

EPOXY NANOCOMPOSITES FOR ENHANCED FIRE RETARDANCY AND METAL-TO-METAL BONDING PROPERTIES OF AIRCRAFT ALUMINUM ALLOYS

A Thesis by

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Bachelor of Technology, JNTU, 2013

Submitted to the Department of Mechanical Engineering
and the faculty of the Graduate School of
Wichita State University
in partial fulfillment of
the requirements for the degree of
Master of Science

May 2016

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

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DEDICATION

To my parents, my sister, my teachers and well wishers

ACKNOWLEDGEMENTS

I would like to thank my advisor and committee chair, Dr. Ramazan Asmatulu, for his continuous support and guidance throughout this research. I would like to thank Dr. Krishna Krishnan and the Department of Industrial and Manufacturing Engineering at Wichita State University (WSU) for allowing me to use the manufacturing lab. I would like to thank Dr. Rajeev Nair for his valuable suggestions towards my research and for readily agreeing to be a committee member. I would like to thank Greg Bunn from Magnolia Advanced Materials, Inc., for providing materials. I also thank Royal Lovingfoss, for giving an opportunity to carryout thermal analysis tests at National Institute for Aviation Research (NIAR) at WSU. I thank my brothers of Phi Delta Theta for their support. Last but not the least; I am indebted to my friends who have helped me in this research work.

ABSTRACT

Epoxy adhesives have a wide range of applications in aerospace, automotive, marine, and construction industries. Epoxies reduce the weight of a structure by minimizing fasteners. By application of epoxy adhesive, a structure can achieve uniform stress distribution, structural integrity, durability and cost effectiveness. A mechanical weakness of epoxy adhesives is their lack thermal stability and failure at post-curing-cycle temperatures. Fire retardancy can be improved by incorporating graphene nanomaterials as reinforcements. These graphene additions have potential to improve the epoxy's thermal, mechanical and electrical properties.

The epoxy nanocomposites of different weight percentages of graphene nanomaterials were prepared using a three-roll milling machine, Single-lap, shear-strength tests were carried out for evaluating the mechanical properties of the epoxy using a tensile test method. The flame retardancy values for the epoxy nanocomposites were determined using the ASTM UL-94 vertical burn tests. The thermal characterization of the epoxy nanocomposites was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Surface morphology analysis was carried out for epoxy nanocomposites by using scanning electron microscopy. The test results showed that fire retardancy was improved by 3wt% and 5wt% with graphene nanomaterial inclusions when compared with pristine epoxy. The DSC results, when compared to 0.5wt and 5wt% graphene inclusions showed the glass transition temperatures increased by 6.2%. The TGA results showed a decrease in mass reduction by 6.2%, due to inclusion of graphene nanomaterials. The lap shear strength when tested under tensile tests were improved by 27%, compared to pristine epoxy. Thus, graphene nanomaterial inclusions improved both mechanical and thermal properties while increasing thermal stability of the epoxy when compared to pristine epoxy.

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LIST OF ABBREVIATIONS

3-D	Three-Dimensional
ASTM	American Society for Testing and Materials
Br	Bromine
Cl	Chlorine
CNF	Carbon Nanofibers
DGEBA	Diglycidyl Ether of Bisphenol-A
FAA	Federal Aviation Administration
GO	Graphite Oxide
LOI	Limited Oxygen Index
PEEK	Poly-Ether-Ether-Ketone
PET	Polyethylene Terephthalate
PHRR	Peak Heat Release Rate
PP	Polypropylene
Wt%	Weight percentage
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
SWCNT	Single Wall Carbon Nanotube
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
DSC	Differential scanning calorimetry

CHAPTER 1

INTRODUCTION

This research primarily focuses on four important parameters of epoxy adhesives: fire retardancy, thermal stability, single-lap joint theory and surface morphology analysis of epoxy adhesives. These parameters not only give the information about mechanical properties, but also the thermal properties of an adhesive joint, which widens the scope for improvement.

1.1 Epoxy

Epoxies are from the family of polymers which specifically represent the thermosetting polymers. Epoxies are differentiated into high viscous and low viscous epoxies depending on the viscosity. High viscous epoxies include bisphenol, cycloaliphatic-, trifunctional- and bio-based epoxy resins. Low viscous epoxies include tetra-functional, nova-lac, fluorine- and silicone-based epoxies [1]. Epoxies undergo basic mechanisms of thermoset polymers, mainly a curing cycle, which is an exothermic reaction. In this exothermic reaction the polymer chain tends to synthesize into a highly cross-linked polymer chain, which transforms the material from high viscous liquid state to a solid state. This transformation makes the material more brittle and rigid [2]. Unlike thermoplastic polymers, epoxies can cure at a different range of temperatures depending on the curing cycle. The curing cycle (or) exothermic reaction mainly depends on the cure kinetics, chemical structure and the curing agents. This unique behavior of epoxy helped to gain its importance in the material industry in replacing traditional isotropic metals. Epoxies have extraordinary material properties, mainly high strength, electrical resistance, adhesion strength, damping resistance, flexibility and chemical resistance as illustrated in Figure 1.1 [3].

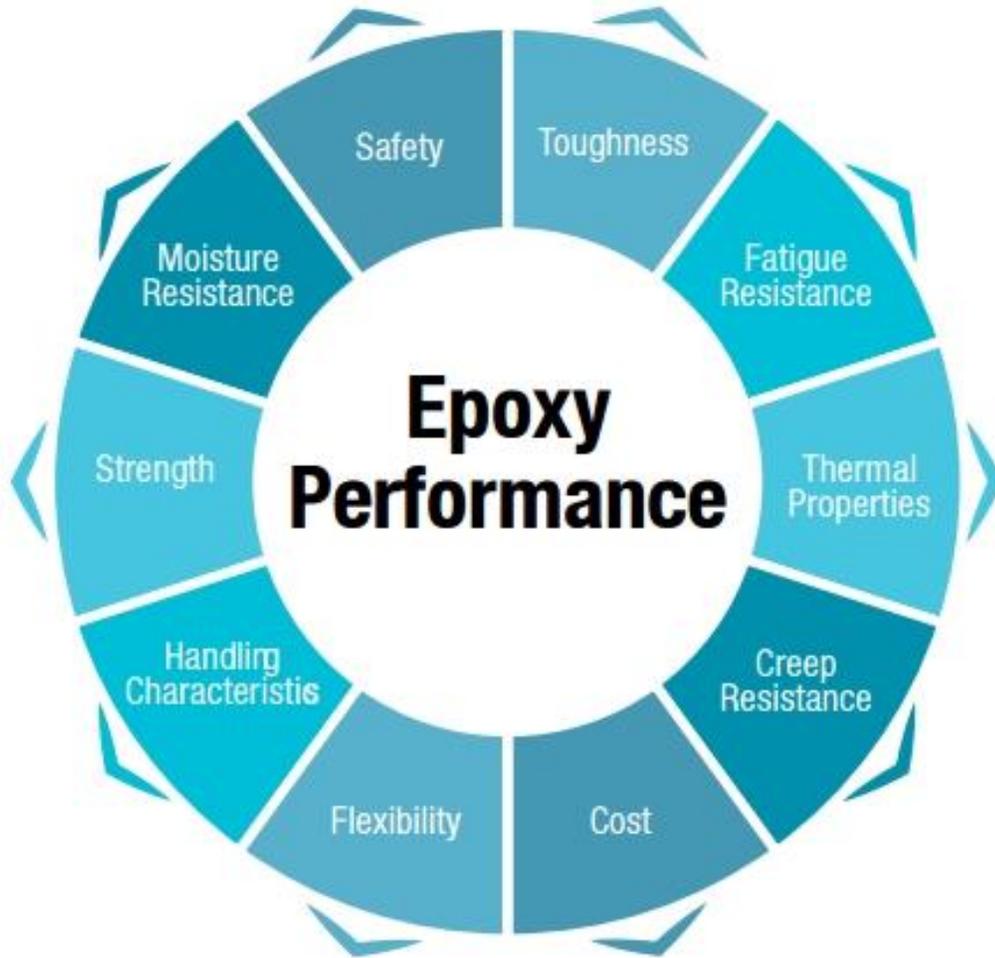


Figure 1.1 Important features of epoxy

Furthermore, epoxies have a weak thermal stability as it contains oxygen groups in the chemical structure, which make them deteriorate faster when imposed to fire. All these conditions lead to innovations of fire retardant epoxies, which have applications in electronic, paint, sport, aerospace, automotive, marine, civil, and composite industries [4, 5].

1.1.1 Fire Retardancy

Every year around 20 deaths per million are recorded due to the fire accidents involve the failure of polymeric materials. Many polymeric materials when imposed to fire release significant amount of noxious smoke which poses a health hazard [6]. Fire accidents lead to a new subject of fire

retardancy, and the growth in research of this specific field was shown in Figure 1.2. [7]. Fire retardancy is defined as a process to delay the time taken for decomposition, when a material exposed to the fire.

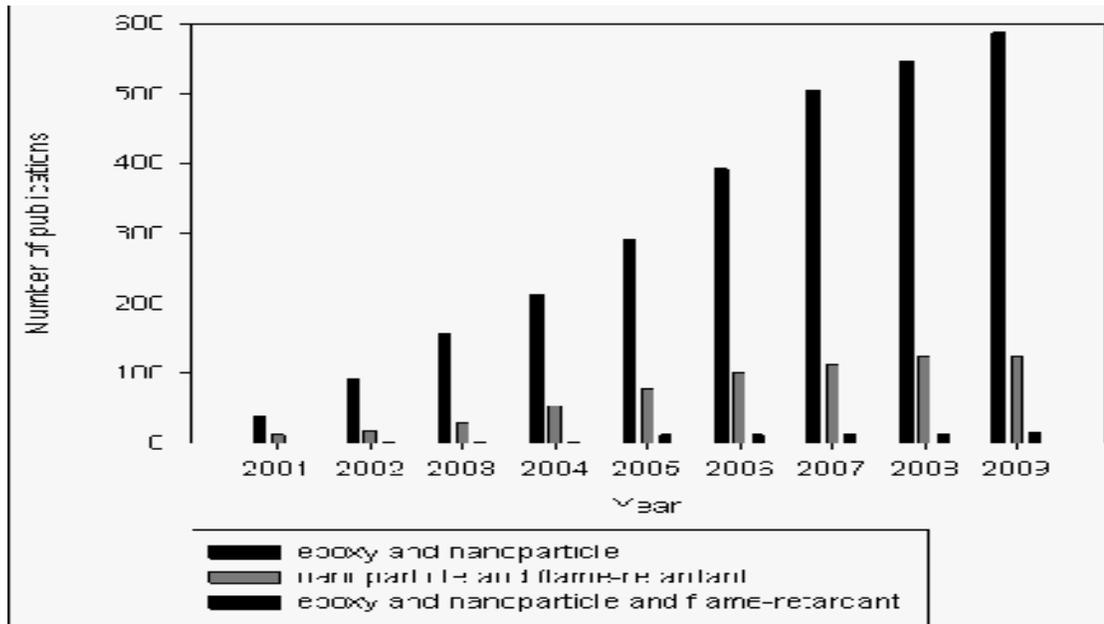


Figure 1.2. Researches on epoxy and fire retardancy.

Improved fire retardancy of a material can be achieved by modifying the backbone of the polymer structure either physically or chemically. The chemical modification process is known as reactive flame retardancy, whereas a physical process is known as additive flame retardancy. Chemically modified polymers emit highly volatile emissions, which mainly use the metallic compounds of P, Si, B or N [7]. The physical modification of these polymers utilizes advanced technologies, which can add reinforcements to these fire retardants easily. The additive flame retardants usually are nanomaterials which emit low toxic gases when compared with the chemically modified flame retardants. This technique is mainly used in producing fire retardant epoxies, textiles, and composites. These modifications in the polymer produce intumescence, char and residue which further act as fire retardants.

1.2 Motivation

The thermosetting polymers specifically epoxy is an important class of material from the family of polymers, which is used in structural applications. The weight reduction is the major factor in aerospace industry and automotive industries. As these thermosets lack in thermal stability, they bring down the mechanical properties. This area has been focused by many researchers, which began inclusion of other materials into this pristine epoxy system. Researchers used many metallic powders, chemical functionalization techniques and presently nanomaterials for improving the thermal stability and mechanical properties.

Nanomaterials not only maintain the weight within the limit, but also aid in enhancing mechanical, thermal, chemical properties of the epoxy. Typical epoxies fail mostly when the temperature is elevated to higher temperatures, especially beyond their curing temperature. The graphene nanomaterials have the exceptional properties in mechanical, electrical, thermal and also have better thermal stability when compared with other metallic reinforcements.

1.3 Research Objective

This research has considered different factors for improving the thermal stability and mechanical properties of an epoxy. The graphene was chosen as a material of reinforcement due to its excellent behavior in enhancing the thermal stability, fire retardancy and mechanical properties. The dispersion of nanomaterials was a challenging factor, which has been considered for this research. Another major objective of this research is to study the surface morphology and to test the epoxy nanocomposite samples to analyze the thermal and mechanical characteristics.

CHAPTER 2

LITERATURE REVIEW

2.1 Mechanism of Fire

Fire is a destructive force and is fatal. Mostly unwanted fires are responsible for losses of property and life. According to the most recent available study, every year around 600 lives are lost in UK, due to unwanted fires. These unwanted fires were caused by synthetic polymers, which have lower thermal stability when compared with natural polymers [8].

The basic mechanism of fire was explained by the fire triangle. The fire triangle includes three main constituents: fire, fuel and oxygen as shown on the Figure 2.1. The oxygen helps in initiation of combustion process and combustible material acts as the fuel. This leads to a chemical reaction, which is an exothermic reaction. The process of decomposition of the material is called as thermo-oxidative reaction, which converts carbon and other constituents into carbon dioxide and water. The major steps in fire growth include ignition, development of fire, fully developed fire and decomposition. New techniques and methods were studied during the test, to control the fire growth by limiting the fuels. Furthermore, fire can be controlled at any of these stages [8].

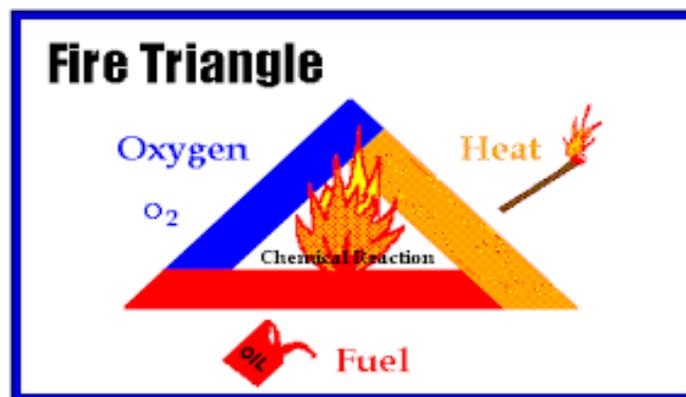


Figure 2.1. Fire growth mechanism

2.1.1 Mechanism of Polymer Degradation

Polymer degradation undergoes a pyrolysis process, which is a free radical process as shown in Figure 2.2. In this pyrolysis process the polymer chains break down into thousands of small carbon atoms. These carbon atoms then emit products of CO₂, smoke, nitrogen and other compounds depending on the fuel [9]. The polymer can undergo four degradation mechanisms by the action of oxygen:

- 1) End chain scission – polymers break down at the ends of particular polymer chain.
- 2) Random chain scission- polymers break in the middle of polymer chains.
- 3) Chain stripping- polymers break down from the backbone of polymer.
- 4) Crosslinking- polymers tend to form new bonds [10].



Figure 2.2 Polymer degradation mechanism involving pyrolysis

2.2 Polymers

The search and quest for new materials for minimizing metals as the basic materials lead to improved polymers. They are diverse and versatile. The initial concept started in 1920, for development of polymeric materials. The polymers are known as macromolecules since they form long chains of molecules called monomers. They form a variety of structures due to their chemical structure, which includes covalent bonds as the primary bonds and have Vander walls forces

between the molecules. These bonds between the molecules help the formation of long molecular chains, which can be linear or branched with many repeating units in the polymer chain [11].

The basic structure of a polymer is formed by polymerization technique, which involves both physical and chemical interactions between the molecules at a molecular level. Polymers undergo two different polymerization techniques, mainly addition polymerization and condensation polymerization. In addition polymerization, the polymer compounds have an interface of carbon - carbon double bonds, where molecules are added to each other and form a long chain. In condensation polymerization, polymer compounds form a polymer chain with an attachment of extra molecule. Polymers have the intermolecular reactions between the monomer molecules and reactive functional groups, which aid in forming a long polymer chain.

The polymers are classified by many different factors, which is clearly shown in Figure 2.3. The most important factor to be considered is the thermal response, as this differentiates the thermoplastic and thermosetting polymers.

Basis of Classification	Polymer Types
Origin	Natural, semisynthetic, synthetic
Thermal response	Thermoplastic, thermosetting
Mode of formation	Addition, condensation
Line structure	Linear, branched, cross-linked
Application and physical properties	Rubbers, plastics, fibres
Tacticity	Isotactic, syndiotactic, atactic
Crystallinity	Non-crystalline (amorphous), semi-crystalline, crystalline

Figure 2.3. Classification of Polymers.

The viscosity of the polymer mainly depends on the length of polymer chains. The entanglements are high in the polymers if they have high viscosity. The molecular weight plays a major role in choosing a particular polymer and is illustrated in the Figure 2.4. Thus, all these material properties of a polymer gave an upper hand in replacing traditional isotropic metals.

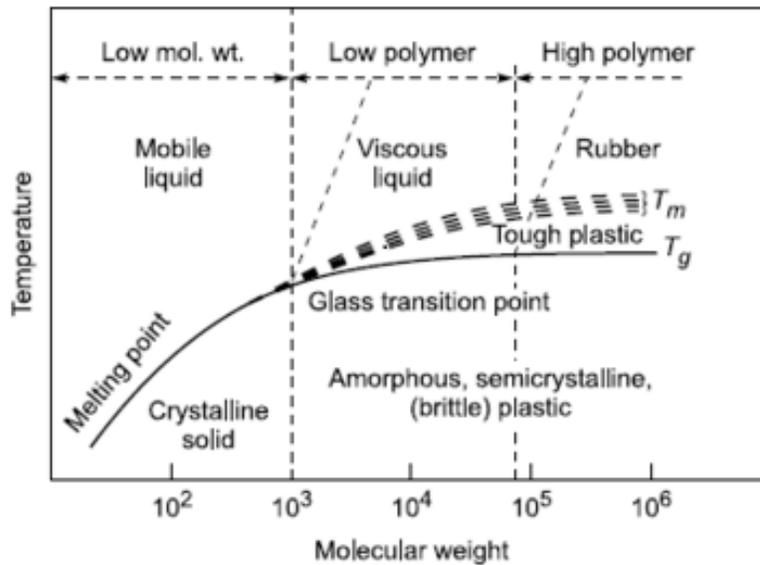


Figure 2.4. Different phases of material at different molecular weight.

2.2.1 Thermosetting Polymers

The thermosetting polymers have a branched structure. Due to application of heat these branched structures tend to transform into a very high density material. This transformation of material is totally irreversible due to the crosslinking of molecules. When thermosetting polymers reach the post curing temperatures they become more brittle and rigid, which make them suitable for structural applications. The different types of thermoset polymers are alkyds, acrylics, amine, Bakelite, epoxies, phenolic, polyester, silicone, polyurethane, vinyl ester and others [12].

