpha_g$</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Peak Factor</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>Volumetric Packing Fraction</td>
</tr>
<tr>
<td>$\gamma_L$</td>
<td>Liquid Surface Energy</td>
</tr>
<tr>
<td>$\gamma_S$</td>
<td>Solid Surface Energy</td>
</tr>
<tr>
<td>$\gamma_{SL}$</td>
<td>Liquid-Solid Surface Energy</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Coefficient of Friction</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact Angle</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

1.1 Background

The use of polymers and polymer composites in a wide variety of tribological applications, e.g. seals, prosthetic joints, gears, tires, dry bearings, brake pads and clutches has been continuously increasing [1]. One of the most challenging applications of these materials is in automotive parts such as brake pads and clutch plates. Clutch and brakes are used to perform the same function. For example, in the case of a clutch, the initial condition is that the driving member rotates and the driven member is at rest, after the clutch is engaged, both the members rotate at the same speed. In a brake, the drum rotates, whereas the braking member is at rest. After the brake is applied both the members are at rest. It may be noted that in both cases the two members having some relative speed are brought to the condition of zero relative speed by the use of either a brake or a clutch. Thus, the function of brakes and clutches is similar [2]. The sliding process between the two members results in energy loss and temperature rise at the interface of friction material.
Note that both these applications demand high and stable friction, low wear, and noise- and vibration-free performance of automobile for reasons of comfort and durability at affordable cost [3].

1.2 **Friction and Wear**

The friction and wear processes for the polymers and polymer composites are complex due to the interaction of two or more materials in the fracture process leading to the formation of a wear particle. There are four basic mechanisms: adhesion, abrasion, corrosion and surface fatigue, which are commonly used to explain the wear of these materials. In adhesive wear situation, adhesive bonding at the asperity contacts occurs between two sliding surfaces and the fragments from weaker of the two materials are generally removed. Abrasive wear is produced as result of the penetration and ploughing of the softer material by the asperities on the harder counterface. Corrosive wear arises due to thermal or thermo-oxidative degradation of polymers resulting in the formation of highly-reactive low-molecular weight compounds. Fatigue wear is usually associated with the localized fatigue on an asperity scale and is being increasingly recognized as an important wear mechanism.

Friction is the resistance to motion that exists when a body is moved tangentially with respect to the surface of another body or when an attempt is made to produce such a motion. Three laws of sliding friction have been proposed:

1. The friction force $F$ is proportional to the normal force $L$: $F \propto L$

2. The friction force is independent of the apparent area of contact $A_0$. Thus, large and small objects have the same coefficients of friction.
3. The force required to initiate sliding between two bodies will be the same as the force to maintain sliding at any specified velocity.

Of these rules, the first two were proposed by the French physicist Guillaume Amontons and the third one was proposed by Coulomb. It must be remembered that the precision of these laws is often not high and there are exceptions when these laws do not apply. A brief literature survey on the friction and wear behavior of several filled and reinforced polymer composites was conducted and is discussed in the following sections.

1.2.1 Friction and Wear Behavior of Reinforced Polymers

A number of workers have studied the tribological behavior of polymers and polymer composites due to their lightweight, wear, corrosion and solvent resistance, self lubrication, easy moldability and machining characteristics [1]. However, polymers have low thermal stability and poor mechanical strength, which affect their tribological performance at high loads, large sliding speeds and temperature. This problem is over come by reinforcing polymers with fillers and/or fibers to improve their tribological behavior. For example, the reinforcement with short fibers (glass or carbon) is mostly used to increase their mechanical strength, consequently the load capacity. Solid lubricants such as polytetrafluoroethylene (PTFE), graphite, and molybdenum disulphide (MoS₂) are added to polymers to improve the formation of the transfer films on the counterface, to reduce wear and stabilize the coefficient of friction (COF) [4].

Short carbon fibers (SCF) are a good option to reinforce polymers because they have a graphitic structure and the wear debris is less abrasive than that of glass fibers.
Lancaster [5] suggested that incorporation of high aspect ratio filler such as carbon or glass fibers to polytetrafluoroethylene (PTFE) can improve the polymer wear resistance because these fibers support part of the load applied on the composite material. In the case of SCF, the wear performance is governed mainly by the process of fiber thinning, cutting and pulling out of the matrix [6]. Zang et al. [6, 7] explored the wear performance of epoxy resin filled with SCF, graphite, PTFE and nano-TiO2 (titanium dioxide). The results showed that the best wear resistance was reached by a combination of epoxy + 15 vol% graphite +5 vol%nano-TiO2 + 15vol% of SCF. For this composite, the wear rate was about 100 times lower than that for the neat epoxy. They concluded that the wear performance of SCF reinforced composites was strongly related to the formation of a thin uniform transfer film on the counterface. Khedkar et al. [8] investigated the tribological behavior of PTFE and PTFE filled with MoS2 and reinforced with glass and poly-p-phenyleneterephthalamide (PPDT) fibers. They found that filler addition increased the hardness and wear resistance of all the composites. In the presence of glass fibers, MoS2 particles were found to be very effective in improving the wear properties of PTFE; while PPDT fibers were effective in interrupting large-scale fragmentation due to their high aspect ratio and favorable mechanical properties. They concluded that wear process in composites mainly depends on three factors: thermal conductivity, thermal stability and the characteristics of the filler materials.

Graphite is extensively used as a lubricant in friction materials. Many types of graphite are available today, including the naturally occurring graphite flakes and several synthetic forms of graphite that can have an even higher structural perfection [9]. Bahadur and Tabor explored the effect of polar graphite as a filler in PTFE. The graphite
reduced the wear rate of PTFE by a factor of about 100 and increased the coefficient of friction by about 30%. The filler produced fine wear particles and a uniform and coherent transfer film. The unfilled PTFE presented fragmented sheets of worn material and the transfer film was patchy and loosely bonded to the surface. The reduced wear rate of filled PTFE was attributed to changes in shape and size of the wear particles, their bonding to the counterface, and the relative ease with which they were dislodged during sliding [10]. Other study evaluated the tribological effect of PTFE powder and graphite flakes filled epoxy. The results showed that both solid lubricants positively contributed to the development of transfer films, reducing the wear rate of the composites; but the transfer films were quite different. For PTFE filled epoxy, a thick transfer film was observed; that reduced the running-in period, while for graphite the transfer film was rather compact and smooth with many thin graphite flakes [11].

Suresha et al. [12] studied the influence of graphite on wear behavior of epoxy composites reinforced with carbon fabric. They found that the wear resistance increased with the addition of graphite, even more, higher loads showed better results. In unfilled composites, carbon fibers were pulled out of the epoxy matrix due to debonding at the worn surface. The improved wear resistance of graphite filled composites was attributed to carbon - graphite interaction and uniform dispersion of filler in the composite. Kadiyala et al [13] investigated the tribological behavior of two epoxy composites: epoxy treated with graphite fabric and epoxy + graphite fabric treated with hexagonal boron nitride (hBN). Scanning electron microscopy (SEM) showed the transfer of uneven film for the fabric graphite composite, which resulted in high coefficient of friction for this
compound. The composite reinforced with hBN treated graphite fabric exhibited low wear and low COF and produced a thin uniform film of carbon.

1.3 Graphene

1.3.1 Atomic Structure

The layered molecular structure of graphite crystallites is compared to a deck of cards [14, 15], where each card is a single layer of graphite with carbons atoms covalently bonded in sp\(^2\) configuration to three other carbon atoms. This individual “card” is graphene, that is, a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice, as showed in Figure 1.1. Graphene is a substance, which has the highest surface area per unit mass, and it is even superior to carbon nanotubes and fullerenes [16]. Graphene is also one of the stiffest known materials with a Young’s modulus of approximately 1TPa. Since graphene does not have interlayer interaction as in graphite, graphene’s thermal conductivity is even higher than graphite, and similar to carbon nanotubes (CNT) at certain temperatures (Figure 1.2).
Figure 1.1  Layered structure of graphite showing the sp² hybridized carbon atoms tightly bonded in hexagonal rings [17]

Figure 1.2  Comparison of thermal conductivity of graphene, CNT and graphite [18]
1.3.2 Graphene Production

Initially, graphene was considered thermodynamically unstable because it tends to form curved structures, such as, fullerenes and nanotubes. In general, 2-D materials are rarely found in nature because of their instability, however in 2004, graphene and other 2D atomic crystals, such as boron nitride and half-layer bismuth strontium calcium copper oxide (BSCCO) were experimentally discovered. These crystals were obtained on top of non-crystalline substrates as suspended membranes in a liquid suspension [19]. Novoselov and Geim [20] obtained single and few layers of graphene using a simple cleavage process. This method for preparation of graphene sheets is called “Scotch tape method”. They used adhesive tape to peel graphene layers off from bulk graphite and then repeatedly peeled off further layers from the original cleaved flake until they managed to get down to flakes that were only a few atoms thick. The graphene layers were then transferred onto an oxidized silicon (SiO$_2$) wafer [20, 21]. The SiO$_2$ electrically isolates the graphene and weakly interacts with it, providing nearly charge-neutral graphene layers. They found that by repeated sticking and peeling back the Scotch tape, the graphene sheets are pulled apart leading to a single-layer of graphene sheets or a few layer thick graphene sheets. In spite of the simplicity of this process, its use is limited to experimental applications because the amount of graphene obtained from this method is not adequate for macro-scale applications.

