SILANIZATION EFFECTS OF CARBON BLACK NANOPARTICLES ON CURING KINETICS OF NANOCOMPOSITES

A Thesis by

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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 and my family

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First and foremost, I would like to thank God for showing me the right path to continue on my education and complete this research. I would like to thank my advisor and committee chair, Dr. Ramazan Asmatulu, for his support, guidance, interest and enthusiasm throughout my college education, along with this project. I would like to thank my committee member Dr. Lankarani who was always supportive and encouraging, not only for this research, but also my college education. I would like to thank Dr. Krishna Krishnan for agreeing to be my committee member. I would like to thank Dr. Seyed A. Soltani for obtaining the Differential Scanning Calorimetry and performing numerous tests for this research. I would like to thank Hinman Max for obtaining Scanning Electron Microscope images and Kevin Langenwalter from the Chemistry Department for his help in obtaining Fourier Transform Infrared Spectrometer results. Last but not least, I would like to thank Vamsidhar Patlolla for his encouragement and his guidance in writing this thesis report.

ABSTRACT

This study presents the development of a nanocomposite using carbon black and Epoxy Resin 828 to improve the curing kinetics of nanocomposite. There is little to no data on curing kinetics of silanized carbon nanocomposite. In this study, carbon black was modified using silanization process to improve its dispersion in epoxy resin which resulted in a change of curing kinetics. Silanization is a surface modification technique to improve carbon black stability and decrease agglomeration of carbon black during the mixing process. Different methods such as stability in acetone, Fourier Transform Infrared Spectrometer (FTIR), and Scanning Electron Microscopic (SEM) were used to confirm the silanization process of carbon black. Differential Scanning Calorimetry (DSC) was used to test the curing kinetics of carbon black nanocomposite.

In order to find the curing kinetics of nanocomposite using DSC, finding a baseline was essential. Epoxy resin 828 and 12%wt curing agent were mixed and samples were tested in DSC at different temperatures to find the baseline. After finding the baseline, nanocomposite was prepared using unmodified and modified (silanized) carbon black at 2%, 4% and 8% weight percentage of carbon black. Curing kinetics of modified and unmodified carbon black nanocomposite revealed that curing temperature of 110ºF for modified CB nanocomposite had a higher Degree of Cure (DOC) than unmodified. Curing kinetics for 220ºF for unmodified and modified did not show significant differences, since curing occurred faster at a higher temperature. However, curing time was shorter for modified CB than unmodified. Acceleration in curing kinetics could have a positive effect on processing of nanocomposites by decreasing cure time at a lower temperature. This study may open up some new opportunities for curing kinetics of various nanoparticle nanocomposites used in many nanocomposite manufacturing industries.

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LIST OF ABBREVATIONS

CNT	Carbon Nanotube
SWNT	Single-Wall Nanotube
MWNT	Multi-Wall Nanotube
POSS	Polyhedral Oligomeric Silsesquioxane
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
CB	Carbon Black
EG	Expanding Graphite
DOC	Degree OF Cure
FCB	Functionalize Carbon Black
EDS	Dispersive X-ray Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

The general meaning of “composite” is a combination of two or more materials which are mixed together to improve their physical, thermal or electrical properties compared to each material individually. There are one or more discontinuous phases called matrix and a continued phase called reinforcement in a composite material. In nanocomposite, at least one of the components is a nanosize 10^{-9} m. Matrix is usually a resin and its mechanical performance is improved by adding the reinforcement [1]. The role of reinforcement is adding more mechanical performance to the composite, while the role of the matrix is to spread the load to the fiber and protect the fiber from external violence. The type of nanoparticle used in nanocomposite, depends on the application of the nanocomposite materials and the designer’s limitations such as high mechanical properties, cost, corrosion resistance or good thermal stability. One the most important microstructure feature of nanocomposite is having a large surface area to their volume. Figure 1.1 shows three types of nanocomposite [1].

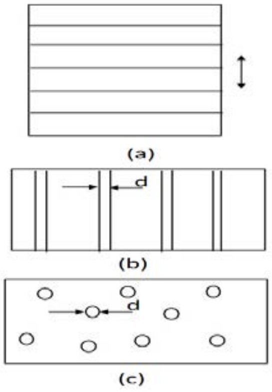


Figure 1.1: Three types of nanocomposite a) nanolayered b) nanofilament c) nanoparticulates [1]

Nanolayered (a) composite is made of layers of nanosize material. For example layered silicate clays are good nominees to make an organic or non-organic nanocomposite because they are chemically stable and have a very large siloxane surface. These layers increase the interfacial contact between the organic and non-organic phases, and as a result the overall performance in nanocomposite increases [1]. Nanofilament (b) composite is nanosize material filament surrounded by matrix. One of the most important uses of nanofilament is to be used as conductive additives in polymers. Alignment of nanofilament is important to transfer the stress between the nanofilament [1]. Nanoparticulate (c) composite is made of matrix surrounded by nanosize particles. Suspension of nanoparticles depends on interaction between the nanoparticles and solvent. It must be strong enough to overcome the density difference; otherwise it will result in falling or floating in liquid. For many applications of nanocomposite having a homogenous dispersion of nanoparticles and desired mechanical, thermal, and conductivity properties is really important [1].

One of the most important benefits that nanocomposite matrix can give to fiber composite is to increase its flexural and compressive strength. Fibers can simply buckle under the compressive load. Modulus of matrix determine the compressive strength therefore a higher modulus increases the cross protection of the fiber. Increase in cross protection of the fiber reduces the buckling or kinking of the fiber. Failure of fibers usually starts from weakness in compressive strength due to buckling and/or kinking. Carbon fiber composites show more sensitivity to decrease of the lateral support of the fibers and that’s because the carbon fiber has lower failure strain. Lower failure strain in carbon fiber leads to buckling, and buckling leads to failure of the fiber which ends in composite failure.

Figure 1.2 shows comparison of flexural strength versus matrix modulus for glass fiber PA6 composite and carbon fiber PA6 composite. The figure shows decrease in modulus of matrix decreases the strength for both glass and carbon composites, but this decrease is stronger for carbon fiber composite. When modulus matrix drops approximately below 1 GPa there is a stronger decrease in strength for both glass and carbon composites [2].

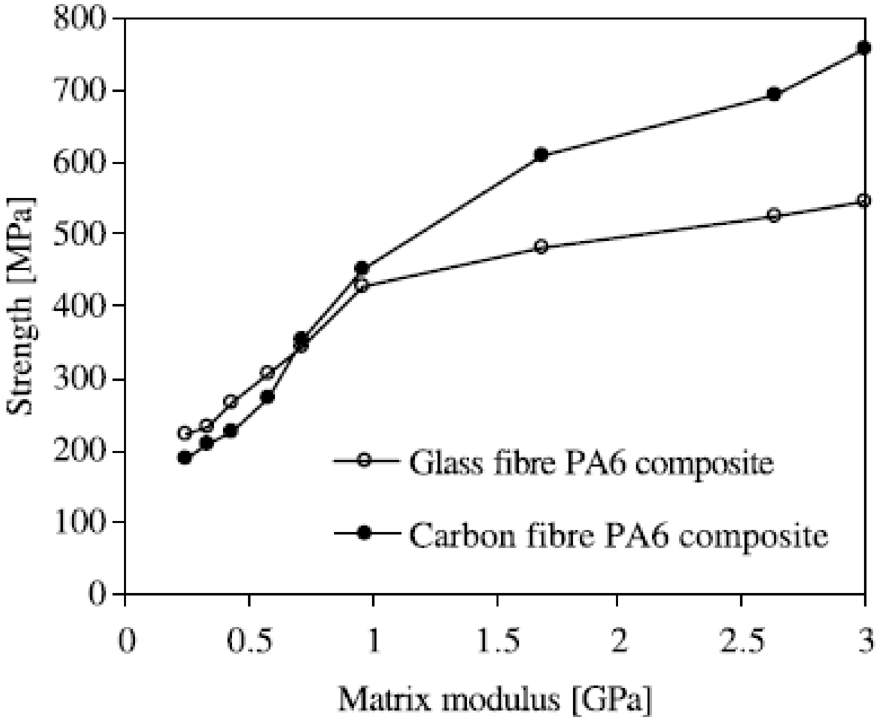


Figure 1.2: Flexural strength of glass fiber PA6 composite and carbon fiber PA6 composite vs. matrix modulus [2].

Nanocomposite can be used in many applications with significant improvement such as producing batteries with more power output. In the human body, they can be used to speed up the healing process for fracture bones. Nanocomposite can also be used in biological sensors to detect very small amounts of chemical vapor. In the defense industry, they are used in nanobattlesuits which has a thin spandex layer and it can monitor health conditions and communication. Nanocomposite improves display screens on electronic devices. Some other applications of nanocomposite are light weight sensors and flexible batteries [3]. The property improvement of epoxy nanocomposite filled with carbon black is far from anticipations based on the outstanding properties of carbon black. Nevertheless, studies recommended that the properties can be improved much more by homogeneous dispersion and interaction between the carbon black and epoxy resin. Based on the studies, one of the most capable ways of property improvement is to have a chemically surface treatment on carbon black. Figure 1.3 shows some application of nanocomposite [3].


(a)
(b)

Figure 1.3: TPO Nanocomposite: Application for automotive parts: a) 1st commercial lunch b) 2nd nanocomposite application on Chevy Impala [3].

With that being said, there are some challenges and difficulties in this fast paced nanotechnology. Homogenous dispersion of nanoparticles in the polymer matrix is a big issue and many methods of dispersion are being used to address this issue. Agglomeration of nanotubes is very typical and causes a severe cost for mechanical properties. Another difficulty is alignment of carbon nanotubes in nanocomposite with strong bonding between CNTs and polymer matrix.

Some other challenges are production and assembly of these nanoscale materials is difficult for engineers. In research and experiment, there are not any clear design guidelines to initiate an invention of nanomaterials. There are many communication and commercial needs between the manufacturing and engineering research to fulfill the future of this revolutionary industry. Neither engineers nor research scientists have the developing experience in nanotechnology. Both health and environment can be affected with nanoscale materials. For example, graphite can cause skin disease and respiratory infections. There are many controversies on nanotechnology regulations. In this recently launched technology, regulatory bodies such as Food and Drug Administration (FDA) do not have any regulation for labeling, production, and handling of these materials [4]. Figure 1.4 shows potential translocation pathways of nanoparticles in the human body.

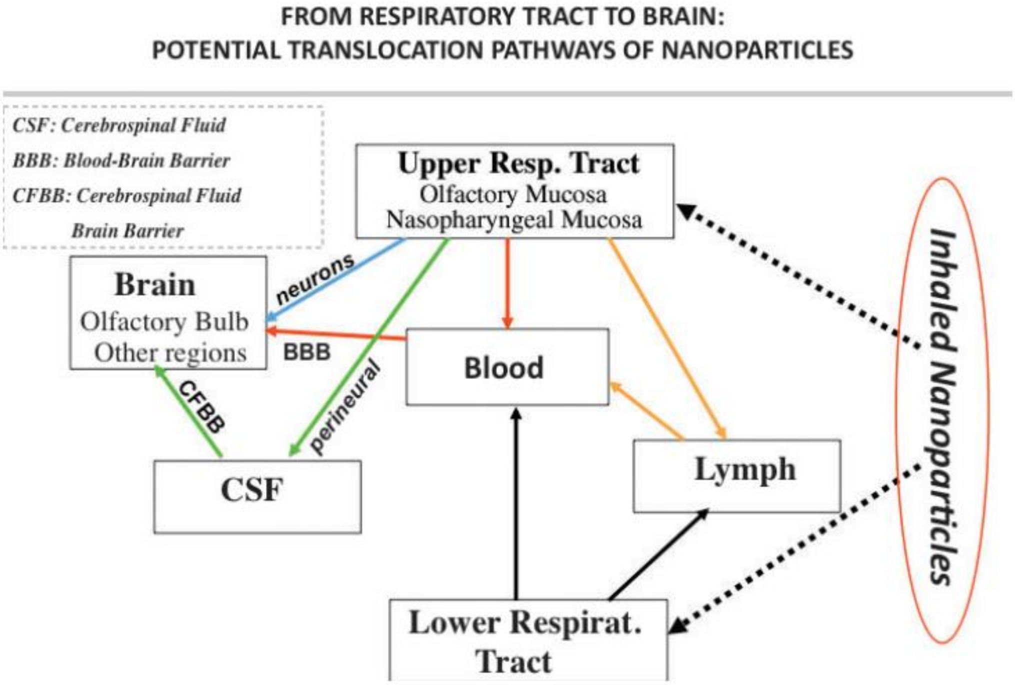


Figure 1.4: Potential translocation pathways of nanoparticles [4].

1.2 Introduction to Epoxy Resin

The epoxy resins were first founded by Pierre Castan in Switzerland and S.O. Green Lee in the U.S in the late 1930's [5]. Epoxy resins are polymers containing epoxide groups, which are sometimes referred to as oxirane group (or glycidyl). The epoxies contain oxides or 1 to 2 epoxides. Oxirane group contains an oxygen atom bonded with two carbon atoms. The epoxy resins are usually thermosetting materials, which after adding a curing agent become hard. On the other hand, thermoplastic resins are fusible composites. They are a collection of long linear chains lying together in three dimensions, but these chains are not interconnected. Mostly epoxy resins used in a liquid phase have a viscosity rang 8000-20000 centipoises. The high viscosity epoxy resin used in highly polymerized products such as diglycidyl ether of bisphenol and since it has high homolog, it can be considered as a representative of its class.

As a reaction of bisphenol A (BPA) with epichlorhydrine (ECH) the basic epoxy resin can be prepared and depends on the applications the value of *n* can have a range from 0-25 [5]. Reaction or curing which is cross linking of epoxy resin can happen with themselves or with other reactants such as acids, alcohols, phenols, and thiols. Reactants are called curing agents or hardeners. As a result of reaction of epoxy resin, either with themselves or with the use of curing agents, thermosetting polymer will form with strong mechanical properties and releasing high temperatures. Curing agents are often an amine which by adding to epoxy resin chemical reaction will take a place. It is necessary to not only find out the proper amount of curing agent needed to achieve the cross linking system, but also need to find the degree of cure (DOC). DOC is cure time and/or cure temperature needed to achieve the cross linking system.

At the early stage of curing, before the entire cross linking takes place, semithermoplastic or B-stage resins are in presence. Cross linking completes with either more time or higher temperature and compound reaches its thermoset. The best characterizations of resins such as physical, chemical and electrical can be obtained from a cured- resin [5]. There are many advantages in epoxy resins that make them great candidates to be used in composites. Epoxy resins have tensile strength, stiffness, and durability. They are light weight compared to polyester and vinlyester. Figure 1.5 shows the tensile strength and stiffness for different resins.

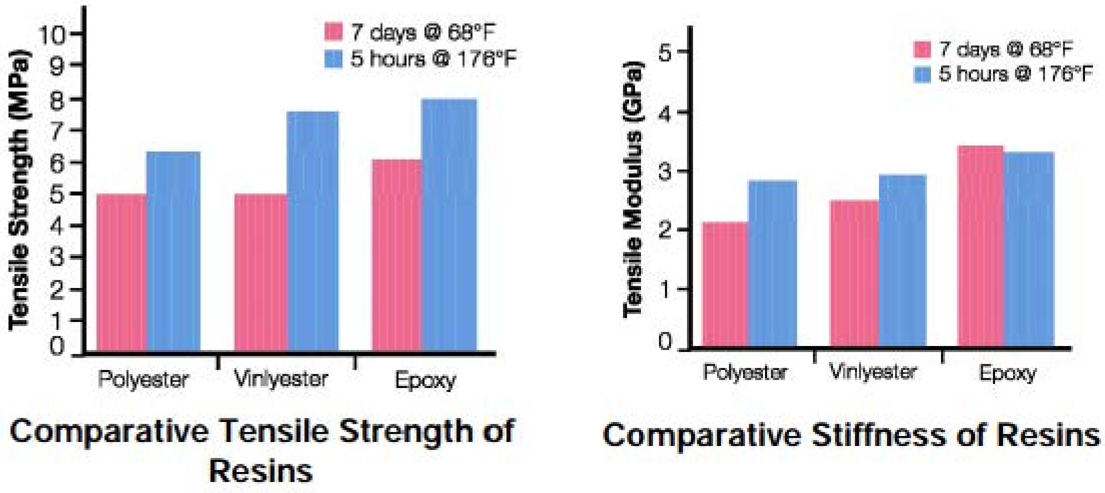


Figure 1.5: Comparative tensile strength and stiffness of resins [6].

Other advantages of epoxy resins are resistance to fatigue and micro cracking, as well as resistance to surface degradation because of water permeability. Epoxy resins shrink less than 2% vs. 7% for polyester and vinyl ester [6]. Epoxy resins have a long shelf life. Application of epoxy resin materials are in paints and coating such as powder coating, primer, and adhesives. Epoxy resins can also be used in industrial tooling and composites such as casting and molds. They are used in electrical systems and electronics, such as integrated circuits and transistors. In consumer, marine, and aerospace industries, epoxy resins can be used as glue. In biology, epoxy resins are used in embedding electron microscopes. In art, epoxy resins are used in paint [6].

1.3 Introduction to Nanotechnology and Nanoparticles

Nanotechnology is the engineering of practical systems at the molecular size. Any particles less than 100 nm are called nanoparticles. Richard Feynman, a physicist in 1959, discovered nanotechnology theories and capabilities. Eric Drexler in the 1980's introduced nanotechnology to building mechanisms and machines with all the components, such as motors, robot arms, and even computers which are all made from nanoscales molecules. The U.S National Nanotechnology Initiative (NNI) was developed to fund nanotechnology. The NNI has invested 3.7 billion dollars in nanotechnology. The European Union has invested 1.2 billion, and Japan 750 million dollars [3]. Physical properties of microparticles are significantly different from nanoparticles. Nanoparticles have a large surface area for a given volume called aspect ratio. Aspect ratio is really important since many physical and chemical interfaces are ruled by surface area. Figure 1.6 shows the aspect ratio; a change in diameter of particles or thickness of layers from micrometer to nanometer.

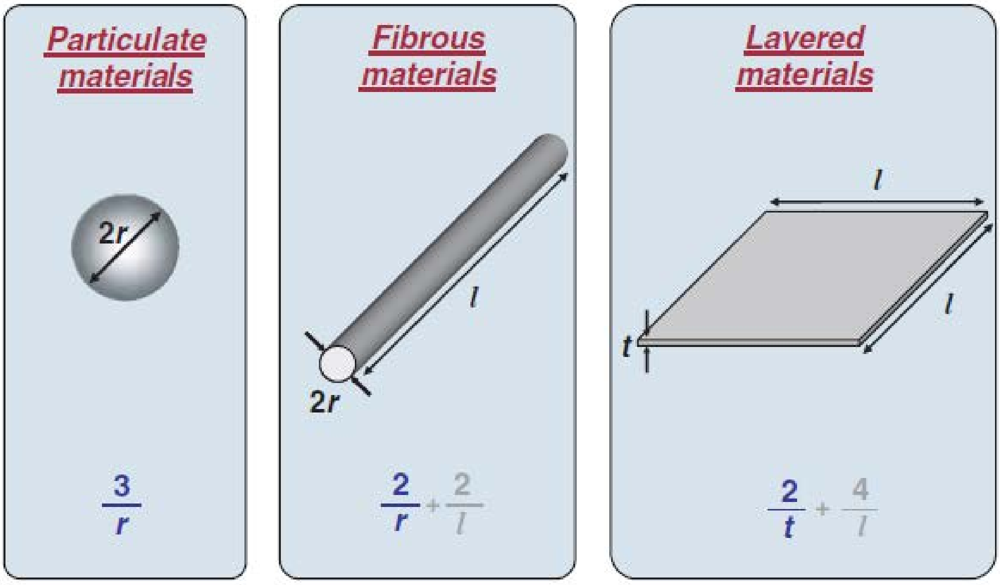


Figure 1.6: Common particle reinforcement geometries and surface area to volume ratios [3].

Some typical nanomaterials are made from nanoparticles, nanotubes, nanofibers, nanowires, and fullerenes. Generally these materials are categorized by their geometry which can be three classes:1-Particles: Carbon black, Silica nanoparticles, Polyhedraloligomeric sislesquioxanes (POSS) 2-Fibrous: Nanofibers, Nanotubes 3-Layered: Organosilicate. Size of the nanocomponents, ratio mixing of nano nanocomponents, and matrix have a great influence in properties of nanocomposite [3].

1.3.1 Graphite Nanoplatelet

Natural Flake Graphite (NFG), is made of nanosheets layers which are carbon atoms linked by strong covalent bonds. When carbon atoms are located in bordering planes, they bond by Van Der Waals, a weaker bonding. The NFGs with a 0.4-60μm thickness can be expand up to 2-20000μm in length and the layers can be divided to a thickness of 1nm. These graphite nanosheets have a high aspect ratio of 200-1500 and high modulus of 1 TPa. Graphite nanosheets contribute a huge interface surface area of 2630 m^2/g, when they are dispersed in a matrix system and as a result, physical and mechanical properties of nanocomposite improves significantly. By rapid heating of graphite nanosheets, expanded graphite (EG) can simply be prepared. Figure 1.7 shows how graphite sheets which are black lines can be expanded [3].

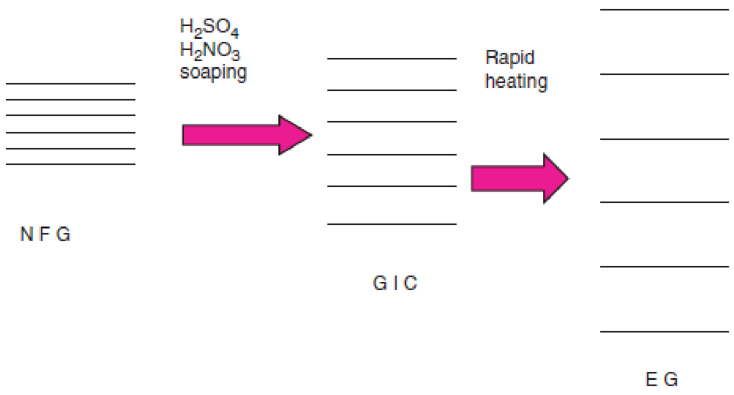


Figure 1.7: Schematic illustration of expanding graphite (EG) [3].