2.2.2 Thermoplastic Polymers

The thermoplastic polymer structure is mainly composed of linear chains, which have primary covalent bonds. Thermoplastics are the class of polymers, which are capable of curing reversibly. They can be softened or plasticized by the application of heat. They typically transform into these phases, when they reach the glass transition temperature. By the action of heat, the intermolecular bonds are broken making a material soft and solvable. This property of thermoplastic polymer gives the capability to recycle. The different types of thermoplastics are acrylonitrile butadiene styrene, acrylics, poly carbonates, polyethylene, poly propylene, polyvinyl chloride, poly phylline sulfide, polystyrene, cellulose, vinyl, fluorocarbons, polystyrene and others.

2.3 Composites

Composites by definition are a combination of two or more different materials [13]. They have a tendency of being tailorable according to needs. The main purpose of choosing the composites is their quality as illustrated in the Figure 2.5. The quality of a composite material depends upon three major factors, design, material selection and processing technology.

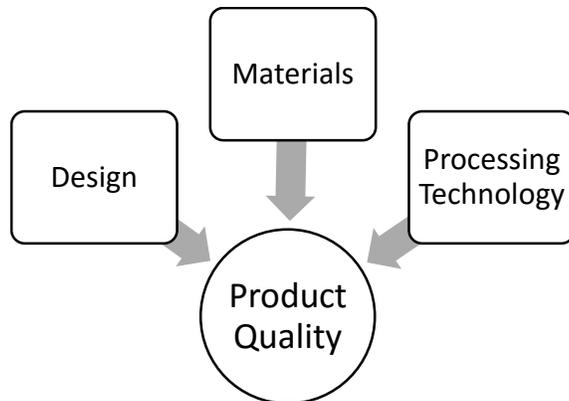


Figure 2.5. Composite material and its quality.

When a new material is in developing stage, it should have a capability to transform intrinsically and extrinsically. Intrinsic defines an internal change due to alloying or heat treatment. Extrinsic defines an external change due to inclusion of reinforcements. These reinforcements can be metallic powders, rods, fibers, whiskers and particles and are illustrated in the Figures 2.6 and 2.7 [14]. These are some of the main features that should be considered when making a new composite material.

Furthermore, composite is an advanced material which has an excellent strength-to-weight ratio and high stiffness-to-weight ratio. These are the two main properties of a composite which make them more adaptable in producing light weight material. Thus, these are some traditional approaches for making the composites that are used for different purposes.

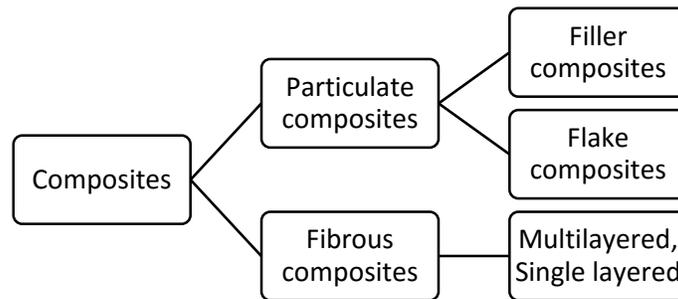


Figure 2.6. Classification of composites and types of fillers.

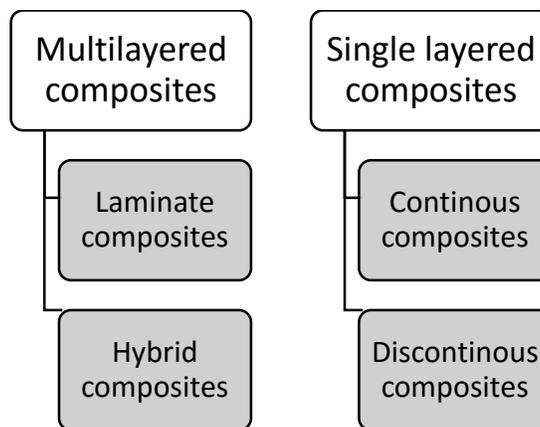


Figure 2.7. Classification of composites.

2.4 Polymeric Composites

The polymers can also evolve into composites when combined with artificial fibers and aramid fibers known as polymeric composites. Polymeric composites have high strength, high stiffness, fracture, abrasion, impact, corrosion, and fatigue resistant properties. Polymeric composites have a wide range of applications in aerospace, automobile, marine, equipment and sports [15].

As the polymers are thermally unstable, the composition of different reinforcements can improve these thermal properties. Depending upon the low- and high-temperature applications the material reinforcements are chosen. For instance, low temperature reinforcements include glass fibers and particulate fibers. The high-temperature reinforcements include carbon fibers.

2.4.1 Polymeric Nanocomposites

The polymeric nanocomposites are attractive to many industries, since they produce lighter materials with superior mechanical properties [2]. The traditional composite material has different kinds of fillers, mainly particulate fibers, uni-directional, and bi-directional fillers. These traditional reinforcements increase the density within the material, which gradually reduces the mechanical properties [16]. This lead to a new concept called polymeric nanocomposites. A typical preparation of a polymeric nanocomposite is shown in the Figure 2.8. The interfacial bonding between polymers and nanomaterials tend to improve the material property and thermal stability of the material.

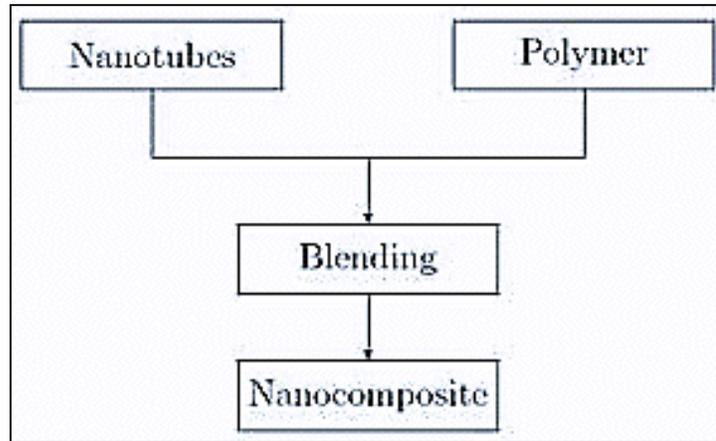


Figure 2.8. Preparation of polymeric nanocomposite.

2.5 Fire Retardancy of Polymeric Composites

2.5.1 Silica as Fire Retardant

Silica is a synthetic polymer, which has applications in aerospace, defense, textiles, cosmetics, and electrical industries [17]. Silica is used as silicon-based compound in the aerospace industry which is also known as poly-methyl-siloxane (PDMS) [18]. Silica has many distinctive compounds like silicate, silicone, silica and organosilanes. As these compounds of silica show exceptional thermal stability, making them ideal for applications in the polymer industry.

When these silicon compounds transform into a nanoscale, they show improvements in mechanical and flame retardant properties. The typical forms of silica in nanoscale are nanosilica and silicate nanoclays. These provide excellent fire retardant properties to epoxy when added in the form of layered silicates. They develop an insulating layer by the formation of carbonaceous silicate char as they are distributed in to this epoxy [19, 20]. The heat release rate and the toxic gases evolved in using of silicone are less when compared with other halogenated flame retardants [18].

2.5.2 Phosphorous as Fire Retardant

Phosphorous is one of the major elements in chemistry which is available in many forms as shown in Figure 2.9. The red phosphorous is one of the allotropes which have the tendency to develop long molecular chains. Due to advances in fire retardancy, the halogenated fire retardants were gradually minimized as they release volatile gases into the atmosphere. Phosphorus has exceptional properties like thermal stability, oxidation, flame retardant and halogen free, which makes them applicable in the production of flame retardant materials.

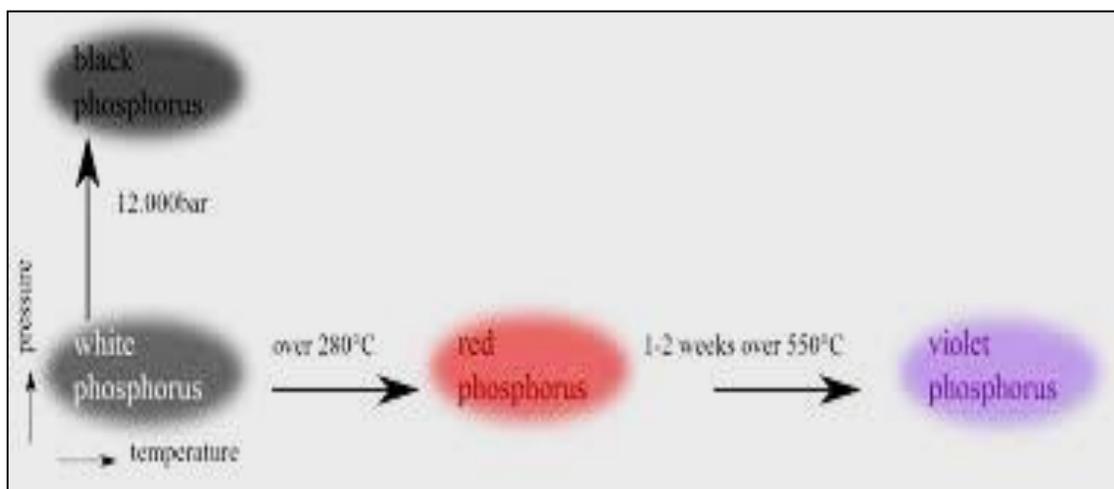


Figure 2.9. Formation of different forms of phosphorous at different temperatures.

Phosphorous has the tendency to act as a flame retardant by developing intumescence and char formation with the increase in temperature. [21] These properties make phosphorous one of the most used materials for enhancing the flame retardancy issue in aerospace, automotive, marine and electrical and electronic industries. Phosphorous, when used as a major reinforcing material in an epoxy, enhances the epoxy's fire retardancy. The incorporation of phosphorous helped achieve an improved fire retardancy either by condensed-phase or gas-phase mechanisms. Condensed phase phosphorous tends to form char, which acts as a barrier for the dissipation of heat. In the gas phase phosphorous evolves toxic gases due to reactions.

Paul et.al (2005) [22], incorporated phosphorous into an aerospace epoxy to improve the fire retardancy. Paul used Tertglycidyl-4, 4'-methylenedianiline (TGMDA), which is a cycloaliphatic epoxy and 4, 4'-diaminophenylsulfonate (DDS) as the base material. Paul introduced the phosphorous as a reactive diamine in different weight percentages to the epoxy to improve the thermal stability. The end results showed that the 3 wt. %, phosphorus inclusions were very helpful in improving the fire retardancy of epoxy.

Toldy et.al (2011) [23], used the technique of adding phosphorous as reactive amine to improve the cross-linking of the epoxy. The epoxy was utilized in preparation of composite panels using the technique of hand lay-up. The composite panels were prepared to have a thickness of 4mm after the curing process. The panels were put to different fire retardant tests, including a lower oxygen index (LOI) (ASTM 2863) and a cone calorimetry test with the heat flux rate of 50kw/m². The composites prepared with the aliphatic resins showed better results in improving fire retardancy and mechanical performance of a composite panel. They improved fire retardancy by obtaining the UL-94 ratings of (V-0) for these composite panels. The phosphorous inclusions enhanced the fire retardancy by forming intumescence layers.

Kandola et.al (2003) [24], utilized phosphorous as the material to improve fire retardancy of a composite panel by intumescence. Kandola conducted fire tests using cone calorimetry to discover positive fire retardant properties for the composite panel. After thermal analysis using cone calorimetry Kandola observed char development at 400°C. The morphological analysis using scanning electron microscopy revealed better formation of intumescence layers in the burned sample.

2.5.3 Carbon Based Fire Retardants

Carbon is one of most the versatile elements from the periodic table. Carbon atoms have a variety of allotropes in the solid phase which lead them to form graphite, diamond and buckminsterfullerene, as shown in Figure 2.10 [25]. Carbon has covalent bonds between atoms, which tends to form large and complex structures.

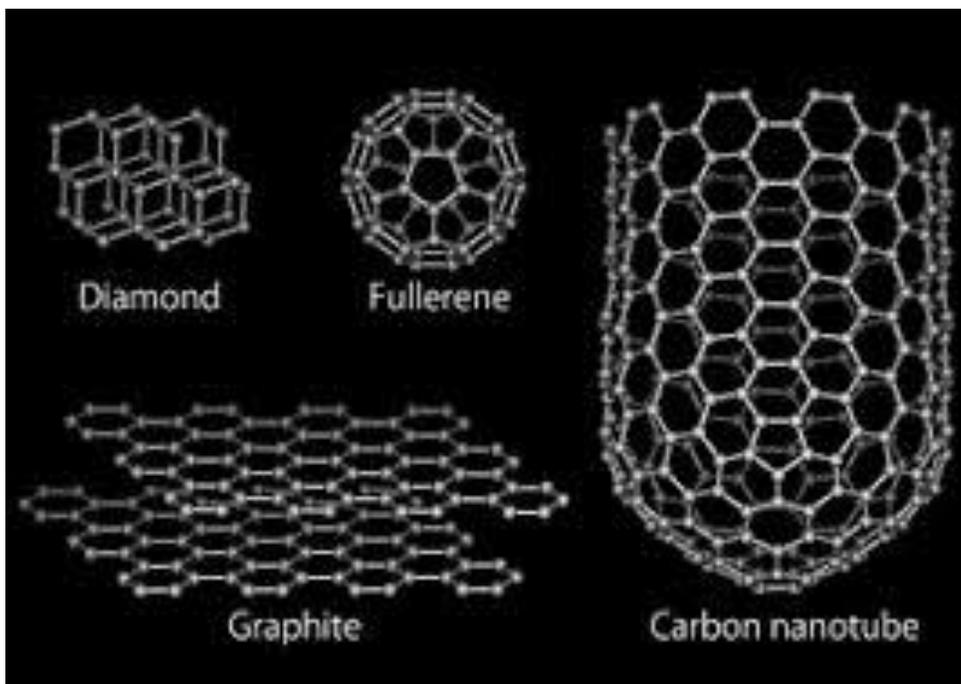


Figure 2.10. Carbon and its allotropes.

Rick Smalley initially discovered fullerenes in 1985. Rick later discovered C₆₀ and named it as soccer ball [25]. The C₆₀ consist of carbon atoms with hexagonal and pentagonal structures. The C₆₀ has extraordinary properties, mainly semiconducting, chemical, physical, electronic, electrical and magnetic [26, 27].

These discoveries by Rick led to extensive research on carbon allotropes. Ijima showed evidence in the formation of carbon nanotubes from the fullerenes [28, 29]. Ijima stated that the carbon nanotubes are the sheets of graphene, which are rolled concentrically. He discovered multi-

walled carbon nanotubes (MWCNT) using the transmission electron microscope (TMA) and discovered that MWCNT has layers of graphene that range from 2 to 20 [28]. Later Ijima's research was extended by one of his coworkers who observed single walled carbon nanotubes [30].

Due to extensive applications of these carbon nanotubes, the production rate has increased. The most important methods used for synthesis and production of carbon nanotubes are arc discharge method, chemical vapor deposition, and plasma enhanced chemical vapor deposition methods [31, 32, 33, 34]. These are some important techniques used in the production of carbon nanotubes, which further led to innovation of carbon fibers, filled carbon nanotubes, multi-walled carbon nanotubes, crystalline ropes and bundles of carbon nanotubes [35].

2.5.4 Graphite, Graphene and Graphene Oxide as Fire Retardants

Graphite was under consideration for almost 150 years due to its interesting properties and its cost effectiveness [36]. Graphite is a three-dimensional carbon allotrope which has a honey comb structure stacked in many layers in a sequence. Each single layer from the stack is built from sp^2 hybridized carbon atoms, with a two-dimensional molecular structure known as graphene. Graphene is an allotrope of carbon which has a two-dimensional molecular structure with a tightly packed pie-pie stacking interaction and weighs about $10^6 - 10^7 \text{ gmol}^{-1}$. As graphene is a two-dimensional crystal structure, it exhibits excellent thermal and electrical properties and high carrier mobility.

Graphene also exhibits excellent properties like stiffness of 1Tpa, electrical conductivity of $5000 \text{ w.m}^{-1} \cdot \text{K}^{-1}$ and specific area of $2600 \text{ m}^2 \cdot \text{g}^{-1}$ [37]. The graphene is produced mainly by chemical vapor decomposition, wet chemical dispersion, exfoliation technique, micro exfoliation technique and epitaxial growth mechanisms [38]. The formation of graphene is clearly illustrated

in the Figure 2.11. These are some of the important techniques used in the production of graphene from raw graphite [39, 40]. Thus, graphene was predominantly used in industries of aerospace, automobile, marine, electrical, electronic, chemistry, and materials science. Several experiments were carried out in justifying the formation of graphene from graphite.

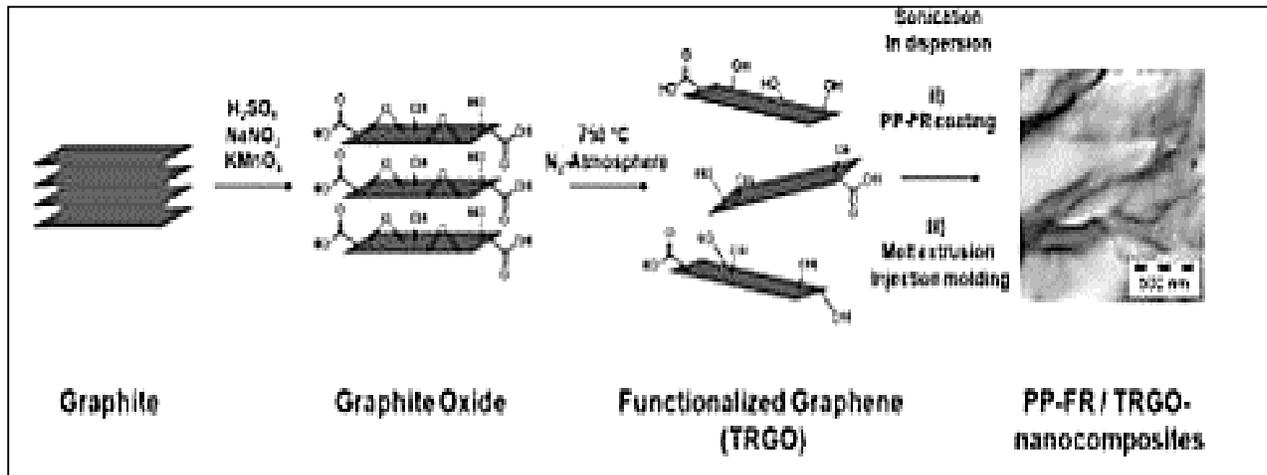


Figure 2.11: Different types of graphite.

Daniel Hofmann et.al (2013) [37] studied graphite and its properties in producing the functionalized graphene. Hofmann chose graphite, which has the carbon content of 96.7%, and stated that the graphite expansions will lead to more than 100 layers of graphene [41]. The study carried out the functionalization process for breaking down graphite and then incorporated the graphene into low viscous isopropyl alcohol. The exfoliation of graphite was done by mechanical stirring and sonication process, which is a liquid assisted sonication process, at 400C. This technique forms perfect graphene [42]. Hofmann examined the thermal stability, mechanical properties and morphology analysis by performing several tests on graphene. The fire retardancy tests, especially cone calorimetry tests, were carried out for different weight percentages of graphene for evaluating the fire retardant properties of graphene. Hofman observed improvements

in fire retardant properties of polypropylene by decreasing the graphene layers by functionalization techniques.