Currently, graphene is produced by two approaches: (i) top-down, it is a low cost production based on mechanical exfoliation of bulk graphite (“Scotch tape” method); (ii) bottom-up, allows extensive tuning of the properties by chemical synthesis approach. The top-down technique includes micromechanical exfoliation of graphite and creation of
colloidal suspensions, whereas the bottom-up methods include CVD (Chemical vapor deposition) and epitaxial growth on electrically insulating surfaces. Among these methods, the chemical method where graphite oxide is converted to graphene has received significant attention, because this method allows large-scale production of graphene at relatively low cost [22].

1.3.3 Production of Graphene Reinforced Composites

Use of graphene in polymer matrices has been attracting great interest from academic and industrial communities. Graphene based polymer composites combine the unique properties of graphene with the benefits of polymers, such as exceptional specific modulus, specific strength and easy processability. The main methods for preparing the graphene-nanocomposites include in situ intercalative polymerization, solution intercalation, and melt intercalation.

In situ intercalative polymerization consists of mixing the nanofiller with neat monomer, polymerization of the mixture, and finally precipitation/ extraction or solution casting is used to produce the finished product. This method achieves a high level of dispersion of graphene in the matrix [23] and is used to produce several nanocomposites, such as, polystyrene (PS)/graphene, polymethyl methacrylate (PMMA)/expanded graphite, poly(styrene sulfonate) (PSS)/ layered double hydroxyl (LDH), polyimide (PI)/LDH, and poly(ethylene terephthalate) (PET)/LDH [24].

Solution intercalation is the most popular method to produce polymer nanocomposites [23]. Here, the polymer is solubilized, then mixed with the solution of
the dispersed suspension of graphene, when the mix is complete, solvent is removed and the compound is molded to create the sample. However, environmental pollution is an issue in this case, that needs to be considered when choosing this method. The use of large amount of solvent and later their removal and disposal have prevented the adoption of this technique due to environmental concerns on a mass scale for the fabrication of composites [17].

Melt intercalation technique utilizes shear forces to disperse the nanofillers in the polymer matrix. Traditional mixing equipment, such as, extruder, internal mixer, or three roll mill can be used for the melting and blending operations. This process is environmentally friendly (does not need the use of toxic solvents), cost effective and is the preferred for industrial applications. On the other hand, this method is less effective in dispersing graphene when compared to solution intercalation or in situ polymerization, because of increase in viscosity due to high filler concentration. Combination of mixing and blending techniques can be a solution to take care of increase of viscosity.

The interfacial adhesion between graphene and polymer matrix is improved by functionalization of the nanofillers. Here, graphene oxide sheets are heavily oxygenated, which modify the van der Waals interactions, becoming more compatible with the polymer matrix [25, 26]. Thus, modified graphene surface shows better dispersion in a polymer matrix. For example, Yang et al. [27] used a coupled hydrogen passivation and ultrasonication technique to improve the dispersion of graphene sheets in epoxy matrix. They found that the inlet hydrogen atoms in the hydrogen passivation served as a source of the second atom to terminate the carbon dangling bonds and form more stable C-H bonds, separating graphene flakes and promoting the binding with the matrix material. As
a result the composite material had a large increase in elastic modulus, fracture strength, and fracture energy.

1.3.4 Properties of Graphene Composites

Graphene is an attractive alternative to other carbon nanofillers (CNT, CNF (Carbon nanofiber), etc) and some of its advantages are: it is easy to produce and is very cost effective [28]. Graphene’s price is between $10/lb to $15/lb while CNT ranges from $100/lb to $750/g depending on the quality and purity of the material [29]. Graphene has been applied in several fields such as, display screens, electric circuits, solar cells and medical, chemical and industrial processes due to its unique physical, chemical, and electrical properties. Graphene filled polymer nanocomposites show superior mechanical, thermal, electrical and flame retardant properties compared to other nanocomposites [30].

Addition of graphene into polymer resins improves mechanical properties such as tensile strength, Young’s modulus, fracture, toughness and resistance to fatigue. The improvement in fracture and fatigue properties of graphene composites is mainly due to its high aspect ratio, which provides them a good resistance to propagation of cracks and absorption of great amount of energy. Graphene’s rough and wrinkled surface improves the interlocking with the surrounding matrix enhancing load transfer. Moreover, the large, planar surface area of graphene increases the contact with the polymer matrix and the two-dimensional plate geometry of graphene provides greater tolerance to in-plane misalignment between the loading direction and the nanofiller orientation [31].
Graphene has exceptional thermal properties, and when combined with polymers, it can improve the thermal stability and conductivity of the polymer matrix. Improvements in thermal conductivity were achieved in graphene nanocomposites, with conductivities increasing from 0.2W/mK for neat epoxy to 3~6W/mK for a graphene concentration of 20wt% [32]. The effect on the thermomechanical properties of the matrix depends on the work temperature. For temperatures below the glass transition temperature ($T_g$) of the polymer, sufficient interactions between the polymer chains and the filler occurs. On the other hand, for temperatures above $T_g$, the graphene interaction with the polymer diminishes due to the higher mobility of epoxy chains. In addition, $T_g$ is expected to increase when the filler-matrix adhesion is strong, whereas a decrease in $T_g$ is expected for weakly adhering fillers due to decreased and enhanced mobility of polymer chains in the interfacial region [31].

Graphene has an excellent electrical conductivity, and it may greatly improve the electrical conductivity of the polymer composite. However, the graphene concentration must exceed the electrical percolation threshold to obtain a conductive network in the polymer matrix. The electrical performance depends on the dispersion and alignment of the filler. However, a high level of dispersion does not necessarily promote the onset of electrical percolation. The reason is that a thin layer of polymer may coat on the well-dispersed fillers and avoid the formation of a conductive network. The electrical conductivity of the nanocomposites is related to the aspect ratio of the graphene, higher the aspect ratio, higher the conductivity. In contrast, wrinkled, folded, or other non-flat morphologies may increase the electrical percolation threshold [32].
1.4 Friction and Wear of Nanocomposites

Nanoparticle fillers have been investigated as a way to improve the wear resistance of polymers. Due to the higher surface area to volume ratio than for microsize particles, physical and chemical properties of the nano materials are controlled more by their surface characteristics than by the bulk. The benefits of nanoparticles in comparison to microparticles additives on the wear behavior of polymers are: (1) nanoparticle has lower angularity, it reduces abrasiveness; (2) improve reinforcement of the polymer matrix, due to enhanced mechanical properties of nanoparticles, such as, strength, modulus, and toughness; (3) higher specific surface areas and thus, improved adhesion; (4) high effectiveness at very low contents [9].

The improvement on wear resistance of nanocomposites can be explained by three different mechanisms. First, the presence of nanoparticles in the matrix improves the toughness, leading to reduced wear by sub-surface fatigue or asperity plowing actions. The second is related to the increase in the thermal conductivity of the composite compared to the pristine polymer. When the composite has a high thermal conductivity the frictional heat generated at the interface is transferred to other parts of the machine faster, then lowering the interfacial temperature of the system. The third mechanism is not completely clear, but some researchers noticed that the nanoparticles change the properties of the transfer film, forming a thin and tenacious transfer film.

Wang et al. [33] investigated the influence of nano Si₃N₄ (Silicon Nitride) on friction and wear properties of PEEK (Polyether ether ketone) composite. They found that the filler considerably reduced wear of the composite than that of pure PEEK. A thin,
uniform, and tenacious transfer film was observed on the counterface for the nanocomposite, while the transfer film was patchy and discontinuous for pure PEEK, which was responsible for the higher wear rate. They concluded that the improvement in the tribological behavior of nanocomposite was related to the improved characteristics of the transfer film. Furthermore, the lowest wear rate was obtained for a nanofiller concentration of 7.5 wt%, for samples with higher concentration, the wear rate increased due to the weakened adhesion of the nanocomposite and deterioration in the quality of transfer film.