Carbon-based system has an unlimited number of diverse structures and large selection of physical properties because of its flexibility and bonding. Graphene geometry is hexagons that make honeycomb structures out of carbon. Fullerenes are wrapped up graphene and because of their geometry of arranging spherically by carbon atoms, from a physical point of view they are zero dimensional with a distinct energy state. Carbon nanotubes are made out of rolling graphene, and reconnect the carbon bonds. They are hexagons considered one dimensional object. Figure1.8 shows the graphene structure:

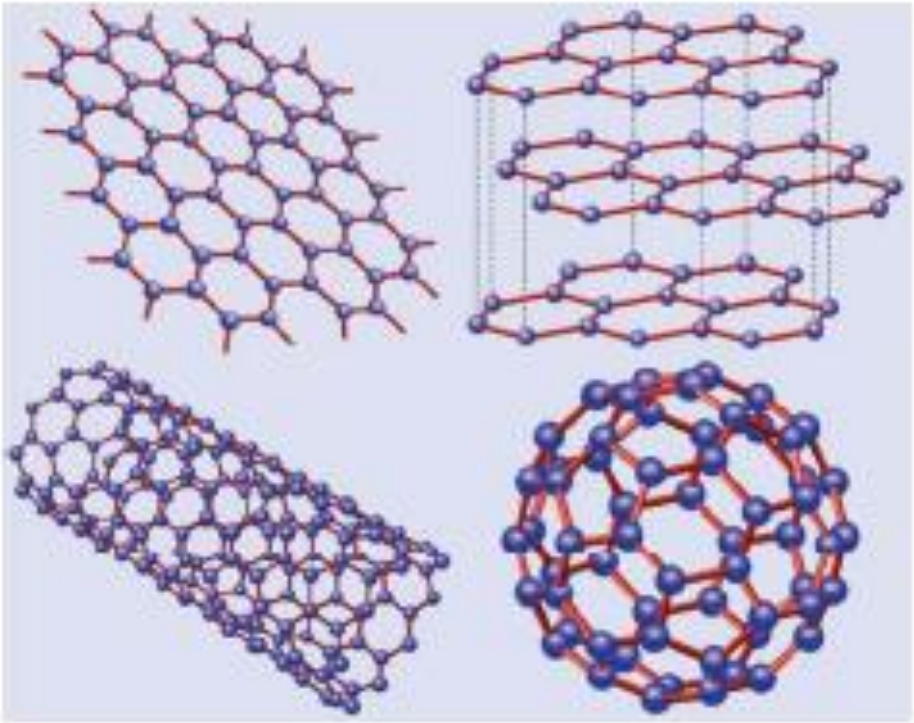


Figure 1.8: Top left is graphene honeycomb lattice of carbon atoms. Top right is graphite, which is stacks of graphene layers. Bottom left is nanotubes, which are rolled up cylinders of graphene. Bottom right is fullerenes, (C60) which is a wrapped graphene [7].

After the invention of pencil in 1564, graphite, a three dimensional allotrope, became widely known. Graphite is made of stacks of graphene and coupled weakly by van der Waals bonding. The weak bonding between the layers of graphene can be easily broken by pressing a pencil on a sheet of paper. Each time someone writes on a paper with a pencil, layers of graphene are being isolated. There are two reasons for this, nobody was anticipating seeing the graphene in a free state, and technology/tools weren't existent to search on one atom layer thick.

Later on using substrate SiO2, helped to observe the graphene on the ordinary optical microscope. As a result graphene is not easy to find, but rather is easy to make [7]. Graphene can be adapted chemically and structurally in many different ways and that's because of its extraordinary structural and electronic flexibility. From stacks of graphene layers, the tight bonding model can be developed. Figure 1.9 shows the bi-layer structure of 3D graphite.

a) Bi-layer graphene: Tight binding approach:

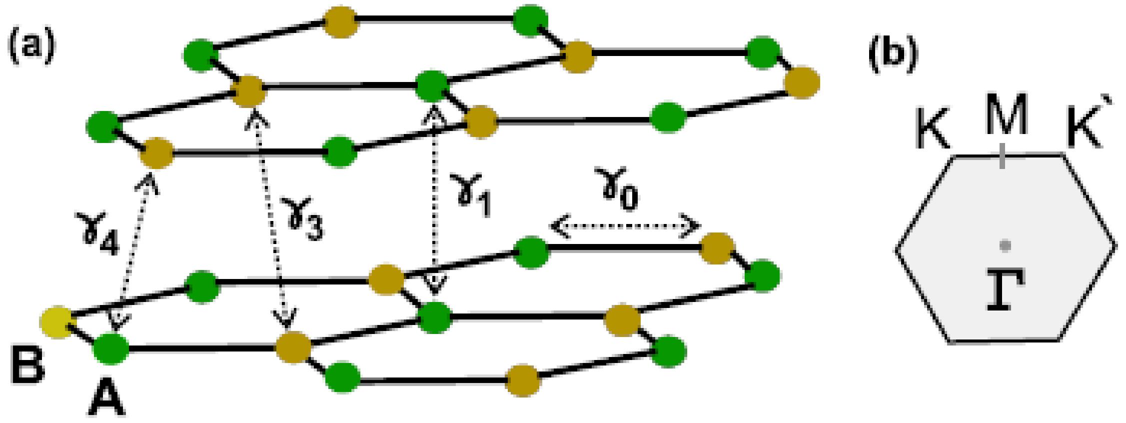


Figure 1.9: a) Lattice structure of bi-layer graphene representing electronic hopping energies based on the SWM model b) Brillouin zone [7]

b) Graphene Stacks

The comparative position of two adjacent layers allows for two unlike orientations of the third layer. Because of the weak bonding between planes the graphene layers can be rotated relative to each other. Due to the different orientations of the layers, quasidegenerate in energy appears in bonding and at certain angles leads to a decreasing in the electronic energy. Super lubricity in graphite is the disappearing of the friction between layers, and results from rotation angle between graphene layers [7].

Graphene has three remarkable qualities:

- Electron transport by the Dirac equation allows contact to quantum electrodynamics in a simple strong substance experiment.
- Scalability of graphene devices to nanosize and chemical and mechanical stability. Graphene can appear in various forms such as graphite, nanotubes, and buckyballs [8].

Graphene can be produced by processes such as micromechanical cleavage of graphite. Only multilayer of graphene can be produced by exfoliation and growth. Atomic Force Microscopy (AFM) was the only technique of recognizing single and few layers, until using the Transmission Electron Microscopy (TEM) on some samples was measured by Raman spectroscopy. Figure 1.10 shows some images of graphene by TEM. Having projected atomic potentials by Fourier transform proves that multilayer of graphene has the same stacking as graphite. Figure 1.11 shows the result from Raman spectra comparison between graphene and graphite. Having projected atomic potentials by Fourier transform proves that multilayer of graphene has the same stacking as graphite. Figure 1.11 shows the result from Raman spectra comparison between graphene and graphite.

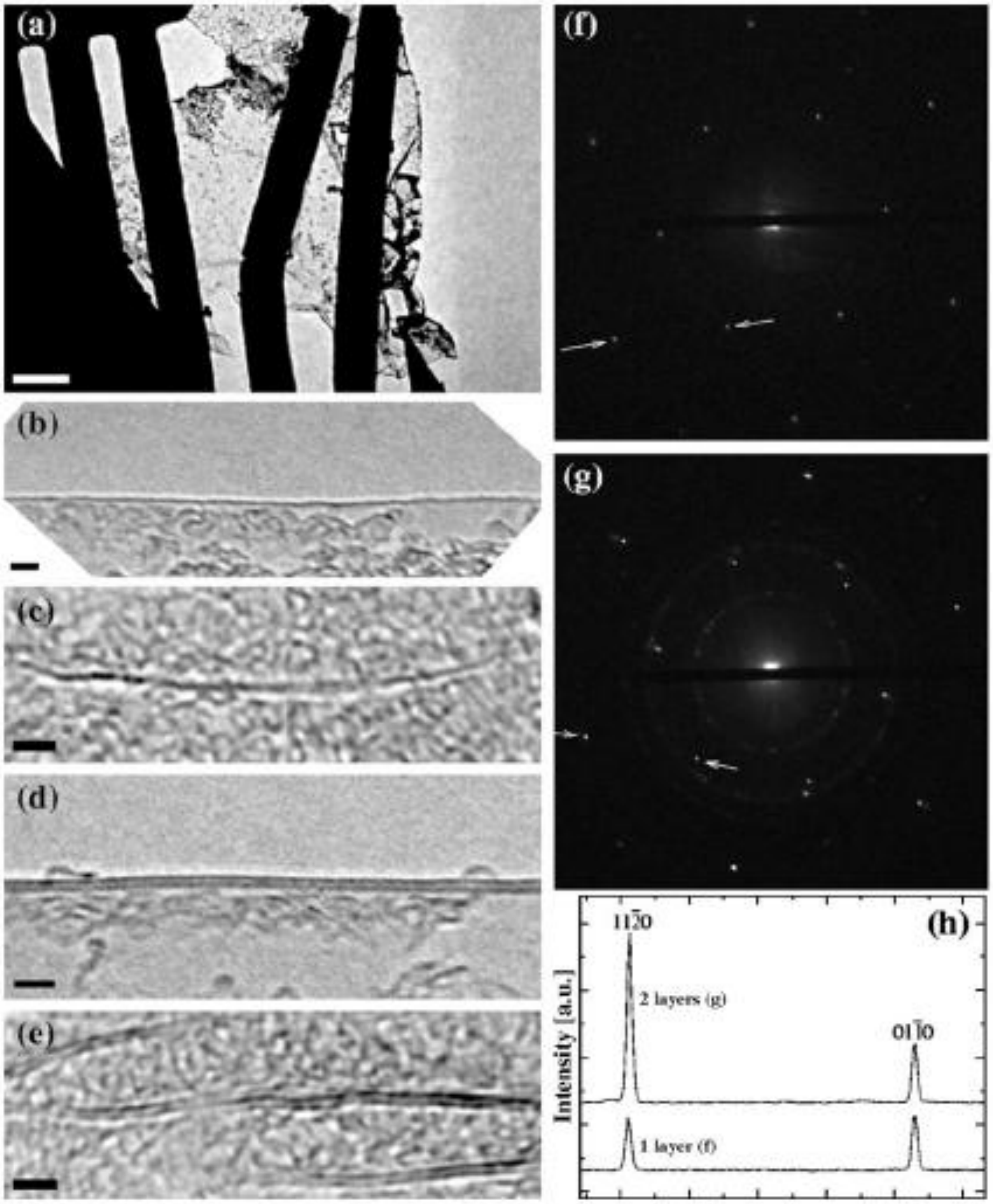


Figure 1.10: a) TEM of suspended graphene b) Folded edge of a single layer c) Layers with wrinkle in between d) Two layer in a folded edge form e) Two layers in a internal folding form f) Single layer electron diffraction pattern g) Weak diffraction peaks from two layers h) Intensity profile plot [8].

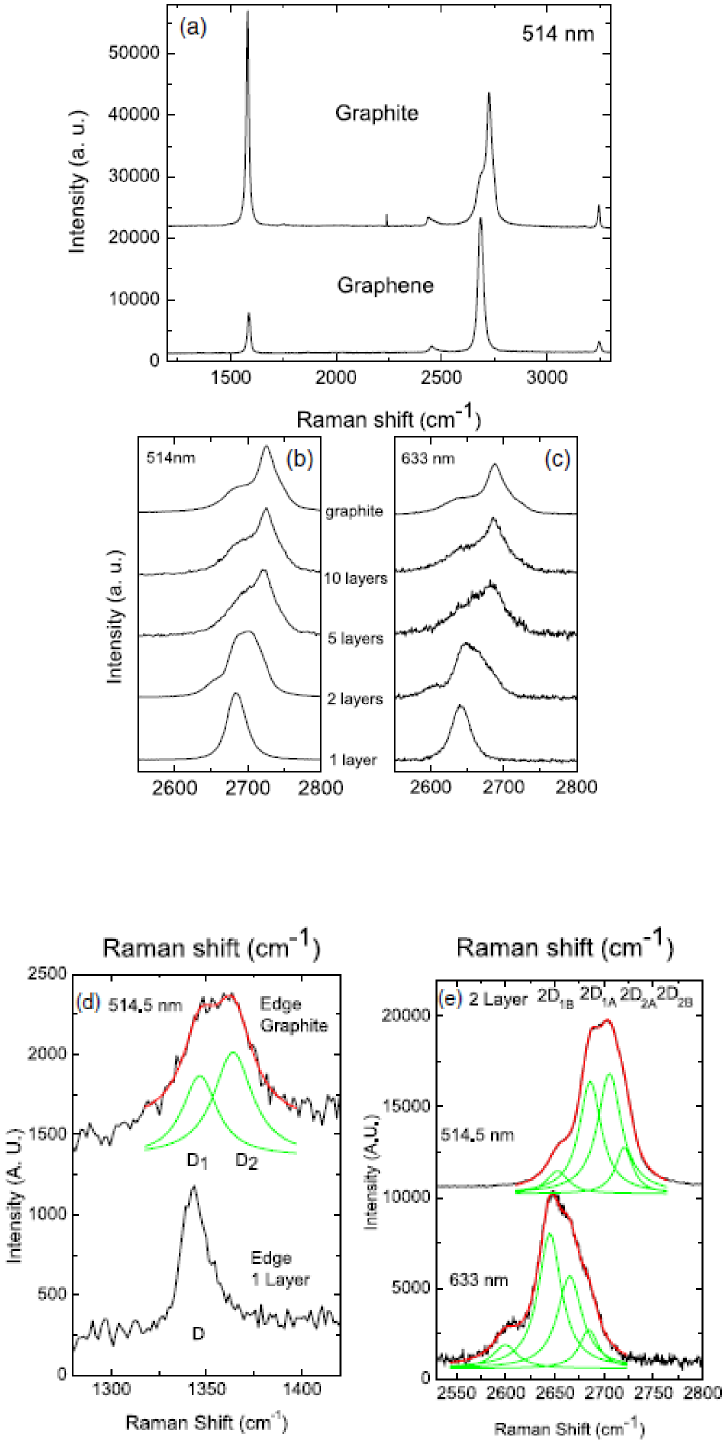


Figure 1.11: a) Comparison between graphene and graphite b) at 514 nm spectra is showing evolution with the number of layers c) at 633 Raman spectra is showing evolution with the number of layers d) comparison between the single layer of graphene and bulk of the graphite with D band at514 n [8].

1.3.2 Carbon Black (CB)

Carbon black is a practically pure element of carbon, number six on periodic table of elements. In the west it was called “soot” and in the east, “shouen”. After production started in the 1740’s in the U.S it was called lampblack because of the production method. In 1870, when the natural gas was used for production, the term of carbon black was used and since then it has been called carbon black. Carbon black is a colloidal particle form, manufactured by partial combustion or thermal decomposition of oil or gas, with an excessive deal of oxygen inside large furnaces under controlled environments. By changing the amount of oil and air the temperature will be affected and as of result of different particle size and connection of carbon black will be produced. Carbon black’s physical appearance is black, finely divided pellet or powder [9]. Manufacturing process can be incomplete combustion or thermal decomposition.

a) Incomplete combustion:

The raw material for this process method is Aromatic hydrocarbon oil, and the manufacturing method is oil furnace, the most common method to produce carbon black. In the oil furnace method, feed stock is used to generate heat by the combustion of fuel and air. The heat reaction section is insulated by heat resistant material. Hot air and hot oil are injected to this section to continue the complete combustion and this rises the temperature to 1300°C. Hot gas with carbon black produced downstream of the reactor will be atomized with water to decrease the temperature to 1000°C, and that is the end of the reaction. Time period from formation of carbon black to the end of the reaction can be as short as a few milliseconds, or up to 2 seconds. Figure 1.12 illustrates the oil furnace method [9].

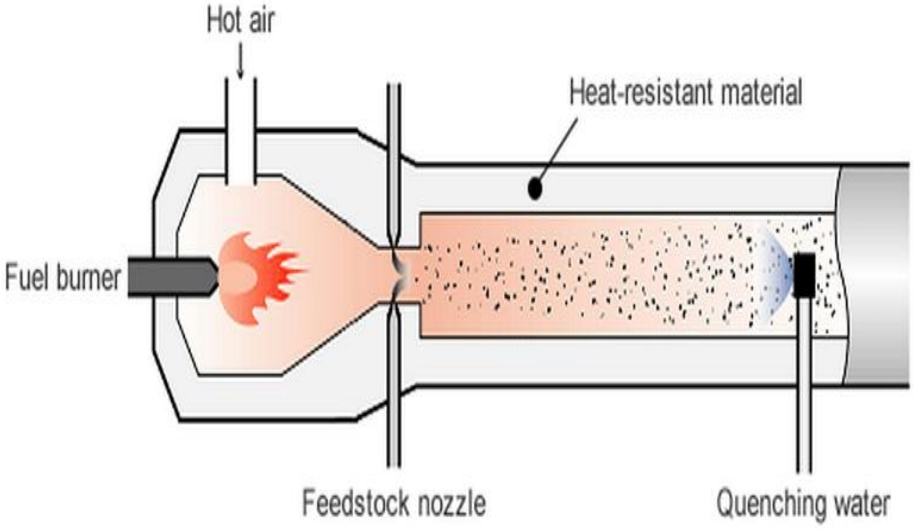


Figure 1.12: Internal diagram of production reactor in the oil furnace method [9].

If manufacturing method is lampblack, then the raw material would be mineral or vegetable oils and this is the oldest manufacturing method of producing carbon black. The lampblack method was used since ancient times in order to produce carbon black resin from heated trees. Until the 1930's this method was used in Europe and later replaced by the furnace method. Equipment for this method would be a metallic plate to place the raw material such as vegetable oil, a cover for gathering, and between the plate and cover there is a space for air injection. Quality of carbon black is depends on the amount of air injected into the system. After the cover heats up, the heat radiation will vaporize the raw material and cause partial combustion and produce carbon black [9]. Figure 1.13 shows the lampblack method. Some other manufacturing methods are Channel and Gas furnace.

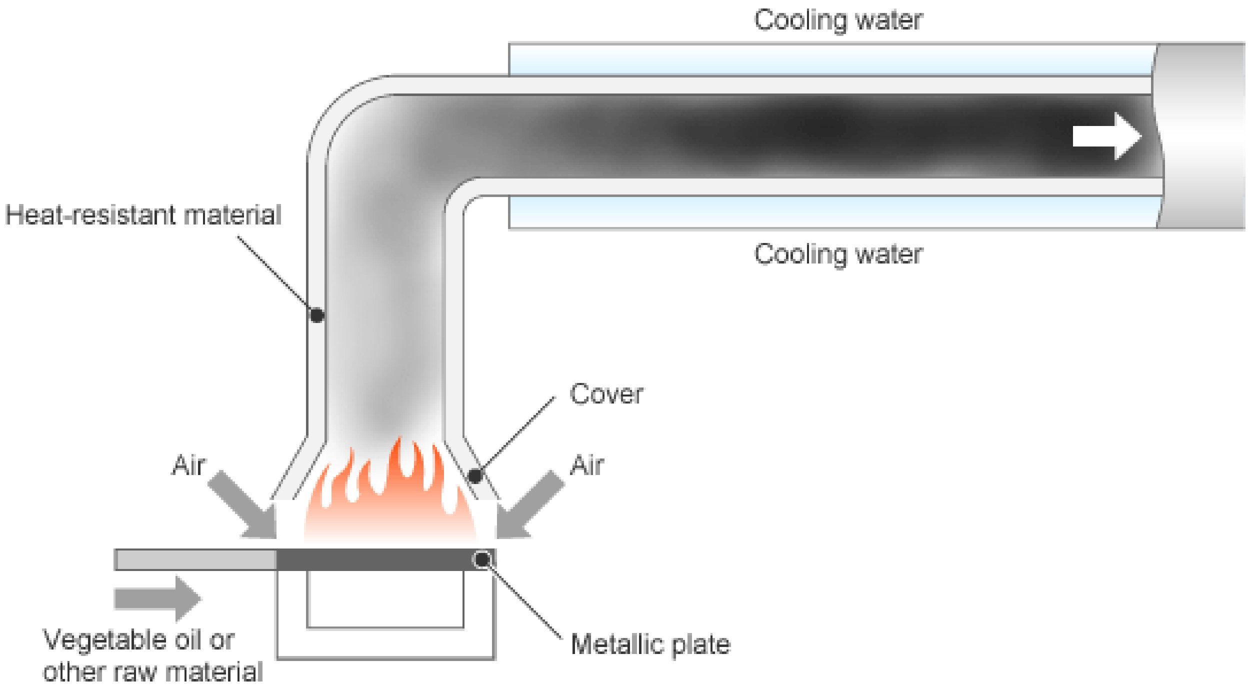


Figure 1.13: Lampblack method diagram of production reactor to produce carbon black [9].

b) Thermal Decomposition

If raw material is acetylene then the manufacturing method would be Acetylene decomposition. In this method, since it is a heat generation reaction, it is possible to have a continuous production. Thermal method is used if the raw material is natural gas, in which combustion and thermal decomposition are repeated in cycles [9]. Figure 1.14 shows the complete process diagram of carbon black. In the channel method, the raw material, natural gas and flames make contact with the lower surface of the H-shaped steel beam channel. In the gas furnace method, raw material is again natural gas, and used to produce a very fine carbon black.