Furthermore, researchers have studied different techniques to improve the thermal stability of an epoxy system. Researchers used the same procedure of functionalizing the graphene initially, before incorporating into the pristine epoxy.

Peipei et.al (2016) [43] used the functionalization and exfoliation techniques for improving flame retardancy of the epoxy by incorporating graphene powder inclusions. Graphene was approximately less than 20 μ m, which later exfoliated by dissolving it into the ZnSO₄, 7H₂O and then stirred using the centrifuge process, until the solution is evaporated leaving the graphene powder. Afterwards, the samples were cleaned using the deionized water until the residual ions were removed from the graphene. This functionalized graphene was subsequently introduced into the polymer amine (M2070) epoxy. Thermal stability tests, including cone calorimetry and UL-94 vertical tests, were carried out on the samples. According to the results obtained by cone calorimetry and lower oxygen index scenarios, factors like peak heat release rate, total smoke release reveal that the graphene inclusions improve the fire retardancy of the epoxy. Most of the UL-94 vertical tests showed the ratings of V-2 along with low volatile emissions.

Furthermore, the percentages of graphene content play a major role in improving fire retardancy. As the graphene content increases, the surface area increases. These transformations will improve a variety of material properties.

Sasha et.al (2007) [44] conducted several experiments on the graphene oxide and its exfoliation using hydrazine hydrate to improve reduction of oxygen content, thereby enhancing the surface area of graphene sheets. Most of the moisture is removed at 200C in the graphene oxide

and yielding better thermal stability by removal of oxygen functional groups, which has enhanced the graphene structure with this exfoliation process. Thus the graphene obtained from the process like these will gradually reduce the rate of fire by decreasing the smoke evolution and acts as a flame retardant.

2.5.5 Carbon Nanomaterials (Tubes, Flakes, Fibers, SWNT, MWCNT) as Fire

Retardants

Due to their exceptional properties, the carbon nanomaterials were used as reinforcements for enhancing the fire retardancy. Different types of nanomaterials like nanofibers, single-walled carbon nanotubes and multi-walled carbon nanotubes were used as additive reinforcements into the polymers to improve the thermal stability.

Alberto Fina et.al (2008) [45] conducted experiments on the multi-walled carbon nanotubes and the single-walled carbon nanotubes which were dispersed into the polyhedral oligomer siloxane. Fina conducted tests for evaluating the thermal stability of the nanocomposite, using Thermogravimetric analysis and cone calorimetry tests. Fina observed that carbon nanotubes were able to develop the char on the surface of the polymeric nanocomposite, due to oxidative dehydrogenation. The surface morphology tests on the burned samples reveal that the crosslinking of the polymers tend to deteriorate by forming thin carbonized layer which intend act as a potential fire barrier.

Kashiwagi et.al (2002) [46] conducted many experiments to determine the thermal stability and the behavior of the carbon nanotube inclusion into the polymer matrix. He added the carbon nanotubes into the poly methyl methacrylate with the better dispersion rates. The samples were tested under the cone calorimeter and the thermogravimetric tests. Kashiwagi observed that the carbon nanotubes aid the polymers by producing the protective layers at the high temperature. He

also observed the mass loss rate was decreased with the better dispersion of carbon nanotubes under the thermogravimetric analysis.

Furthermore, the carbon nanotubes were used to improve the damping properties of the epoxy. By inclusion of carbon nanotubes into the epoxy, Abhinav Alva and S. Raja observed improved damping stiffness. They made the samples of epoxy nanocomposite using multi walled carbon nanotubes and epoxy which are mixed at the ratio of 100:12 and then cured at 50°C. The 0.5% inclusion showed good results when compared with the 1% inclusion because the interfacial slippage is low due to less percentage of inclusion. The epoxy nanocomposite was very helpful in achieving better damping properties [47].

2.6 Adhesive Joints

Structural adhesives are used in the preparation of metal or composite joints. The adhesives are mainly epoxy-based. These epoxy based adhesive joints have a tendency to bond dissimilar materials without any gaps or voids [48]. These adhesive joints play a crucial role in maintaining the structural integrity. They can distribute the loads uniformly when they are perfectly spread between two adherend [49, 50, 49]. Adhesive joints improve fatigue resistance, improve surface smoothness, corrosion resistance and reduce stress concentration. 70% of the structures fail due to shear loads that are experienced on the adhesively bonded joints [51]. Other factors that affect the performance of an adhesive joint are adhesive type, temperature, joint preparation, moisture, adherend, bond line thickness, type of load applied, etc.

Kairouz et.al (1993) [52] carried out experiments on the adhesive thickness property and stated that the adhesive thickness played an important role in the structural integrity. He also stated that the failure rate significantly increased by an increment in adhesive bond layer thickness.

Abdullah al-khanbashi et.al (2012) [53] conducted experiments on the life time of creep growth of adhesively bonded single lap joints. Abdullah have tested the samples of single lap joints were tested using tensile tests to find out the shear strength. The samples were kept under a constraint of glass transition temperature at 50°C and then tested for properties of creep. At the end the test results reveal that strain energy was improved by the increase in the adhesive bond line thickness. Abdullah have also observed a significant growth in creep with an increase in bond line thickness.

Banea et.al (2010) [54] explained the behavior of the single lap joints with the effects of temperature. The temperature was the major issue in the polymers as it causes the shrinkage due to the curing cycle. Banea observed the reduction of fracture toughness at the temperature of 200C [55]. He has also observed the different modes of transitions in an adhesive with the increase in temperature. Banea observed cohesive failure at 100°C, and adhesive failure at 200°C. This shows that the temperature plays an important role in adhesively bonded joints.

Many other reinforcements are added into the polymers to improve the mechanical properties of the adhesive bonded joints. Ramazan Kaharaman et.al (2008) [4], investigated the mechanical properties of adhesively bonded single lap joint by adding aluminum powder which is 50µm in diameter into the epoxy. The adhesive joint was prepared according to the standards of ASTM D1002, for different bond line thicknesses ranging from 0.03mm-1.3mm. Ramazan observed reduction of adhesive strength with the increase in bond line thickness. But reinforcements of aluminum powder inclusion improved the material properties.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials

- **Magnolia 6380 A/B Epoxy**

Magnolia 6380 A/B is a two-component epoxy system, which was a thermosetting polymer. The mixing ratio of this epoxy system was 100:27 by weight percentage according to specifications of the technical data sheet.

The material was generously provided by Magnolia Advanced Materials, U.S.A. It was a high viscous epoxy system, especially designed for structural joints. The epoxy adhesive is well-known for its high performance and low moisture content. It has a wide range of applications in the aerospace industry. Magnobond 6380 A/B was used in different aerospace companies, like Boeing/Sikorsky 2000-777-016, 0-02-DASH-001A, Rockwell MBO-120-037, Type II, Class-I and Sikorsky SS 8622-007A. This epoxy system has a wide range of substrates, which was beneficial for curing procedures at a distinctive set of temperatures.

- **Graphene N006-010-P**

The Graphene N006-010-P nanomaterials were purchased from Angstrom materials, Dayton, Ohio. The graphene powder or graphene oxide had a true density less than 2.20 (gm/cm³). The graphene powder has carbon content of 95.0%, which makes it black or greyish in color. It has a thickness of 10-20nm, x-y dimension of 5.0µm and have the surface area around 110m²/gm. This material was well known for its application in the manufacturing of nanocomposites.

- **Acids and Chemicals**

Sulfuric acid, sodium bicarbonate, sodium dichromate, acetone and ethanol were purchased from Fisher Scientific Inc., Philadelphia.

- **Alodine**

Alodine is an instant chromate conversion liquid, which was manufactured by Henkel Corporation, North America. This conversion kit was a nonflammable liquid, which consists of chromic acid for chromate conversion coating. This uses an activator, which activates the reaction between the metal and the solution through oxidation process. The chromate conversion coating from the alodine solution provides roughness to the metal, which enhances adhesion property for adherend. Due to this chromate conversion process, the corrosion resistance was also improved.

- **Aluminum 2024-T3**

Aluminum 2024-T3 was purchased from Online Metals. The T3 represents that the material was heat treated. The thickness of the aluminum sheet was 1.62mm. Aluminum 2024-T3 has better mechanical properties and was used in multitude of applications. Aluminum alloy have excellent properties which make it attractive in aerospace and mechanical industries, including being light weight, corrosion resistant, high reflectivity, high conductivity and high strength. Aluminum 2024-T3 has been used in the manufacture of aircraft wings, aircraft fittings, rivets, structures, bolts, nuts, hydraulic systems, worm gears, couplings, etc.

3.2 Experimental Methodology

3.2.1 Preparation of Aluminum Test Panel Strips

The prerequisites for the preparation of aluminum was degrease, abrade with degrease, and chemical pretreatment along with degrease.

The aluminum 2024-T3 sheet was machined into metal strips with the dimensions of 102mm x 25mm x 1.62mm, as shown in Figure 3.1a. They were machined using the milling machine for maintaining perfect dimensions. The protection layer was completely removed and checked thoroughly for any sort of defects prior to use.

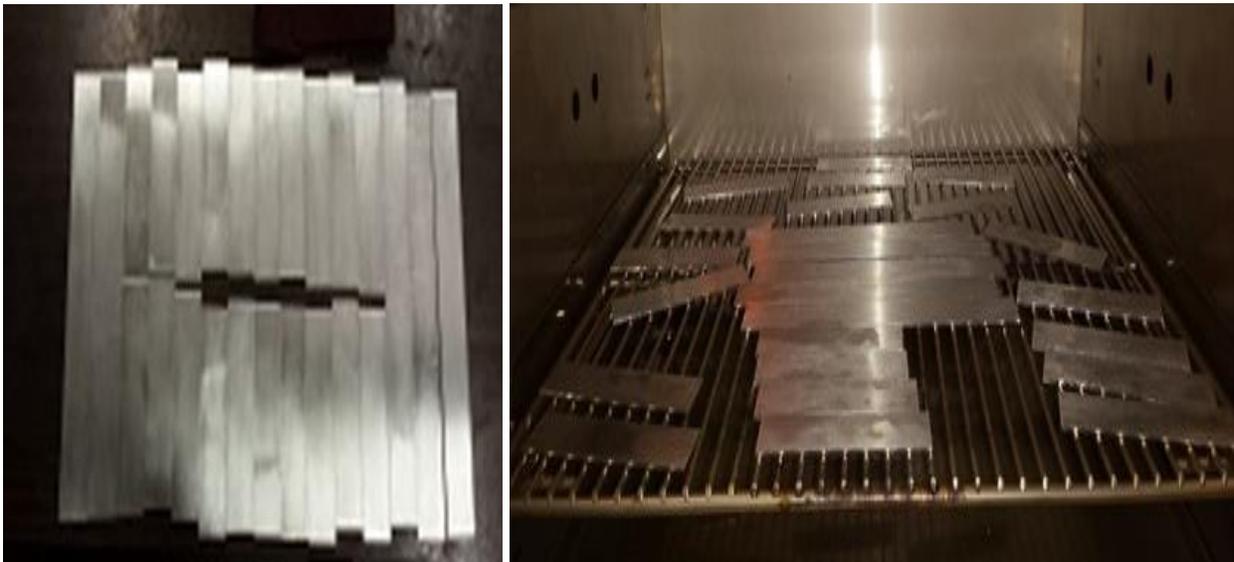


Figure 3.1. a) Preparation of aluminum test panels, b) Specimens dried in the oven.

The test specimens of aluminum metal strips were sanded using fine 220-240 grit sand paper for improving the surface roughness of the aluminum. Metal strips were cleaned with distilled water and acetone to remove the dirt on the surface. Aluminum metal strips were then cured in the oven for one hour at 60°C and were set to dry, as shown in Figure 3.1 b. The surface

preparation of the aluminum plays a vital role in the adhesive bonding. As the adhesive joints produce higher stress concentrations at the edges of the specimen, the edges were sanded perfectly.

3.2.2 Etching Process of Aluminum Test Panel Strips.

The etching chemical process was mainly used to prepare the metal surface free from contaminants of dirt. An isotropic etching process was carried out in this research for preparing aluminum test specimens. The isotropic etching process provides etching rates in both vertical and horizontal direction. By performing chemical etching process, the corrosion resistance and surface roughness of specific metal will be improved. The main reason to choose the wet etching process is its cost effectiveness, low solution wastage and reusability.

3.2.3 Chemical Etching

Traditional chemical etching process was carried out at the initial stages of research for preparing aluminum test strips. The surfaces were cleaned thoroughly with trichloroethylene slowly by spraying on the surface and then wiped with a cloth. Then the surfaces of aluminum were separated using the screws and nuts in making a batch. The etching process of aluminum metal sheet was carried out in the oven, as it needs a heating element.

A glass pan was taken and filled with deionized water of 531ml. The sulfuric acid of 96% concentration was then added to the water. The sodium dichromate weighed 62.5grams was added slowly to the solution and then mixed till it was dissolved completely. The molarity of the complete solution was 3M, which was sufficient to produce better etching rates. The prepared aluminum sheets were slowly submerged into the etching solution as shown in Figure 3.2.e. The solution mixture was constantly agitated for maintaining etching rates. The etching solution was then transferred into a different container, so that it can be reused for other specimens.

The left over solution was neutralized, using the sodium bicarbonate powder. The neutralization was done to remove the hazardous contents of chromate. After neutralizing the solution, the metal plates were cleaned with deionized water and wiped thoroughly with a free cloth. The aluminum plates were dried in the oven for 30 minutes at 70°C as shown in Figure 3.2.h. The aluminum plates were then machined into small test strips, and surface cleaning was done using the same procedure that's been carried out for aluminum plates. The test strips were flipped on each side for 20 minutes, so that the etching process was carried out properly. The collected aluminum strips were dried in oven at 70°C, so that all the moisture content gets evaporated. The procedure for preparation of aluminum metal strips was illustrated in the Figures 3.2.a to 3.2.h.

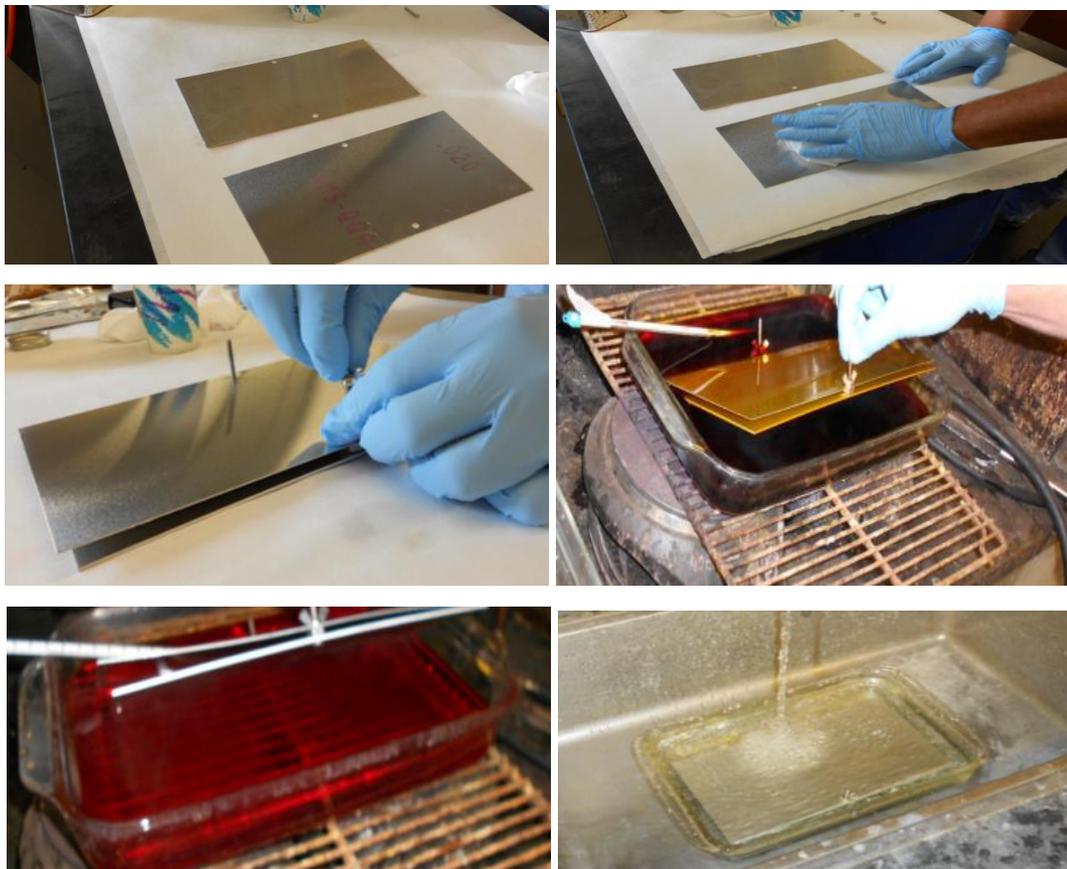


Figure 3.2 a) Aluminum alloy, b) Machined aluminum alloy, c) Cleaning aluminum, d) Fixing nut and bolts, e) Immersion of Al plates into etching solution, f) Heating element, g) Cleaning.



Figure 3.2. h) Dried aluminum metal strips in oven.

3.2.4 Alodine Etching Process

The alodine etching process is a surface preparation technique which was used for aluminum metal plates. The etching process undergoes two steps, oxidization and chromate conversion coating. Alodine etching process was well-known for its self-etching process and chromate conversion coating, which made it applicable in preparation of aircraft or automobile adherend.

The alumini perp was used as an oxidizing agent before etching process. The pot was filled with 150ml of alumini perp and then the aluminum metal strips were submerged into solution for 5 minutes. The aluminum metal strips were cleaned from dirt and grease due to oxidization. Aluminum metal strips were then cleaned with acetone and then transferred into oven for 30 minutes and were set to dry at 70°C.

Alodine contains chromic acid, which was a source for chromate conversion process. Alodine of 200ml was taken into a tray, and then the aluminum specimens were submerged into solution for five minutes as shown in Figure. As the etching process proceeds the aluminum metal strips were flipped to maintain constant consistent etching rates. As etching rates of alodine were very high, it can damage the material when kept in solution for long time. The time for submersion

plays a vital role in chromate conversion coating due to its high oxidation rates. Subsequently, the samples were cleaned with ionized water and then dried in the oven for 30 minutes at a constant temperature of 70°C. A prepared aircraft wing structure using chromate conversion coating was shown in Figure 3.3 b.



Figure 3.3. a) Alodine etching process, b) Aircraft wing etched using alodine.

3.2.5 Sonication Process

Sonication is a dispersion process in which the sound waves are utilized to mix thoroughly. The vibrations produced by these sound waves at high frequency break down the particle lumps in the solution. This procedure was used in the preparation of the epoxy resins.

The acetone of 50 ml was taken in a beaker and then epoxy weighing 30grams was added to the solution. Then the solution of acetone and epoxy were mixed together using the sonication method. Then heating element was set to room temperature, and the speed of the mechanical stirrer was set to 400 rpm. The agitation of mixture is then continued for one hour until all the remains of acetone evaporate by leaving the epoxy. The dispersion of nanomaterials in this epoxy was tough, as the epoxy was highly viscous even after sonication process.

3.2.6 Three Roll Milling Method

Due to extensive use of nanomaterials in improving the material properties, the dispersion was the major factor that needed to be considered. A three roll milling method was used for better dispersion. The three roll milling process was not only limited to nanotechnology but has applications in color, food, cosmetics, chemical and pharmaceutical industries.