Zhao and Bahadur [34] studied the tribological behavior of polyphenylene sulfide (PPS) filled with nickel sulfide (NiS) and lead selenide (PbSe). When PPS was filled with NiS the wear rate decreased, while for PbSe filler the wear rate increased. The transfer film for each of the fillers was different: for the unfilled PPS the transfer film was thick and grainy; while for NiS filler, the transfer film was thin and uniform, and a reaction with the counterface was observed, it probably enhanced the adhesion of the transfer film to the counterface. However for PbSe no transfer film was observed and the maximum reduction in wear was obtained with 20-30vol% of NiS.

1.4.1 Effect of Particle Size on Wear of Composites

The effect of filler particle sizes on the wear of polymer composites have been investigated by several workers [35-42]. Olea-Mejia et al. [43] investigated the low density polyethylene (LDPE) composites containing 10wt% micro- and nano-sized particles of aluminum (Al), silver (Ag), and nickel (Ni). They used both the micro- and
nano-particles of Al and Ag while the Ni particles were only micro-size. They observed several wear mechanisms of LDPE wear depending on the type and size of metal particles used: abrasion, delamination, and adhesion. The presence of Al (micro- and nano-) particles lowered the wear rate of LDPE significantly. The wear rate for Ag (micro- and nano-particle filled) and Ni composites was found to more than that of the neat LDPE. They concluded that nanoparticles, when well dispersed, were more effective in reducing the wear than the micro-particles, due to improved reinforcement of the polymer.

Chauhan et al. [37] evaluated the effect of particle size and particle concentration on the tribological behavior of vinylester composites. Cenosphere of three different sizes (21μm, 900nm and 400nm diameter) and concentrations (2, 6 and 10wt%) were used in their research. They found that submicron particles were more effective in improving the wear resistance than micro particles. The best particle content was 6 wt% of submicron particles to reduce the specific wear rate with further increase of particle concentration, the filler agglomerated increasing the wear rate. A similar finding was reported by Wang et al. [42], who analyzed the tribological behavior of PEEK filled with different sizes of nano- zirconium oxide (ZrO₂). They found that wear behavior of the composite improved as the particle size decreased, moreover, the wear of PEEK filled with large size nanoparticle was higher than that of unfilled PEEK. They concluded that the reason for this was the transfer of thick and discontinuous film and its weak adhesion for micro-particle filled PEEK. While for smaller nanoparticles, a thin, uniform and tenacious transfer film was formed on the counterpart surface during the sliding, which reduced the wear of PEEK.
1.4.2 Role of Nanofiller Concentration

The nanofiller concentration plays an important role on the tribological behavior of nanocomposites, usually the optimum filler content ranges between 1 to 4 vol% [35]. At higher contents the nanofillers start to agglomerate, deteriorating the uniformity of dispersion and wear properties of the nanocomposites. Thus, the nano particles have to be uniformly dispersed in the matrix to improve the performance of the nanocomposites. Usually an optimum amount of filler content exists for minimizing the wear rate, while for coefficient of friction the optimum concentration may be altogether different. It can be stated that nanoparticles affect the friction and wear behavior of polymers in different ways and that the filler concentration for a lower coefficient of friction does not necessarily correspond to a decreased wear rate [9].

Wetzel et al. [40] investigated the effect of several concentrations of micro scale wollastonite (CaSiO₃) and nanoparticles of TiO₂ in epoxy matrix. They found that tribological properties are strongly influenced by the volume fraction of fillers and the lowest wear rate was reached at a nano particle content of 4 vol% TiO₂. Afterwards they used this optimized nanocomposite as a matrix for the CaSiO₃ micro-particles, to examine a possible synergistic effect between the micro- and nanoparticles. The wear resistance was remarkably improved at 3 vol% of CaSiO₃, the fillers had a distinct effect on the wear mechanism: nanocomposites undergo a transition from severe to mild abrasive wear due to formation of a compacted wear debris layer that reduce the roughness of the counterface by filling the valleys and protected the composite surface from extreme wear. On the other hand, the large CaSiO₃ particles protruded out of the
matrix and acted as spacers between the composite and counterbody, partially relieving the matrix from severe wear.

### 1.4.3 Tribology of CNT and CNF Filled Composites

Previous research investigating the tribological properties of polymers reinforced with either CNT or CNF showed positive effects on friction and wear behavior, which were related to the formation of continuous, smooth and stable transfer film [44-54]. One study investigated the effect of different concentrations of CNTs on the tribological properties of PMMA. CNT content was varied from 0.05 to 2.5 wt%. COF decreased with increasing CNT content up to 1wt% and then stabilized at higher contents. The incorporation of CNTs also decreased the wear rate of PMMA. The worn surfaces of PMMA and PMMA-1wt% CNTs nanocomposites were analyzed by SEM. They observed different wear mechanisms for each material. Pure PMMA surface showed signs of adhesive and abrasive wear, with a very rough surface displaying plucked and ploughed marks. This phenomenon corresponds to the relatively poor wear resistance of the pure PMMA. In the nanocomposites, the worn surfaces were relatively smooth and uniform, which explains the reason of increased wear resistance of this nanocomposite. During the course of sliding, CNTs are released from the PMMA- matrix and transferred to the counterface. The self-lubricating properties of CNTs resulted in reduction of the wear rate and the friction coefficient [44].

In another study, the effect of CNT on tribological behavior of Ultra-high molecular weight polyethylene (UHMWPE) was explored [45]. It was found that addition
of CNT improved the wear resistance of UHMWPE, but the coefficient of friction increased slightly. The worn surface examined by SEM showed that pure UHMWPE has a smoother worn surface than the composite surface. The pure polymer showed a broader and deep track, whereas the nanocomposite exhibited locally smashed regions, probably due to the CNT addition. These different morphologies of surface damage indicate that CNT reinforcement altered the wear mechanism of the polymer. The increase in coefficient of friction was attributed to the increase in shear strength of the CNT filled UHMWPE. Galetz et al. [54] also investigated the tribological behavior of 10wt% CNF reinforced UHMWPE. In their study, the nanofiber percolation threshold was at lower concentration, 5wt% of CNFs, for higher concentrations they found difficulties in the dispersion of CNF, which affected the tribological performance of the nanocomposite. They concluded that the presence of dispersed CNFs leads to a significant reduction in wear rate of the polymer, but large amount of nanofibers limit this improvement to some extent. Vail et al [50] investigated the influence of single-walled carbon nanotube (SWCNT) on tribological behavior of PTFE. A number of CNT concentrations in PTFE were analyzed: 0, 2, 5, 10 and 15 wt% SWCNT. The addition of SWCNT to PTFE increased the coefficient of friction and decreased the wear rate significantly. Their hypothesis is that the nanotubes effectively immobilized the amorphous regions, arresting crack propagation and disabling the low friction mechanism of PTFE at lower speed. The friction coefficient varied with loading and sliding distance as wear debris and transfer films were generated. At higher sliding speed, SWCNT reduced the speed sensitivity and the coefficient of friction varied by less than 10%. As the filler concentration increased, they observed reduction in debris size, increase in the number of
A debris particle, reduction in transfer film thickness and improvement in its uniformity. At 5wt% SWCNT, the wear resistance improved by more than 20 times and friction coefficient increased by 50%.

Werner et al. [53] studied the influence of CNF on the wear behavior of PEEK. Composite samples with weight fractions ranging from 0 to 15 wt% of CNF were evaluated. The results showed that CNF reduced the wear rate of PEEK significantly. The percolation threshold was found to be 10 wt% of nanofibers, where the nanocomposite showed a smaller wear rate. Possible reasons for the wear reduction were attributed to an increased shear strength of the nanocomposite compared to the pure polymer and the lubricating effect of the CNF. It was observed by SEM that no CNFs were present on the wear surfaces. They concluded that CNF degraded to small graphitic debris particles, which acted as a lubricant similar to graphite flakes. Optical microscopy of worn surfaces of PEEK showed that unfilled polymer had the depositions of polymer debris forming large plaques on the surface. However with addition of CNFs, the nanofiller tended to reduce the agglomeration of the PEEK wear debris, and the sliding surfaces became smoother with increasing CNF content due to the lubricating effect of the nanofibers.

The tribological studies involving the effects of carbon nanofillers to friction materials are fairly limited. Hwang et al. [55] investigated the effect of CNT addition to brake friction materials. The compounds were made substituting barite with 1.7, 4.7 and 8.5 wt% CNT. They found that the addition of CNT improved the thermal and friction stability of friction materials. The wear resistance was also evaluated and the specific wear rate decreased with increasing CNT content, which was attributed to the reinforcing effect of CNT. Lee et al. [56] also observed the same trend, i.e., increasing CNT content
improved wear and thermal stability of the compound. However, in both cases the friction coefficient decreased with increasing content of CNT, probably due to the lubricity of CNT bundles.