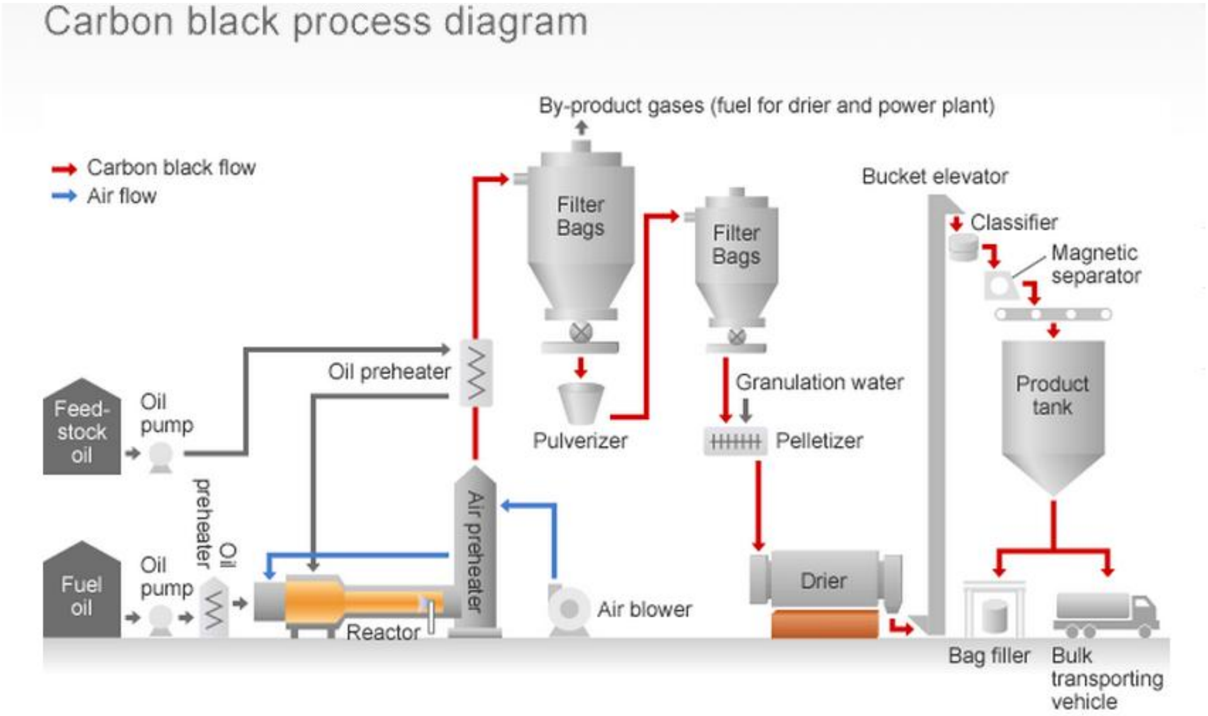


Figure 1.14: Furnace black manufacturing process to produce carbon black [9].

Carbon black has two main properties:

a) Physicochemical properties which includes:

- Particle size: The size of each particle of carbon black. The smaller the carbon black, the larger the specific surface.
- Structure: Size of particle chain and oil absorption indication. The greater the oil absorption, the more multifaceted is the arrangement.
- Surface chemistry: different functional groups such as hydroxyl and carboxyl group can be found in the surface of the carbon black and this can change the compound characteristics.
- Aggregate distribution: The size of the aggregates can vary, and if the distribution is spiky then there are many aggregates of the same size. Figure 1.15 shows these properties of carbon back [9].

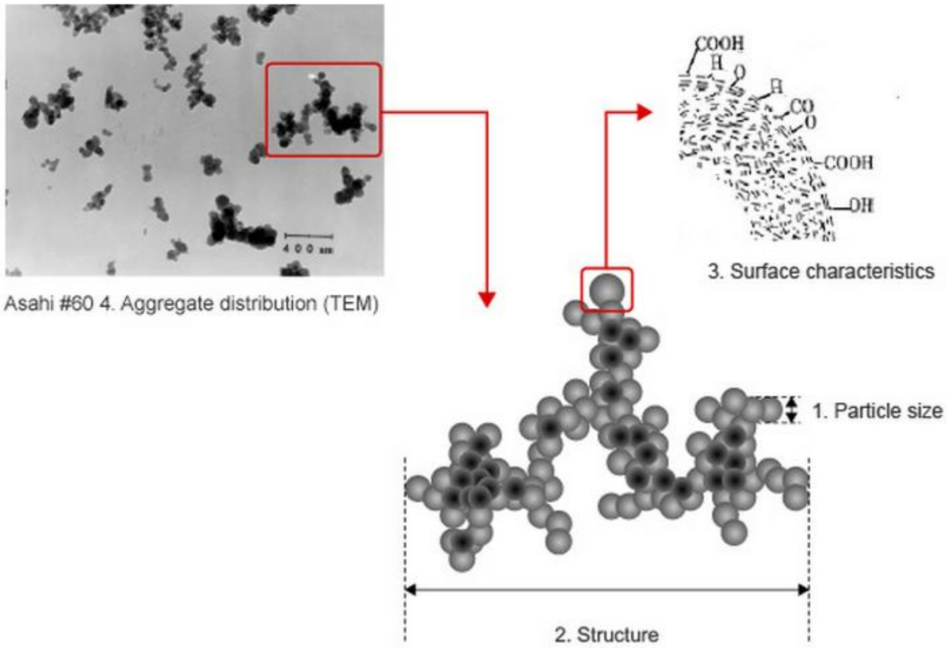


Figure 1.15: Properties of carbon black from physicochemical point of view [9]

b) Compound properties include :

- Reinforcement: Carbon black is added to many materials to increase strength, such as rubber used in tires or high pressure hoses as a material reinforcement.
- Conductivity: Adding carbon black to natural rubber results in a decrease of resistance in their electrical resistance. This conductivity is because of the channels of electrons jumping from one particle to another.
- Pigmentation: Carbon black has physically powerful tint properties, because thermal stability makes it suitable for plastic and film coloring. This property of carbon black comes from its size and structural interaction with light.
- Ultraviolet degradation protective properties: Ultraviolet light can be absorbed by carbon black and this protects the materials from degradation. This is because the carbon black stress-fissure prevention in plastics refines their crystals [9].

Carbon black can be used as a rubber reinforcement preservative in different rubber products. For example carbon black can be used in tires and shoe soles. Carbon black also has colors and pigments used in the plastic industry. Carbon black has a very good coloring power compared to other colorants. For example carbon black can be used as ink for printing magazines and newspapers, or as ink-jet toner. Application of carbon black as a pigment to heat-molded plastics is used in car body parts such as bumpers and coating for electrical wires. Carbon black can be used in electrical equipment and a conductive component [9]. For example carbon black is used as a pigment in magnetic tapes and semiconductors. Figure 1.16 shows some applications of carbon black.

Figure 1.16: Application of carbon black in different industries [9].

1.3.3 Carbon Nanotubes

Carbon nanotubes were discovered in 1991, and since then attract huge attention because of their structural characteristics, mechanical, and electrical properties. Geometry of carbon nanotubes is similar to rolled graphene layers having a planar hexagonal array of carbon – carbon bonds. Carbon nanotubes bonding array and topological defects needed for rolling up the sheet of graphene gives them outstanding properties. Carbon nanotubes can be multiwall nanotubes (MWNTs) or single walled nanotubes (SWNTs), and this depends on the synthesis during growth. Nanotube diameter has a range from a nanometer to tenths of a nanometer and their lengths have a range from micrometers to centimeters. Synthesizing of nanotubes can be done by several techniques such as: arc-discharge, laser ablation, and catalytic chemical vapor deposition (CCVD) [10].

- Arc-discharge method: This technique is used to synthesize SWNTs and double wall nanotubes (DWNTs) which have a narrow diameter. In this method, under a helium or argon environment and between two graphite electrodes, an electric arc is generated which results in vaporizing graphite and condensing the cathode. There are other deposits other than the nanotubes on cathode such as: fullerenes, catalyst particles, and amorphous carbon materials. Later some purification is required to separate the CNTs from other deposits.
- Laser ablation method: In this method in the flowing argon and at the temperature of 1200ºC a laser ablates a graphene target. The graphite target has some other metal catalyst such as iron and nickel and this is because bimetallic catalysts are more productive than single ones.

Characterization of carbon nanotubes:

Transmission Electron Microscopy (TEM) is used to investigate the morphology and condition of dispersion of the CNTs. Figure 1.17 shows the TEM image of a toluene suspension of MWNTs after sonication. Figure 1.17A shows distribution in length range from 0.15 μm and diameter range from10-50 nm. Figure 1.17B shows the rounded structure of a single nanotube. Figure 1.17C shows interconnection structures between the nanotubes caused by highly entangled nanotubes. Figure 1.17D shows enlarged nanostructure of a MWNT with several layers of graphite carbon and unfilled center. Figure 1.17E-H shows the TEM images of nanocomposite which MWNTs used as filler and base was styrene-butadiene rubber. Figure 1.17E shows a bundle of MWNTs. Figure 1.17F and G show the aggregation of MWNTs as black spots [10]. Figure 1.17H shows an orientation of MWNTs taking place during hot pressing of the film which effects on mechanical properties of nanocomposite [10].

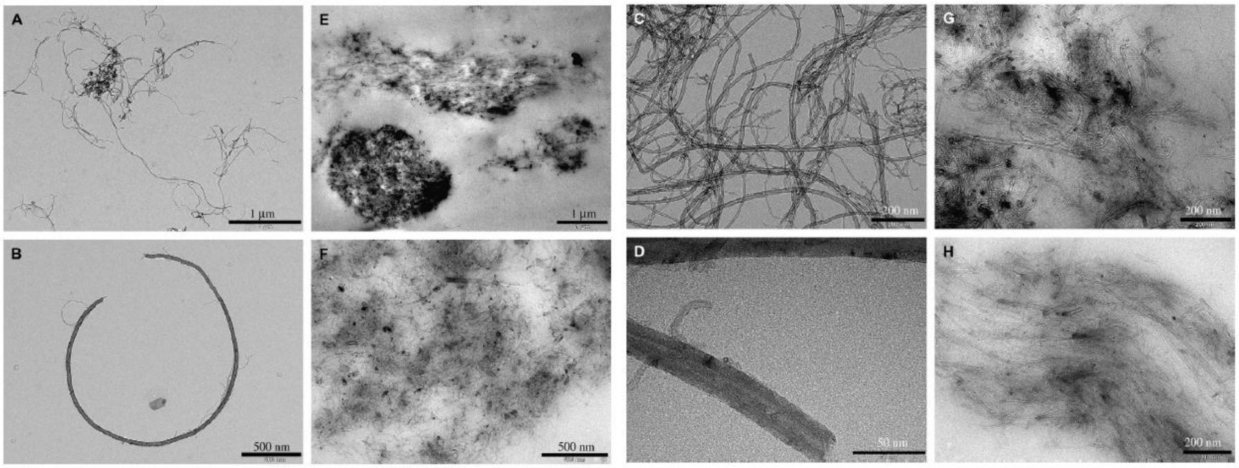


Figure 1.17: TEM Images A-D: MWNTs Pourely and E-H as MWNTs Composite [10].

a) Mechanical properties of nanotubes composites:

Addition fillers such as carbon black and silica to elastomeric cause an increase in the modulus which is a result of increasing in the cross-linking interaction between polymer and filler. Carbon nanotubes expected to create better and stronger reinforcement effects result in a higher modulus of elasticity. Considerable improvements in mechanical properties of nanocomposite have been reported by addition of CNTs, and some measurements shows elastic modulus of elasticity of SWNTs up to 1Tpa. Figure 1.18 shows stress-strain curves comparing pure styrene butadiene rubber (SBR) and MWNTs nanocomposite [10].

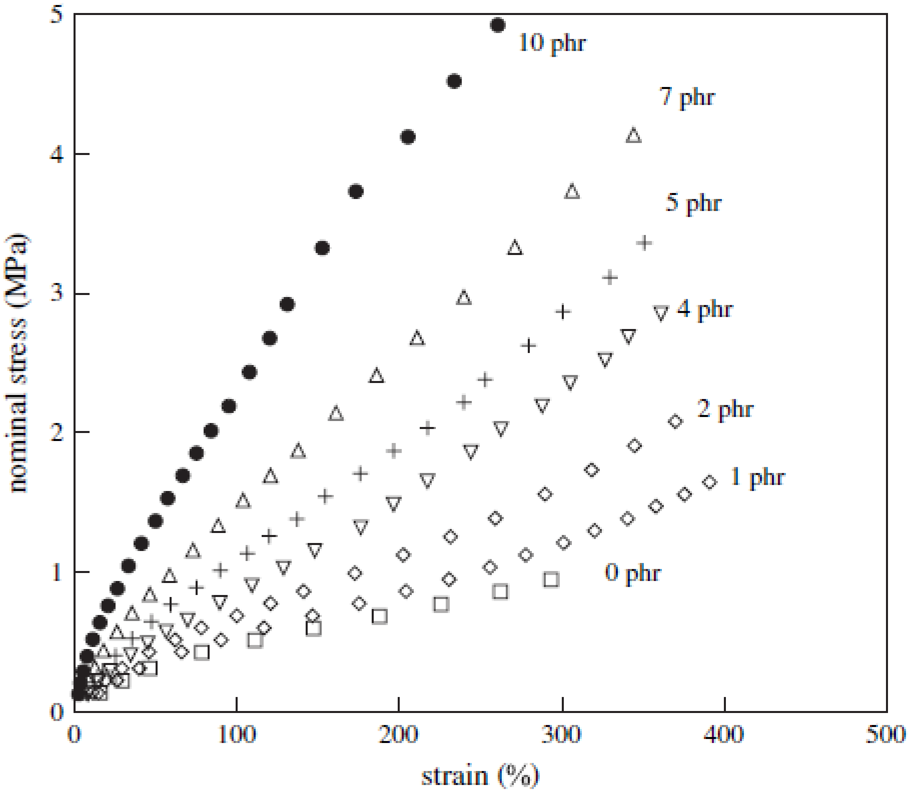


Figure 1.18: Stress- Strain Curve Comparing SBR and MWNTs Composite. Amount of MWNTs is in phr (parts per hundred parts of rubber) [10].

b) Electrical properties:

Carbon nanotubes bring low resistivity to elastomeric nanocomposite. Filler concentration has large influence in electrical properties. Matrix interface of filler –filler, filler-matrix, and filler particle size and structure determine the dispersion condition. Electrical conductivity is also influenced by nanotube orientation. Percolation threshold is a critical volume fraction that leads to a quick drop of electrical resistivity, as a result of interconnecting filler by conducting inclusion. Figure 1.19 shows the effect of filler loading on the volume resistivity of carbon black and MWNT. The volume resistivity ρ can be calculated after measuring resistance R using this equation: $\rho = \frac{RS}{d}$

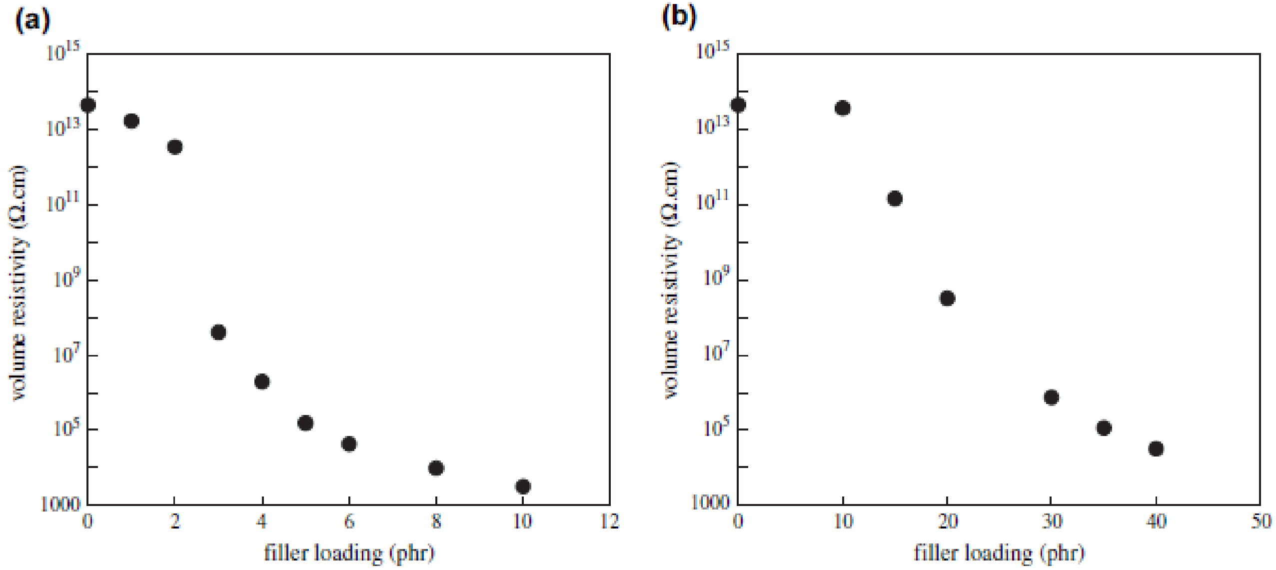


Figure 1.19: Volume Resistivity vs. Filler Loading for Composite made out of a) MWNT c) CB [10].

Nanotube composites have many applications in different industries. In the health care industry, adding the nanotubes to the surface of implants improves the properties of the implant. Nanotubes can also be used to monitor the level of nitric oxide by injecting under the skin. In the environment, nanotubes can be used to make a sponge to absorb oil in case of oil spill. Also flexible food cover can be detecting spoiled food by spraying carbon nanotubes on to the surface of plastic. In effecting material, addition of nanotubes to concrete stops the crack forming to avoid leaks. Adding nanotubes to aerobatic aircraft engine cowling increases the strength to weight ratio. In electronics nanotubes can be used to make the transistor from nanotubes as small as a few nanometer dimensions. Nanotubes can be used to make integrated circuits. Figure 1.20 shows some application as grow rate of nanotubes [11].

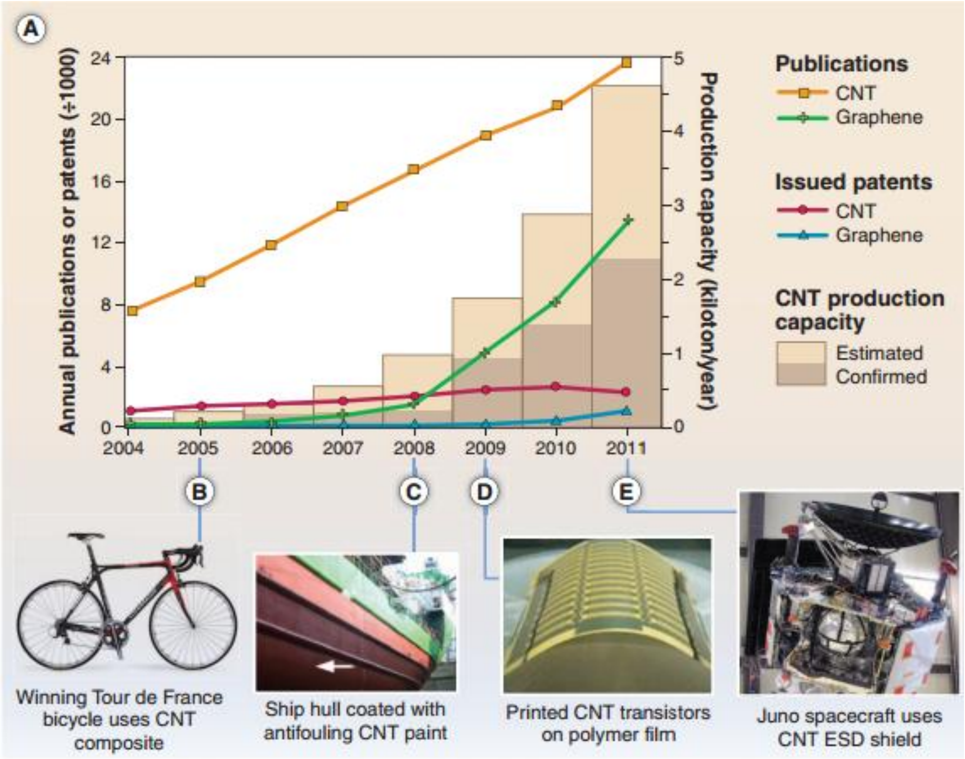


Figure 1.20: Graph shows the widespread CNTs research production since 2004 and some applications of nanotubes [11].

1.4 Silanization

The physical and mechanical properties of epoxy nanocomposite are far from expectation, since CNTs have excellent properties. However these properties can be improved by having better dispersion of CNTs in epoxy resin systems. Better dispersion of CNTs in resin creates more efficient interfacial adhesion to reach the expected properties. One of the most potential methods is to chemically modify the surface of CNTs before mixing into epoxy. Silane mixture agent can act as link between hydrophilic CNTs and hydrophobic epoxy. Surface treatment of CNTs by using silane is an efficient method to have a homogeneous dispersion and prevention of agglomeration of CNTs. Another advantage of functionalized CNTs compared to non-functionalized, is the functionalized CNTs have more functional groups to make chemical bonding with epoxy resin system. There are different types of silane used for silanization of

CNTs such as Aminopropyl-triethoxysilane (A1100) [12]. By using different chemical modification on CNTs, properties of nanocomposite can be changed. Functionalization of CNTs also affect on thermal stability of epoxy nanocomposite [12].

Silanization process:

a) Make a solution with silane and ethanol at 0.001g/ml concentration and 10% of weight ratio of treated carboxylic- functionalized MWCNTs (COOH-MWCNTs) [12].

b) Add dried COOH-MWCNTs to the solution then stirring by using magnet stirrer at 60ºC for 30 minutes, and to having a dispersion put the solution in sonicator for 1 hr [12].

c) Use the filtration separate the silane treated particles and then rinses it with ethanol several times [12].

d) Dry the treated particles in vacuum at 110ºC for 1hr.

Fourier –transform infrared (FTIR) was used to confirm the success of silanization process. Figure 1.21 shows the result of FTIR [12].

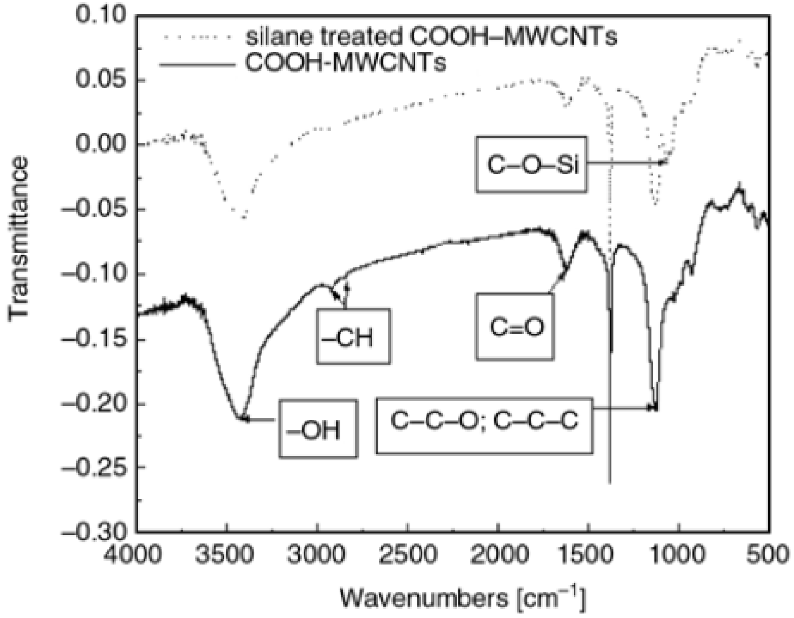


Figure 1.21: FTIR Spectra of Non-Treated COOH-MWCNTs and Treated COOH-MWCNTs [12].