The three roll milling machine has three rollers: feed, center and apron. They have a roller speed ratio of 1:3:9, which produce extremely high shear forces between the rollers. The agglomerations produced by nanomaterials can be reduced by constantly shifting the gaps between the rollers.

At first, the machine was calibrated for gap, tray, and nip gap errors. These should be calibrated by cleaning normally or cleaning it using the reverse method. Afterwards, the accessories of three roll mill were fitted for collecting the material easily. Subsequently, the epoxy was introduced in appropriate weight ratios, i.e. (100:27). The epoxy was put through several cycles to decrease the viscosity, and then the nanomaterials were added slowly into the mixture of epoxy, as shown in Figures 3.4 and 3.5. The mixing cycles for producing an epoxy nanocomposite range from 40 to 50 cycles. Subsequently, the hardener was added to the epoxy and nanomaterial mixture, which reduced the viscosity of an epoxy. The chemical reaction between the epoxy and hardener and the shear forces between roller gaps disperse the nanomaterials into the epoxy. At the end of the process, the material was transformed in to a low viscous liquid with nanomaterials, which could then be utilized in the preparation of epoxy nanocomposite specimens.

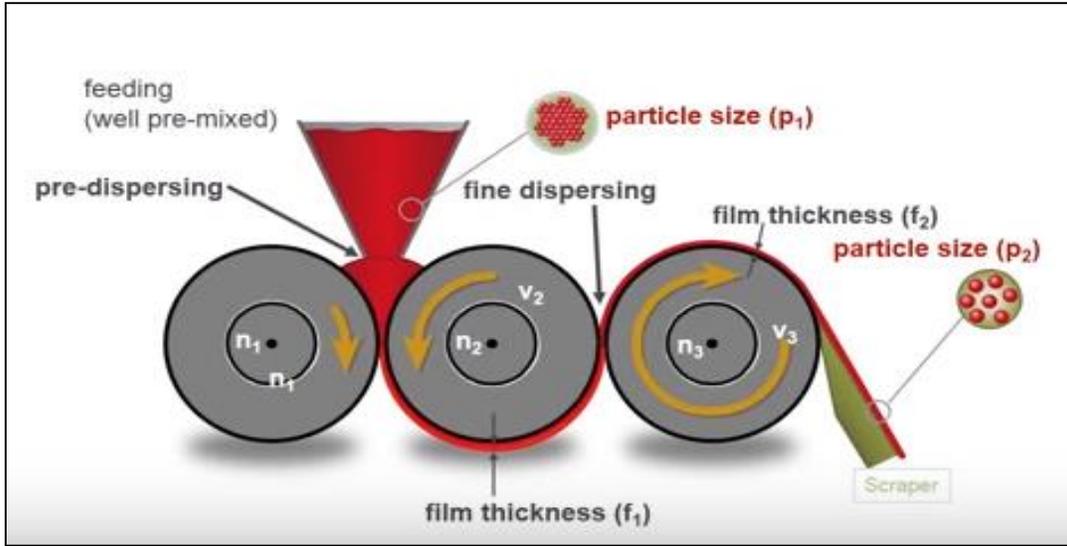


Figure 3.4. Methodology of three roll milling machine.

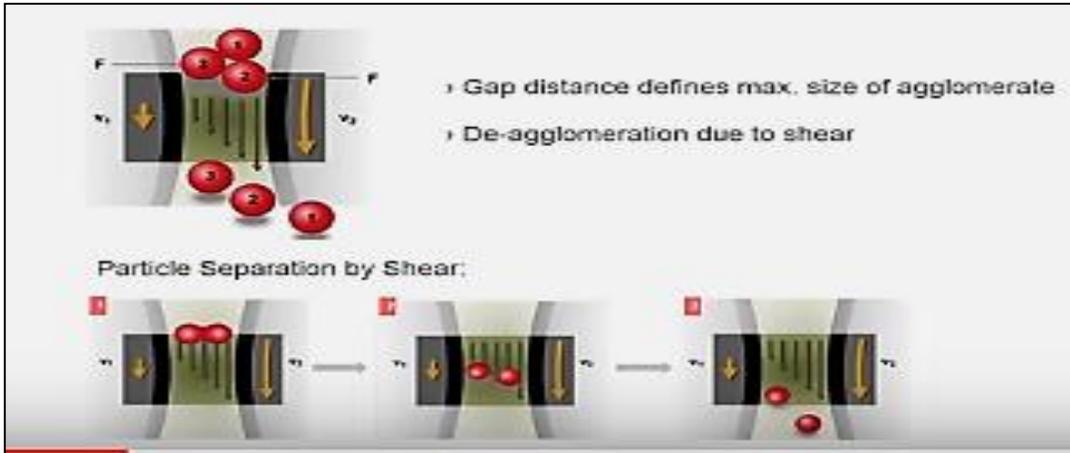


Figure 3.5. Shear force mechanism of the three roll milling machine.

List of nanocomposite batches made using three roll milling process.

Table. 1:

Epoxy nanocomposite batches for Tensile test.

Epoxy (Magnolia 6380 A/B)	Inclusion
Batch 1	0 wt% Nanomaterial inclusions
Batch 2	0.5 wt% Nanomaterial inclusions
Batch 3	1 wt% Nanomaterial inclusions
Batch 4	2 wt% Nanomaterial inclusions
Batch 5	3 wt% Nanomaterial inclusions

Table 2

Epoxy nanocomposite batches for Tensile test.

Epoxy (Magnolia 6380 A/B)	Inclusion
Batch 1, 5 samples	0 wt% Nanomaterial inclusions
Batch 2, 5 samples	0.5 wt% Nanomaterial inclusions
Batch 3 , 5 samples	1 wt% Nanomaterial inclusions
Batch 4, 5 samples	2 wt% Nanomaterial inclusions
Batch 5, 5 samples	3 wt% Nanomaterial inclusions
Batch 6, 5 samples	5 wt% Nanomaterial inclusions
Batch 6, 5 samples	10 wt% Nanomaterial inclusions

Table 3

Epoxy nanocomposite batches for DSC pans.

Epoxy (Magnolia 6380 A/B)	Inclusion
Batch 1, 3 pans	0 wt% Nanomaterial inclusions
Batch 2, 3 pans	0.5 wt% Nanomaterial inclusions
Batch 3, 3 pans	1 wt% Nanomaterial inclusions
Batch 4, 3 pans	2 wt% Nanomaterial inclusions
Batch 5, 3 pans	5 wt% Nanomaterial inclusions
Batch 6, 3 pans	10 wt% Nanomaterial inclusions

3.2.7 Preparation of Mold for UL-94 Test Specimens

The mold was prepared to minimize the waste due to high viciousness of the epoxy. Another factor considered for preparation of the mold was maintaining precise dimensions for making epoxy nanocomposite specimens according to technical standards of ASTM and FAA standards

The mold was designed using CATIA-V5 software. The designed model was exported to MASTER CAM software, which generated a code for machining process for this particular mold model. A steel plate of dimensions (380mm x 225mm x 3mm) was machined into the required sample size using the milling machine as shown in Figure 3.7 b. The slots made were consistently maintained with a tolerance of 1mm on all the sides and this is shown in Figure 3.6. The 1mm tolerance space allows the cured epoxy sample to be later machined after the epoxy has cured.

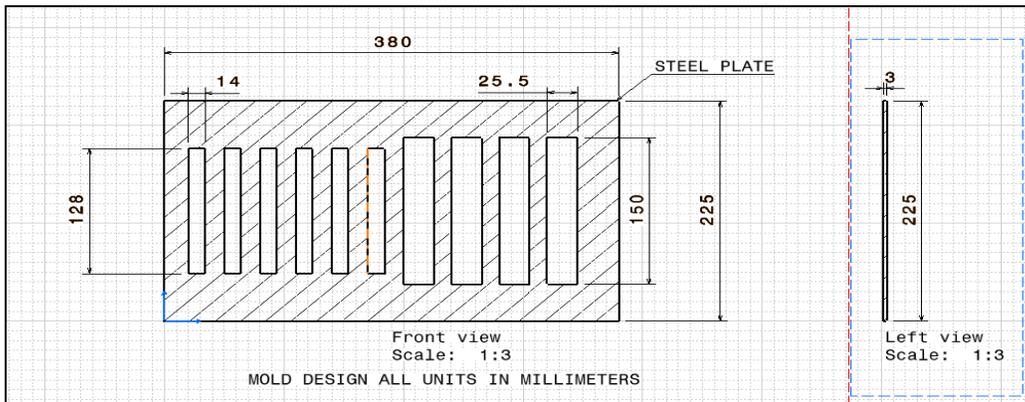


Figure 3.6. Geometrical drafting of mold.

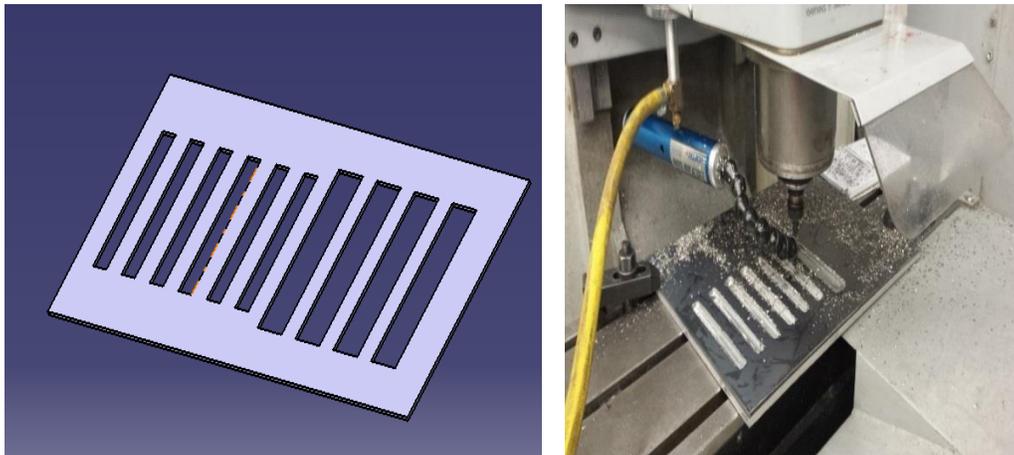


Figure 3.7. a) CATIA model of mold, b) Mold prepared using milling machine.

3.2.8 Preparation of UL-94 Fire Test Epoxy Nanocomposite Samples

The nanocomposites were cast using the mold prepared for UL-94 vertical fire tests. The mold was cleaned with acetone before preparation of every batch of epoxy nanocomposite. The base of mold was then covered with aluminum foil to improve the surface finish of prepared sample. A releasing agent was sprayed into the rectangular slots to ease the removal of sample after curing process. The prepared epoxy nanocomposite mixture was then slowly spread in to the slots and scraped on the top for perfect finish. Figures 3.8 a, b show the preparation of pure epoxy samples for UL-94 fire tests.

The samples of epoxy nanocomposite were then set to a ramp up temperature to 80°C. The temperature was then maintained at 80°C for two hours. The oven cured samples were then further cured for two days, until they attain a complete curing process. Then samples were subsequently cut from the mold and machined to perfect size according to technical standard.



Figure 3.8.a) Epoxy nanocomposite dispersed for curing process, b) Collecting prepared specimen.

3.2.9 Scanning Electron Microscopy

Scanning electron microscopy was used to study the surface morphology of epoxy nanocomposite samples. SEM uses the primary and secondary electron beams to produce an image of a specific sample. The cured samples of the pure epoxy and epoxy nanocomposites were cut into small square bits as shown in Figure 3.9. The prepared samples were run through scanning electron microscopy tests at various magnification rates. Resolutions of 200nm, 1 μ m, 2 μ m, 10 μ m and 20 μ m were used to analyze the structure of the epoxy nanocomposites.



Figure 3.9. Epoxy nanocomposite samples prepared for SEM analysis.

3.2.10 Differential Scanning Calorimetry

DSC was used to examine the thermal properties of an epoxy. DSC mainly specifies glass transition temperature, crystallization temperature and heat flow rates.

The DSC tests were carried out for pure epoxy and epoxy nanocomposites. The methodology used a QA 1000 DSC instrument, shown in Figure 3.10 a. The DSC test pan preparation was shown in Figure 3.10 b, and then the weight was recorded. The calorimetry testing was done under the environment of nitrogen, which has a purge gas flow rate of 50ml. The experiments were conducted on both wet and cured epoxy samples. The temperatures ranged from

-100°C to 300°C with an increasing rate of 10°C/minute. These temperatures clearly specify the properties of an epoxy at cryogenic and high temperature limits.



Figure 3.10 a) QA 1000 Differential Scanning Calorimetry, b) Sample pan preparation

3.2.11 Thermogravimetric Analysis

Thermogravimetric analysis was mainly used to determine the material mass loss rate with respect to temperature. This machine can plot a variety of graphs related to phase changes and the decomposition of a particular sample. Especially induced heat flow of an epoxy nanocomposite sample will determine the heat conductivity and material characterization.



Figure 3.11 a) Prepared epoxy samples, b) Prepared sample pan for the TGA test

The prepared epoxy samples were collected as shown in Figure 3.11a, and cured according to the curing temperatures specified by the technical sheet. The sample pans were prepared and weighed appropriately as shown in the Figure 3.11 b. Then the prepared samples of epoxy nanocomposites were sent into a furnace. The temperature ranged from 100°C to 1000°C with an increment of 10°C/minute under nitrogen environment. The phase changes and mass loss percentages of pure epoxy and epoxy nanocomposite were recorded and compared with the baseline. Thus, this experiment was essential in determining the thermal properties of an epoxy nanocomposite.

3.2.12 Adhesive Lap Shear Strength Test

The tensile tests were carried out to predict mechanical properties of an epoxy adhesive. The strength of an adhesive depend on density, flow characteristics of epoxy, curing cycle, gel time, carrier composition, cooldown rate, pressure induced and temperatures. All these factors were considered for the evaluation of a specific adhesive joint. Many test runs were made to achieve the consistency in maintaining the bond line thickness of the single lap joints. The epoxy weighing 0.5 grams, when applied on lap joint showed a promising bond line thickness of approximately 0.15mm to 0.2mm. This specific bond line thickness was acceptable according to the technical standards of ASTM D1002.

The aluminum metal strips were prepared using the milling machine for better surface finishing. Perfect dimensions were maintained according to technical data sheet of ASTM D1002 standard. Then the machined metal strips were cleaned with acetone and dried in the oven at 60°C to remove moisture. Each aluminum metal strip had the dimensions of (177.8mm x 25.4mm x 1.62mm), which included the bonding surface area of 12.7mm. The samples were then sent through etching process for improving the adhesion properties. Five sets of samples were prepared

having different weight ratios of 0wt%, 0.5wt%, 1wt%, and 2wt% and 3wt% graphene nanomaterial inclusions. The epoxy adhesive was applied slowly on the bonding area and clamped using the binder clips, as shown in Figure 3.12.c. These binder clips were consistent in maintaining pressure throughout the curing process. Afterwards, the samples were then transferred into an oven for two hours. The curing cycle required a temperature change from room temperature to 80°C, as shown in Figure 3.12.d. Then the samples were removed and cured for one more day at room temperature for better adhesion between adhesive and metal. Then the samples were sand blasted for any external remains of unwanted epoxy, which is spilled on the metal strips.

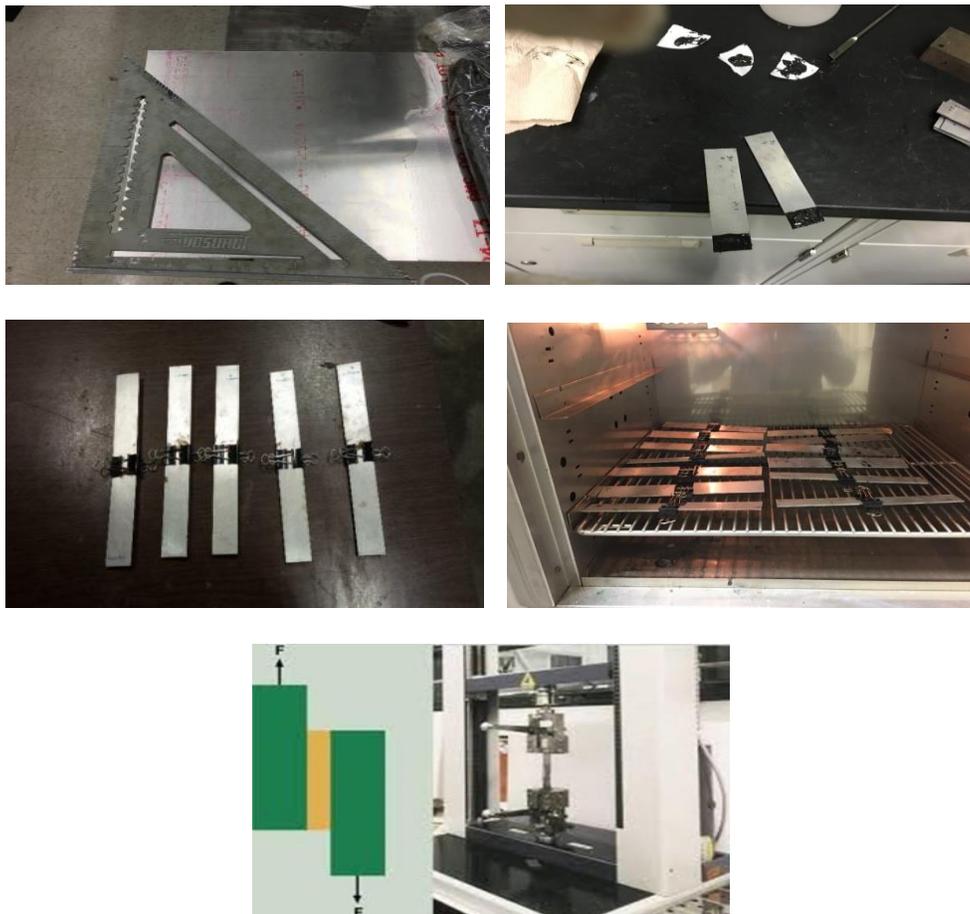


Figure 3.12. a) Surface preparation of aluminum, b) Application of epoxy, c) Adhesive bonding using binder clips, d) Curing process in oven, e) Tensile test apparatus.

The prepared adhesive single lap joints were subsequently tested using the tensile test machine as shown in Figure 3.12 e. The machine is calibrated first for any kind of internal errors and then set to application with a loading rate of 1.27 mm/minute. The rate of loading was maintained as specified by standards, which play a major role in the behavior of the single lap joint. A record is maintained for adhesive bond line thickness and the length of the bonded area for each specimen that is being tested. The tested samples give a better picture for characterization of epoxy by evaluation of stress-strain curves. The material characteristics like ultimate stress, fracture stress, yield stress, and elongation were evaluated. The same testing procedure is repeated for the different percentages of nanomaterial inclusion and then comparison of the results with the baseline epoxy results.

CHAPTER-4

RESULTS AND DISCUSSION

4.1 Electron Scanning Microscopy for Surface Morphology Analysis

Nano material inclusion plays a vital role in improving the mechanical properties and material behavior. These changes occur due to the dispersion rate, and the amount of nanomaterials utilized. Electron scanning microscopy was used to visually analyze the structure of the nanomaterials, through images which were generated at the nanometer scale. Surface morphology analysis using scanning electron microscopy can significantly improve the dispersion rates of nanomaterials in enhancing the mechanical and thermal properties of an epoxy nanocomposite.

The scanning electron microscopy tests were carried out to see the dispersion rates of different weight percentages of graphene inclusions. The unburned and burned samples of the epoxy nanocomposites were analyzed to determine the fire retardant properties. The Figure 4.1 show the surface characterization of unburnt pure epoxy.