1.4.4 Friction and Wear of Graphene Composites

Kotov [57] states “When carbon fibers just won’t do, but nanotubes are too expensive, where can a cost-conscious materials scientist go to find a practical conductive composite? The answer could lie with graphene sheets”. Graphene is the building block of the most common macroscopic graphite, also exhibits excellent friction reduction and wear resistance properties [58]. When graphene is exposed to sliding surface, graphene platelets which are exposed at the surface are easily sheared off due to the stacked layer morphology of graphene. However, this debris can lead to the formation of a stiffer transfer film, effectively providing a stable coefficient of friction over longer periods of time [9].

To date, tribological investigation involving graphene has been quite limited. Studies revealed that the frictional behavior of graphene is related to the number of graphene layers [59-61]. According to this research, the friction of graphene is higher than that of graphite. This relationship was attributed to the interaction of surface attractive forces [59] and the effect of electron-phonon coupling [60]. The lubrication of graphene is related to the bond with the matrix, the strong adhesion between them appears to be most promising from the tribological point of view.
Kandanur et al. [62] examined the wear behavior of graphene reinforced PTFE. The results showed that incorporating 10 wt% of graphene platelets drastically reduced wear rates of PTFE from $0.4 \times 10^{-3}$ mm$^3$/Nm to $10^{-7}$ mm$^3$/Nm for the composite. They also compared the wear behavior of graphene filled polymer with micro graphite filled polymer. The conclusion was that graphene provided 10-30 times lower wear rate than the micro graphite with the same filler concentration. The reason for this improvement in wear can be due to stronger bond between graphene and PTFE and the smaller wear debris sizes of the composites.

Shen et al. [63-64] investigated the tribological performance of graphene in epoxy resin. They used a very low concentrations of graphene (0.05 to 0.5 wt%). The results showed that the wear resistance improved due to the addition of graphene. The specific wear rate was reduced by a factor of 6 – 7 in comparison to the neat epoxy. They attributed this behavior to the high specific surface of graphene, strong graphene-epoxy adhesion, interlocking arising from the wrinkled rough surface of graphene and the enhanced glass transition temperature due to the introduction of graphene. Comparing with other nanofillers such as SiO$_2$, TiO$_2$, Al$_2$O$_3$ (Aluminum Oxide), Si$_3$N$_4$ and carbon nanotubes, the effect of graphene was superior in enhancing the wear resistance of epoxy resins at low concentrations. At the same time introduction of graphene increased the coefficient of friction, which is very useful for application to friction materials.

In another investigation [64], graphene was combined with 0.5 parts per hundred of resin (phr) of multi-walled carbon nanotubes (MWCNTs) to reinforce the epoxy. Results showed that the best hybrid formulation contained 0.5phr of MWCNTs and 0.1phr of graphene. The wear resistance and coefficient of friction increased for this
composition. Here, the specific wear rate reduced by a factor of 11 when compared to neat epoxy resin and the coefficient of friction increased by a factor of 2. Once again, the behavior was attributed to the wrinkled surface morphology of graphene and the wavy morphology of MWCNTs, which might have roughened the surface of the composite. However, the coefficient of friction of the composite decreased when the graphene content was increased to 0.5 phr. This was attributed to the formation of a solid transfer film on the counterpart. Once a uniform and tenacious transfer film is formed, the sliding occurred between the composite block and the transfer film, and not between the rough surface of the composite and the steel counterpart. They concluded that there are two reasons for the improvement on tribological behavior of the polymer when combined with both nanofillers: (i) the dispersion of MWCNTs is greatly improved in the presence of graphene compared to that when only MWCNT is used in the composite, and (ii) the existence of reactive OH and carboxyl groups on the graphene nanosheets, which provided good mechanical interlocking arising from the wrinkled rough surface of graphene and an excellent interfacial adhesion with the epoxy.

The above literature search indicates that the research involving the friction and wear behavior of epoxy reinforced with graphene and CNF is very scant. Furthermore, nobody has studied the friction stability of polymer composites. In the present work, the tribological behavior of graphene-reinforced epoxy was studied. Graphene was used because of its lower cost as compared to CNF and CNT. The concentration of graphene was varied from 1 to 10wt%. Attention was focused on the effect of graphene content on friction stability of various composites.
CHAPTER II

EXPERIMENTAL

2.1. Sample Preparation

This study investigated the effect of graphene concentration on tribological behavior of epoxy resin. The composite samples were produced using the conventional dry mixing method and adding 1, 5 and 10 wt% of graphene to epoxy. To maintain uniformity and produce sound samples, the unfilled polymer and the composites were processed under identical conditions. Graphene used in this study was produced by exfoliation and reduction of graphite in our own laboratory.

The polymer was a low viscosity liquid epoxy resin: Epon 862 (Diglycidyl Ether of Bisphenol F) and the curing agent was Epikure W (diethyl toluenediamine, or DETDA), both compounds were acquired from Momentive Specialty Chemicals Inc. This epoxy was chosen here due to its low viscosity and long shelf life at room temperature, which make the system versatile and easy to process. The aromatic amine curing agent has the advantage of providing excellent performance and chemical resistance at elevated temperatures. The molecular formulae, of both the compounds are given in Figure 2.1.
Figure 2.1  Molecular formulas of (a) Epoxy, Epon 862 and  
(b) curing agent, Epikure W
Graphene tends to agglomerate in chunks because of its small particle size, large surface area and superior particle activity. In order to improve the dispersion of graphene in epoxy resin, the graphene bundles were dry-blended in a blender to obtain a uniform density graphene. It was then weighed to obtain three concentrations 1, 5, and 10wt% with the epoxy resin system. It may be noted that one of the previous studies investigated the effect of low graphene content on the tribological performance of epoxy [63]. The graphene content in their study was varied from 0.05 to 0.5wt%. Therefore, it was decided to evaluate the epoxy composite with higher graphene contents. The lowest graphene concentration selected was 1wt%, an intermediate value of 5wt%, and the maximum concentration used was 10wt%. It was found that for concentrations higher than 10wt%, the mixing process became challenging and a well dispersed compound was very difficult to obtain.

The nanofiller was added, based on the desired filler concentration, to the epoxy resin, which was previously mixed with the curing agent in a plastic container by hand for 5 minutes in a weight ratio of 100/26.4 (epoxy/ curing agent). This blend was subsequently loaded in a three-roll mill mixer to obtain a homogeneous dispersion of graphene in the epoxy. The procedure was same for all compositions, with the exception of 10 wt% of graphene. As the amount of nanofiller increased, the viscosity of the compound increased. Therefore, the 10wt% compound was prepared in several steps. Here, a small amount of graphene was added to the resin, then it was mixed in the three roll mill until the viscosity of the compound was reduced, subsequently more graphene was added. This step was repeated until all the graphene was incorporated in the resin.
A three-roll mixing mill, from Lehmann Mills (Figure 2.2), was employed to mix graphene in epoxy and obtain a uniform mixture. According to Gojny et al. [65], a laboratory scale three-roll mill is most capable equipment to uniformly mix the nano-fillers in polymers. The three horizontal rolls rotate in opposite directions at different speeds relative to each other, by means of an electric motor and gear box assembly. The rotational speed of center and apron rolls (Figure 2.2b) is increased in order to apply large shear stress on the mix and improve mixing and dispersion. The standard speeds for rollers 1, 2, and 3 were 21, 64 and 200 rpm, respectively. The gap between the rolls was kept as small as possible to produce large amount of shear stresses. Here, a feeler gauge was used to set a 25μm gap between the rolls. It was further decided that for all formulations the compound would be passed through the roll mill five times, and the feed roll speed be increased with increasing graphene content (Table 1). Since the shear stress produces heat, the temperature of the rolls was controlled by a cooling system, where chilled water at a temperature of 70°F was used.
Table 2.1 Feed roller speed

<table>
<thead>
<tr>
<th>Formula</th>
<th>Nanofiller %</th>
<th>Feed roll Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>333</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>550</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>600</td>
</tr>
</tbody>
</table>

The mixing of the compound was started by slowly pouring the pre-mixed compound (graphene, epoxy and curing agent) between feed and center rolls. The mixture then automatically passed between center and apron rolls by sticking to them, and a knife edge blade scraped the processed material off the apron roll and stored in the pan (Figure 2.2). When all the mixture was collected in the pan, it was poured again between the feed and center rolls. The process was repeated 5 times for each compound. As the mixture became homogeneous, it started presenting a shiny metallic surface due to the presence of exfoliated graphite.