CHAPTER 2

LITERATURE REVIEW

It was reported adding nanopartilces increased the curing time as result of high cross linking between epoxy resin and nanopartilces. Silanization process of nanoparticles was improved in homogeneous dispersion and using Fourier Transform Infrared (FTIR), showed silane as a coupling agent created a covalent bond. Using Differential Scanning Calorimetry (DSC) was used to measure the activation energy by using Friedman was showed catalytic effects of the functionalization act as a hardener and more accelerated cure reaction. This suggests acceleration in curing kinetics could have positive effects on processing of nanocomposite by decreasing curing time at the lower temperature. However, some studies reported curing behavior at four different temperatures. Using DSC curing reaction at lower temperatures didn't change the auto catalytic cure reaction, and that might be because of higher surface area of nanoparticles. During fabrication of nanocomposite, higher surface area eventually was required a higher post curing temperature. Also some studies showed the effect of adding nanotubes to epoxy resin on its curing kinetics by using DSC resulted in different temperatures at initial curing slopes, but after 15 min there was no significant change in slope. One study result was determined as well dispersion of Carbon Nanotubes (CNTs) being lowered the heat reaction of curing epoxy and concluded that condition of dispersion plays a big role in curing of resin. Another study was demonstrated using Dynamic Mechanical Analyzer (DMTA) to measure the energy dispersion as a function of temperature. It resulted in decomposition temperature and improved thermal stability by silanization of Multi-Walled Carbon Nanotubes (MWCNTs). Improvement in thermal stability of composition was because of molecule diffusion from matrix at high temperature. Higher transition glass (Tg) was reported as a result of cross linking reaction and covalent bonding between nanotubes and epoxy resin.

2.1 Unfunctionalized Nanoparticle Nanocomposites

Nanoparticles were used as they were received from the manufacturer without any modifications to prepare nanocomposites. Nanoparticles such as: Carbon Nanotubes (CNTs), Single Wall Nanotubes (SWNTs), Multi-Wall nanotubes (MWNTs), Graphene, and Metallic nanoparticles were used. As matrix system epoxy resins such as: bisphenol M dicyanate ester (BMDC), tetraglycidy-4-4 diaminodiphenylmethane (TGDDM), EPIKOTE 826, and Araldite GY 251 were used by addition of curing agents to study the effects of unfunctionalized nanoparticles on curing kinetics of nanocomposites.

2.1.1 Carbon Nanotubes

Puglia et al. [14] have conducted a study on the effects of carbon nanotubes (CNTs) on curing reaction of DGEBA epoxy resin using diethylenetramine (DETA). To make the nanocomposite samples 5% and 10% of SWNTs was mixed separately with epoxy resin in a sonicator and samples were cured using DETA. DSC was used to test the isothermal and was showed acceleration on curing reaction at low temperature, however no effects were observed on maximum degree of curing on presents of SWNTs. High frequency Raman spectra was used to measure the mode frequency. The result showed a 5% increase on concentration of SWNTs and thermal degradation increases; however 10% SWNT had no effects. Raman spectroscopy showed carbon nanotubes dispersion in epoxy resin and caused a well high thermal conductivity.

Tang et al. [15] have conducted study effects of carbon nanotubes (CNTs) on curing kinetics of epoxy resin. Different weight percentages of CNTs were mixed with epoxy resin. FTIR was used to confirm the dispersion of CNTs in epoxy resin. The result showed the speed of imidization because of well dispersion of CNTs in resin. DSC resulted in a decrease of decomposition temperature of poly which can be used by better dispersion of CNTs and that result in acceleration of cyclodehydration of the poly (amic acid).

Li and Simon [16] conducted study on the effects of nanoparticles and nanotubes on curing behavior of bisphenol M dicyanate ester (BMDC) resin. In this study, catalyst was not used to allow the liquid monomer absorbed by nanopores above its melting point without a significant degree of cure .DSC was used to measure the calorimetric and two types of measurements were used one to measure Tg at 180º F as a function of cure time, and another to measure the residual heat of reaction to show the relationship between Tg and conversion. It resulted in an increase of nanoparticles and the curing rate of resin, but it didn't affect the glass transition vs. conversion. Addition of nanoparticles increased the curing rate of resin. Concluded from data, there is no change in heat of reaction and glass transition vs. conversion.

Xie et al. [17] have conducted a study of effect of carbon nanofibers (CNF) on curing kinetics of tetraglycidy-4-4 diaminodiphenylmethane (TGDDM) epoxy resin. To prepare the samples TGDDM resin was dispersed in sonicator with CNF for 2h. Then mixture of resin and CNF was placed in an oil bath at 120ºC and then 4,4 diamminodiphenylsulfone (DDS) curing agent was added while mechanical stirrer was mixing. After about 10 min when uniform dispersion observed several samples was taken for DSC testing. Different weight percentages of CNT were taken for samples. Isothermal DSC was used to measure the curing kinetics of samples. This resulted in the effects of CNF on TGDDM are negligible at initial and maximum reactions but addition of CNF slightly was decreased the overall curing temperature range.

2.1.2 Single -Walled Nanotubes

Gerson et al. [18] is about the effects of single-walled carbon nanotubes (SWNTs) and Hysol 9309.2 as an epoxy host material on curing kinetics and the mechanical properties of the resin. Because the SWNT exhibits extraordinary mechanical electrical properties, this makes it great for the next generation of composite. This study focused on curing effects of SWNTs on property of epoxy by itself. High powered sonicator was used to have a good dispersion of nanotubes on resin. After making the sample, Dynamic Mechanical Analyzer (DMA) was used to measure the stored and dissolute energies of a visco-elastic sample. The dissipated energy shows the loss modulus caused by molecular friction. Thermal analysis (TA) was used to analyze the dynamic mechanical of the product. Digital Image Correlation (DIC) was used to show the bending deformation and verify that it is negligible. Results showed an increase in SWNTs to resin will increase surface area and the effects on thermal and mechanical properties. Results also showed by increasing in SWNTs, it also increases the strength and stiffness of epoxy. Glass transition temperature (TGs) also increases by adding more SWNTs because of increase in cross-linking which is caused by more interaction between SWNTs and epoxy.

Tao et al. [19] have conducted a study on the effects of carbon nanotube on the curing kinetics of epoxy resin (EPIKOTE 826) and hardener (EPIKURE). Short SWNT, Hipco SWNT, and XD-CNT were three kinds of nanotubes that have been used in this study. Differential Scanning Calorimetry (DSC) was used to measure the curing process by using a temperature ramp. Results showed additional nanotubes caused a decrease of curing degree. All three nanotubes showed different initial curing slopes, but after 15 min curing there wasn’t any significant change. CNT caused curing at the lower temperature.

Chakraborty et al. [20] have conducted a study on the effects of uniform dispersion of single wall carbon nanotube on curing of bisphenol F-based (Epikote 862) epoxy resin and dietheltoluenediamine (Epikure 3402) as a curing agent. There are different approaches to perform a good dispersion of CNTs in epoxy resin without damaging the CNTs properties. In this investigation to facilitate a uniform dispersion, a dispersing agent (DAs) was used to improve the dispersion of CNTs in epoxy resin. In this experiment, the DA was added directly to the epoxy resin, and then CNTs was added. By using the high speed mixer at 8000 rpm and using the 3 roll mill, mixing was completed and nanocomposite was ready. To cure the composite heating mould was used. Scanning Electron Microscope (SEM) was used to illustrate the images and the effect of dispersion. This resulted in dispersion of CNT in resin at the high temperature is not stable. Also using hardener was increased in bundling the CNTs. As of result of uniform dispersion of CNTs mechanical properties of composite were improved.

Lau et al. [21] have conducted a study on the effects of different solvent used for dispersion of single –walled carbon nanotubes (SWNT) on thermal and mechanical properties nanocomposite. Araldite GY 251 was used as epoxy resin and curing agent was CIBA HY 956. Some solvent such as ethanol, acetone, and DMF (used for dispersion of SWNT), was traced in nanocomposite. In this study to see the effects of solvent before curing, acetone, ethanol, and DMF were added to individual samples of epoxy resin continued by an evaporation process. DSC showed curing for different solvent samples were different as well. FTIR depends on the type of solvent used, and then different functional groups were formed, which caused variation of thermal and mechanical properties of samples. The order of effects of solvent based on result of this study was DMF>ethanol>acetone.

2.1.3 Multi -Walled Nanotubes

Kim et al. [22] have conducted a study on the effects of uniform dispersion of canbon nanotube (CNTs) on cuing kinetics of epoxy resin. Reinforcement was multi walled CNTs, epoxy resin was bisphenol –A-type, and KBH1089 was the curing agent in this experiment. Since most CNTs aggregate, dispersion process was performed as following: mixed CNT, Epoxy, and Acetone by using high power ultrasonication. Then by using vacuum, residual solvent evaporated, which resulted in well dispersed CNT in epoxy. Curing agent was added to the mixture of CNT and epoxy to have samples for Differential Scanning Calorimetry (DSC). Results showed well dispersion CNTs were lower in the heat reaction of curing epoxy and the condition of dispersion is significant in curing of resin.

2.1.4 Graphene

Qiu et al. [23] have conducted a study on the effects of graphene oxides (GOs) on the curing kinetic, activation energy, and thermal stability of the tetra-functional tetraglycidy1-4-4-diaminodiphenImethane epoxy resin with 4,4-diaminodiphenylSuldone as curing agent. Graphene oxides at different weight percentages have been added to the epoxy resin. After adding hardener with the different wt% of graphene oxides, kinetic analysis of curing reaction was measured by differential scanning calorimetry. The Fourier Transform Infrared (FTIR) used to analyze the X-ray Photoelectron Spectra (XPS). It was reported by adding GOs to TGDDM/DDS, nanocomposite curing process accelerated because of increases in the enthalpy of resin cure reaction. Results showed the thermal stability of resin decreases by addition of GOs. The SEM images of the samples have shown uniform dispersion of GOs in epoxy because of present epoxide groups on the surface of GOs.

2.1.5 Metallics Nanocomposites

Rosso et al. [24] have conducted a study on the effects of nanoparticles on cure kinetics of diglycidyl ether bisphenol A, epoxy resin. Silica nanoparticles at different volume percentages have been added to the epoxy resin. After adding the hardener to the samples with different percentage of nanosilica, DSC analysis has been performed. Differential scanning calorimetry (DSC) is used to measure the curing kinetics and from there activation energy can be calculated. It was reported that by adding nanoparticles such as silica to the epoxy resin system, the time taken for curing increases when there is an increase in the nanoparticle volume percentage. This is the result of high cross linking of the resin and hardener system created by the presence of nanoparticles. The TEM images of the samples have shown uniform dispersion of nanosilica in the epoxy resin. The presence of a rubber-like shell on the outside of the nanoparticles was also caused due to the presence of excess hardener in this region.

Rong et al. [25] have conducted a study on the effects of silver nanoparticles dispersion method in epoxy resin, and how nanoparticles behave in the system. By using different dispersion matrices, self -organization behavior of silver nanoparticles with and without curing agent was studied. By using DSC, melting point of Ag nanoparticles versus Ag crystal were measured and results showed the melting point of Ag nanoparticles was lower than Ag crystal. Increase in temperature will decrease the viscosity of the epoxy resin and self-organization of nanoparticles is possible, and then conductive behavior appears. The DSC measurement shows the interaction between epoxy resin and silver particles helps the uniform primary curing. The curing kinetics depends on the curing system that was chosen. Curing reaction of the present epoxy resin will match the self-organization of particles. Curing kinetics analysis shows the interaction between nanoparticles and resin is very strong.

Sanctuary et al. [26] have conducted the study on effects of the AL2O3 nanoparticles on the curing kinetics of diglycidyl ether bisphenol A, epoxy resin and by adding Dithylene trimine (DETA) hardener. Temperature – Modulated Differential Scanning Calorimetry (TMDSC) was used to study curing kinetics, and at the same time measure the specific heat capacities of the thermosets. Using Rheologic, measurement shows during the isothermal curing, that Al2O3 accelerates the growth of macromolecules. Increase of Al2O3 concentration decreases the specific reaction, and this is because of the transition to a glassy state from rubbery state. Measurements of the zero-shear viscosity from Rheologic show the acceleration of growth of the network by having nanoparticles and gelation.

Zhou et al. [27] have conducted a study effects of two different curing kinetics methods on curing kinetics of Bisphenol- A glycidol ether epoxy resin (DGEBA), 2-ethyl -4-methylimidazole (EMI-2,4) as curing agent, and nano-sized SiC (nano-SiC) as nanoparticle. The epoxy resin EPON828, showed comparing method I versus method II. Reaction mechanism wasn't changed by additional nano-SiC, however activation energy E calculated by method II was decreased initially, and then later cure reaction increased. As a result, method II had a complex calculation process but can be used to study in depth cure reaction mechanism. Method II is also confirmed and agrees with experimental data. However, both methods used in a suitable feature are both effective.

Baller et al. [28] has conducted study on the effects of silica nanoparticles (nanopox A410) on curing behavior of diglycidyl ether of bisphenol-A (DEGEBA) by using diethylene triamine (DETA) as a curing agent. Silica nanoparticles, which already have a silane layer, were homogeneously dispersed in DEGEBA, then curing agent (DETA) was added after stirring mixture was isothermally cured in DSC and Rheometer. DSC was used to measure the Tg. The result showed a very weak interface between the nanoparticles and DGEBA by measuring the specific heat capacity before curing. Tg filler content did not play any role during the isothermal cure. Results of this study contrasted with some other related research results.

2.2 Functionalized Nanoparticle Nanocomposite

In this section are studies using nanoparticles with different methods of functionalizations (modifications) to prepare nanocomposites. Nanoparticles such as were used: Carbon Nanotubes (CNTs), Single Wall Nanotubes (SWNTs), Multi-Wall Nanotubes (MWNTs), Graphene, and Polyhedral Oligomeric Silsesquioxane (POSS). Matrix system epoxy resins such as diglycidyl ether of bisphenol A (EPON 828), crystalline 4,4-dihydroxy-x-methyl-stilbene(DGE-DHAMS), and EPIKOTE resin 862 were used by addition of curing agents to study the effects of functionalized nanoparticles on curing kinetics of nanocomposites.

2.2.1 Carbon Nanotubes

Ma et al. [29] have conducted a study on the effects of functionalization, well dispersion of CNTs on mechanical properties, and curing of diglycidyl ether of bisphenol A(EPON 828) epoxy resin and m-phenylenediamine(mPDA) curing agent. CNT was functionalized via chemical vapor deposition method and has a well dispersion by using an ultra sonicator. Nanocomposite was prepared using different wt% on amino-functionalized CNT. FTIR was confirmed in the functionalization process. The results showed that an increase in amino-functionalized CNT increases the surface energy as an effect of interfacial energy between CNT and epoxy resin. Agglomerate was also increased during curing of resin which showed higher temperature required for curing process of nanocomposite.

Sui et al. [30] conducted a study of the effects of curing kinetics of pretreated carbon nanotubes (CNTs) and epoxy resin. For treatment process, hydrofluoric acid, hydrated silica, resorcinol, and hexamethylene were used in different weight ratios. To prepare the nanocomposite, treated CNTs were mixed with toluene then the mixture was added to resin and dispersed by a sonicator. Later the mixture was placed in a vacuum at 80 deg to remove the solvent. Nanocomposite was prepared by using a Two–Roll Mill at room temperature. The result showed that the curing rate was decreased and thermal stability was improved with the addition of treated CNTs to epoxy resin. The mechanical properties of nanocomposite increased with the addition of treated CNTs into resin.

2.2.2 Single -Walled Nanotubes

Dominguez et al. [31] conducted a study on the effects of functionalization of Single-Walled Carbon Nanotubes (SWNTs) on curing kinetics of epoxy resin. Chemical funtionanlization of SWNTs by amination of nanocarbons was performed. In this study, non isothermal DSC and iso-conversional kinetics was used to measure the curing reaction. The results showed functionalized SWNTs decreased in enthalpy and significantly increased in Tg and decreased in AE during the beginning of curing stage.

Bae et al. [32] conducted a study of effects of surface treatment of single-walled nanotubes on curing kinetics of crystalline 4,4-dihydroxy-x-methyl-stilbene (DGE-DHAMS) epoxy resin; sulfanilamide was the curing agent. In this study, two types of nanotubes and two types of carbon blacks were used. To surface treat carbon black and nanotubes, they were first oxidized with a preheated HNO3, then washed with distilled water, and finally dried in a vacuum oven. Carbon fillers were separately mixed with resin. DSC was used to measure the cure reaction, and the result showed the curing heat of composite with carbon nanotubes was higher than one with carbon black. Functionalization of both nanotubes and carbon black decreased the activation energy and cure reaction. Homogeneous dispersion of particles improved as a result of functionalization. Also, cure rate of carbon fillers was increased by oxidation.

2.2.3 Multi- Walled Nanotubes

Zhou et al. [33] conducted the study of effect silanization of carbon nanotubes (COO H_MWCNTs) on curing kinetics of epoxy resin (Epon 828) using EMI-24 as hardener. Silanization is a process to improve dispersion of nanoparticles in a matrix system of nanocomposite. Functionalization of CNTs increases functional groups which have a covalent bonding with epoxy resin. Fourier Transform Infrared (FTIR) shows the existance of silane as a coupling agent which creates a covalent bond to COOH-MWCNTs. Differential scanning calorimetry (DSC) was used to measure the activation energy by using Friedman kinetics, and the result showed the catalytic effect of functionalized COOH-MWCNTs acted as a hardener and accelerated the cure reaction. Acceleration in curing kinetics does have a positive effect on processing nanocomposites by decreasing curing time and lowering the temperature.

Jahan et al. [34] conducted a study of the effects of Carboxyl (MWCNT's) functionalized curing kinetics of epoxy resin (EPIKOTE resin 862) and curing agent (EPICURE). Samples were prepared by mixing pre-calculated amount of Carboxyl with acetone in a sonicator. The mix and curing agent were then added to the epoxy resin and mixed using a magnetic mixer. Using differential scanning calorimetry (DSC), the effect of different percentage of MWCNT's on curing kinetics, heat of reaction, peak temperature and activation energy was observed. Heat reaction decreased by adding up to 2% of CNT to polymer but further addition of CNT increased the heat reaction. Increase in heat rate increased the peak temperature. Also, the onset temperature (Ti) increased with increase in CNT. Curing behavior in four different temperatures using DSC was found to lower curing reaction temperature with addition of CNTs; but in epoxy systems, the autocatalytic cure reaction did not change possibly because of the higher surface area. During fabrication of composite, higher surface area eventually requires a higher post curing temperature.

Shen et al. [35] conducted a study on the effects of amino functionalized MWNTs on curing of E51 epoxy resin matrix and JX-011 as a curing agent. MWNTs functionalization was performed by the chemical vapor (CVD) process and oxidization using H2SO4 and HNO3. To confirm the success of functionalization, FTIR was used to record the spectra on the NEXUS670 spectrometer. Functionalized MWNTs was added to resin with curing agent and mixed; then the mixture was placed in a sonicator. DSC was used to measure the thermal properties. Result showed that strong covalent bonds and well dispersed nanotubes cause a stronger interaction between CNTs and epoxy resin; amino-functionalized MWNTs have a higher thermal stability.

Kathi et al. [36] conducted a study on the effects of functionalization of MWNTs on thermal and mechanical properties of diglycidyl ether of bisphenol (DEG-BA) epoxy resin. MWNTs were functionalized using silanization and oxidation process. 3-aminopropyltruethoxusilane was used for silanization process and sulfuric acid was used for oxidation process. FTIR, SEM and TEM were used to confirm the silanization and oxidation process. After fabricating the nanocomposite by adding different wt% of MWNTs to resin and mix, they were mixed with a stirrer and then with a sonicator. The mix was poured into a Teflon mold which was later machined for thermal and mechanical testing. Three point bending was used to measure the flexural strength of samples. Rheometric was used to measure the energy dispersion of samples. This study showed that up to 0.2wt% MWNT improved the mechanical and thermal properties of nanocomposite. Both silanization and oxidation of MWNT increased glass transition temperature (Tg) but adding more than 0.2wt% MWNT caused a decrease of Tg.

Abdalla et al. [37] conducted a study on the effects of modified surface of MWNT by adding carboxyl and fluorine to diglycidyl ether of bisphenol A (DGEBA) and curing agent diethyltolluenediamine (DETA). Fluorination process of MWNT was done using 2-methocyethel ether and 4-fluoroaniline by mixing them with a stirrer, filtering it, and washing it. Carboxylation process was done using sulfuric acid, mixing it with a sonicator, and drying it in the oven with end result of COOH-MWNT. Next step was mixing the treated MWNT and epoxy resin with DETA. DSC was used to measure the curing process of prepared nanocomposite. After collecting data and using some related curing kinetics, formula degree of curing and activation energy was calculated. Results were shown during curing of three samples of neat resin, carboxyl-modified sample, and fluorinated sample; neat resin began to cure first but later the modified samples cured faster.

Gojny et al. [38] conducted a study on the effects of functionalization of MWNT on curing kinetics of DEGBA epoxy resin. Different wt% of MWNT both functionalized and non-functionalized were used to mix with epoxy resin and dispersed with sonicator. Polyetheramine was used as a curing agent. Dynamic-mechanic thermal analysis (DMTA) was used to determine the Tg, and DSC was used to measure the curing kinetics of nanocomposite. The results showed strong interaction between hardener and functionalized MWNT and an increase in thermal stability and Tg with addition of nanotubes. The chemical functionalization of nanotubes increased the surface interfacial between nanotubes and epoxy resin.

Kim et al. [39] conducted a study of the effects of silanized MWNTs on thermal and mechanical properties of DGEBA epoxy resin using polyamidoamine (PAA) curing agent. Silanization is a preferred method where trisilanol which is formed from hydrolysis of silane coupling reacts with hydroxyl on the surface of nanotubes. 3-glycidyloxypropylrimethoxysilane was used for silanization process in this study. Two samples of nanocomposite were prepared; one used unmodified MWCNT and the other used modified MWCNT. An ultrasonicator bath was used to disperse MWCNTs in epoxy resin. After samples cured, they were machined for thermal and mechanical testing. Dynamic mechanical analyzer (DMTA) was used to measure the energy dispersion as a function of temperature. The result showed decomposition temperature and thermal stability were improved by silanization of MWCNTs. Also, because of diffusion of molecules from matrix at high temperature, thermal stability was improved. Higher Tg was as a result of cross linking reaction and covalent bonding between nanotubes and epoxy.