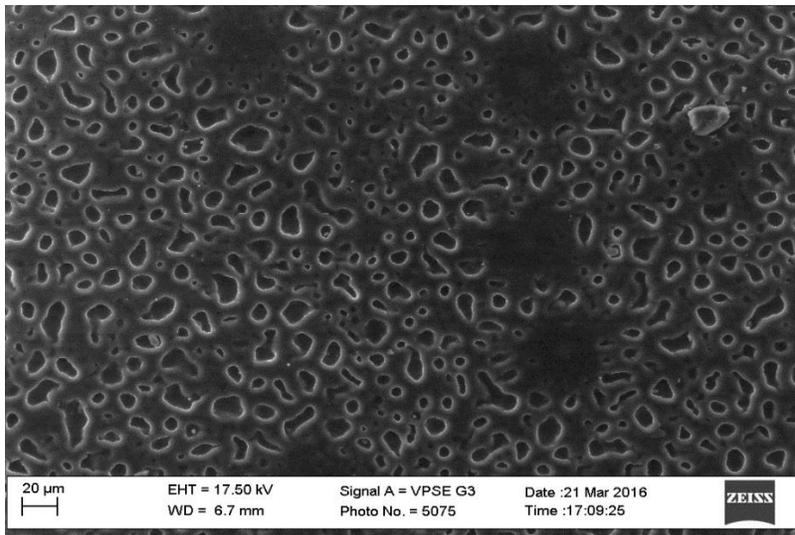


Figure 4.1. SEM image of the pure magnolia 6380 epoxy adhesive.

The Figure 4.2.a show the basic structure of the magnolia 6380 after curing cycle, which consist of pores. These pores determines the basic structure of a pure epoxy. The Figure 4.2a show more magnified images of the pores, which are useful for comparison of epoxy nanocomposite samples.

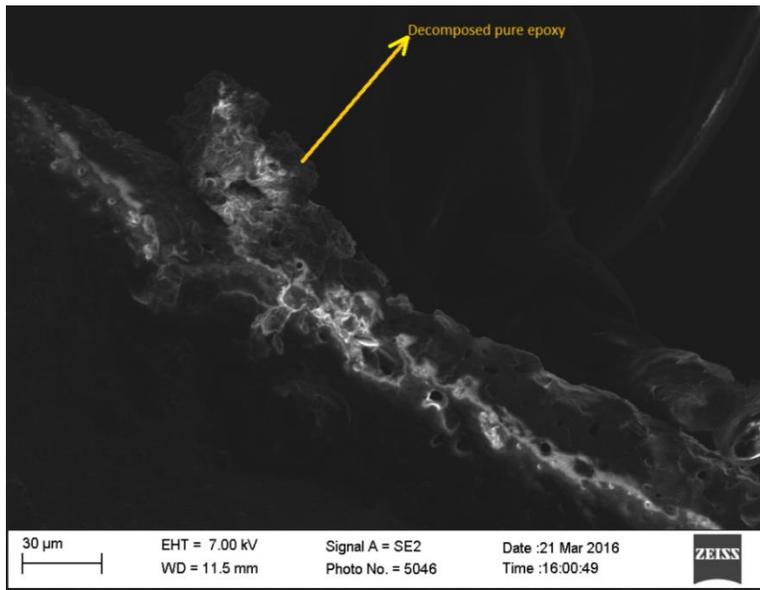
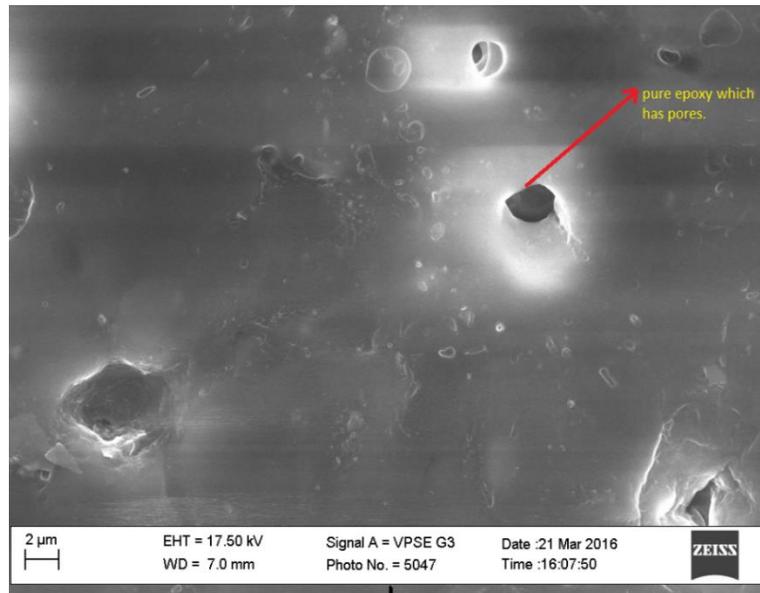


Figure 4.2. a) SEM image of pure epoxy consisting pores b) The decomposed sample under fire retardant test.

The Figure 4.2.b show the decomposition and especially formation of char in the sample in microscale. This formation of char was considered to be an essential factor to make a material fire retardant. Pure epoxy failed in fire retardant tests, but showed low dripping of decomposed materials due to formation of char residue.

The 0.5wt% graphene nanomaterial inclusions were made into the epoxy, which was mixed at 100:27 weight ratio. The graphene was introduced very slowly into the epoxy in order to achieve better dispersion rates. The Figure 4.3.a, shows the dispersion of graphene in the epoxy and some agglomerations. These agglomerations can be minimized by sending the epoxy nanocomposite samples for more mixing cycles, using three roll mill.

The SEM images show the white dots, which were graphene inclusions in the Figures 4.3.a and in Figure 4.3.b, the burned sample and its surface morphology depict the formation of char.

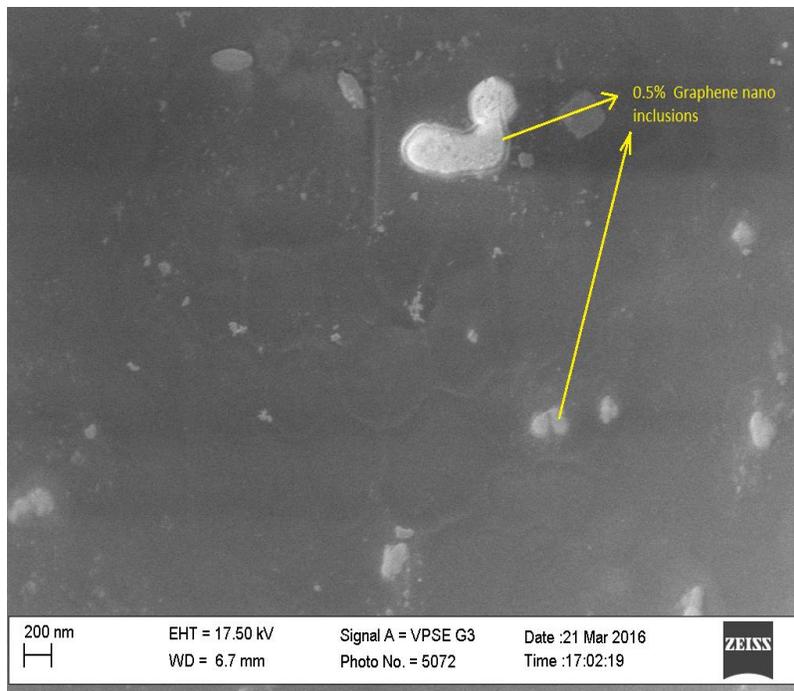


Figure 4.3. a) SEM images of epoxy+0.5wt% graphene nanomaterial inclusion.

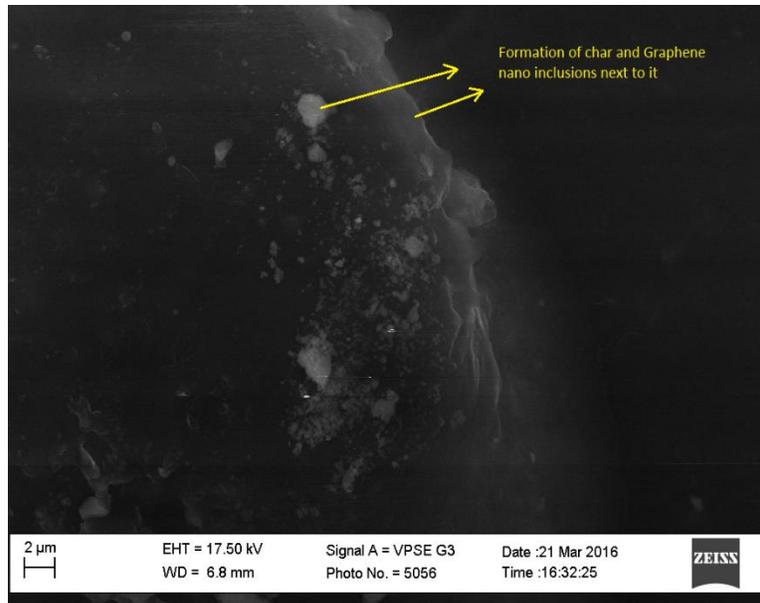


Figure 4.3. b) SEM images of burned sample with the formation of char.

The next level was to introduce the 1wt% of graphene nanomaterial inclusion into the pristine epoxy. The Figure 4.4.a shows better dispersion of graphene, as it had undergone 10 minute mixing cycles. Moreover, in the Figure 4.4.b the burned sample show the formation of bubbles and char. These bubbles and char act as a possible potential barriers for fire retardancy.

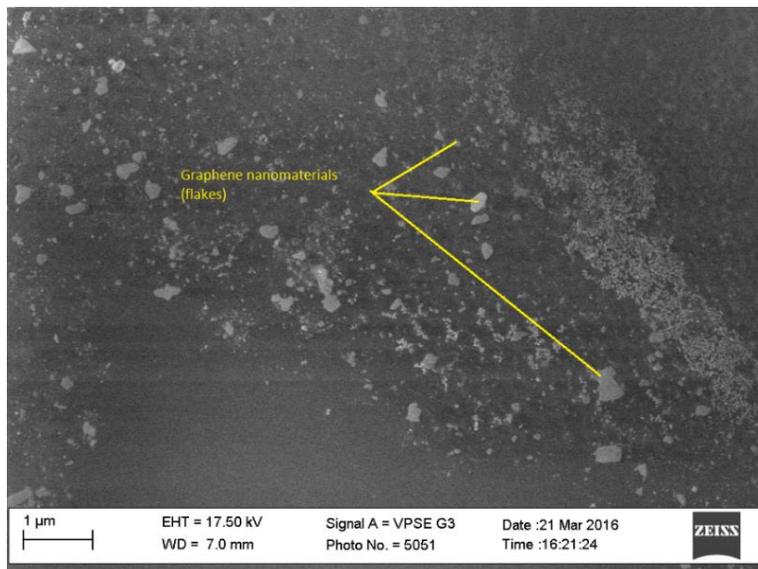


Figure 4.4. a) SEM image of Epoxy+1wt% graphene inclusion.

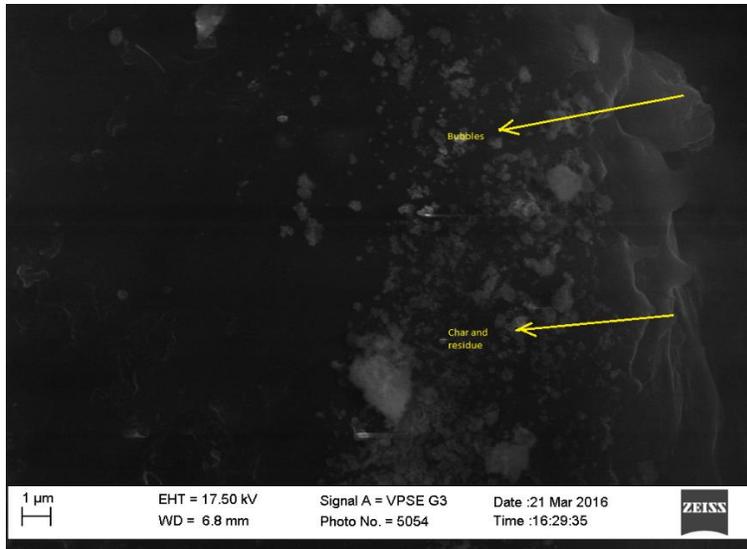


Figure 4.4. b) SEM image of Epoxy+1wt% with formation of bubbles and char.

The same procedures were repeated for 2wt% and 3wt% graphene nanomaterial inclusions with a maximum number of cycles for mixing. The dispersion rates on 3wt% show better images under scanning electron microscope with very fewer agglomerations. The dispersion rates when compared between 2wt% and 3wt% were shown in Figures 4.5 a, b. the 3wt% achieved better dispersions than the 2wt% samples due to increased mixing cycles.

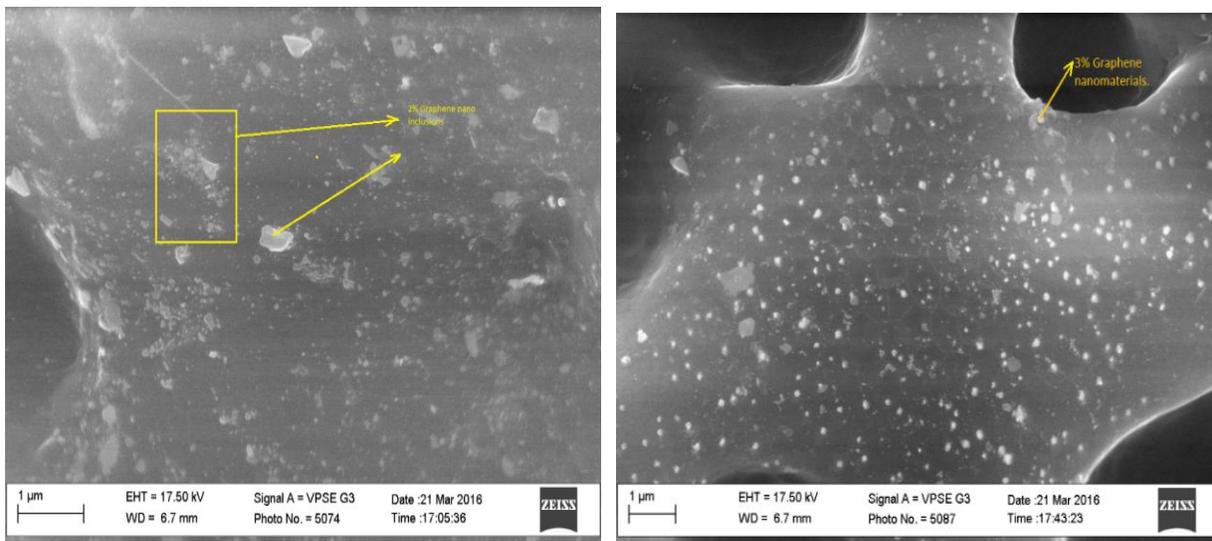


Figure 4.5. a) SEM image of Epoxy+2wt% graphene nanomaterial inclusion, b) Better dispersion of graphene nanomaterial inclusions.

Furthermore, the 5wt% graphene nanomaterial inclusions were made into the pristine epoxy. The Figure 4.6.a, the dispersions of graphene nanomaterials were made consistently with less agglomerations. This tendency of graphene will improve the fire retardancy by the formation of bubbles, char and residue and can be seen in Figure 4.6.b. The 5wt% samples showed extraordinary fire resistivity when compared to other samples due to formation of layers of char and bubbles.

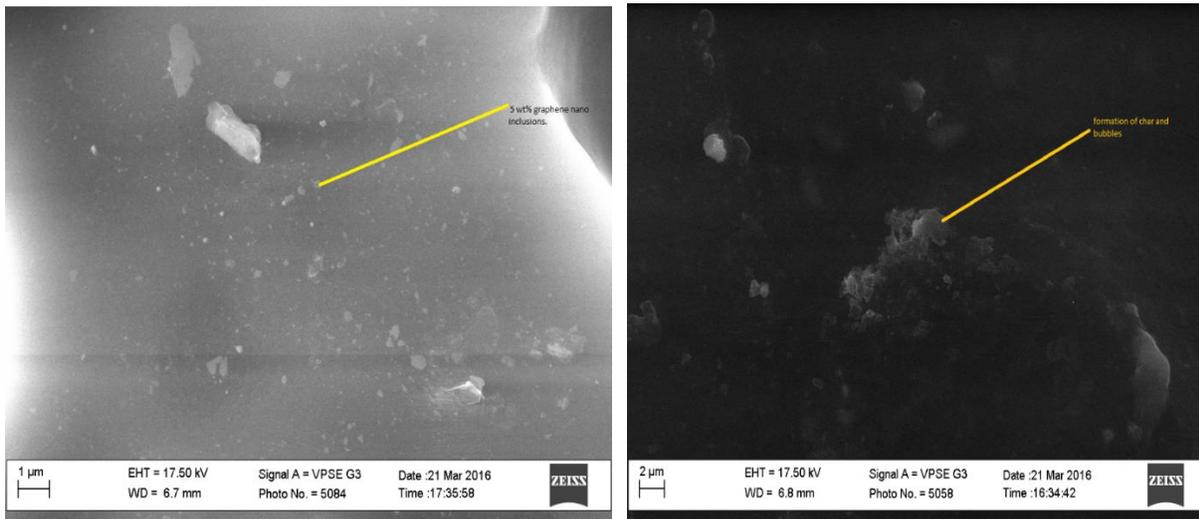


Figure 4.6. SEM images of a) Epoxy+5wt% graphene nanomaterial inclusions, b) Burned sample with the formation of char.

4.2 Differential Scanning Calorimetry

The differential scanning calorimetry was one the major experiments in this research. It played a crucial role in obtaining results related to the glass transition temperatures of the epoxy. The glass transition temperature defines the softening of materials when imposed to different set different temperature profiles. These glass transitions will aid in obtaining data related to the thermal stability of an epoxy and epoxy nanocomposites.

Two sets of DSC experiments were carried out, which include wet epoxy samples and cured epoxy samples. The DSC pans were prepared for epoxy samples, which are cured at different

curing temperatures i.e. 83°C and 103°C, to find out the perfect glass transition temperature of the pure epoxy.