Composite samples were then molded into 10 cm x 10 cm x 0.5 cm plates using a two-piece mold as shown in Figure 2.3. The mold was comprised of two flat plates (aluminum) and a 5 mm thick aluminum plate, which had two 10 cm x 10 cm windows machined in it. First, the mold release agent, Frekote 770-NC from Henkel, was applied on all three pieces of the mold, which were previously cleaned and dried. Two coats of this agent were applied and after the evaporation of the solvent, the composite mixture
was poured into the assembled mold (aluminum and molding plate) (Figure 2.3b), which were held together by high temperature tape. The poured mold was then covered with the silicone rubber plate and transferred to the molding press. This mold was heated to a temperature of 250°F for 10 minutes without applying pressure to eliminate any bubbles, and then a load of 7 tons was applied on the mold. According to the technical data sheet [66] the curing process called for: heating the mold under pressure for 1 hour at a temperature of 250°F, 2 hours at 350°F and finally cooling down to 100°F prior to releasing pressure. The cooling of the mold inside of the press was an effort to obtain a flat sample.

Afterwards both sides of the composite plates were polished by hand for 1.5 minutes each with a 180 grit emery paper, and then they were washed in water and dried. For 5wt% and 10wt% concentration of graphene, the electrical conductivity of the samples was measured to examine the graphene dispersion. The measurements were made using a Mitsubishi Chemical Loresta-GP MCP-T600 Low Resistivity Meter by a 4 point probe method. The probes were applied perpendicular to the sample and a small weight placed on top of them to obtain good contact between the probes and the specimen plate. The electrical conductivity reading was obtained in units of Ωcm.
Figure 2.2  (a) Lehman Mills three roll mixer, (b) schematic of the rolls [67]

Figure 2.3  Two-piece mold, window frame and baseplate
2.2  **Graphene Dispersion**

2.2.1  **Sample Preparation for SEM Analysis**

Scanning electron microscopy and optical microscopy are commonly used to study the homogeneity of graphene dispersion in polymer composites [68]. SEM analysis was performed on the fracture surface of nanocomposite. The micrographs were obtained with Hitachi TM 1000, a tabletop electron microscope that does not require coating the test surface with gold to increase its conductivity; the only preparation the fractured specimen needed is to cover its sides with copper tape to increase its conductivity, reduce charging, and improve the quality of the image. The surface morphology was examined to assess the nanofiller dispersion.

2.2.2  **Sample Preparation for Optical Microscope**

The specimens for the optical microscopic analysis were cut by a wet saw (MK tile saw) from the molded plate in the shape of 0.5 cm x 0.5 cm x 0.5 cm cubes. The specimens were fixed with scotch tape to the base of a cylindrical plastic mold. The epoxy resin (Epon 862 + Jeffamine D230, mix ratio 100g/34g, respectively) was slowly (to avoid bubbles) poured into the mold to the level of the specimen and cured at ambient temperature for 24 hours. Later the molded specimens were removed from the mold and polished in the Ecomet 3000/ Automet 2000 Grinder-Polisher. Here, the specimens were slid against a rotating disc of emery paper under constant pressure. Several emery papers from coarse to fine grit in sequence of: 180, 320 and 600 were used. During each step, water flow, load, and speed were controlled. Between each sequence of grit, the
specimens were washed with water to prevent the contamination of the finer emery paper with coarse grit particles. The final two steps involved the use of 9 µm diamond suspension on a TexMet® 1000 Polishing Pad and MasterPrep® (0.05µm) Alumina Polishing Suspension on a microcloth; this last step took 48 hours on a chemomechanically vibratory polisher (VibroMet 2) to remove the remaining scratches. Finally, the specimens were washed and dried with compressed air.

The pictures from the polished surface were taken, to study the graphene dispersion, under polarized light using the SPOT Insight 2.0-megapixel color camera attached to a BX41 Optical microscope (Olympus) equipped with a 10X objective lens. The optical microscopy with plane-polarized light is appropriate to study the anisotropic materials, for example, graphene. The lattice of crystalline materials presents an extremely ordered arrangement of atoms; this controls the optical properties of the crystal, which commonly change in different directions. When plane-polarized light illuminates this kind of materials, the orientation of the incident light changes due to the crystallographic orientation of the impinged surface. In case of graphene due to its hexagonal crystals structure, the orientations of the anisotropic directions react in different ways to the polarized light and emit two different colors and intensities by constructive or destructive interference. Such effects can reveal information on the character of the sample along with qualitative and quantitative data regarding the anisotropic nature of the material [31].
2.3 **Dynamic Mechanical Analysis (DMA)**

Dynamic Mechanical Analysis (DMA) is a quick and simple technique to characterize polymers. It is very useful for studying the viscoelastic behavior of polymers and provides information about thermal transitions. In addition, the bending elastic modulus and damping properties of polymer nanocomposites are also determined by this technique. The material properties are characterized as a function of temperature, time, frequency, stress, and atmosphere. A sinusoidally varying stress is applied and the strain in the material is measured. The DMA measurements were performed on a DMA242C (NETZSCH) tester operating in three-point bending mode (Figure 2.4) at a frequency of 1Hz (a frequency of 1Hz is most commonly used as a standard value [69]). The tests were performed over a temperature range of 25 to 200°C at a heating rate of 2°C/min. Small specimens 40 mm x 10 mm x 5 mm were cut from the sample plates using a wet saw. A sinusoidally varying load of 0 to 6N was applied at the center of the specimen generating a maximum stress of 0 to 1.44MPa. The oscillatory force applied to the sample produced changes in specimen deflection with time, allowing the calculation of elastic modulus (stiffness), damping, and glass transition temperature.
Figure 2.4  Three-point bending test configuration [70]
2.4 Contact Angle

Consider a liquid drop resting on a flat horizontal solid surface (Figure 2.5). The contact angle is defined as the angle ($\theta$) formed by the intersection of the liquid-solid interface and the liquid-vapor interface. It is determined by drawing a tangent from the end contact point along the liquid-vapor interface in the droplet. The contact angle depends on the properties of the solid and the liquid: intermolecular forces (cohesive and adhesive forces) and repulsive forces between liquid and solid. The balance between the cohesive forces of similar molecules such as between the liquid molecules and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules determine the contact angle created in the solid and liquid interface. For small contact angles, the cohesive forces are weaker than adhesive forces, while for large angles, the cohesive forces are stronger than adhesive forces and the molecules of the liquid tend to interact more with each other than with the solid molecules.

Surface energy is an important surface property, which must be considered in evaluating the friction and wear characteristics of materials. Surface energy affects the interactions between sliding surfaces and can control adhesion between asperities. It is often reported that a low specific surface energy induces slip between two bodies, which is a reason for the reduced friction between two bodies [71]. A poor wetting and consequently low surface energy is reflected by low adhesive interactions accompanied with low friction, which make the sliding easier between surfaces. The surface energy was calculated by the following formula:

$$E_{\text{adh}} = \gamma_L + \gamma_S - \gamma_{LS} = \gamma_L (1 + \cos \theta)$$
where $E_{adh}$ is the total surface energy per unit area (J/m$^2$), $\gamma_L$ the liquid surface energy, $\gamma_S$ the solid surface energy, $\gamma_{SL}$ the liquid-solid surface energy, and $\theta$ contact angle.

The contact angles were measured between deionized ultra-filtered water droplets and the cured nano-composite plates (before and after the wear test) using a drop shape analysis system (DSA 100, Kruss) using the height-width method (H/W). As water has a high surface energy (72.2 mJ/m$^2$) and is a highly polar liquid, it is commonly used to determine solid surface energies [72]. The sample was leveled and placed between a light source and the microscope. A drop of 2\(\mu\)l deionized water was gently placed with a motor-driven syringe onto the sample surfaces. The water volume is generally kept at 1-5\(\mu\)l to avoid the effect of gravity. If the volume is larger than that, the drop cannot form a sphere due to the effect of gravity. After the water drop reached its equilibrium state, zoom and focus was manually adjusted at the camera for a well-focused image of the drop, then the image was taken and subsequently the contact angles were determined (Figure 2.6). The diameter (2r) is the width and ‘h’ the height of the drop, these variables are measured by the equipment and contact angle calculated using the formula:

$$\theta = 2\tan (h/r).$$  

The resultant contact angle was the mean of five individual measurements carried out at different locations on the sample.
Figure 2.5  Definition of contact angle [73]

Figure 2.6  Measurement of the contact angle between the water drop and composite plate
2.5 Tribological Testing

To evaluate the tribological performance of graphene reinforced composites under dry sliding conditions, wear tests were carried out on a laboratory scale dynamometer (Figure 2.7) using a ring-on-disc configuration. The dynamometer consists of a spindle #1 (Figure 2.7a) which is powered by a 20 hp motor. The motor speed can be varied from 0 to 5000 rpm. The counterface ring can be screwed on to the spindle. The specimen plate is attached to an aluminum holder #2 (Figure 2.7c). The specimen is held in position by vacuum drawn between the specimen and the holder. The specimen holder is connected to an air cylinder capable of applying axial force varying from 0 to 4500 N. A lever arm is attached to the specimen holder, which presses against a load cell. The product of lever length and load cell force provides the friction torque.