Ma et al. [40] conducted a study of the effects of silanization on the surface of multi wall carbon nanotubes (MWCNT). 3-glycidoxypropyltrimethoxy silane was use for silanization process. Pretreatment of MWCNT was established by ball milling and oxidation which created active elements on the surface of MWCNT. After oxidization, UV light used to reduce lithium aluminum hydride. To silanize, toluene was added to the reduced MWCNTs, and they were dispersed in ultrasonicator bath. GPTMS were added to the mix and stirred. After reaction and dilution, filtrated MWCNTs were dried in a vacuum oven. FTIR was used to confirm the silanization process and to show the difference in surface morphology of the nanotubes. Suspension stability testing was used to compare the different processing by reducing the agglomerates and improving the dispersion.

Santos et.al (2002) [41] conducted a study on the effects of oxidation and silanization of MWNTs. The treatment surface of nanotubes by oxidation and silanization were bonded to the nanotubes and propylthiol chain by silane. After oxidation process and functionalization of MWNTs 3- mercaptopropyl trimethoxysilane9 (3-MPT) was used to silanize the nanotubes. The silanized MWNTs were the end result of processing. FTIR was used to compare the non-functionalized MWNTs and functionalized MWNTs which confirmed the silanization process and presence of silicon the surface of nanotubes. The result was improvements in the surface and chemical affinity for making new MWNTs based composite.

Visco et al. [42] have conducted a study of the effects of multi walled nanocomposite (CNTs) on curing kinetics and mechanical properties of polymeric resin diglycil ether of bisphenol F (DGEBF). Curing agent for this study was diethyl toluene diamine(DETDA). Different weight percentages of CNT were added to acetone and each of the percentages were added to DGEBF and sonicated for dispersion. Later, the sample was mixed with a magnetic stirrer to reduce gas bubbles. DSC was used to measure the cure kinetics of nanocomposite. Rheometer SR5 was used to measure the activation energy. The results showed 0.5wt% CNT increased the cure reaction, however increased the CNT to 1.0 and 1.5wt% reduced the cure reaction. Also having more wt% of CNT increased the stiffness and strength on nanocomposite but highly reduced its deformability. The result showed functionalization of CNT is necessary to increase the interaction between resin and CNTs. Accordingly, the best weight percentage of CNT is 1.0 or 1.5%.

Chen et al. [43] have conducted a study effect of functionalized multi walled carbon nanotubes on curing kinetics of 4, 4-bis (2,3 epoxypropoxy)biphenyl. H2SO4 and HNO3 used for functionalization of MWNTs. After a series of mixing and filtering, the final result was a black powder. FTIR was used to confirm the surface modification of ef-CNTs. Functionalized CNTs were dispersed in a sonicator with resin. The mixture was ball milled for homogenous mixing and solvent was removed using an evaporator. DSC was used to measure the curing reaction and heat rate. An increase of functionalized CNTs concentration in nanocomposite resulted in an activation energy decrease, and an increase in reaction rate. However, the curing degree decreased.

Prolongo et al. [44] conducted a study effect of functionalized MWCNTs on curing kinetics and electron microscopy of diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The hardener was 4, 4– methylenedianiline (DDM). Nanocomposite was prepared by dispersing MWCNTs in chloroform, and then DGEBA was added to the solution and dispersed in sonicator. Later solvent was evaporated by stirring in vacuum, and finally curing agent was added into mixture. SEM was used to show the cross linking between carbon nanotubes and epoxy resin, and DSC was used to measure the heat reaction and curing rate. The result showed addition of CNTs slowed the curing reaction of nanocomposite. Also, adding hardener affects molecules inside of MWCNTs that cause the decrease in heat reaction. Because of restriction mobility of MWCNTs, glass transition temperature (Tg) was increased in epoxy resin. Due to the covalent bond formation between epoxy and MWCNTs, a strong interface was created.

Choi et al. [45] has conducted study effects of functionalized multi walled nanotubes (FMWNT) on curing kinetics of diglycidyl ether of bisphenol-A type epoxy resin and 4, 40-methylene dianiline as a curing agent. For functionalization both polyphosphoric acid and aminobenzoic acid were used. After some mixing, FMWNTs were washed with acetone and DI water, and then sample was placed in an oven for a day to dry. FMWNTs were mixed with epoxy and then hardener was added to the mixture, which later was molded into silicon rubber. FTIR was used to confirm the functionalization process of the MWNTs. DSC was used to measure the curing kinetics of nanocomposite. Results showed FMWNT increased the curing rate of the nanocomposite because of the cross link bonding between the MWNT and resin. The SEM imaging confirmed the cross link bonding and improvement as a result of functionalization.

Yang et al. [46] has conducted study effects of functionalized multi walled nanotubes (FMWNT) on curing kinetics of EPON828 epoxy resin (DGEBA) using curing agent of EMI-2,4.

To Functionalize the MWNTs, sulfuric acid (H2SO4) and Nitric acid (HNO3) were used. After that, ethylyediamine (EDA), tetrahydrofuran (THF), and sicyclohexylxcarbodiimide (DCC) were used to continue the functionalization process. FMWNT was mixed with DGEBA and curing agent was added to the mixture. Then steel mold was used to make the nanocomposite. FESEM was used and confirmed the uniform dispersion of MWNT in the epoxy resin. DSC was used to measure the activation energy and cure reaction by using Flynn-Wall-Ozawa method. The result was functionalized multi-walled nanotubes increased speed of the cure reactions. FMWNT decreased the activation energy and improved the thermal stability in nanocomposite.

2.2.4 Graphene

Fang et al. [47] have conducted the study of searching for new light weight material that also has high performance structure and is a motivation to research about polymer nanocomposite. To make the nanocomposite, graphite powder was mixed with EPON 828 as a resin system. In this experiment, to have a homogeneous dispersion of graphene was functionalized by Hummers and Offeman method. Having a molecular dispersion of functionalized graphene in matrix system creates a cross linking bonding. As a result of bonding, which creates more energy dissipation, composite can have more strength. The differential scanning calorimetry (DSC) used to measure the activation energy and calculate the enthalpy. Covalent bonding was observed by Raman spectra. Based on the data measured from thermal and mechanical properties of nanocomposite, increase in weight percentage of graphene increases Young modulus, strength, and fracture toughness of nanocomposite. The hierarchical structure during process of curing nanocomposite happens spontaneously. This structure improves bonding between graphene and resin, and increases the fracture mechanics by 93.8%, 91.5% in toughness, and improves the flexural strength by adding only 0.6 wt% graphene.

2.2.5 Polyhedral Oligomeric Silsesquioxane (POSS)

Villanueva et al. [48] have conducted a study effect of modified POSS and using different weight percentages on curing cycle of diglycidyl ether of bisphenol (DGEBA) epoxy resin. Meta-xylylenedialmine, MXDA was used as a curing agent. The results showed no improvement in thermal stability and thermo- degradation by addition of POSS. Increase in POSS content also increased the activation energy. DSC was used to measure the glass transition which showed the increase in POSS was raising the Tg.

CHAPTER 3

EXPERIMENTAL

3.1 Carbon Black

Carbon black ELFTEX 8 manufactured by Cabot was used as nanoparticles for this experiment. This carbon black was used to have silanization process on it and later was used for preparing functionalized carbon black nanocomposite. Also carbon black was used to prepare carbon black as received nanocomposite. Figure 3.1 shows the carbon black used as nanoparticles. To measure the carbon black and epoxy resin, high accuracy weighiting scale of 1/1000th of grams was used for this research. Weighing paper was used to place the carbon back on duing measument. A lab spatula was used to take the carbon black for mearment. Figure 3.2 shows all of the lab eqiupment.

Figure 3.1 : Carbon Black ELFTEX 8

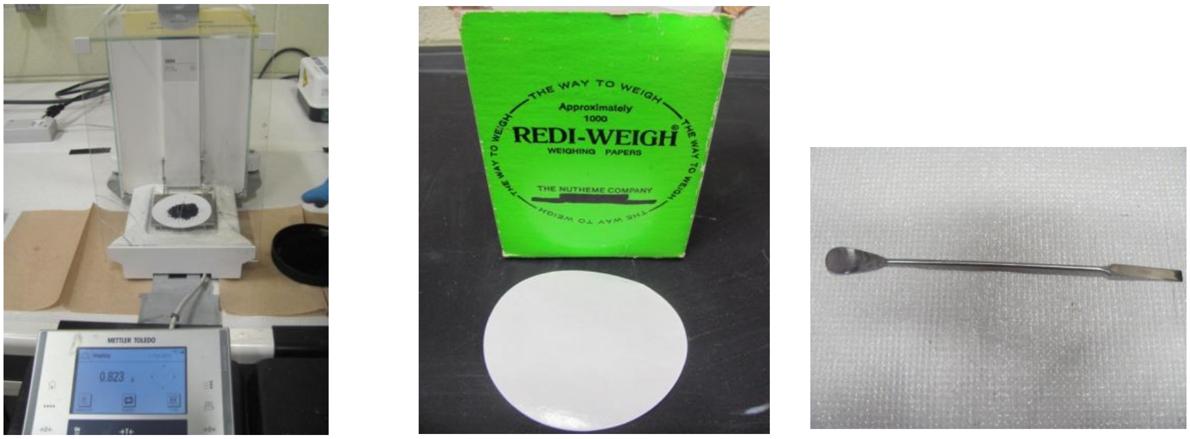


Figure 3.2: Weighing Scale (left), Weighing Paper (middle), Spatula (right)

3.2 Ethyl Alcohol, Beaker and Parafilm

Carbon black and ethyl alcohol was mixed in a 250 ml beaker and then the beaker was placed in an ultrasonicator. Ethyl alcohol was used to disperse the carbon black. Figure 3.3 shows the ethyl alcohol, beaker and parafilm used for dispersion. Parafilm which is a laboratory film for sealing was used to protect the mixture and to waterproof the beaker during the ultrasonicator bath.

Figure 3.3: Ethyl Alcohol (right) and 250 ml Beaker (left)

Figure 3.4: Parafilm was used to seal and waterproof the beaker

3.3 Sonicator

Fisher Scientific ultrasonicator bath model FS60D was used to disperse the carbon black in ethyl alcohol. Sonication is the dispersion of particles in a liquid by applying sound energy. In this research, the sonicator was used once for pre-mixing process. In preparation process (mixing) of nanocomposite, the sonicator was used to homogeneously disperse the nanocomposite after it was mixed by a mechanical mixer. Figure 3.5 shows the ultrasonicator bath.

Figure 3.5: Ultrasonicator bath was used for even dispersion of carbon black in ethyl alcohol

3.4 Erlenmeyer Flask, Magnetic Stirrer and Hot Plate

A sealed flask (Erlenmeyer flask) connected to another sealed flask (Erlenmeyer flask) with a tube was used. (Substitution equipment used for three neck flask with water condenser). A magnetic stirrer for mixing the solution and a water evaporation tube connected to the other flask were used for the mixture of ethyl alcohol and carbon black which were placed on a hot plate to boil. Also, on top of the rubber lid was a hole to allow the injection of silane and then sealed with double tape sealer. Figure 3.6 shows the equipment and magnetic bar used for silanization mixing process. A hot plate manufactured by Fisher Scientific Company was used for mixing and heating process. The hot plate has two displays, one for heat (ºC) and one for stirring (rpm) which were controlled with a knob. Figure 3.7 shows the hot plate.

Figure 3.6: Flask Connection (left) and Magnetic Stirrer (right)

Figure 3.7: Hot plate used for heating and stirring the solution

3.5 [3- (2-Aminoethylamino) propy]trimethoxysilane, Double Sided Tape and Syringe

[3- (2-Aminoethylamino) propy]trimethoxysilane purchased from Sigma Aldrich, Inc. was used for the silanization process of carbon black. This chemical, called silane, is an organosilane which chemically surface treats carbon black. Chemistry of silanization was discussed in detail on section 1.4. Figure 3.8 shows the silane used in this research. Double sided sealing tape was used to seal the cap of the flask. This tape is sticky on both sides and it is perfect for use as a gasket to prevent any leaks. It can be rolled or fold to use in any kind of geometry. A 10 ml syringe was used to inject the silane into the flask and also was used to insert the curing agent to nanocomposite mixture for curing.

Figure 3.8: [3- (2-Aminoethylamino) propy]trimethoxysilane was used for silanization of carbon black

Figure 3.9: Double Sided Tape (left) and 10 ml Syringe (right)

3.6 Buchner Funnel and Filter Paper

A ceramic Buchner funnel was used for filtering the solution. Filter paper was placed in Buchner funnel to separate the silanized carbon black from solution. Filter paper has some important parameters such as: wet strength, flow rate and capability. For this research because of scale size of carbon black, circles of 4.25cm Fisher brand qualitive grade 5 filter paper, which is a cellulose fiber and has particle retention of 5-1-um, were used. Figure 3.10 shows the Buchner funnel and filter paper used to separate the silanized carbon black from solution.

Figure 3.10: Buchner Funnel (left and middle) and Filter Paper (right) used for Filteration

3.7 Buchner Flask and Simplicity Ultrapure Water System

A Buchner flask, vacuum flask, has a short glass tube about one inch from neck of flask which can be connecte to a vacuum via vacuum hose as shown in Figure 3.11; this vacuum was used for filteration process. Simplicity ultrapure water system was used to purify water; this water was used for rinsing the solids left on the Buchner funnel filter paper. Figuer 3.12 shows the simplicity water system used to get the purified water needed to rinse the solids left in filter paper.

Figure 3.11: Buchner Flask to Filter the Solution

Figure 3.12: Simplicity Ultrapure Water System

3.8 Laboratory Oven

Laboratory oven provides uniform temperature by using themal convection. It was used to dry out the washed carbon black. The washed solution was placed in a tempered glass container which was then placed in an oven. Oven has a knob to set the desired temperature.

The oven can supply a heat temperature up to 220ºC. Figure 3.13 shows the glass container and oven used for this research.

Figure 3.13: Laboratory Oven (left and middle) and Glass Container (right)

3.9 EPON Resin 828 and Mechanical Stirrer

EPON resin 828, epoxy resin, was used to make the nanocomposite. EPON resin 828 is a neat clear dis-functional bisphenol A/epichorohedrin liquid epoxy resin. EPON 828 has very good mechanical, dielecric and chemical resistance properties after using a curing agent. EPON resin 828 has a density of 1.16 g/ml, viscosity of 110-150 P, and specific heat of 0.5 BTU/lb/ºF. Laboratory petite digital stirrer was purchased from Caframo and has a range of 50-2500 rpm; it was used for mixing epoxy resin with carbon black. Some other features of stirrer are: 50-2500 rpm at 10 Ncm 1/100 hp, using 7 watts AC 100-240 volts. This stirrer is good for water viscosity, chemical resistance and high impact nylon. Stirrer has a digital LED display button and on/off botton also buttons to increase/decrease rpm. Stirrer assembly was very simple.

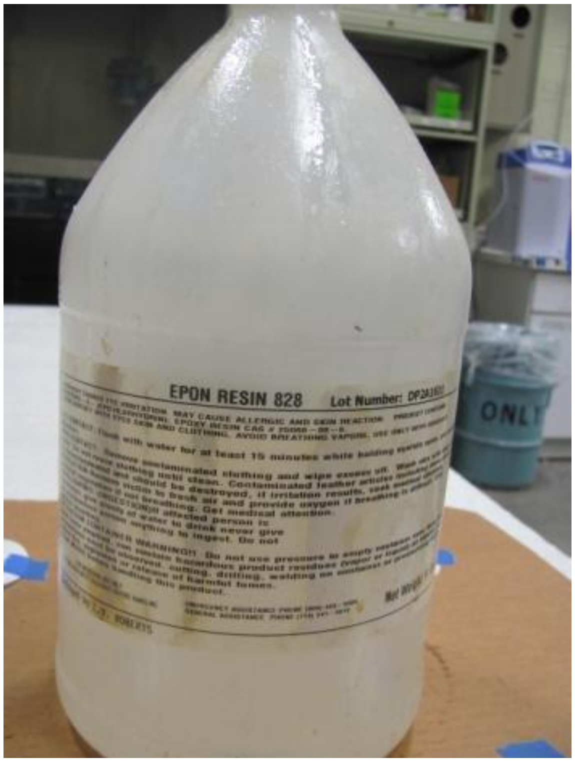


Figure 3.14: EPON resin 828 was used as a epoxy resin to prepare nanocomposite

Figure 3.15: Laboratory Mechanical Stirrer

3.10 Diethylenetriamine,98+% (DETA), Tzero Pan and Tzero Hermetic Lid

Diethylenetriamine,98+% (DETA) which is an organic curing agent and maufactured by ACROS was used to cure the silanized carbon black nanocomposite. DETA has a density of 0.953g/ml,viscosity of 7.16cp at 20ºC and amine value of 1626 mg KOH/g. DETA is clear with an ammonia like odor and it is a single component product. Figure 3.16 shows the DETA used as a cuting agent on nanocomposite. The sample of nanocomposite was placed in the Tzero pan and Tzero Hermetic lid manfactured by TA company. Pans and lids came in a separate boxes and each box contained 100 pans or lids. After placing a sample in a pan and placing the lid on it, the pan was placed in differetial scanning calorimetry to collect the desired data from sample.

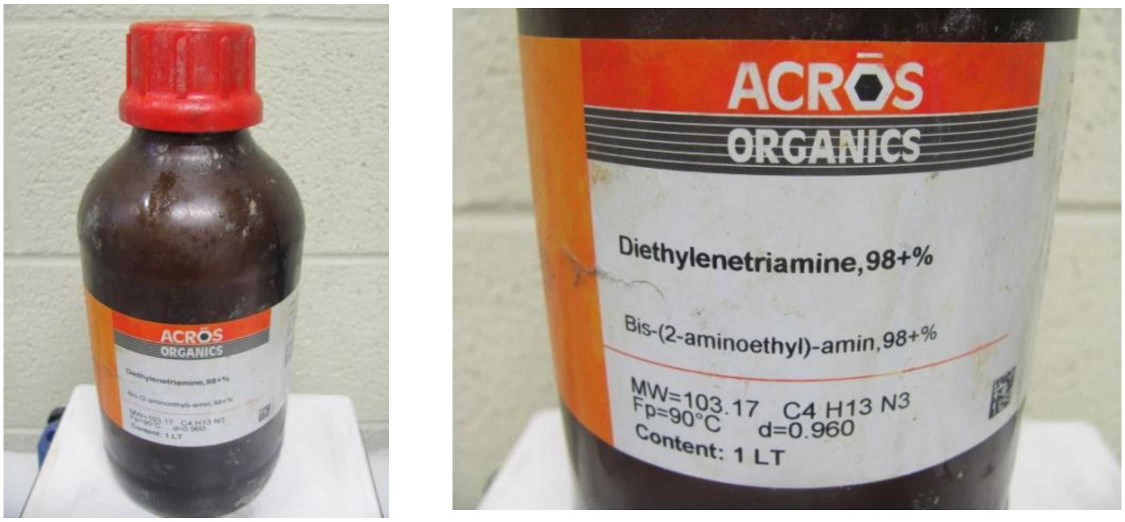


Figure 3.16: Diethylenetriamine (DETA) Curing Agent

Figure 3.17: Tzero Pan (left side of each picture) and Tzero Hermetic Lid (right side of each picture)

3.11 High Accuracy Weight Scale, Dental Probe Tool and Labratory Tweezer

Weight scale Mettler Toledo with 1/10000th accuracy was used to measure the nanocomposite. Becaues of very small amount of sample needed to place in pan using a high accuracy scale is essential. Also because of small amount nanocomposite needed for this testing a dental probe tool was used to place the nanocomposite in the pan. The sharp point of dental probe allowed one to take a very small amount as a sample. Figure 3.18 shows scale and a dental prob. Laboratory tweezers were used to prevent movement on Tzero pan and Tzero hermetic lid since they are very small and sensitive.

Figure 3.18: High Accuracy Weight Scale (left) Dental Probe Tool (right and bottom) and Labratory Tweezer (right and top)

3.12 Encapsulation Press and DSC

Tzero DSC sample Encapsulation press was used to seal the lid onto the pan. Tzero press has a smooth operation mechanism which was used for hermetic sealing. The press has four die sets and are magnetically attached requiring no tools or adjustment. The press has an unparalleled sealing performace. Figure 3.19 shows Tzero DSC sample Encapsulation press used to seal the nanocomposite sample. Differential Scanning Calorimetry (DSC) Q2000 was used to find degree of curing (DOC) for nanocomposite samples. DSC is top of the line in industry for research and has an unmatched performance in base line flatness, precision, sensivity and resolution. DSC 50 autosampler makes the testing flexible and with the use of software permits auto schedueling. DSC has a temperature range of ambient to 725ºC with calorimetric precision of +/-0.05%. Figure 3.20 shows DSC Q2000 used in this research.

Figure 3.19: Tzero DSC Sample Encapsulation Press

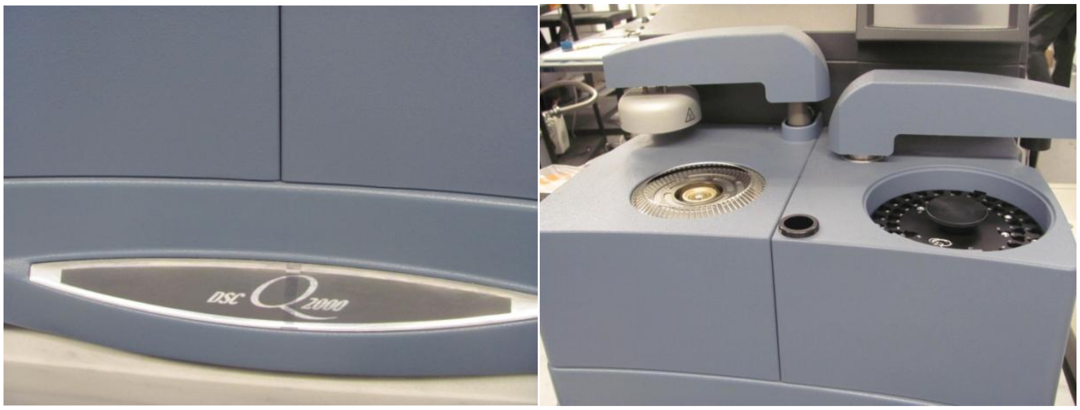


Figure 3.20: DSC Q2000 was used to measure the degree of cure (DOC)

3.13 AVATAR 360 FTIR

AVATAR 360 FTIR was used to measure the wavelength of samples. Energy of sample molecular vibrations corresponded to electromagnetic spectrum. The location of an absorption band in the spectrum is expressed in term of the reciprocal of the wavelength, cm^{-1}. The range of infrared spectrum is 4000 cm^{-1} (high frequency) to 625 cm^{-1} (low frequency). Nanocomposite samples were cured more than 7 days in room temperature and they were solid tested with FTIR. Figure 3.21 shows the AVATAR 360 FTIR used for this research.