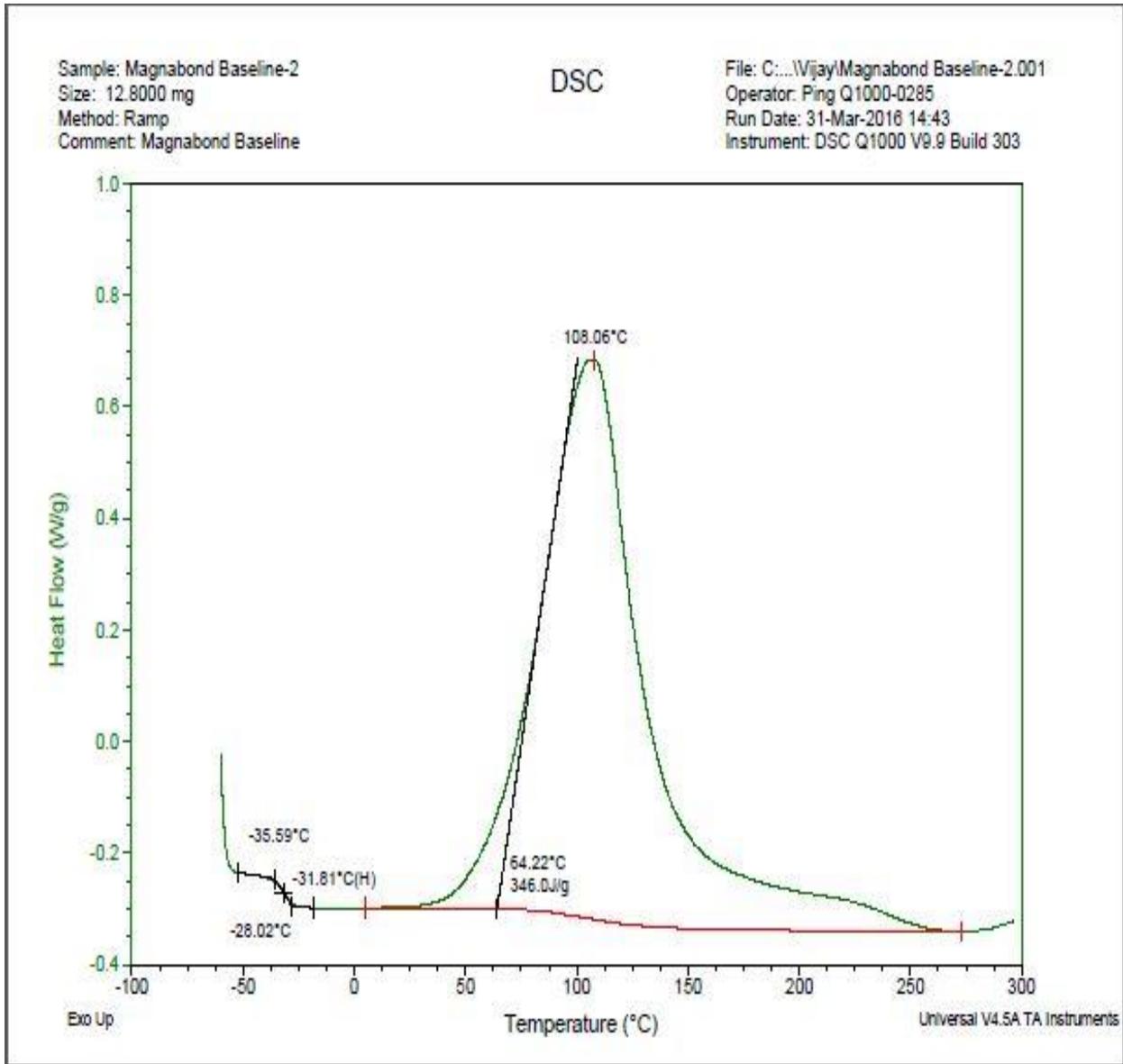


Figure 4.7. The DSC result for baseline epoxy cured at 83°C.

Sample: Magnabond Baseline-1
Size: 18.3000 mg
Method: Ramp
Comment: Magnabond Baseline

DSC

File: C:\...Vijay\Magnabond Baseline-1.001
Operator: Ping Q1000-0285
Run Date: 31-Mar-2016 13:55
Instrument: DSC Q1000 V9.9 Build 303

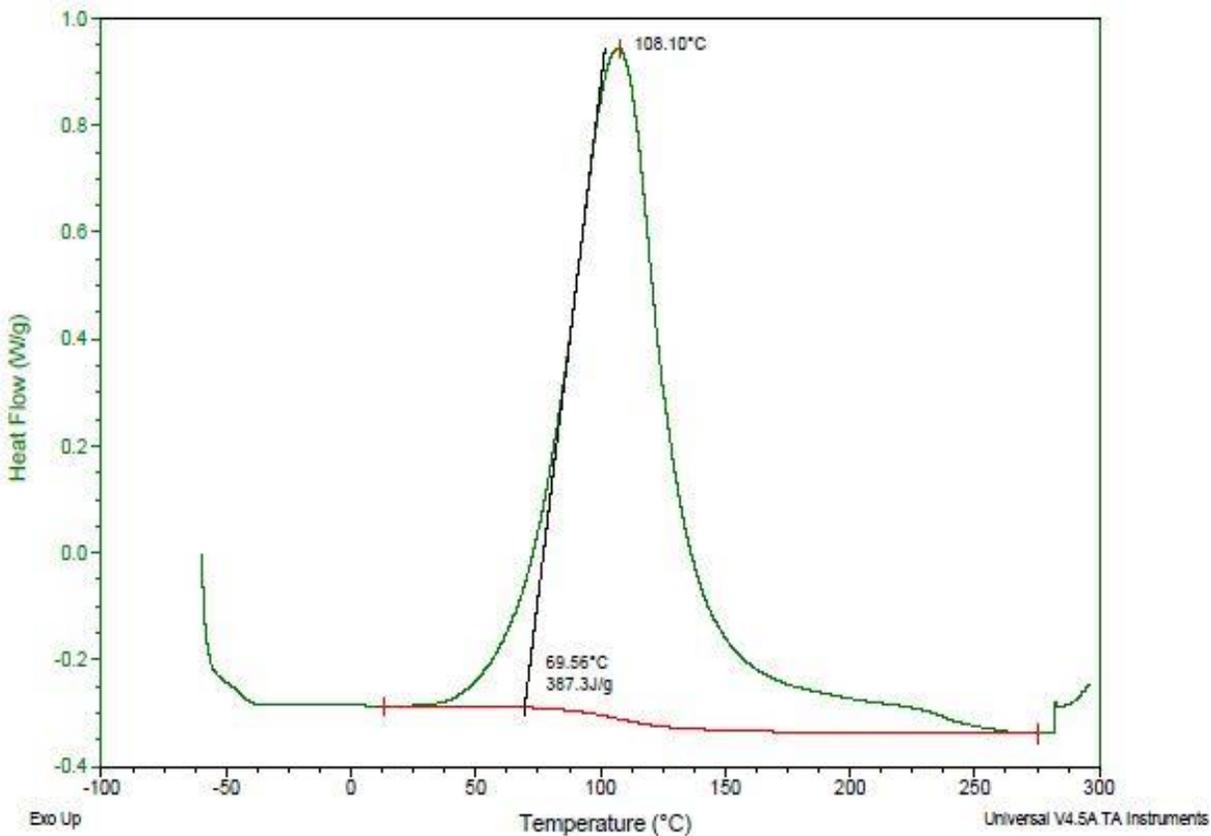


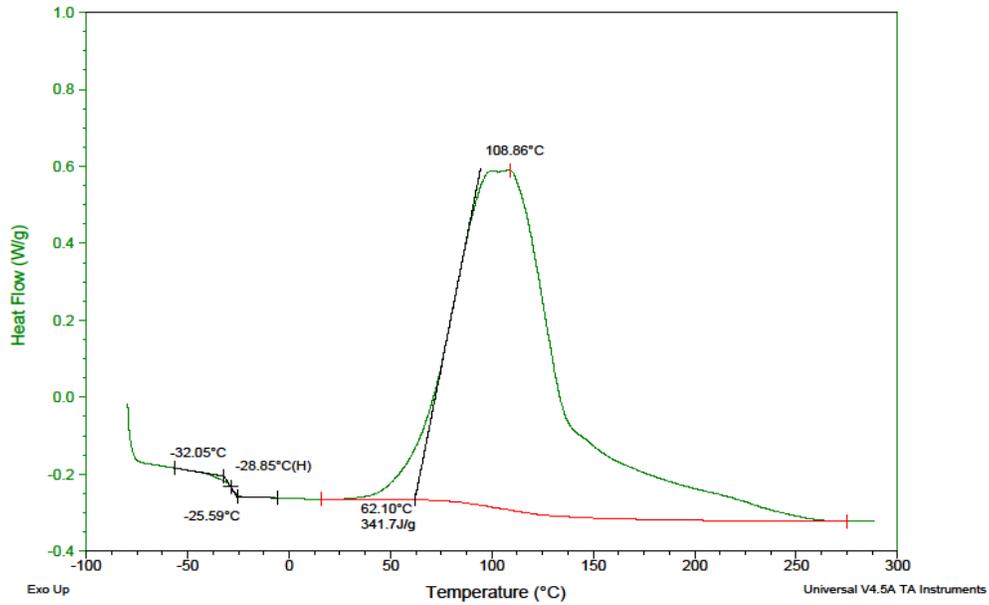
Figure 4.8. The DSC result for baseline epoxy cured at 83°C.

The glass transition temperatures of wet epoxy and cured epoxy samples were between 64°C to 69°C as shown in Figures 4.7 and 4.8. The DSC went through both cryogenic temperatures and high temperatures to perfectly capture the glass transition temperature of the epoxy. In the figure 4.7, the sample was wet and uncured, which was tested to analyze the glass transition temperature. The glass transition temperature was -30.81°C, at cryogenic temperature and the glass transition at high temperature was 65°C. The heat absorption when compared in both graphs they were close.

Sample: Magnabond 0.5wt-1
Size: 13.2000 mg
Method: Ramp
Comment: Magnabond 0.5wt-1

DSC

File: C:\...Vijay\Magnabond 0.5wt-1.001
Operator: Ping Q1000-0285
Run Date: 31-Mar-2016 15:57
Instrument: DSC Q1000 V9.9 Build 303



Sample: Magnabond 0.5wt Cured - 2
Size: 6.1000 mg
Method: Ramp
Comment: Magnabond 0.5wt Cured

DSC

File: C:\...Magnabond 0.5wt Cured - 2.001
Operator: Ping Q1000-0285
Run Date: 01-Apr-2016 14:49
Instrument: DSC Q1000 V9.9 Build 303

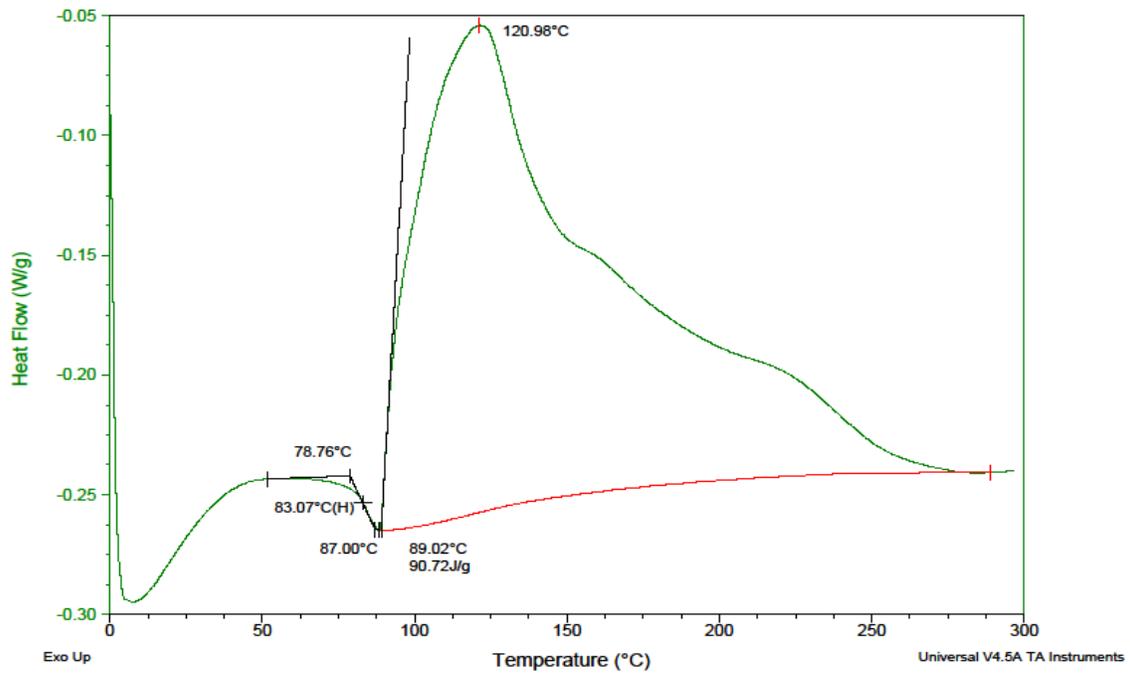


Figure 4.9. a) Wet sample under DSC test b) Cured sample under DSC test.

Both the samples were analyzed for glass transition temperatures at the cryogenic and high temperature. The Figure 4.9.a show the glass transition temperature of wet sample as 62.10°C, when this was compared with the Figure 4.9.b the glass transition temperature was recorded as 87°C. This type of situation clearly explains that the glass transition temperature of the epoxy changes, when it was exposed to different room temperatures. The crystallization temperature was improved at 120°C in the second graph as shown in Figure 4.9.b, which explains that the crosslinking was high at that temperature.

The second phase of the differential scanning calorimetry was to analyze the behavior of the epoxy under the total cure condition in which the epoxy was cured at 103°C that was the highest curing temperature according to the technical data sheet. Different weight ratios of 0.5wt%, 1wt%, 2wt%, 3wt% and 5wt% were analyzed.

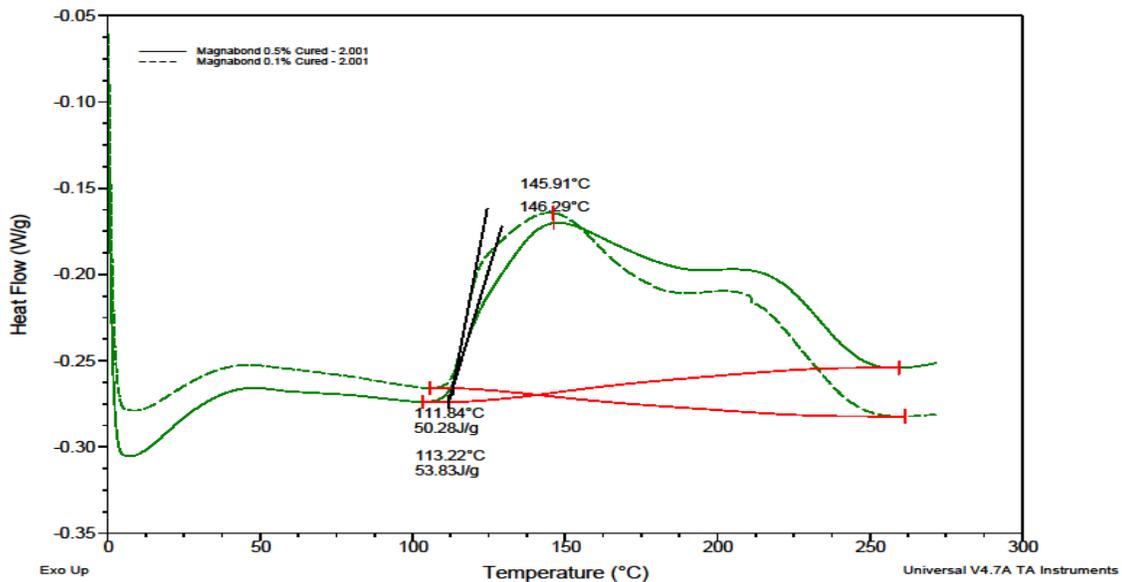


Figure 4.10. DSC analysis of epoxy+0.5wt% vs epoxy+1wt% graphene inclusions.

The glass transition temperature of the 0.5wt% was 111.84°C and for 1wt% graphene inclusion the glass transition was 113.22°C. The heating rate of 10°C was maintained as the ramp from 0°C - 300°C. The Figure 4.10, shows a validation that incorporation of graphene nanomaterials was useful in improving the glass transition temperature of the epoxy nanocomposite.

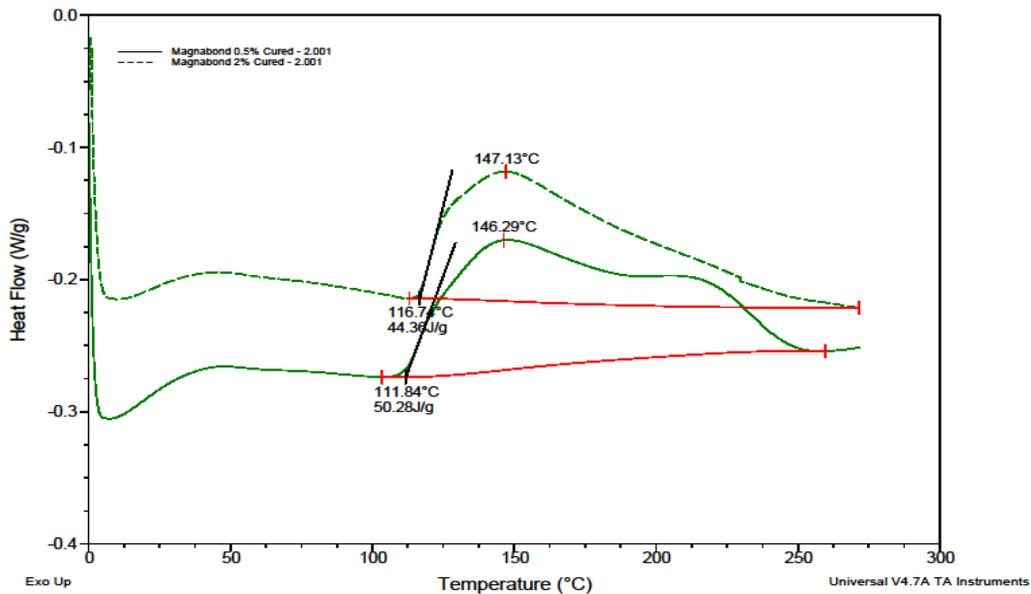


Figure 4.11. DSC analysis of epoxy+0.5wt% vs epoxy+2wt% graphene inclusion.

The glass transition temperature of the 0.5wt% was 111.84°C and for 2wt% graphene inclusion the glass transition was 116.74°C. The heating rate of 10°C was maintained as the ramp from 0°C - 300°C. The Figure 4.11, shows a validation that incorporation of graphene nanomaterials was useful in improving the glass transition temperature of the epoxy nanocomposite. The crystallization temperatures were differed by 1°C when compared between 0.5wt% and 2wt% graphene inclusions.

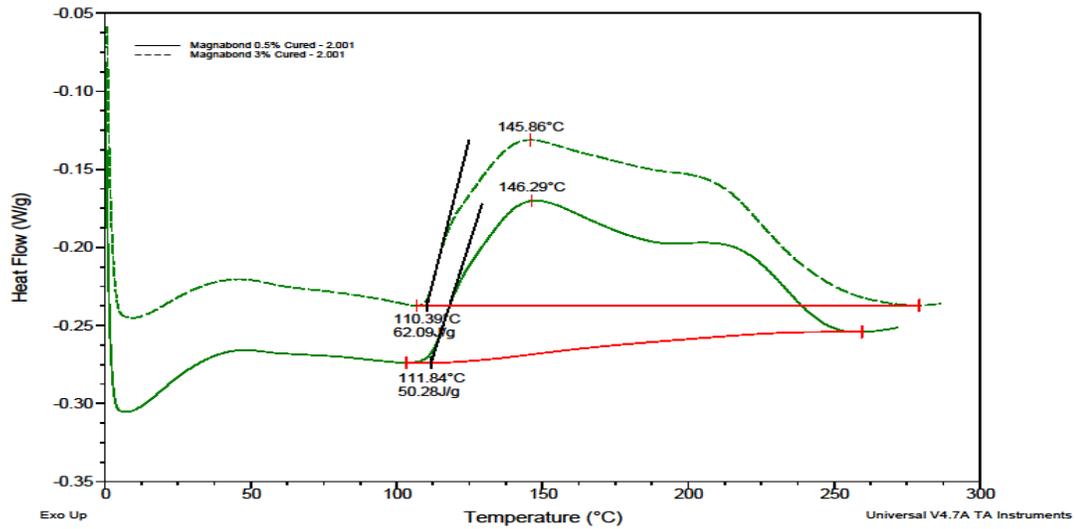


Figure 4.12. DSC analysis of epoxy+0.5wt% vs epoxy+3wt% graphene inclusions.