The counterface ring (Figure 2.7b) was machined from gray cast iron (BHN 241) with an average diameter of 58.8 mm (external diameter, 67 mm; internal diameter, 50.7 mm), and apparent contact area of 1520 mm$^2$. Cast iron was chosen here because one of the possible applications of this study is the development of friction materials for automobiles, for example, brake systems, where drums are usually made of cast iron. The sliding surface of the ring was machined on a lathe machine. The surface roughness can be specified by several parameters, the most common surface parameter is the arithmetic average of surface roughness ($R_a$). For this ring, the $R_a$ values were measured to be 0.4613$\mu$m in the tangential direction and 0.8931$\mu$m in the radial direction. Due to high hardness of gray cast iron, it was expected that even after the friction test the surface roughness and profile would not change.
To start the test, the sample plate was held against the stationary aluminum holder by a vacuum system. The air cylinder was pressurized to produce contact between the spindle and the specimen plate. An axial force varying from 400 N to 600 N was applied on the specimen holder by the air cylinder. This condition resulted in a normal pressure of 0.26-0.39 MPa between the sliding surfaces. The cast iron ring was rotated at a constant speed of 97 rpm (0.3 m/s). These sliding conditions were chosen based on several trials, which gave a reasonable amount of wear. The cyclic normal load was applied to simulate the oscillating pressure that the driver usually applies on the brake pedal to reduce the vehicle speed. The output from various dynamometer sensors was fed to a computer which monitored the rotating speed of the ring (rpm), normal force, and torque. The data were collected every 0.5 seconds using the Labview software and the coefficient of friction was calculated as a function of time using the following formula:

\[ \mu = \frac{T}{F \cdot r} \]

where \( \mu \) is the coefficient of friction, \( T \) the torque, and \( F \) the Normal Force, \( r \) the average radius of the ring. Before starting the test, the cast iron counterface was polished with a 180 grit emery paper and cleaned with ethyl alcohol in order to remove the wear debris, lubricant, dirt, and any transfer film from the surface. After the test, the wear debris from the composite surface was collected to study the morphology of wear particles.

After the test was concluded, it was required to measure the wear volume of the different composites. It was decided to characterize wear by the average depth of wear scar. A typical wear scar as obtained by a Talysurf profilometer was similar to that shown
in Figure 2.8. Note that the depth of wear scar is not constant. Therefore, the depth measurements of the wear scar were performed by an optical microscope with a magnification of 5X. The depth data were collected at 10 different points across the scar in a sample and the average scar depth was calculated. This technique is superior to other methods which are used to calculate the depth of the wear scar because it does not make contact with the sample surface, as in the case of the surface profilometer where the contacting stylus may abrade the wear scar.

To investigate the wear mechanism of graphene filled epoxy composites, the morphology of the wear track was studied by optical microscopy because it is quick, sensitive, and non-destructive analysis. Polarized light was used to identify the dispersion of graphene. The shape of wear particles was studied by SEM.
Figure 2.7 Test dynamometer (a) spindle (b) metallic counterface ring (c) sample holder

Figure 2.8 Typical profile of a wear scar
CHAPTER III

RESULTS AND DISCUSSION

3.1 Graphene Dispersion in Epoxy

The mechanical and physical properties of nanocomposites depend on the dispersion of filler agent into the matrix. Here, the dispersion of graphene in epoxy was analyzed using optical and scanning electron microscopes. The optical microscope specimens were produced by mounting a 5 mm x 5 mm x 5 mm composite cube in epoxy holder and polishing its surface to optical flatness through several steps. The SEM samples were obtained by breaking a thin strip of the composite in tension. The graphene layers in epoxy can be identified via color contrast caused by the polarized light. This method is qualitative because the color contrast often varies from one laboratory to another [74]. However, it is an accurate and reliable technique to evaluate the graphene dispersion and distribution in polymer matrix. Figure 3.1 shows optical microscope images of cured nanocomposites for 1, 5 and 10wt% of graphene filled epoxy. The white spots and streaks as indicated by arrows are the graphene sheets.

In all the cases the graphene can be seen to be dispersed all over the surface. The density of graphene sheets increases with its concentration. As such, these images indicate that the graphene dispersion in epoxy is reasonably uniform, which was further verified by the SEM analysis.
Figures 3.2 and 3.3 show the scanning electron micrographs of the fracture surfaces of graphene filled epoxy strips. Figures 3.2 shows the overview of the nanocomposites identifying the graphene sheets, while Figure 3.3 provides the detailed view of each of the surfaces. In both cases, Figures 3.2 a, b and c are from 1, 5 and 10wt% composite surfaces, respectively. The graphene sheets are again indicated by white spots and their location identified by yellow arrows (Figure 3.2). It may be noted that graphene is reasonably well dispersed in all the three composites. The wrinkled surface morphology of the graphene nanosheets is shown in Figure 3.3. According to Shen et al. [63], it is this morphology which plays an important role in enhancing mechanical interlocking and transferring load from the epoxy matrix to graphene sheets.
Figure 3.1 Optical micrographs of graphene filled epoxy. Arrows indicate the graphene locations. Graphene concentration (a) 1wt%, (b) 5wt% and (c) 10 wt%
Figure 3.2 Overview nanocomposite fracture surfaces showing the graphene dispersion, with graphene content of (a) 1wt%, (b) 5wt%, and (c) 10wt%.
Figure 3.3  Enlarged view of nano-composite fracture surfaces showing graphene morphology, with graphene content of (a) 1wt%, (b) 5wt%, and (c) 10wt%.
3.2 **Electrical Conductivity**

The electrical conductivity indicates a material’s ability to conduct an electrical current; it is reciprocal of electrical resistivity. At room temperature, the resistivity of graphene is approximately $5 \times 10^{-5} \ \Omega \cdot \text{cm}$ [75] which is equal to a conductivity of $2 \times 10^5 \ (\Omega \cdot \text{cm})^{-1}$. Due to its low electrical resistivity and high aspect ratio, graphene can increase the conductivity of its composites by several orders of magnitude. However, this improvement in electrical conductivity of the nano-composite depends on several diverse parameters, such as: (1) sample geometry, for example, if the filler is long enough, it may be able to produce a bridge of conducting material between the electrodes for a sufficiently small test specimen, resulting in a low percolation threshold, which would otherwise not exist in a large composite specimen; (2) alignment of the filler, if the platelets are aligned in the matrix, there will be few contacts between them, thus increasing the percolation threshold; (3) aspect ratio of the platelets, i.e., higher the aspect ratio, higher the conductivity; (4) platelet conformation, wrinkled, folded, or otherwise non-ideal platelet conformations will raise the electrical percolation threshold; (5) the concentration of the conducting filler must be above the electrical percolation threshold, where a conductive network of filler particles is formed; and (6) dispersion, where a poor dispersion will negatively impact conductivity of epoxy by requiring high concentration to obtain a low percolation. Note that high degree of dispersion may not necessarily yield the lowest onset of electrical percolation, as a sheath of polymer may coat the surfaces of well-dispersed filler and prevent direct interparticle contact [76].

The lowest electrical percolation threshold reported in the literature for graphene reinforced epoxy was 1wt% [77] and the highest threshold was 8wt% by Tien et al. [78].
They attributed this result to large thickness of the graphene flakes and low aspect ratio.

In the present work, the percolation threshold for graphene nanocomposite was 5wt%. At 1 wt%, the electrical resistivity was off-scale and could not be quantified. As the focus of this work was the characterization of the composites, measurement of electrical conductivity was also used as an alternate method to qualitatively evaluate dispersion/distribution of graphene. A good distribution of filler in the sample should present similar values of electrical conductivity in different directions at different points on the sample. The electrical conductivity was measured at 25 different points for each sample, on both sides of the plate. Figure 3.4 shows the mean values of conductivity along with their standard deviation. It may be noted that the electrical conductivity values are almost same for both the 5wt% and 10wt% composites on both sides of the plates. Although, it was expected that electrical conductivity would increase with the graphene content, but it did not happen. It may be due to the dominant effect of epoxy conductivity, measurements errors, or poor contact between composite plates and electrodes. The low value of standard deviation of electrical conductivity indicates a small variation of electrical conductivity, which implies a uniform distribution of graphene in composites as concluded earlier.
Figure 3.4  Average values of electrical conductivity for 5wt% of and 10wt% of graphene
3.3 Mechanical Properties of Composites

3.3.1 Storage Modulus ($E'$)

Dynamic mechanical analysis was used to obtain stiffness (storage modulus), glass transition temperature ($T_g$) and loss factor (tan\(\delta\)) of the nanocomposites. For this test, rectangular specimens 40 mm long, 10 mm wide, and 5 mm thick were used. A sinusoidal load varying from 0 – 6 N was applied at the center of the specimen in a three-point bending made. The test temperature was varied from 25 °C to 200 °C at a rate of 2°C/min. The storage modulus indicates the elastic behavior of the material, and is closely related to the modulus of elasticity measured with a standard stress-strain mechanical test.