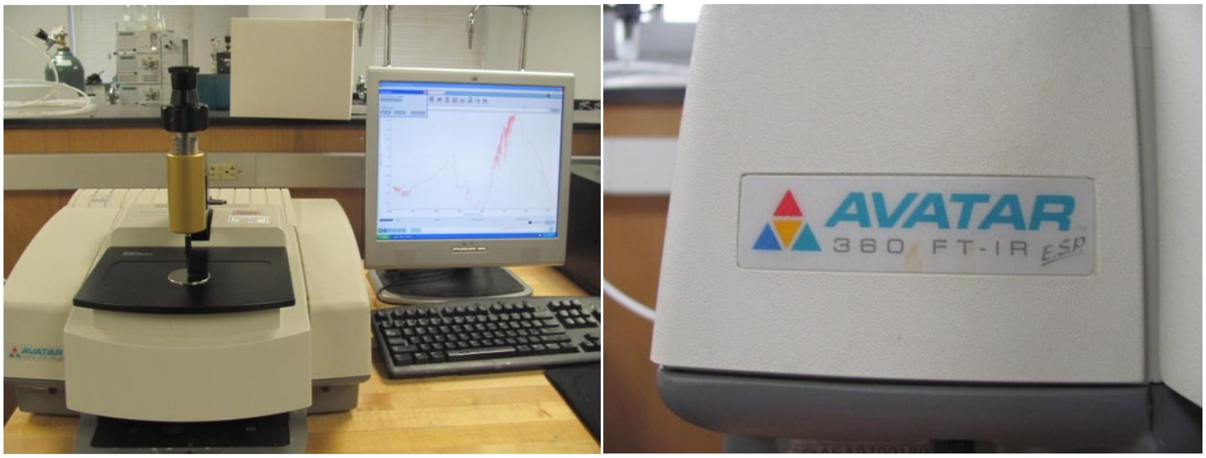


Figure 3.21: AVATAR 360 FTIR

3.14 ZEISS SEM and Specimen Mount

Specimen Mount, a 1/8” aluminum pin with a 1/2” slotted head, was manufactured by TED PELLA, INC; it was used to place sample of epoxy resin carbon black nanocomposite. After pouring the sample onto the specimen mount, it needed to cure seven days at room temperature. The specimen mount was used to hold the sample for the scanning electron microscope (SEM) so that microscopic image of the samples could be collected for comparison. Zeiss Scanning Electron Microscope (SEM) was used to get surface images of both modified and unmodified carbon black nanocomposite. Also same equipment was used for Energy Dispersive X-ray Spectroscopy (EDS); it was used for elemental analysis and chemical characterization of samples. SEM can provide image as small as 1.5 nm. Figure 3.23 shows the ZEISS SEM used to get images of specimen.

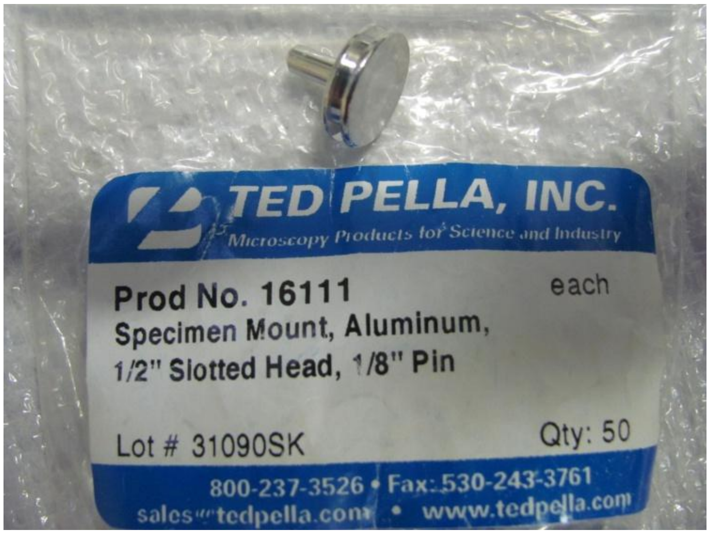


Figure 3.22: Specimen Mount, Aluminum, 1/2” Slotted Head, 1/8” pin

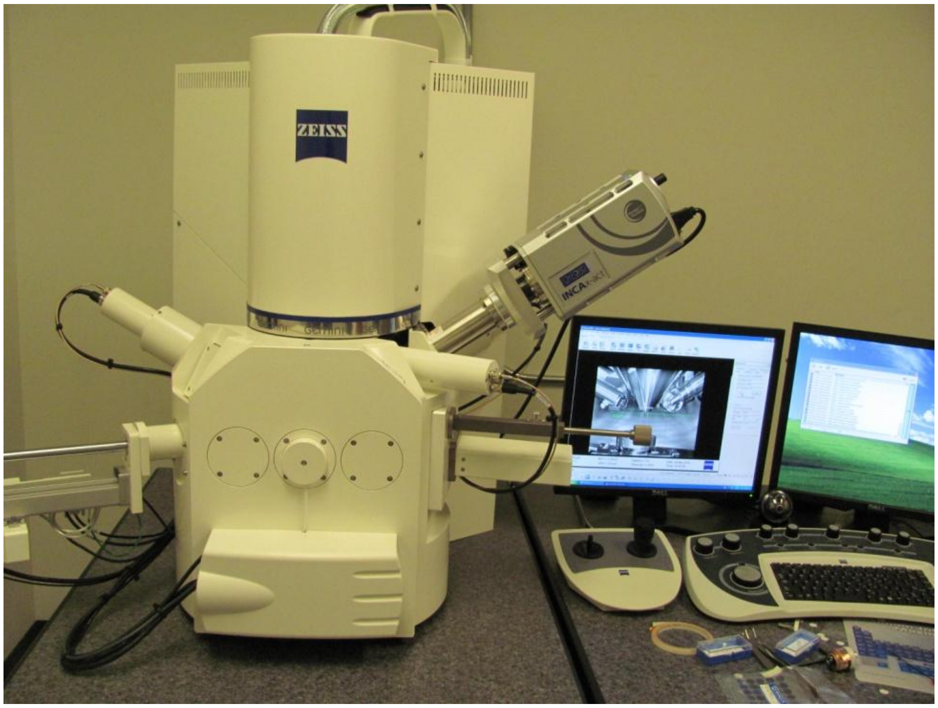


Figure 3.23: ZEISS SEM Equipment.

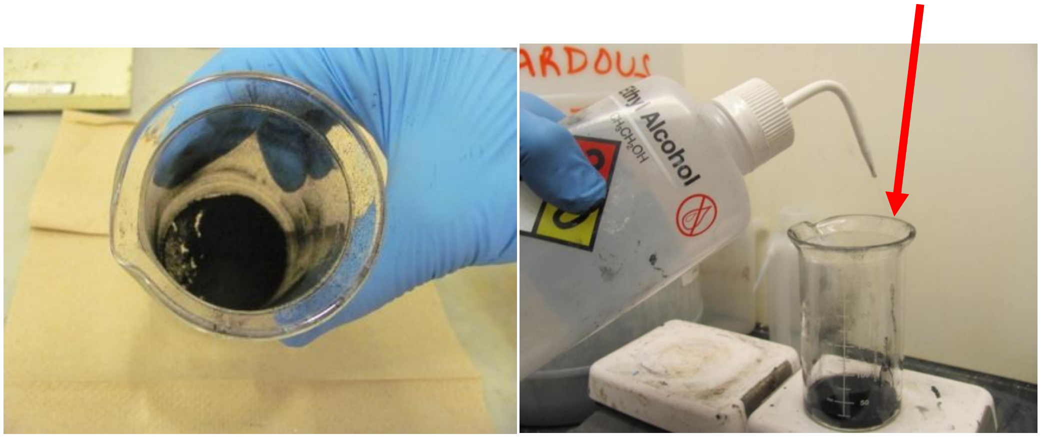
3.15 Silanization Process

In this study in order to silanize the carbon black, [3- (2-Aminoethylamino) propy]trimethoxysilane organosilane purchased from Sigma-Aldrich , Inc was used.

First, a weighing paper was weighed and then by using a spatula 2 grams of carbon black as shown in Figure 3.24(a) was measured. A 300ml beaker was taken and the measured carbon black was poured into the beaker. 200ml ethanol alcohol 95% was added to the beaker and the carbon black, Figure 3.24(b). The beaker was sealed by using parafilm, Figure 3.24(c). The beaker was placed in ultrasonicator bath for 1hr to disperse the carbon black into ethanol alcohol Figure 3.24(d).


Weighing Carbon Black

Figure 3.24 a: Weighing Carbon Black



Adding Ethanol Alcohol to Carbon Black

Figure 3.24 b: Adding Ethanol Alcohol

Covering the Beaker with Parafilm

Figure 3.24 c: Cover the Beaker with Parafilm

Placing the Beaker
in Sonicator

Figure 3.24 d: Placing the beaker in ulatrasonicator bath

After 1hr, the beaker was taken out of sonicator; and the solution of carbon black and ethanol were poured into the flask (Erlenmeyer flask). A magnetic stirrer was put into the flask and the cover was put back on the flask. By using the double sided tape around the lid of the flask, it was sealed and the flask was placed on a hot plate. Temperature was set to 120ºC and rpm was set to 800, Figure 3.25a. A 10ml syringe was taken and used to draw 12ml of silane from bottle. It was injected into the hole provided on the cap of the flask; the hole was covered with a piece of double sided tape, Figure 3.25b. Running time was set to 5 hr [48].


Insert a Magnetic Stirrer into the Flask

Figure 3.25 a: Pouring the mixture in to flask (left) and Inserting a magnetic stirrer into the flask (right)


Injecting Silane into the Flask

Figure 3.25 b: Drawing silane with a syringe (left) and injecting into the flask through a prepared hole on the cap (right)

After 5 hrs, the flask was taken off the hot plate and was cooled to room temperature. A Buchner funnel was put on a Buchner flask and a filter was placed inside the funnel, and vacuum hose was connected to the flask. Solution was poured into the Buchner funnel and vacuum was turned on, Figure 3.26a. Solution went through the filter and silanized carbon black was left on the filter, Figure 3.26b. After all the solution was poured into the funnel, silanized carbon black was rinsed several times with DI water to remove all chemicals such as ethanol and silane Figure 3.26c.

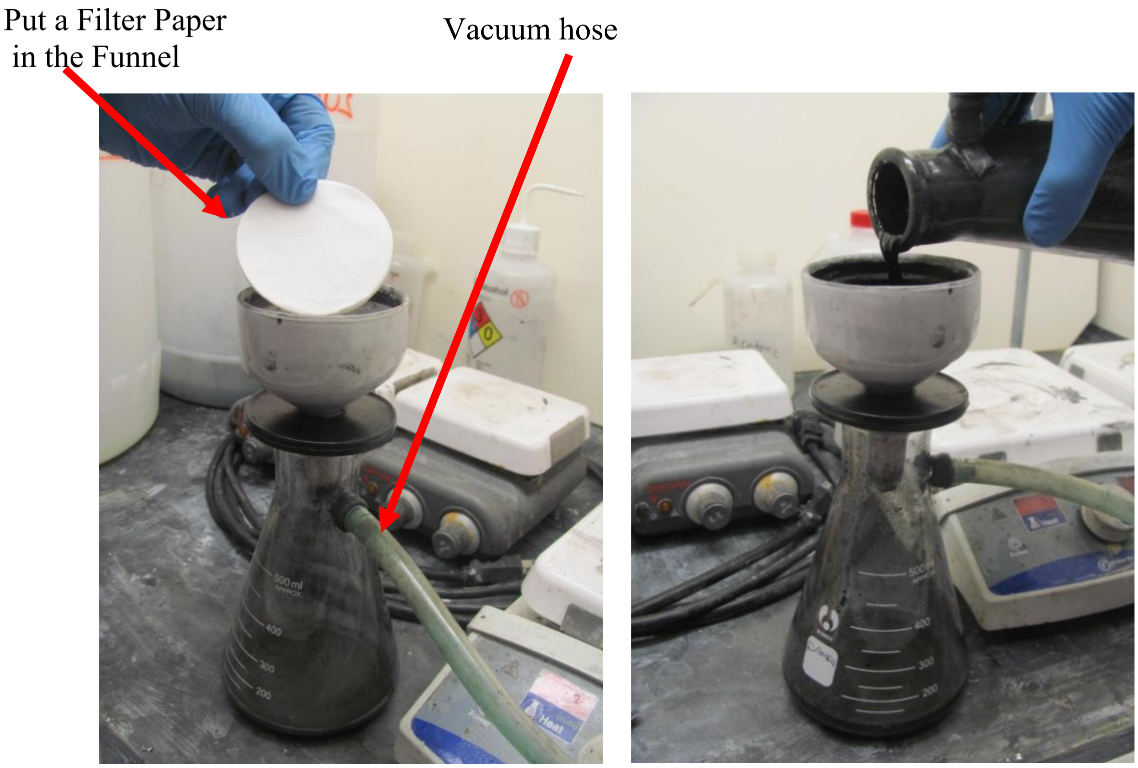


Figure 3.26 a: Placing the Buchner funnel on the Buchner flask and turning on the vacuum, placing a filter into the funnel and pouring the solution into the funnel

Silanized Carbon black on the filter

Figure 3.26 b: Filtering the Solution

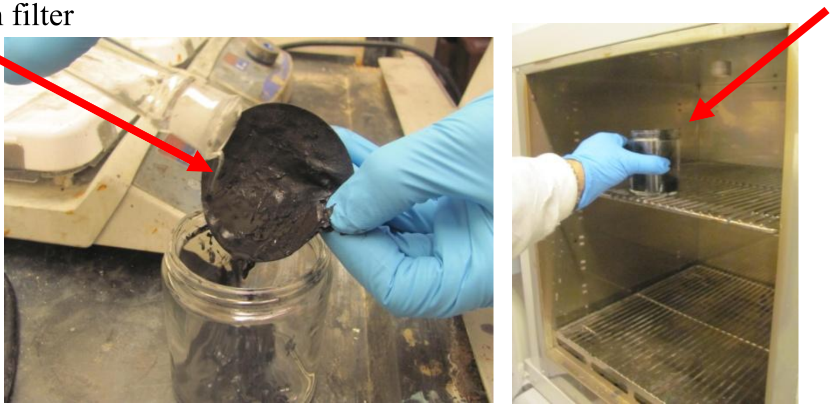
Rinsing the Silanized
Carbon black with DI water

Figure 3.26 c: Rinsing the remained silanized CB with DI water.

Next step of the process of silanization of carbon black was to use a spatula to remove the filter which has silanized carbon black on it. The filter was very gently scraped off with a spatula into a tempered glass container and then with DI water filter was rinsed to wash off the remainder of silanized carbon black, Figure 3.27a. The open lid container was placed in a laboratory oven and temperature was set on 50ºC for 12 hr to evaporate all the water and dry out the silanized carbon black, Figure 3.27b. The container was taken out to cool down to room temperature [48].

Scraping off Silanized
Carbon black from filter

Figure 3.27 a: Scraping off the silanized carbon black from filter



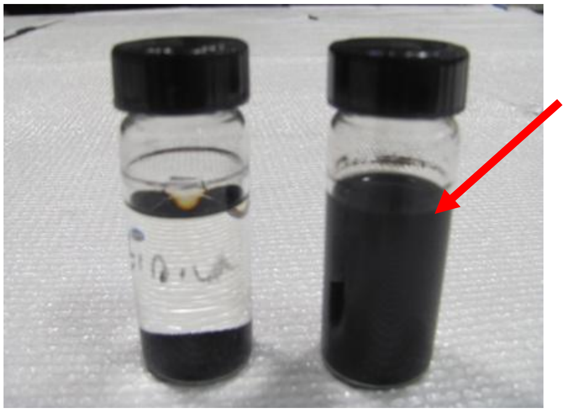
Washing off Silanized
carbon black from filter

Place the container in the lab oven

Figure 3.27 b: Wash off the remainder of silanized carbon black into the container and put the container in the laboratory oven

3.16 Stability Dispersion Test

To confirm the success of silanization process, 5 g of non-silanized carbon black and 5 g silanized carbon black was put into separate 20 ml tempered glass containers. 15 ml acetone was added to each container, and containers were capped. Both containers were placed in the ultrasonicator for 5 min and then were taken out and were set aside. After 3-5 days, observation showed that one of the containers was clear with solids settled, the solution of non-silanized carbon black; and the other container was homogenously dispersed, the silanized carbon black, Figure 3.28. By using this method, stability of both samples in acetone was tested and it confirmed the success of silanization process on carbon black.



Stability dispersion
of Silanized
Carbon black

Figure 3.28: Testing stability dispersion of carbon black (left) and silanized carbon black (right) in acetone

3.17 Nanocomposite Preparation

To prepare samples of nanocomposite, 2%wt, 4%wt and 8%wt of carbon black was added to epoxy resin; silanized carbon black, previously prepared, was also added to epoxy resin the same weight ratios. Method of mixing for both carbon black and silanized carbon black was the same. 5 g of EPON resin 828 was measured into a 30ml beaker and placed on a hot plate; a clamp held the beaker in its place. Temperature was set to 40ºC for 15 min to reduce the viscosity of the epoxy resin. A mechanical stirrer was set and adjusted to mix the resin in the beaker. Rpm was set to 50; and then the height of the mechanical stirrer as well as any other necessary movement was adjusted for a smooth and effective mixing, Figure 3.29(a). 2% carbon black was calculated, 5g x 2%= 0.1 g of carbon black; and by using scale, weighing paper and spatula, carbon black was measured. Rpm of stirrer was increased to 300 and carbon black slowly was added to the EPON resin 828 with the help of the spatula, Figure 3.29(b). After all of the carbon black was added to the resin, the speed of stirrer was increased to 1000 rpm and the hot plate was turned off, Figure 3.29(c). Mixer ran for 2 hr. Figure 3.29 shows the processing of mixing.

EPON resin 828

Place the EPON resin 828 on hot plate and setup the Mechanical Stirrer

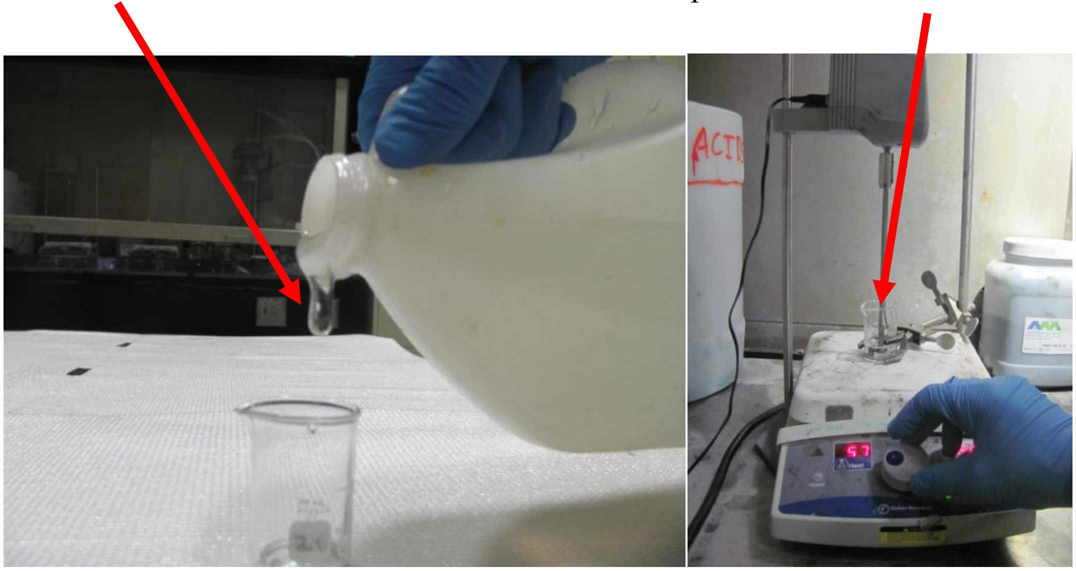


Figure 3.29 a: Measure 5g EPON828, placed on a hot plate and adjust temperature to 40ºC for 15min

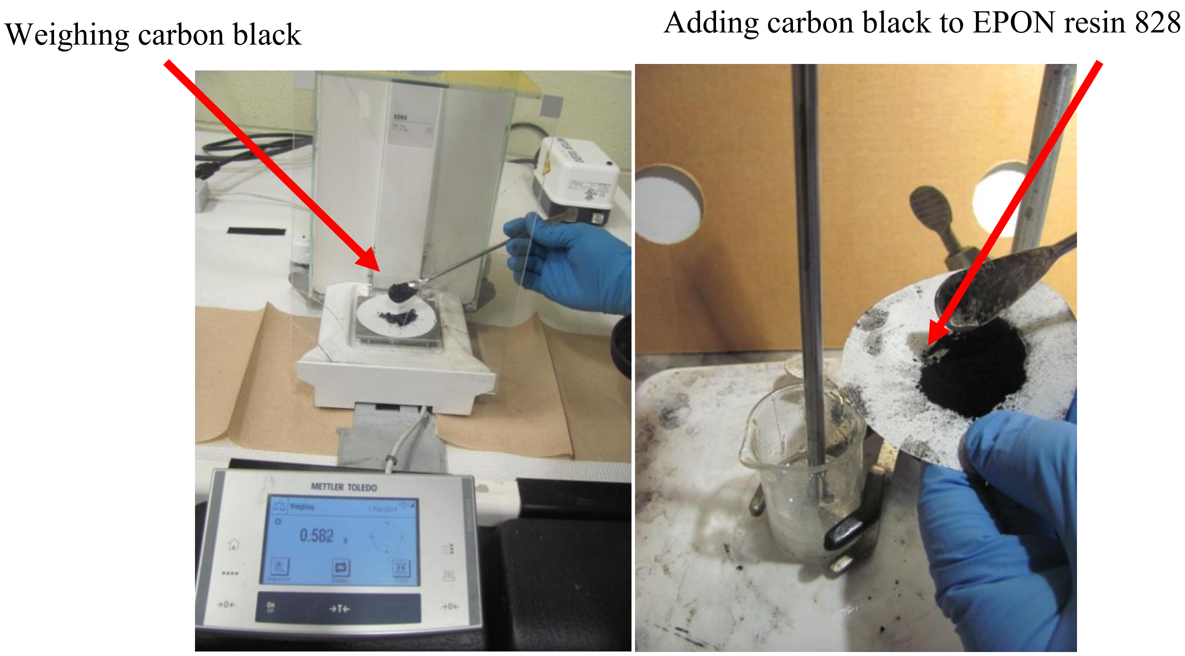


Figure 3.29 b: Measuring CB (left) and adding to the resin slowly and carefully (right)

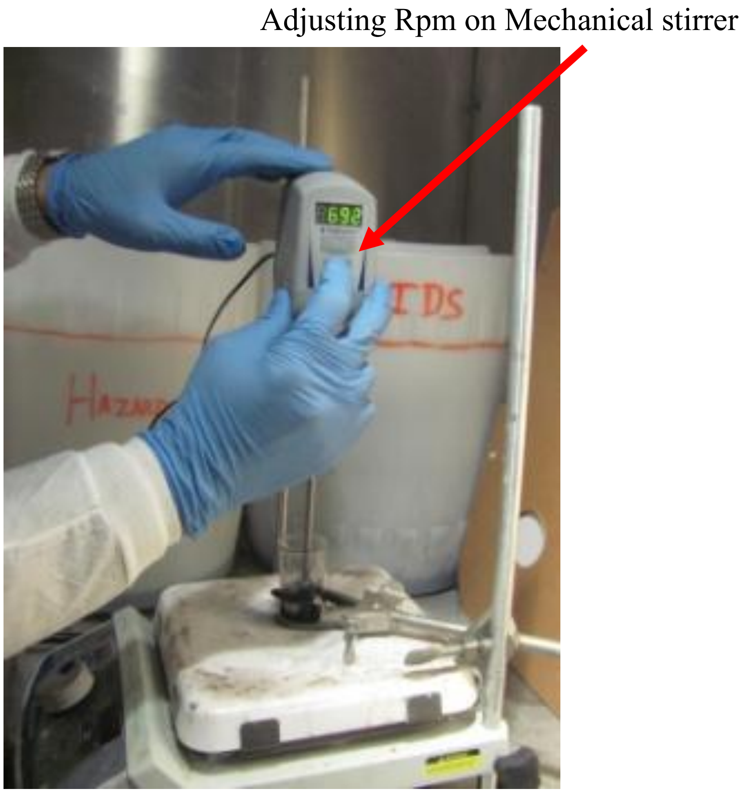


Figure 3.29 c: Hot plate was turned off and mechanical stirrer speed was set to 1000 rpm for 2 hr.