The Figure 4.12 illustrates that the glass transition temperature of the 3wt% was low when compared with the 0.5wt% epoxy nanocomposite. The decrease of glass transition temperatures can clearly show the effects of room temperature and the testing condition. The heat flow was high due to the carbon content in the sample.

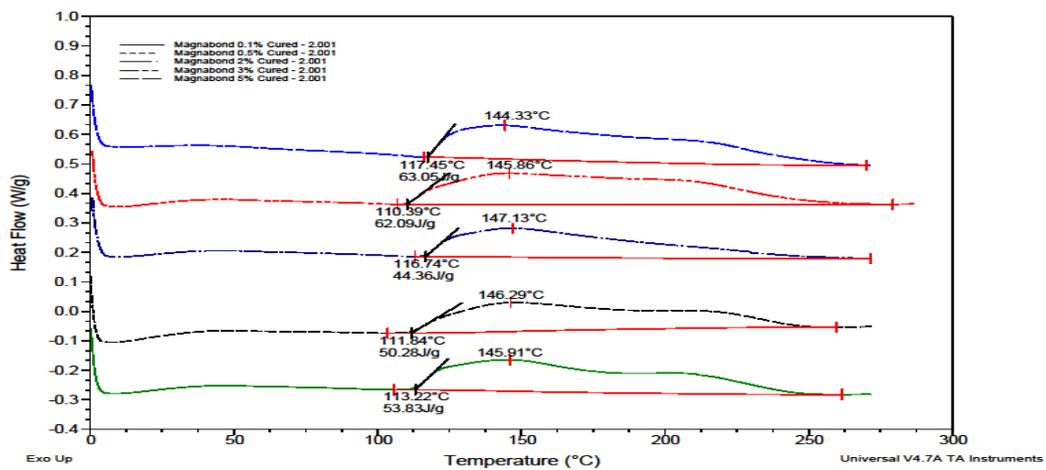


Figure 4.13. Overlay of DSC analysis for epoxy glass transition temperatures.

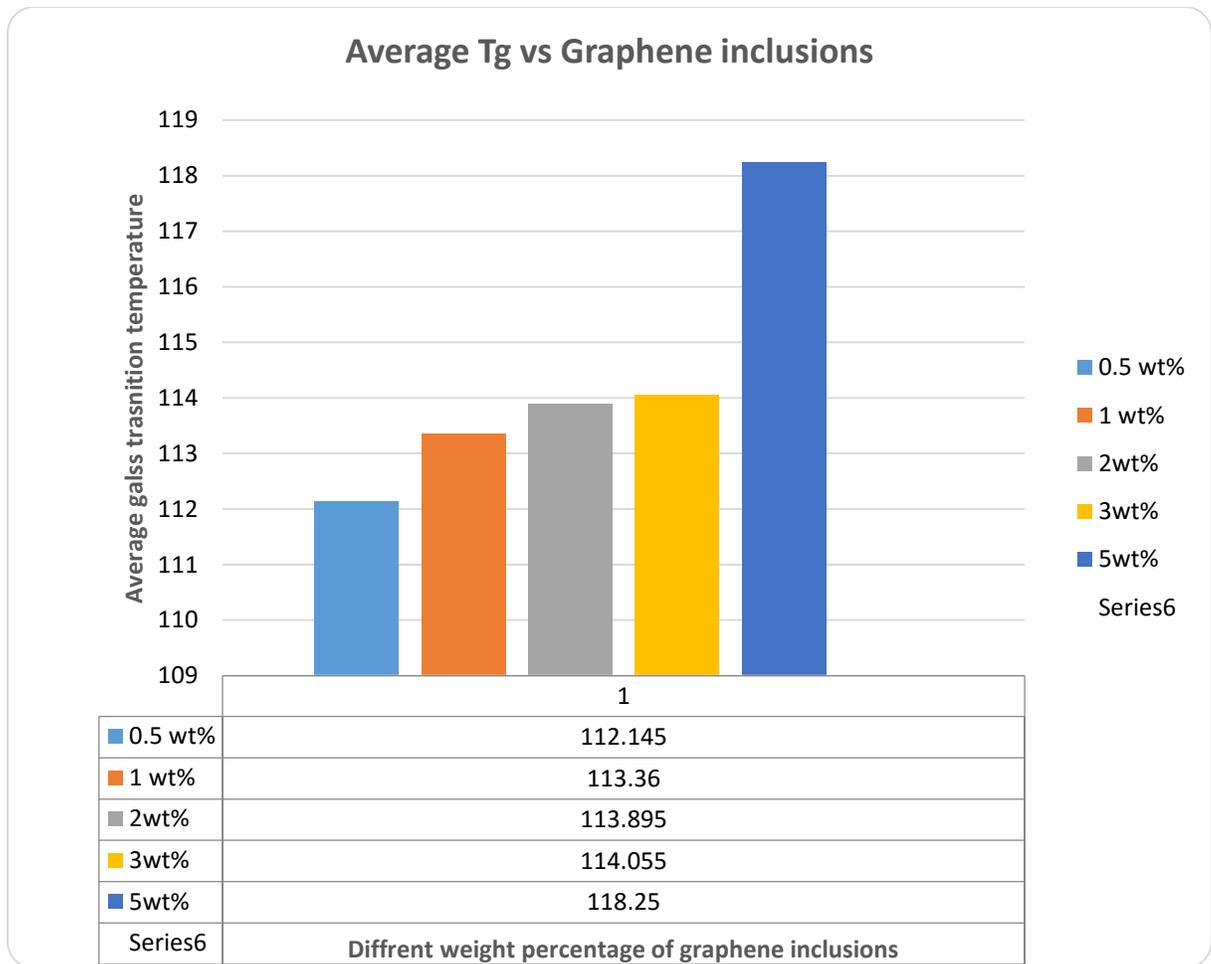


Figure 4.14. Average glass transition temperatures vs Graphene inclusions.

In depth analysis of these epoxy nanocomposites show that the graphene inclusions played a major role in improving the glass transition temperatures of an epoxy as shown in Figure 4.13 and 4.14. The heat diffusion rates were improved with the improvements in graphene nanomaterial inclusion, which states that graphene nanomaterials acted as potential barriers. There was an increment of 6.36% in glass transition temperature, which shifted from 110°C to 117°C, when compared with the 0.5% graphene nanomaterial inclusions.

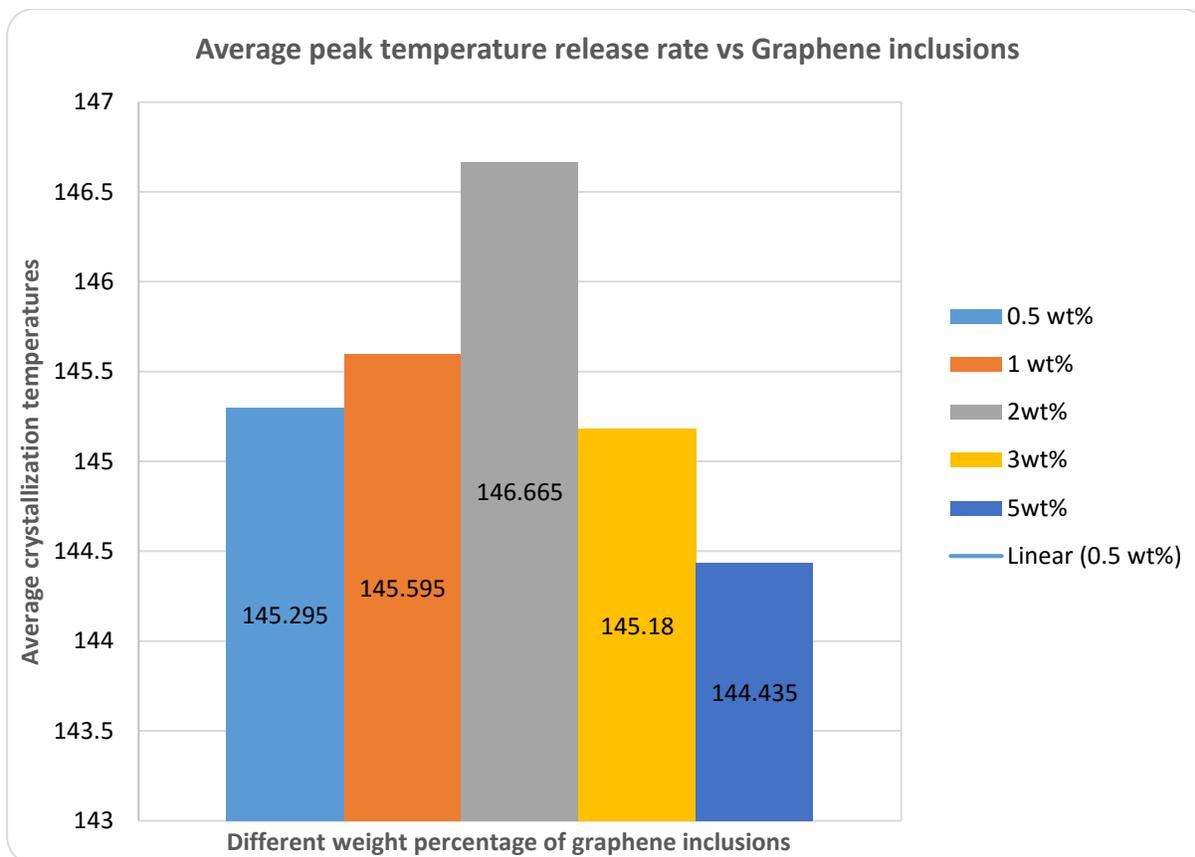


Figure 4.15. Average crystallization temperatures vs Different wt. % of graphene nanomaterial inclusions.

The crystallization temperatures were in the range of 144°C - 146°C. There was a time delay of 50minutes for each test, so the material properties change according to the environmental conditions and this effect the behavior of the sample. Due to delay in test time and room temperature variations, there was a shift in crystallization temperatures. The variations in crystallization were sometimes depend on the material composition too.

Thus, in context graphene nanomaterial inclusions were very helpful in enhancing the thermal properties of a pure epoxy. The thermal stability was improved by shifting the glass transition temperatures of the epoxy. The energy of heat flow was improved, due to inclusion of graphene nanomaterials into the pristine epoxy.

4.3 Thermogravimetric Analysis

The thermogravimetric analysis tests were carried out the samples of pure epoxy along with different weight percentages of graphene nanomaterial inclusions mainly 0.5%, 1%, 2%, 3% and 5%. The Figure 4.16, illustrates that with the inclusion of 0.5wt% graphene nanomaterials 62.86% of mass was lost at 439.06°C and for 1wt% 70.24% of mass was lost at the temperature of 433.05°C.

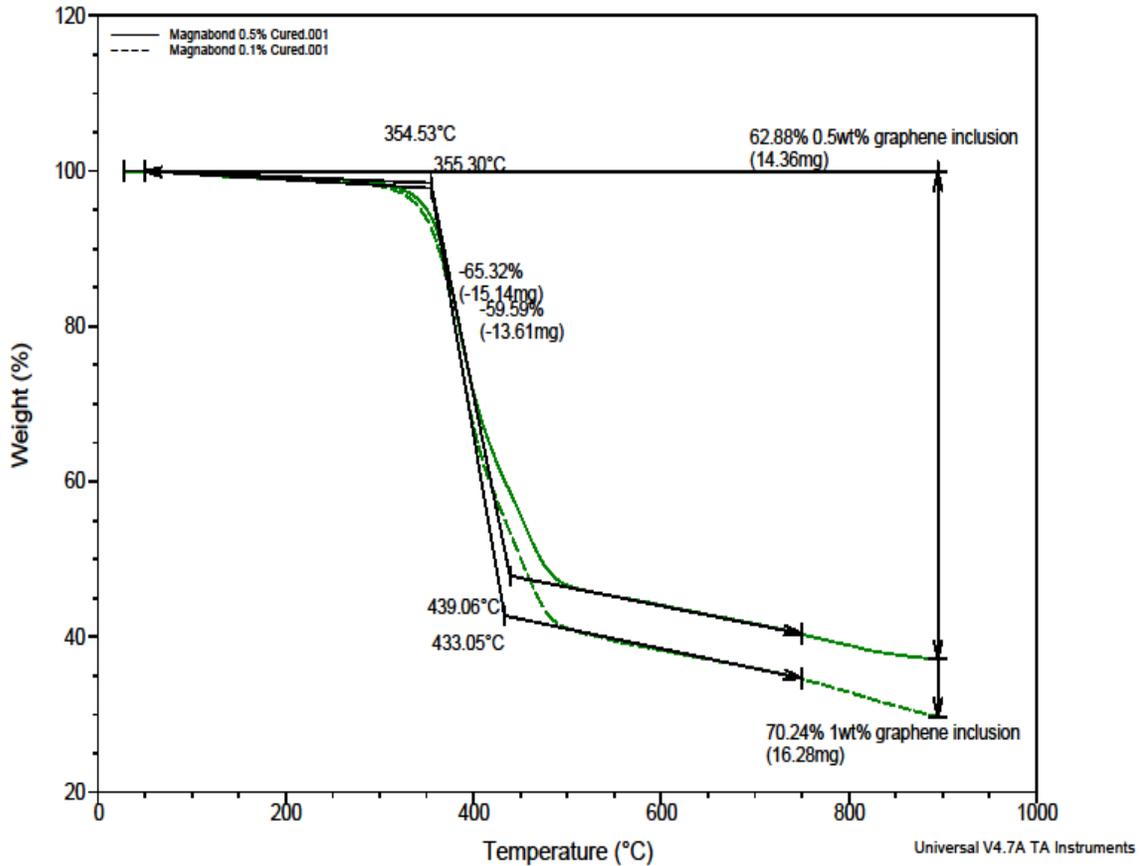


Figure 4.16. TGA analysis of 0.5wt% vs 1wt% graphene nanomaterial inclusions.

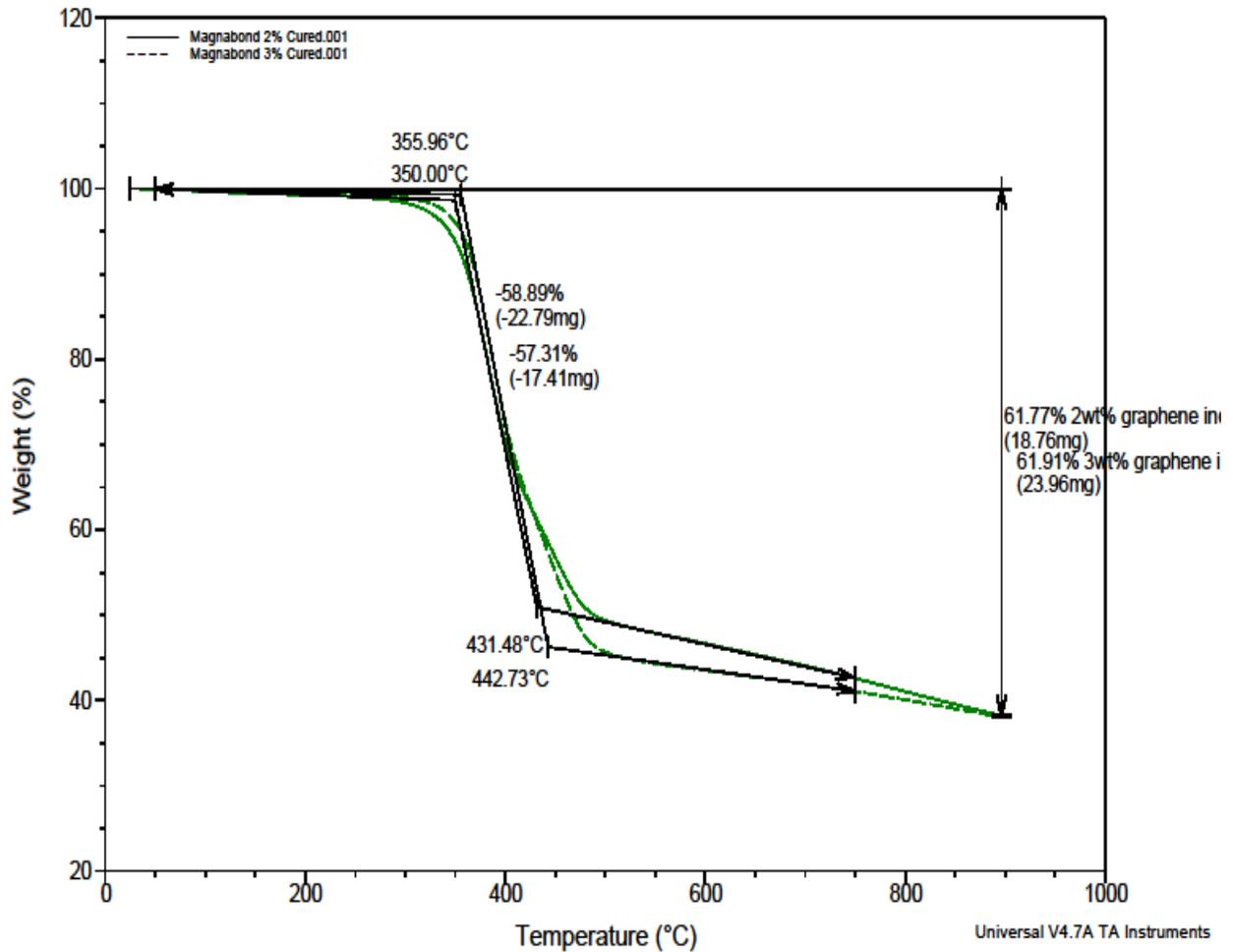


Figure 4.17. TGA analysis of 2wt% vs 3wt% graphene nanomaterial inclusions.

The Figure 4.17, illustrates that with the inclusion of 2wt% graphene nanomaterials 61.77% of mass was lost at 431.48°C and for 1wt% 61.91% of mass was lost at the temperature of 442.73°C. The values of mass loss were close due to 1% increment in the epoxy. This clearly states that the 2wt% and 3wt% have similar thermal stabilities.