The variation of storage modulus ($E'$) was studied as a function of temperature (Figure 3.5). The stiffness increases with graphene content and decreases as the temperature rises. The storage modulus increases because the nanofiller inhibits the movement of epoxy molecular chains around the nanofiller and any stress imposed on the nanocomposite is transferred to the nanofiller, which is stiffer than epoxy. The addition of 10wt% of graphene produced a 62.5% increase of the storage modulus at 50°C.

The stiffness of the composite can be predicted by the rule of mixtures, this rule assumes: (1) the fillers are uniformly distributed throughout the matrix; (2) perfect bonding between fillers and matrix; (3) the matrix is free of voids. The estimated values of composite stiffness were calculated by the following formula:
E\text{c} = E_f V_f + E_m V_m, where E and V are Young’s modulus and volume fraction, respectively, and the subscripts c, f and m represent composite, filler and matrix, respectively. Considering the experimental storage modulus of 2.6 GPa for the epoxy and the theoretical modulus of 1000 GPa for graphene, the estimated values of \( E' \) were computed for the composites. Figure 3.6 shows variation of composite modulus with graphene concentration. It may be observed that there is a large difference between the two stiffness values. The difference may be attributed to the fact that the assumed value of graphene’s modulus is too large and that the rule of mixtures cannot be applied for nanocomposites, because this rule assumes a perfect bonding at the interface. In the absence of perfect chemical bonding, the load transfer between the nanofiller and the matrix will be incomplete and therefore the storage modulus would be lower.

A more realistic mathematical model to estimate the storage modulus for nanocomposites is the Halpin–Tsai model \[79\], which is based on the geometry and orientation of the filler and the elastic properties of the filler and matrix materials. For randomly oriented nanofiller in the polymer matrix, the nanocomposite modulus \( E_c \) is given by:

\[
E_c = E_m \left[ \frac{3}{8} \frac{1 + \eta_L \xi V_C}{1 - \eta_L V_C} + \frac{5}{8} \frac{1 + 2 \eta_T V_C}{1 - 2 \eta_T V_C} \right]
\]  

(1)

where \( \eta_L, \eta_T \) and \( \xi \) are given by

\[
\eta_L = \frac{(E_g / E_m) - 1}{(E_g / E_m) + \xi}, \quad \eta_T = \frac{(E_g / E_m) - 1}{(E_g / E_m) + 2}, \quad \xi = \frac{2 \alpha_g}{\sqrt{3}} = \frac{2 \gamma_g}{3t_g}
\]
where $E_c$ is the storage modulus of the nanocomposite; $E_g$ and $E_m$ are the storage modulus of the nanofiller and the polymer matrix respectively. $\alpha_g$, $l_g$, and $t_g$ refer to the aspect ratio, length and thickness of the nanofiller, respectively and $V_c$ is the volume fraction of nanofiller in the nanocomposite. Substituting these parameters in Equation 1, the storage modulus was calculated and plotted for graphene composites (Figure 3.7). Figure 3.7, shows the variation of experimental and estimated storage modulus as a function of graphene content, good agreement may be observed between the two sets storage moduli. However, at high filler concentration the theoretical value was lower than the experimental result. It is because the Halpin- Tsai model does not consider the maximum volumetric packing fraction ($\phi_m$), and studies have shown that $\phi_m$ has a significant effect on the modulus for higher filler contents [79]. The smaller the $\phi_m$, the larger the increase in modulus. In addition, the model assumes that the filler dispersion is related to filler volume, which may not be true.
Figure 3.5  Storage modulus of the graphene nanocomposites

Figure 3.6  Estimated and experimental storage moduli of graphene nanocomposites based on the Rule of Mixtures
Figure 3.7  Comparison of estimated Halpin-Tsai model and experimental storage moduli of graphene nanocomposites.
3.3.2 Loss Factor (\(\tan \delta\))

The loss factor (\(\tan \delta\)) is the ratio of the viscous behavior to elastic behavior. The experimental values of loss factor as a function of temperature are shown in Figure 3.8. The ratio increases with temperature reaching to a peak and then drops down. The loss factor is related to the energy absorption capacity of a material when a cyclic load is applied, and it goes through a peak at the glass transition (glassy phase to rubbery phase). The higher the peak, the larger is the energy dissipation (also referred to as damping). The decreasing height of the \(\tan \delta\) peak with increasing graphene concentration relates to increasing elastic behavior and less damping. The damping decreased because the introduction of graphene reduced the mobility of the polymer chains, consequently reduced the capacity of the composite to absorb energy by polymer chain sliding. The temperature corresponding to the peak is referred to the glass transition temperature. It is 149°C for the epoxy and between 151°C and 153°C for the composites. Typically, a difference of 2 or 3°C is significant when using DMA. In the past, some workers reported an increase of \(T_g\) of up to 30°C [63-64] when epoxy was reinforced with graphene, but this behavior has been anomalous because it depends on the interactions between molecular chains and nanofiller. The \(T_g\) may also decrease if the filler has a negative effect on the cure reaction and resulting network structure.
Figure 3.8  Tanδ of the graphene nanocomposites as a function of temperature
3.3.3 Peak Factor, $\Gamma$

The peak factor, $\Gamma$, is defined as the width of tanδ-curve at one-half of maximum peak height divided by its height. It can be qualitatively used to assess the homogeneity of epoxy molecules network in the matrix [80]. The peak factor values as a function of graphene content are shown in Figure 3.9. Neat epoxy showed a low value of peak factor, $\Gamma$, indicating a uniform crosslink density of epoxy molecules. The factor increased as the nanofiller content increased to a maximum value of 56 °C for 10wt% graphene composite. The higher value of peak factor with increased nanofiller content (Figure 3.9) indicates a less uniform crosslink density and greater heterogeneity, which suggests the intercalation of graphene into the epoxy network.
Figure 3.9  Peak factor for graphene compounds
3.4 Contact Angle

Surface energy is an important material property, which is considered in evaluating the friction and wear characteristics of materials [9]. Here, the contact angle between a water drop and worn and unworn surfaces of composite plates was determined to calculate this property. The surface energy per unit area was determined using the formula:

\[ E_{\text{adh}} = \gamma_L (1 + \cos \theta) \]

where \( E_{\text{adh}} \) is the total energy per unit surface area (J/m²), \( \gamma_L \) the liquid surface energy (J/m²), \( \theta \) contact angle. Figures 3.10 to 3.11 show the variation of contact angle and surface energy with graphene content, respectively. It may be noted that as the graphene content increased, the contact angle decreased and surface energy increased. In fact the nanocomposite containing 10wt% of graphene presented the lowest contact angle and highest surface energy, indicating good wettability and high friction forces. The reason is that graphene has high aspect ratios, large surface area, wrinkled surface, and good bonding with the matrix. All these characteristics improved the mechanical properties of nanocomposites (stiffness). This behavior is supported by the fact that material hardness and therefore the mechanical properties increases with the surface energy [81]. The contact angle values for the worn and unworn surfaces cannot be compared because the two types of surfaces are almost different. The worn surfaces are (a) rougher, (b) the graphene is exposed, and (c) composite is porous.

Moreover, the experimental results indicate that the contact angles for the worn surfaces increased for all samples except that for 10wt% of graphene (Figure 3.10). The
possible reason was that the roughness of the composite surface increased after sliding, while for 10wt%, a smeared graphene film covered the whole surface and improved the adhesion forces of the nanocomposite.
Figure 3.10  Contact angle for graphene nanocomposites

Figure 3.11  Surface energy for graphene nanocomposites
3.5 **Friction and Wear**

Sliding between the unfilled and graphene filled epoxy plates and cast iron ring was conducted using a tribo-test dynamometer. The epoxy plates were held in a specimen holder and the cast iron ring was screwed on to the spindle. The spindle was rotated at a speed of 97 rpm and an axial load varying from 400 N to 600 N was applied. The tests were run for 1 hour duration and the axial load, friction torque, and spindle speed was monitored at 0.5 second intervals, using the Labview software.

3.5.1 **Coefficient of Friction**

Figure 3.11 shows the variation of coefficient of friction for the duration of the test with time for the neat epoxy. The friction value oscillated throughout the test, probably because the axial load was varied from 400 – 600 N at a frequency of 0.4 Hz. The initial value of COF was approximately 0.6, it dropped to about 0.42 after 1000 seconds, then increased to about 0.5 between 2000 and 2700 seconds, finally stabilizing at about 0.42. This variation of friction can be attributed to the interface temperature. Initially, the epoxy plate was at room temperature, the polymer strength was high, exhibiting a large COF. As the sliding continued, the interface temperature increased, the polymer softened and the friction dropped. The intermediate increase in friction may be due to enhanced contact between the sliding bodies which occurred due to further softening of the epoxy. Finally, the temperature continued to rise, and the friction dropped down to approximately 0.42.
To verify the above hypothesis, the wear track (Figure 3.13) was examined. It may be noted that the polymer underwent thermal oxidation at number of location as indicated by blackened patches of polymer. The sequence of events may be summarized as: hard epoxy softens (friction decreases), as the polymer softening continues, the real contact area and friction increases, and finally the epoxy degrades leading to lower friction.