3.18 Adding Curing Agent to Nanocomposite

After 2hr, mechanical stirrer was stopped; and beaker was covered by parafilm. Beaker was placed in an ultrasonicator bath, and temperature was set to 40ºC for 30min to homogeneously disperse carbon black into EPON 828. After sonicator was finished, beaker was put back on the mechanical stirrer; and rpm was set to 300. 12% wt of 5.1 g mixture, 0.612g, was measured from Diethylenetriamine (DETA) curing agent by using a 10 ml syringe; while the stirrer was running, hardener was slowly added to the mixture. After 15 min, stirrer was stopped and carbon black nanocomposite was ready to test. Figure 3.30 shows the measuring and adding the curing agent to the mixture.

Injection of DETA curing agent to nanocomposite

Figure 3.30: Adding Diethylenetriamine,98+% (DETA) curing agent to the carbon black nanocomposite and making it ready for testing

3.19 Taking Samples for SEM, EDS and Testing

After nanocomposite was ready, samples were taken for different testing. Three tests were needed for this study. First test was Differential Scanning Calorimetry (DSC) to measure the curing kinetics of nanocomposite. Second test was Scanning Electron Microscope (SEM) to produce image of nanocomposite by scanning it with a focused beam of electrons. To make a specimen for both SEM and FTIR, seven days curing time was required, but the specimen for DSC was needed right after mixing was completed. To make a specimen for SEM, Specimen Mount 1/8” aluminum pin with a 1/2” slotted head was pushed down onto a cardboard box; and with a spatula, carbon nanocomposite was carefully put on the mount. The box was kept in a secure place far from any dust for seven days to cure at room temperature. Figure 3.31 shows the process of making specimen for SEM.


Putting Nanocomposite on Specimen Mount for SEM

Figure 3.31: Aluminum Specimen Mount ½” Slotted Head, 1/8” Pin (left)
Putting Nanocomposite on the Mount for SEM

After the mounts were placed in a cartridge, it was placed in a chamber. A camera showed inside the chamber; and by using controller, aimed the scanner at the top of the specimen. Figure 3.35 shows the cartridge holding specimens and Figure 3.36 shows inside of the chamber of SEM. For SEM and EDS, specimens were cured for 7 days; but the first attempt showed that there was still moisture in the specimen. Then 2% and 8%, modified and unmodified, CB was placed in lab oven at 180ºC for 6hr. In second attempt, speciment was fully cured and SEM was able to get the images. Images were collected in different magnifications at the best possible resolution.

Figure 3.32: Cartridge Holding Specimens

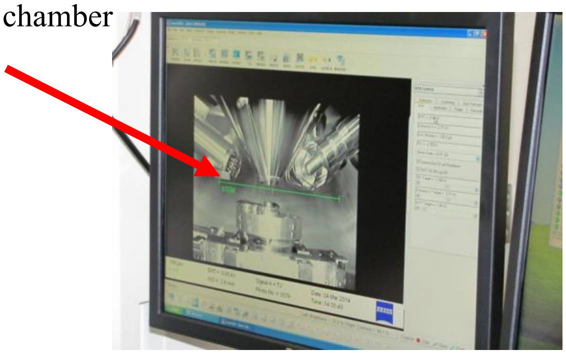
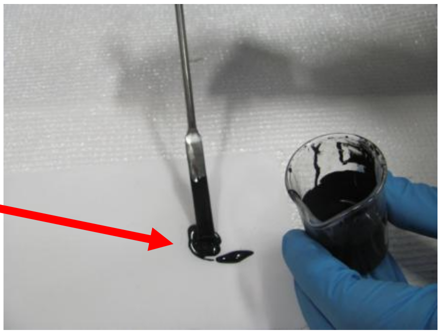


Figure 3.33: Computer screen shows inside the SEM chamber

3.20 Taking Samples for FTIR and Testing

Third test was Fourier Transform Infrared Spectroscopy (FTIR) to measure intensity of nanocomposite over a small range of wavelengths at a time. For FTIR, specimen needed to cure for seven days at room temperature. To make a specimen for FTIR, a piece of non-stick cloth called Peel Ply was used, and with a spatula small amount of carbon black nanocomposite was poured onto the peel ply. Peel ply with specimen was put in a secure place far from any dust for seven days to cure at room temperature. Solid specimen, Figure 3.34, was placed in the holder; and by turning the handle, pressure was placed on the specimen. Test was run and data was collected. Figure 3.34 shows the process of making specimen for FTIR on a piece of peel ply.



Putting Nanocomposite on
Peel Ply for FTIR

Figure 3.34: From left to right process of making specimen for FTIR on a piece of Peel ply

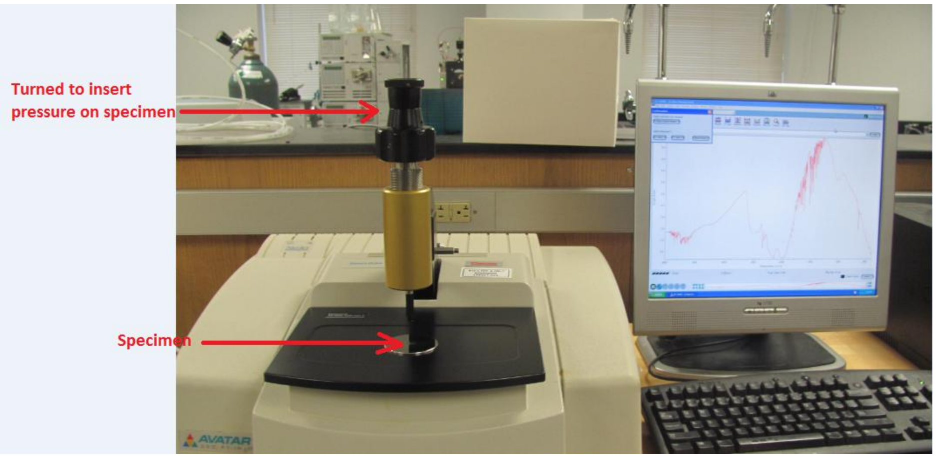
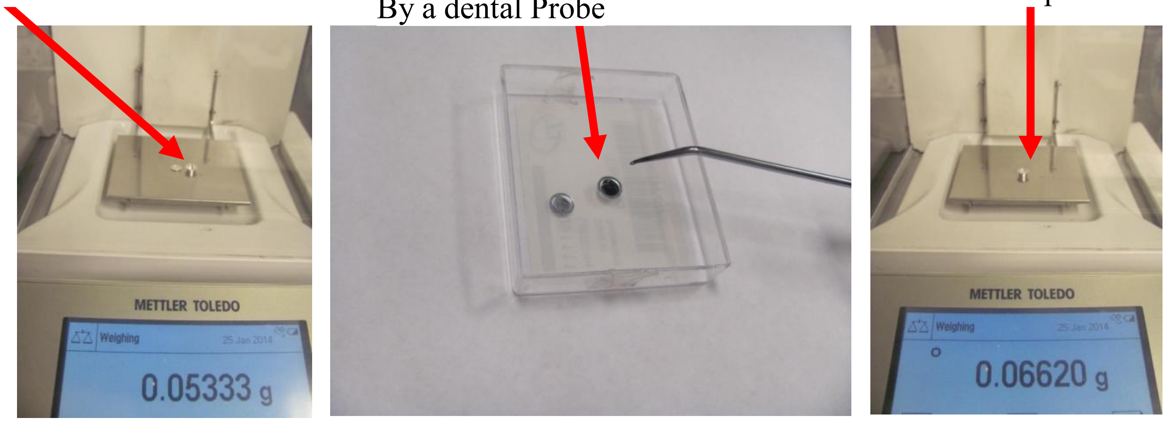


Figure 3.35: FTIR Testing Specimen and Collecting Data

3.21 Taking Sample for DSC and Testing

To make a specimen for DSC, a Tzero Pan and a Tzero Hermetic Lid were weighed on a 1/10000th scale; and to pick up and prevent any movement on the Tzero Pan and a Tzero Hermic Lid, tweezers were used to avoid entering any foreign object to the Tzero pan. Then with the help of a dental probe, very small amount (10-15mg) of carbon nanocomposite was put into the Tzero pan. Then with tweezers Tzero lid was put on and weighed again; by subtracting weight before and after adding specimen, the net weight of specimen was calculated and recorded. After weighing was done, specimen was placed on Tzero DSC sample Encapsulation press to seal the T zero lid and Tzero pan. After sealing was finished, specimen was placed on the circular rack of DCS Q2000. Figure 3.36 shows the process of making specimen for DSC.



Weighing empty Tzero pan
and Tzero hermetic lid

Putting Nanocomposite to
Tzero pan
By a dental Probe

Weighing Tzero pan
and Tzero hermetic lid
with Nanocomposite

Figure 3.36a: Weighing Tzero pan and Tzero hermetic lid, Putting sample of carbon black nanocomposite on the Tzeropan and weighing again to find the weight of specimen

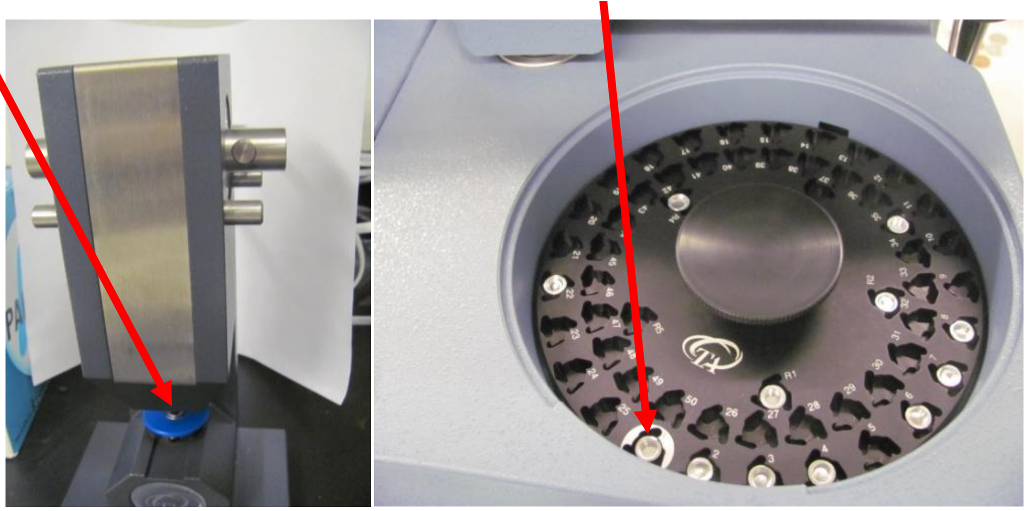


Figure 3.36 b: Encapsulation Press (left), Cicular Rack on the DSC Q 2000 (right)

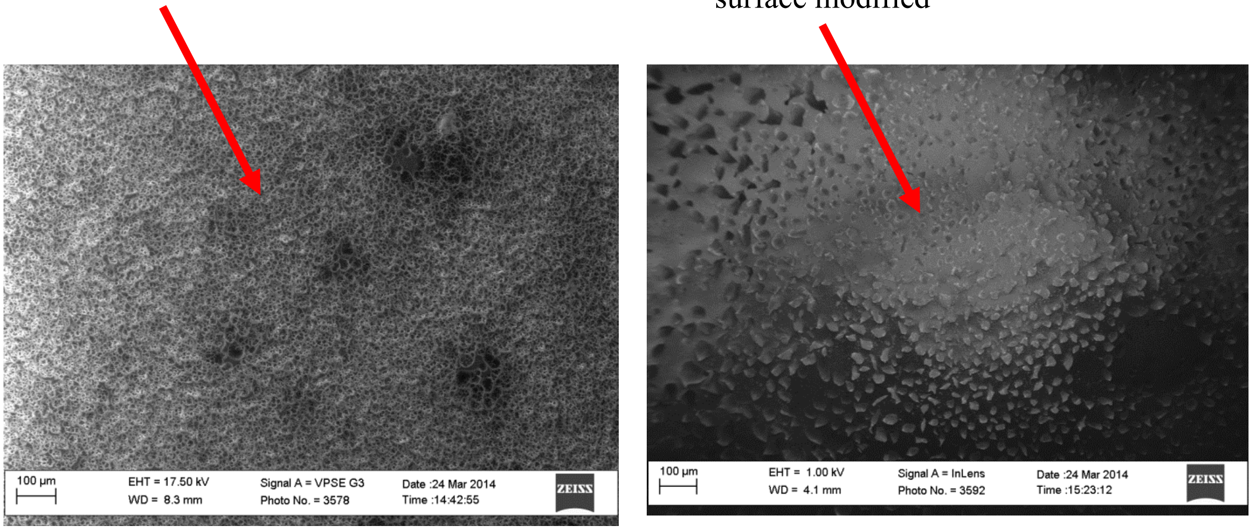
Same process of prepration of samples was repeated for 4% and 8% carbon black. Also same process of prepration was done for silanized carbon black. Several samples of EPON 828 and hardener without any carbon black were made just to find the base line for DSC. After finding the base line, it was decided to run carbon black nanocomposite and silanized carbon black nanocomposite at 110ºF, 140ºF and 220ºF. As a result of this decision, a total of 18 samples were needed. After specimen was placed in the DSC Q2000, tempearature of curing was set. In this study, the temperature was set to 110ºF, specimen was run, and data was collected for analyzing.

CHAPTER 4

RESULTS AND DISCUSSION

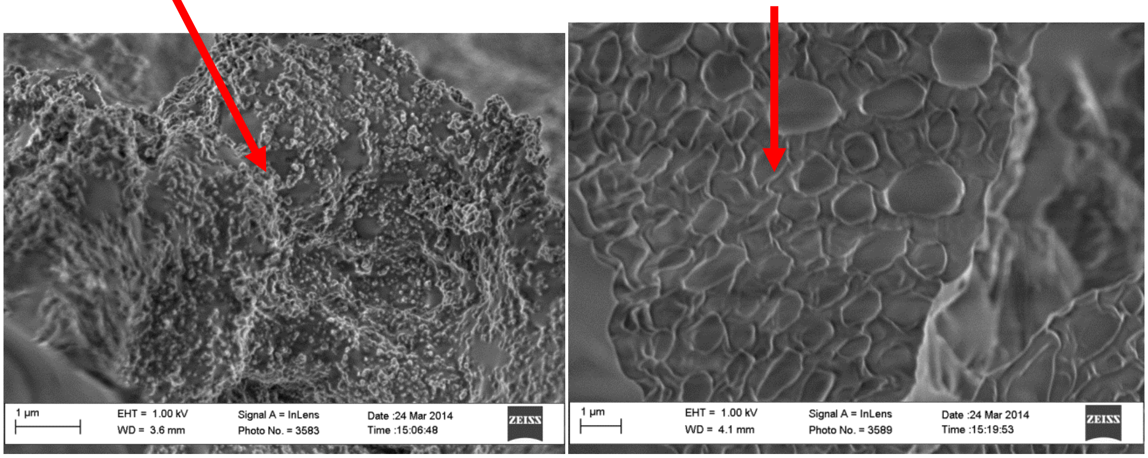
4.1 SEM on Unmodified and Modified CB

SEM images for unmodified and modified (silanized) carbon black nanocomposite at 2%wt showed some differences in structure of samples. Unmodified carbon black had some agglomerations and didn't have good dispersion. Image of modified (silanized) carbon black nanocomposite showed a homogeneous dispersion and no agglomerations. This suggests silanization process of carbon black was successful. Figure 4.1 shows modified and unmodified 2% CB nanocomposite at 100µm magnification. At higher magnification, images of same samples showed a rubber like shell around carbon black particles and confirmed successful silanization process. Figure 4.2 shows modified and unmodified 2% CB nanocomposite at 1µm magnification.


Carbon black surface unmodified

Silanized carbon black particles surface modified

Figure 4.1: SEM images of unmodified (left) 2% carbon black nanocomposite and modified (right) 2% carbon black nanocomposite at 100µm magnification.



Carbon black Paticles Agglomeration

Silanized Carbon Black uniform distribution inside EPON resin 828

Figure 4.2: SEM images of unmodified (left) 2% carbon black nanocomposite and modified (right) 2% carbon black nanocomposite at 1µm magnification.

SEM images for unmodified and modified (silanized) carbon black nanocomposite at 8%wt showed some differences in structure of samples. Image of modified carbon black nanocomposite showed a homogeneous dispersion and no agglomerations. This suggests silanization process of carbon black was successful. At higher magnification, images of same samples showed a rubber like shell around carbon black particles and confirmed of successful silanization process. Figure 4.4 shows modified and unmodified 8% CB nanocomposite at 1µm magnification.

Comparing result from SEM with other sutdies such as Li et al. [16], surface modification by silanization showed consistancy in results. Silanization resulted in strong interface bonding between carbon black and EPON resin 828. Also, silanization technique was used in this study to produce good dispersion quality of carbon black in EPON resin 828. On the other hand, unmodified carbon black nanocomposite showed large agglomeration and poor interface bonding between carbon black and EPON resin 828. SEM images clearly illustrate voids on the fracture surface within unmodified carbon black. In modified carbon black, voids and gaps between carbon black and EPON resin 828 were not observed, indicating the interface bonding strength was good.

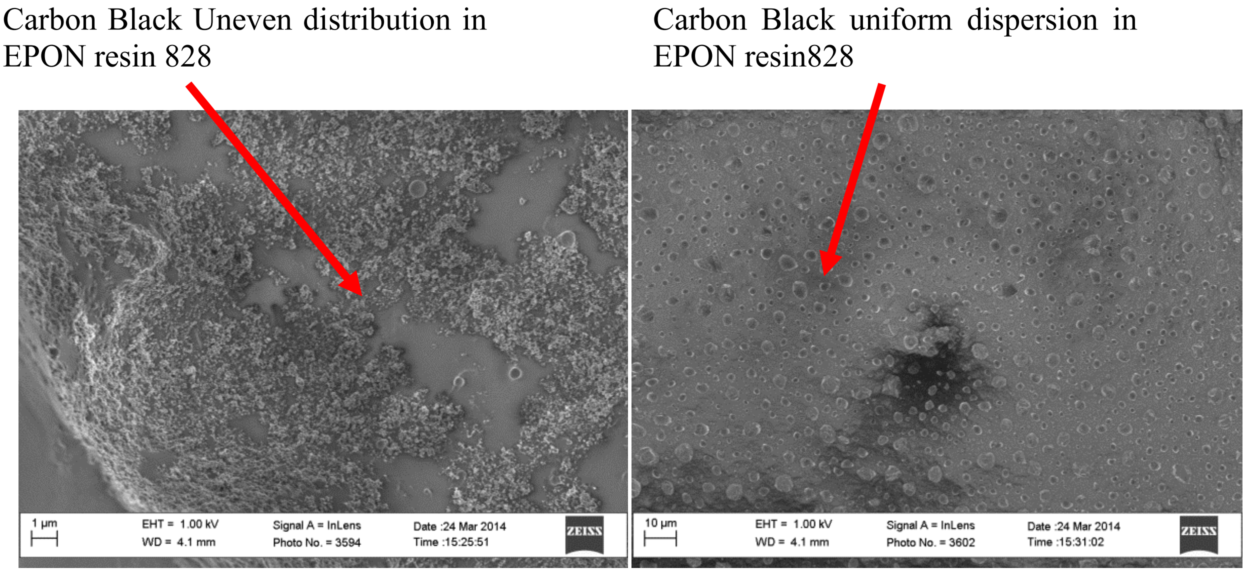


Figure 4.3 : SEM images of unmodified (left) 8% carbon black nanocomposite and modified (right) 8% carbon black nanocomposite at 1µm magnification.

4.2 EDS on Unmodified and Modified CB

Energy Dispersive X-ray Spectroscopy (EDS) showed some differences in element analysis of specimens.This suggests carbon element in modified CB nanocomposite was higher than unmodified for both 2% and 8% CB. Nitrogen in modified CB nanocomposite was less than in the unmodified one. Oxygen did not significantly change; Figure 4.4 shows unmodified 2% CB nanocomposite, 67.5% carbon, 13.69% nitrogen and18.81% oxygen. Figure 4.5 shows modified 2%wt CB nanocomposite with 74.05% carbon , 6.12% nitrogen and 19.83% oxygen. Figure 4.6 shows that unmodified 8% CB nanocomposite element analysis was approximately the same as 2% ; the composition was 69.40% carbon, 12.71%wt nitrogen and17.89% oxygen. Figure 4.7 shows that modified 8% CB nanocomposite had a higher carbon concentration of carbon (73.98%), lower nitrogen concentration (5.66%) and slightly higher oxygen concentration (20.36%).