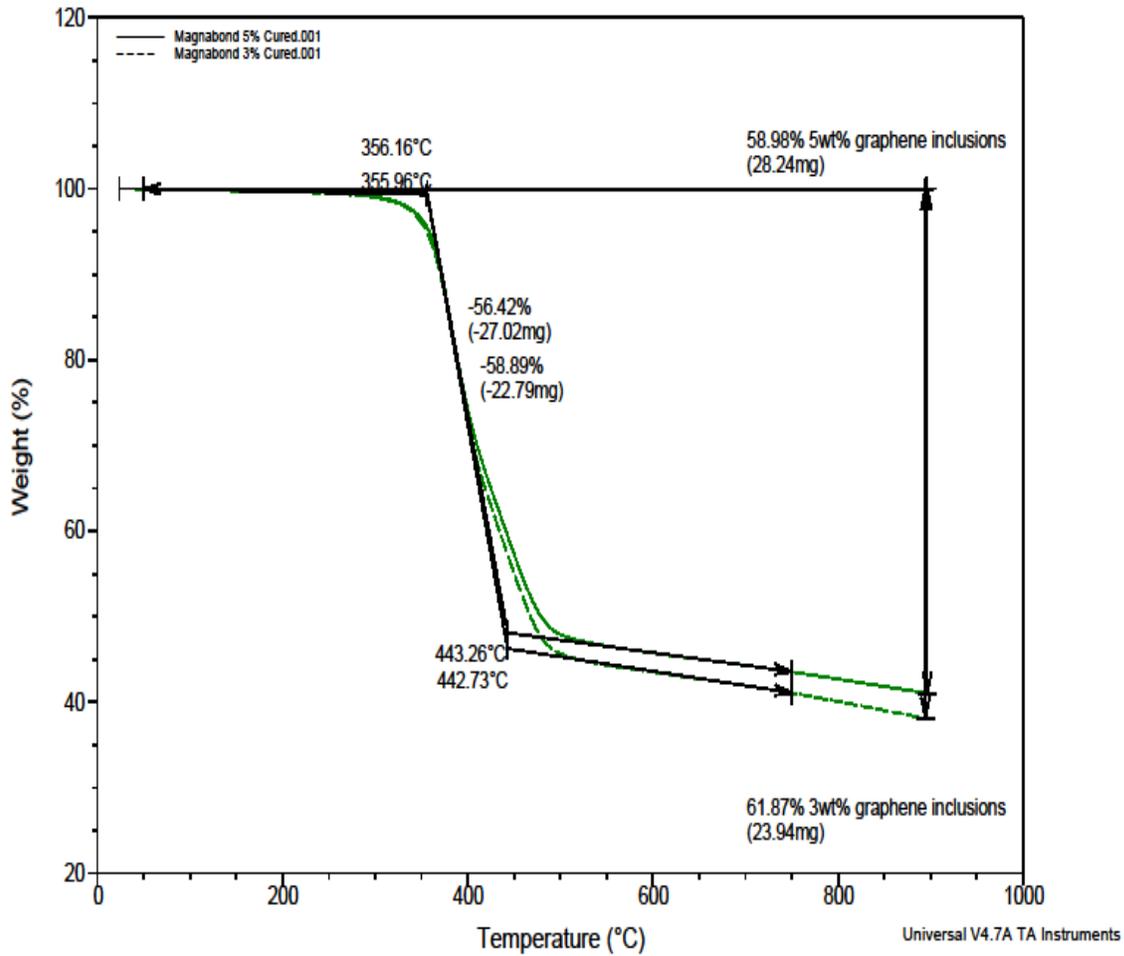


Figure 4.18: TGA analysis of 3wt% vs 5wt% graphene nanomaterial inclusions

The Figure 4.18 illustrates that with the inclusion of 3wt% graphene nanomaterials 61.87% of mass was lost at 443.26°C and for 5wt% 58.98% of mass is lost at the temperature of 442.73°C. This clearly explains that the mass loss rate was decreased when compared 3wt% and 5wt% epoxy nanocomposites

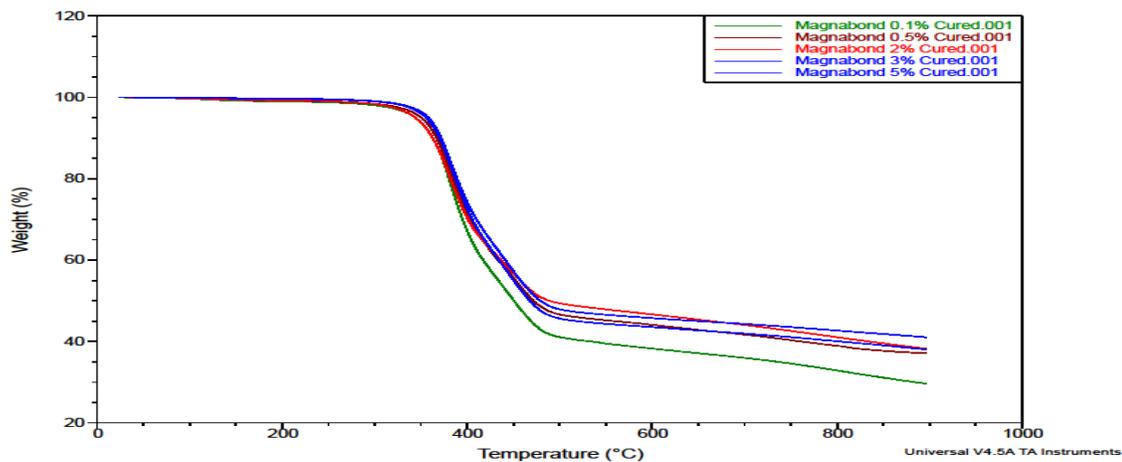


Figure: 4.19. The overlay of TGA results for different epoxy nanocomposites and its mass loss rate.



Figure 4.20. Mass loss temperature vs Weight percentages.

Figures 4.19 and 4.20, clearly shows that graphene nanomaterial inclusions have improved the thermal stability of the epoxy. Mass loss rate was gradually decreased by the increase in graphene nanomaterial inclusions.

According to the methodology of the thermogravimetric analysis, the mass loss rate was decreased when compared with the 0.5wt% graphene inclusions. The mass reduction explains that the fire retardancy was improved by graphene nanomaterial inclusion. These graphene inclusions act as the potential barrier in production char at the time of decomposition. Thus the graphene inclusions reveal 6.2% decrease in mass loss rate when compared with 0.5wt% and 5wt%.

4.4 Fire Retardancy Tests

The UL-94 tests were conducted on the pure epoxy as well as, the epoxy nanocomposite with the graphene inclusions of 0wt%,0.5wt%,1wt%,2wt%,3wt%and 5wt%. The tests were conducted according to the standards of UL-94, which define the various ratings.

Table 4

Results obtained by fire retardancy tests.

UL-94 TEST SPECIMENS	V-0 (fire retardancy achieved)	V-1 (moderate fire retardancy)	V-2 (failed to achieve fire retardancy)
Pure epoxy			✘
Epoxy+0.5wt%			✓
Epoxy+1wt%			✓
Epoxy+2wt%			✓
Epoxy+3wt%		✓	
Epoxy+5wt%		✓	

The results from the fire tests depict that dispersion of graphene nanomaterials in the preparation of epoxy nanocomposites were very useful in enhancing the fire retardancy. From the fire tests, it was depicted that the voids in the epoxy nanocomposite samples can lead to rapid fire growth. The

3wt% and 5wt% show better results by maintaining the after flame time less than 30seconds without any kind of dripping material. The char was formed after the burn tests, which acted as the intumescent layer and reduced the fire growth mechanism. Thus, the graphene inclusions were helpful in maintaining the thermal stability of the epoxy.

4.5 Mechanical Tests for Pure Epoxy and Epoxy Nanocomposites

The mechanical tests mainly include apparent lap shear strength tests which were useful to evaluate the mechanical properties of a pure epoxy as well as epoxy nanocomposites. Two different surface preparation techniques were used to evaluate the mechanical performance of the adhesively bonded lap joints.

The epoxy nanocomposites were prepared with different weight percentages of graphene nanomaterial inclusions. The weight ratios considered for the mechanical tests were 0wt%, 0.5wt%, 1wt%, 2wt% and 3wt%. The bond line thickness of the epoxy was maintained according to the mechanical testing standard ASTM D 1002. A minimum of 4 samples were prepared for each condition and are tested using the MTS machine for finding the shear strength of an epoxy. The bond line thickness was maintained around 0.20mm - 0.23mm using the binder clips for overlapping the adhesive joints.

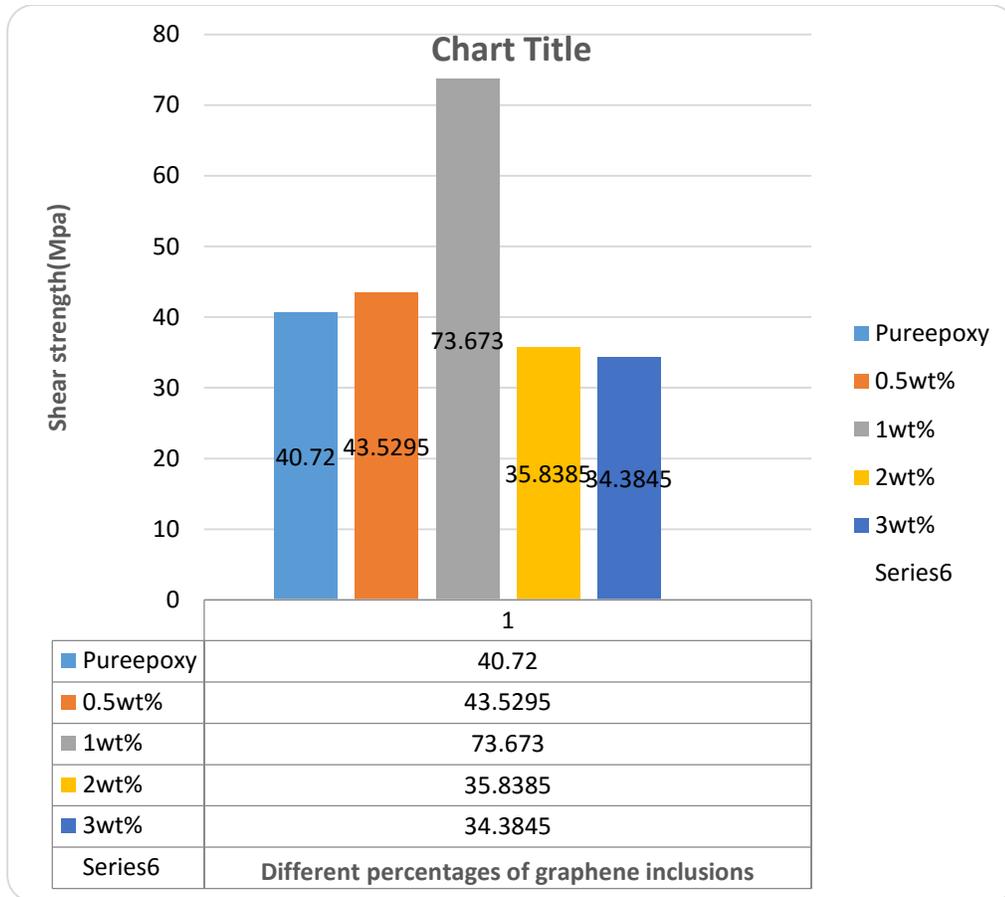


Figure 4.21. Average shear strengths vs Different weight ratios of graphene nanomaterial inclusions.

This was the test data for the samples that went through traditional surface preparation process, which is a chromate conversion coating. The Figure 4.21, shows the comparison of the average shear strength of different weight ratios nanoscale inclusions. Results from the single lap joint tests depicted that the load bearing capacity and lap shear strength of adhesive joints were improved by the additions of 0.5wt% and 1wt% nanomaterials. There was an increment of 3% by load bearing capacity and lap shear strengths between baseline and 0.5wt% graphene samples in the adhesive, and 68% increment between baseline and 1wt%, which has been the highest improvements among these tests.

A gradual decrease of 14% -15% in load bearing capacity and lap shear strength was also observed in 2wt% and 3wt% of the nanoscale inclusion samples when compared to the base line tests.

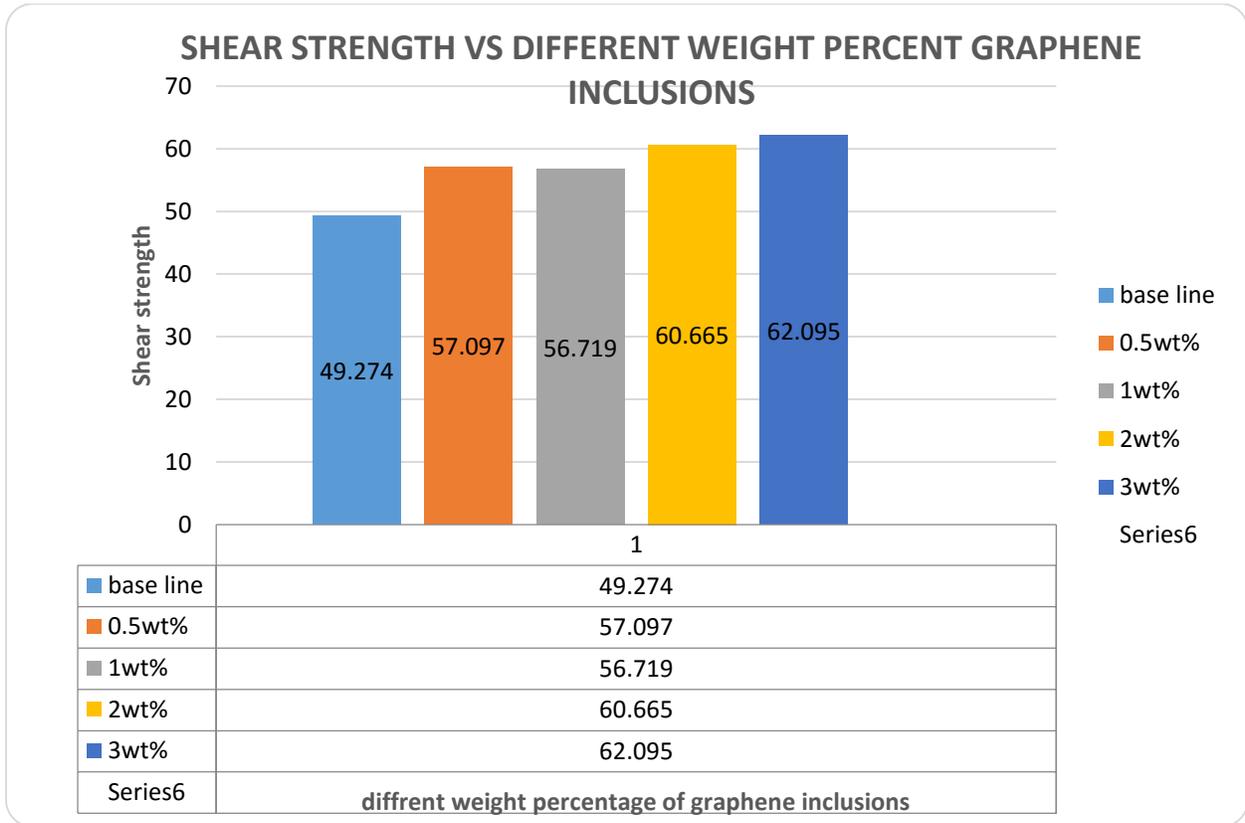


Figure 4.22. Average shear strength vs different weight percentages of epoxy nanocomposites.

The samples prepared by automatic etching. The chromate conversion process carried out using the alodine solution. The samples were then tested using the tensile test machine with the same loading constraints set as the previous testing condition. There was a gradual increase in the shear strength of the adhesively bonded lap joints and was shown in Figure 4.22. The results illustrate that there was a 26.05% increase in the shear strength when compared with the baseline.

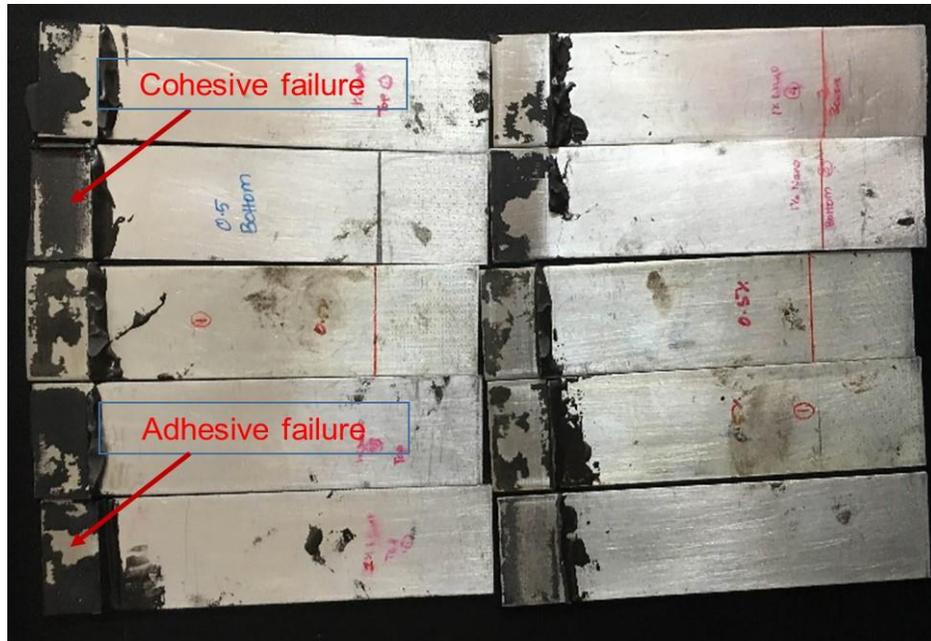


Figure 4.23. Cohesive and adhesive failures of epoxy system.

After the lab shear tests, the broken surfaces of the nanocomposite epoxy adhesives between the Aluminum coupons were investigated in detail for the failure analysis. It was observed that the major failures were cohesive failure in the epoxy adhesives, and some of them were adhesive failures. Usually, the samples with lower graphene concentrations gave cohesive failures, while at high concentrations, adhesive failures were caused because of the interfacial interactions between graphene and metal surfaces. Figure 4.23, shows the test panels with cohesive failures and adhesive failures occurred during the tensile test loadings.

This explains that the surface preparation techniques play a major role in the performance of the epoxy nanocomposite. Moreover, the graphene nanomaterials were very crucial in improving the performance of mechanical properties of the epoxy adhesive. The better dispersion of nanomaterials was another major criterion to be considered for the improvements in the mechanical strengths of the epoxy adhesive lap joint.

CHAPTER 5

CONCLUSIONS

In this research, the major area of concern was improvement of the mechanical properties and fire retardancy of thermosetting epoxy resin. Epoxy was modified by graphene nanomaterial inclusions, which act as reinforcements to enhance these specific properties of the epoxy. The better dispersion of the graphene nanomaterials was achieved by using the three roll milling machine. As all the experiments were in need of epoxy nanocomposites, this was the main priority. The surface morphology was analyzed under scanning electron microscopy show that graphene was well dispersed in to the epoxy. The ul-94 vertical fire conducted on epoxy nanocomposites show that the 3wt% and 5wt% graphene incorporated epoxy nanocomposites achieved the fire retardancy rating of (V-1). This fire retardancy rating was considered as moderate flame retardant situation according to the standards of UL-94. The thermal stability of the epoxy nanocomposites was analyzed using the thermogravimetric analysis and the differential scanning calorimetry. The differential scanning calorimetry results when analyzed, show that the glass temperature got improved when compared with neat epoxy with the temperature ranging form 110°C to 118°C. Thermogravimetric analysis run on epoxy nanocomposites show reduction of mass loss rate, due to inclusion of graphene nanomaterials into the epoxy. The mechanical properties especially, load bearing capacity was improved by graphene nanomaterial inclusions. Samples prepared using traditional etching method, when tested using tensile tests, showed 68% increase in lap shear strength when compared with baseline. Whereas, samples prepared from alodine etching method showed 27% increase in lap shear strength when compared with baseline. Thus, the graphene inclusions have improved both mechanical and thermal stability issues of the pristine epoxy.

CHAPTER 6

FUTURE WORK

- A perfect glass transition can be achieved for the epoxy nanocomposite, if tested with Dynamic mechanical analyzer.
- The mechanical properties, especially lap shear strength should be modelled and analysis should be carried out using Finite element method simulation.
- The thermal responses can be analyzed using simulations of COMSOL, to reduce time in preparation of epoxy nanocomposite.
- Different types of nanomaterial inclusions should be made into epoxy mainly multi walled carbon nanotubes for enhancing better thermal and mechanical properties.

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