A possible technique to reduce this friction variation is by increasing the thermal conductivity of the epoxy, because the increased thermal conductivity would reduce the interface temperature and therefore the polymer degradation. Figure 3.13, shows the variation of coefficient of friction with time for unfilled, 1, 5 and 10wt% graphene filled composites. It may be noted that as the graphene content increased, the fluctuations in friction decreased. The difference in friction behavior for unfilled and 1wt% graphene filled was very little. For the cases of 5wt% and 10wt% composites, the friction reaches to an almost stable value of 0.45. The reason why large graphene content can stabilize COF is that graphene can reduce the surface temperature by increasing the thermal conductivity of the bulk material and prevent the softening and degradation of epoxy. It is for this reason that friction coefficient approached to a stable value as the graphene content increases. This happened in spite of the fact that the axial load was varied from 400 N – 600 N, which indicates that COF becomes independent of load for this graphene content.

Figure 3.15 shows the variation of average coefficient of friction for filled and unfilled epoxy. The COF varied from 0.42 to 0.52 and it was highest for 5wt% graphene composite. This behavior can be explained based on the lubricity, improved thermal
conductivity, and atomic bonding provided by graphene. As the graphene content increased, the epoxy thermal conductivity increased, which reduces the interface temperature. At the same time, the composite mechanical properties including the shear strength improve. Finally, the composite lubricity increases due to the presence of graphene. The interplay among these factors provided the largest COF for 5wt% graphene composite. These results are in agreement with the literature, in that an optimal graphene content for a large value of friction is between 1 to 4 vol% [9].
Figure 3.12  Coefficient of friction of neat epoxy

Figure 3.13  Picture of the neat epoxy wear track showing the presence of blackened areas
Figure 3.14  Variation of coefficient of friction as a function of time (a) epoxy, 1wt%graphene and 10wt%graphene and (b) 5wt%graphene and 10wt%graphene
Figure 3.15  Variation of coefficient of friction with graphene concentration
3.5.2 Wear Rate and Morphology of Wear Particles and Wear Track

3.5.2.1 Wear Behavior of Composites

The wear of unfilled and graphene filled epoxy was determined by measuring the depth and width of wear scars. The wear scar depth was measured using an optical microscope at 10 different locations across the wear track and the average depth was used to specify the wear of composite plates. Figure 3.16 shows the variation of wear scar depth with graphene concentration. The wear of composites decreased as the graphene concentration increased. The reduction in wear was very steep for 1wt% composite. For other composites the reduction was less steep. However, the wear of 10wt% graphene filled epoxy was reduced by a factor of 43. This wear behavior can be attributed to the improvement in thermal and mechanical properties of the composites that occur due to the addition of graphene. This is in line with wear behavior of epoxy reported by Shen et al [63].
Figure 3.16  Variation of depth of wear scar
3.5.2.2 Microscopic Examination of Wear Tracks

The wear tracks of the filled and unfilled epoxy plates were examined by optical microscopy under polarized light to investigate the probable wear mechanisms. It may be mentioned here that this type of investigation is hampered by the complication that the fracture features produced by the separation of wear particles are instantaneously marred by the following sliding action. Therefore, the determination of exact wear mechanism operating at the interface is fraught with many uncertainties and complications.

Figure 3.17 shows the wear tracks for neat epoxy and 1, 5 and 10wt% of graphene reinforced epoxy, as observed by optical microscope under polarized light. The polarized light was used here because it generates interference color patterns when illuminates a graphite surface. The colors range from purple to blue, yellow, and white depending on the orientation of the graphite layers. Figure 3.17a shows the wear scar of unfilled epoxy plate. The surface was covered with some shallow grooves in the direction of sliding indicating that the polymer was plowed by the asperities on the counterface resulting in abrasive wear process during the sliding. It was also covered with some transverse markings, which were probably caused by adhesive wear of the epoxy. Thus, both the adhesive and abrasive wear processes were active in this case, which produced large amount of wear on the plate.

As the graphene concentration increased the worn surfaces became flat and smooth. The grooves and transverse markings started disappearing. The graphene shows up either as white spots or as white streaks. The concentration of these spots and lines increased as the graphene concentration increased. For 1wt% graphene plate, only few
graphene spots were observed on the wear surface (Figure 3.17b), however, for 5wt% composite several lines of graphene can be seen, and for 10wt% plate (Figure 3.17d) a shiny track is visible. This was a smeared, highly oriented graphene film that prevented direct contact between the nano-composite and the counterface. It reduced plowing of polymer by the counterface asperities, thus eliminating abrasion. It is for this reason that the wear track was featureless. In summary, as graphene is added to epoxy, both the abrasive and adhesive wear component decreased, it is for this reason that the wear of the 10wt% composite is 43 times smaller than that of the neat epoxy.
Figure 3.17  Wear track (a) pure epoxy (b) 1wt% of graphene composite (c) 5wt% of graphene composite (d) 10wt% of graphene composite
3.5.2.3 Morphology of Wear Particles

The examination of wear particles can also provide useful information to explain the wear mechanism. After each test, the wear particles from the wear track were carefully collected with a copper tape and examined under scanning electron microscope to determine their shape and size. Figure 3.18 shows the shape and size of the particles collected from the four specimens. Figure 3.18a shows the large flake and cylindrical shaped particles for the case of neat epoxy. It appears that originally flake shaped particles were produced, which were then rolled into cylindrical shape due to continued sliding. As the graphene is added to epoxy, particle size starts to decrease. This happened for 1 and 5wt% composites (Fig. 3.18 b and c). In both the cases, both flake shaped as well as cylinder shaped particles can be observed. For 10wt% graphene composite the particle size increased. Here, all the particles are flake shaped. However, this composite exhibits the lowest wear rate. It appears that originally, smaller wear particles were produced for this composite due adhesion, which later on agglomerated in to large size particles under continued sliding.
Figure 3.18 SEM Analysis of wear debris (a) neat epoxy (b) 1wt% of graphene composites (c) 5wt% of graphene composites (d) 10wt% of graphene composites
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

4.1 Conclusions

The tribological behavior of graphene reinforced epoxy has been studied. Four formulations: neat epoxy, and 1wt%, 5wt% and 10wt% graphene filled composites were used. The physical and mechanical properties, such as storage modulus, electrical conductivity, surface energy were determined to characterize these composites. The following conclusions can be made based on this work:

1. The storage modulus (stiffness) of the nanocomposites was found to increase as the graphene content increases. A 10wt% addition of graphene increased the stiffness of epoxy from 2.5 GPa to 6.0 GPa.

2. As the graphene content increases, the coefficient of friction becomes stable, showing the highest stability and largest value of COF at 5wt% of graphene.

3. As the graphene content was increased, the wear rate of the composites decreased. For example, the 10wt% composite resulted in a wear reduction of almost 98% when compared with the neat epoxy.
4. The probable wear mechanisms for neat epoxy was a combination of adhesion and abrasion, while for the graphene filled epoxy the major contribution from adhesion.

5. The enhancement of the tribological properties with the increasing amount of graphene is due to the unique properties of graphene, such as, high specific surface area, two dimensional planar geometry, and wrinkled surface, which improved the mechanical interlocking and therefore the transfer of load from epoxy matrix to graphene sheets.

6. The surface energy of both the worn and unworn surfaces increased with the addition of graphene because of its superior mechanical properties.

7. The measurement of electrical conductivity showed the percolation threshold at 5wt% of graphene content. However, the electrical conductivity values for both the 5 and 10wt% composites were almost identical and similar in all the directions.

8. The glass transition temperature increased a little bit with the addition graphene, but the change was insignificant.
4.2 Recommendations for Future Work

The following recommendations are made for future work:

1. Study the effect of different sliding conditions, for example, speed and load on the friction and wear behavior of graphene filled composites.
2. Repeat these studies by using CNF as the nanofiller.
3. Study the tribological behavior of temperature resistant thermoset polymers, for example, phenolic resin and cyanate ester resin reinforced with graphene.
4. Control the temperature of the sliding surface and study the effect of temperature on the tribological behavior on the nanocomposites.
REFERENCES


nanocomposites. *Composites Science and Technology, 70*(7), 1120-1125. doi:10.1016/j.compscitech.2010.02.023