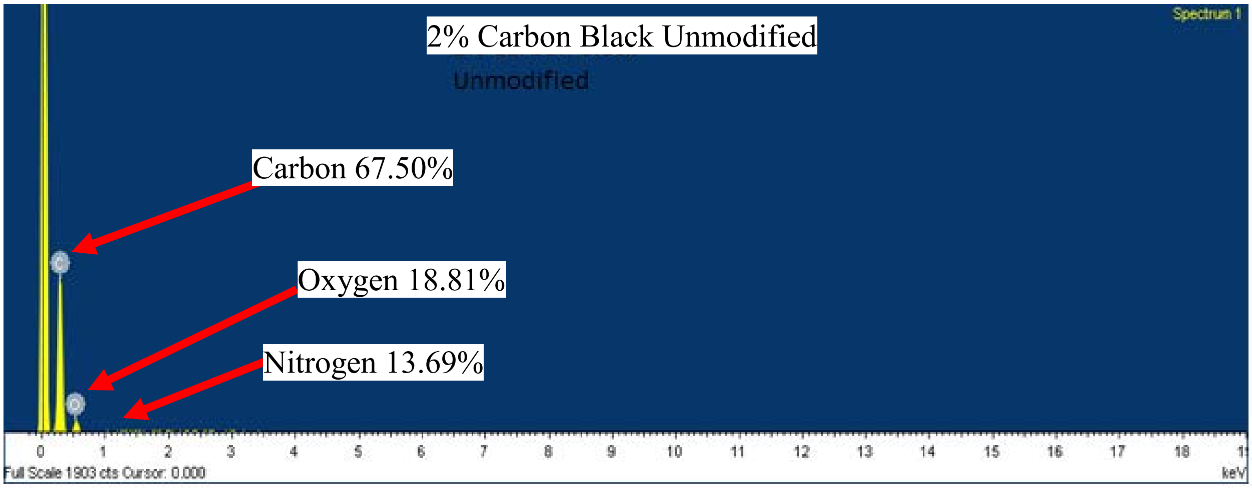


Figure 4.4 : EDS Analyzation of Elements in Unmodified 2% CB Nanocomposite.

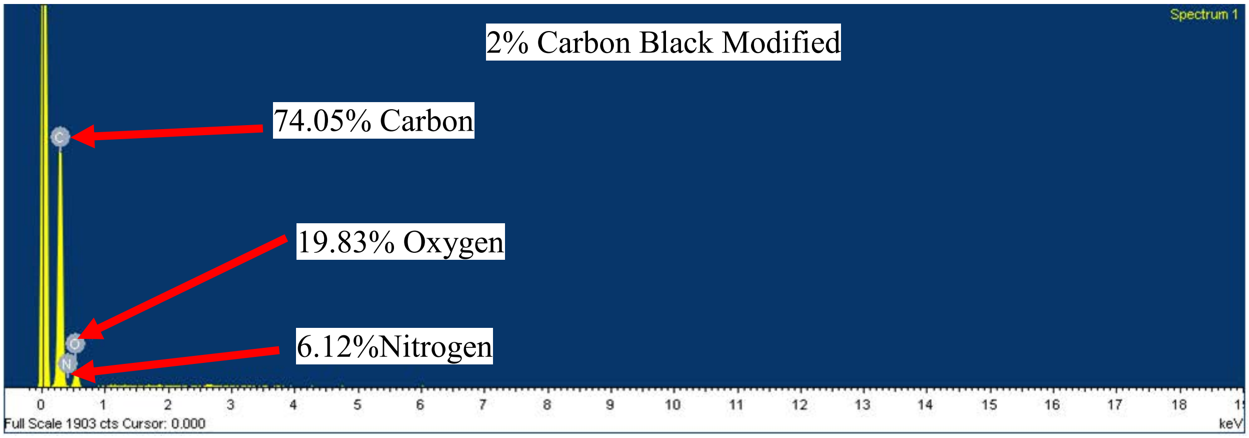


Figure 4.5: EDS Analyzation of Elements in Modified 2% CB Nanocomposite.

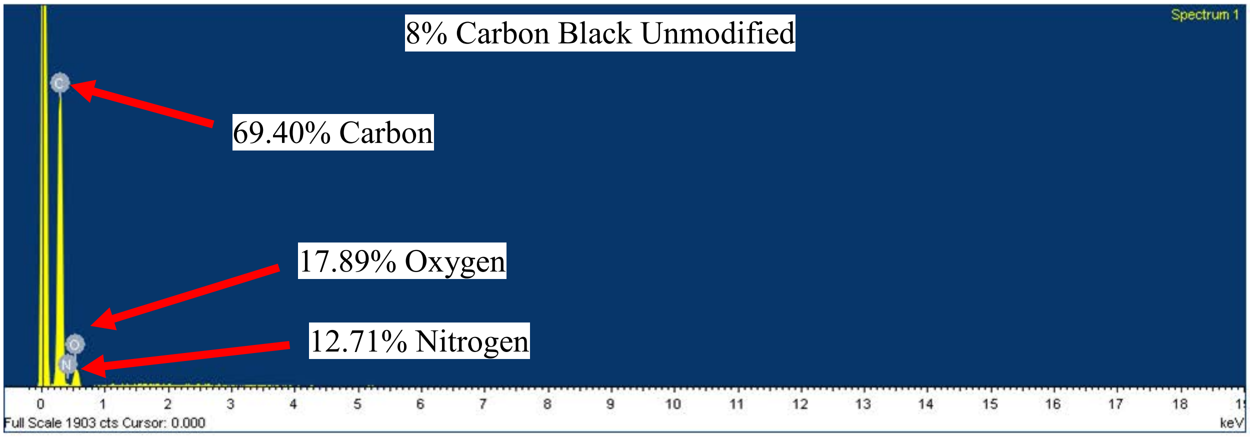


Figure 4.6: EDS Analyzation of Elements in Unmodified 8% CB Nanocomposite.

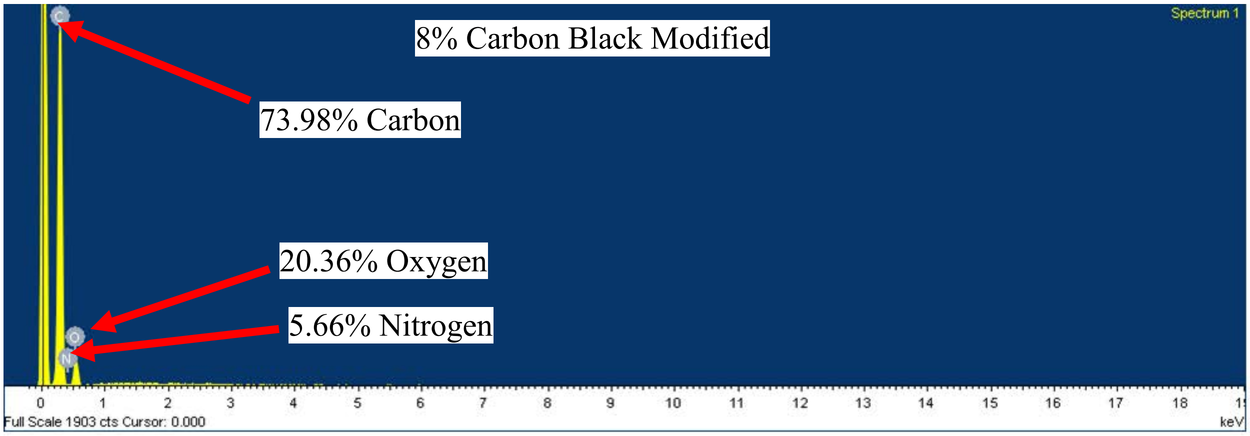


Figure 4.7: EDS Analyzation of Elements in Modified 8% CB Nanocomposite.

Comparing results of EDS from this study with other studies such as Kathi et al. [36] showed that the results were not consistant. The expected result for the element compostion was to show Silicon in the composition. EDS results however didn't show attachment of silane molecules to the funtionalized surface of carbon black. Conclustion of comparison was percentage ratio of [3- (2-Aminoethylamino) propy]trimethoxysilane was not sufficient to appear in EDS. In future study, this inconsistency may be solved by adding a larger weight percent of [3- (2-Aminoethylamino) propy]trimethoxysilane.

4.3 FTIR 4% Unmodified and Modified CB

FTIR was used to confirm the silanization process on carbon black was successful. Transmittance percentage was between 97% and 105% with wavelength range of 500 cm^{-1} to 4000 cm^{-1}. Numbers of sample scans were 64 and numbers of background scans were 32. Resolution was set to 4.0 and sample gain to 8.0. Figure 3.1 shows the FTIR spectrum of neat resin specimen (0% carbon black). Spectrum showed various peaks, and peaks showed whether or not chemical bondings were breaking or forming. Wavelength Range of 500 cm^{-1} to 1500 cm^{-1} is a fingerprint region; and results showed 559.64 cm^{-1}, 825.41 cm^{-1}, 1033.75 cm^{-1}, 1180.40 cm^{-1}, 1232.44 cm^{-1}, 1448.02 cm^{-1} formation of epoxy group with bonding in C-O group. At peak wavelength of 1506.55 cm^{-1}, there was stronger C=O group bonding between oxygen and carbon. In hydrogen stretching region, wavelength peak at 2917.15 cm^{-1} showed N-H bonding. Figure 4.8 shows bonding in different regions of spectrum.

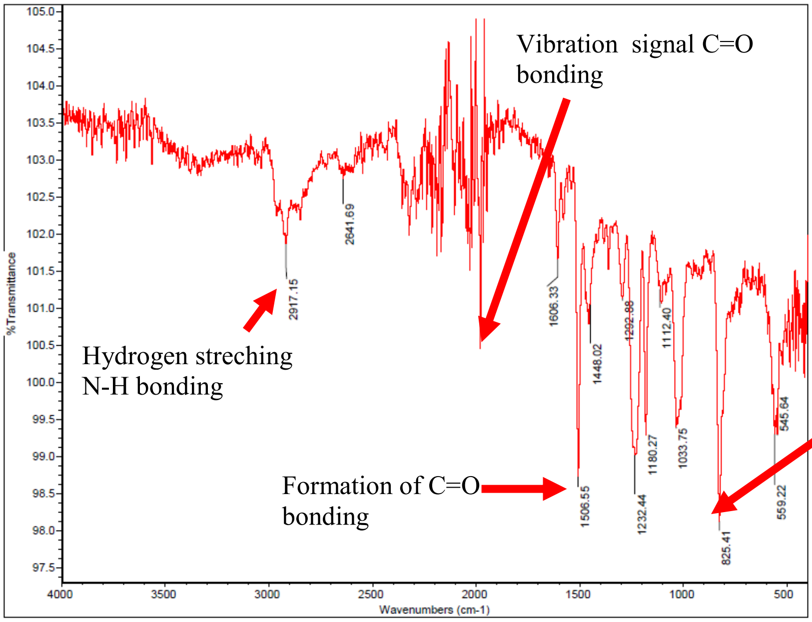


Figure 4.8: FTIR spectrum of neat resin (0% carbon black) cured in room temperature for 7 days with 12% Diethylenetriamine,98+% (DETA) curing agent.

FTIR spectrum for 4% unmodified carbon black nanocomposite was mostly the same as neat resin spectrum except for a minor peak. Spectrum showed a peak at 911.71cm^{-1}, suggesting an increase bonding on C-O. Increase in bonding C-O is caused by addition of carbon black to the epoxy resin. Rest of the spectrum such as fingerprint and hydrogen stretching regions didn't show any significant changes.

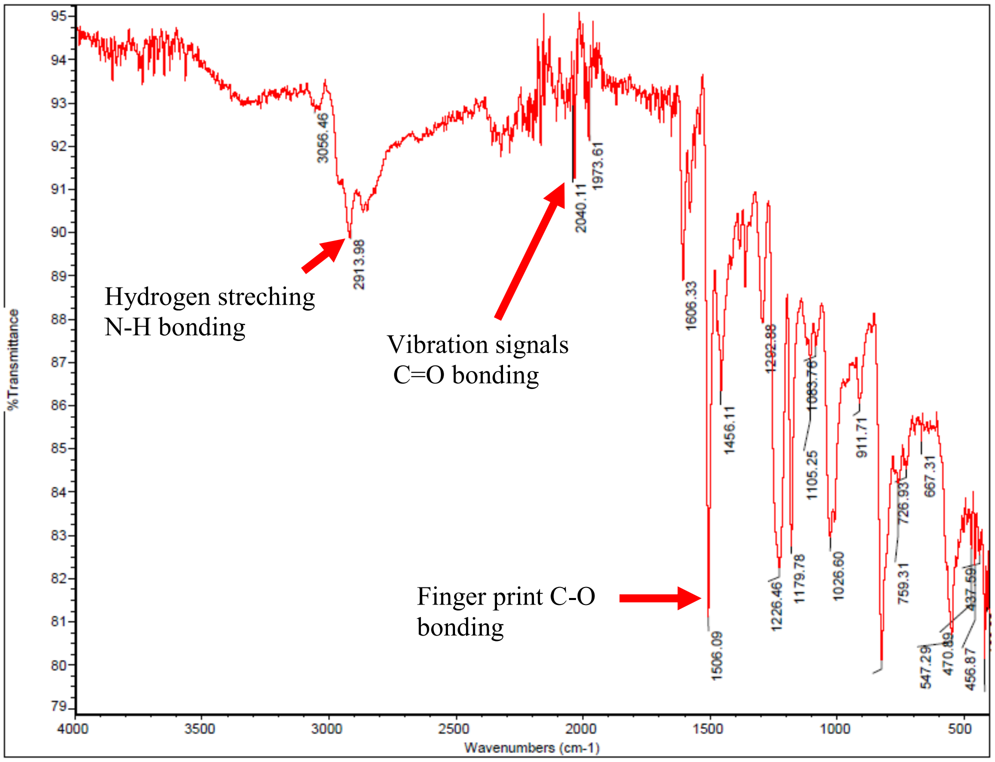
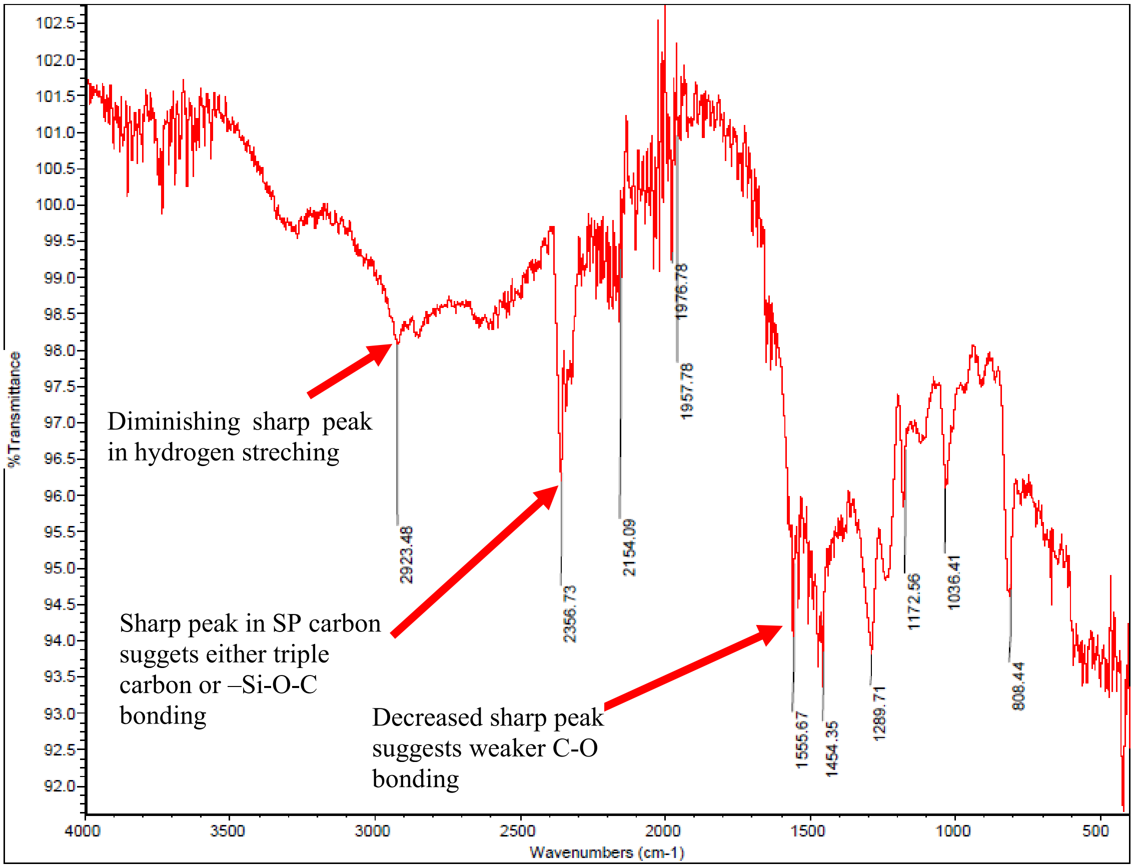


Figure 4.9: FTIR spectrum of 4% unmodified carbon black nanocomposite cured specimen in room temperature for 7 days with 12% Diethylenetriamine,98+% (DETA) curing agent.

Spectrum for 4% modified carbon black nanocomposite specimen in room temperature for 7 days with 12% Diethylenetriamine,98+% (DETA) curing agent showed that some peaks diminished and one appeared. For the range of 1200 cm^{-1} to 1300 cm^{-1}, some of the peaks were diminished, showing decrease in fingerprint region and weaker C-O bonding. Also, the sharp peak at 1500cm^{-1} showed that neat resin and 4% unmodified CB nanocomposite were diminished in this spectrum. However, spectrum showed appearance of sharp peak at 2356.73cm^{-1} suggesting stronger covalent bonding: either -C ≡ C- or –Si-O-C. Both of the new covalent bondings resulted in stronger cross linking bonding and confirmed the difference for silanized carbon black nanocomposite. On the other hand, diminished peak at 2932.48 cm^{-1} showed the decrease in hydrogen stretching region and weaker C-H bonding. Figure 4.10 shows the FTIR spectrum for 4% silanized CB nanocomposite.



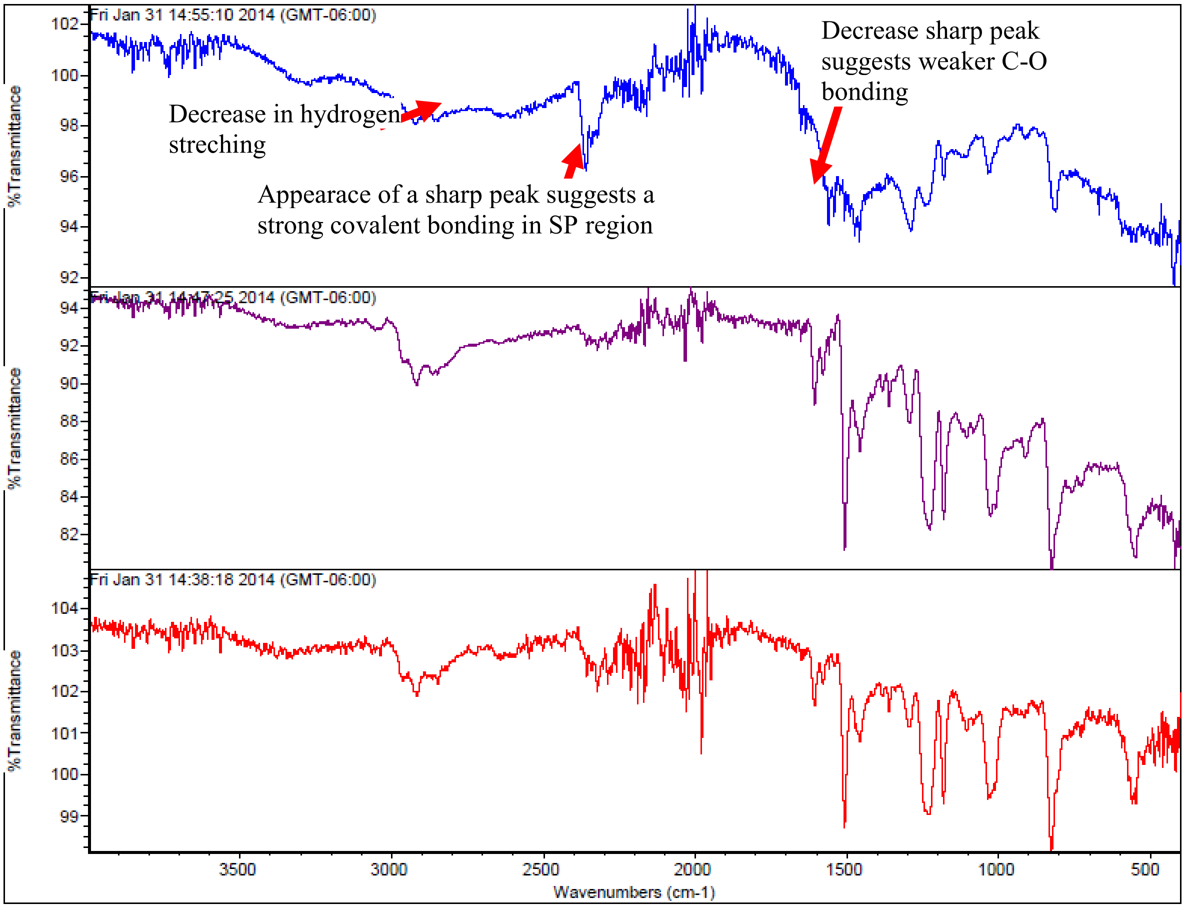
Diminishing sharp peak in hydrogen streching

Sharp peak in SP carbon suggets either triple carbon or –Si-O-C bonding

Decreased sharp peak suggests weaker C-O bonding

Figure 4.10: FTIR spectrum of 4% modified carbon black nanocomposite cured specimen in room temperature for 7 days with 12% Diethylenetriamine,98+% (DETA) curing agent.

FTIR spectrum stack showed a comparison for all three specimens. Diminished peaks in range of 1200 cm^{-1} - 1300cm^{-1}, 1500cm^{-1} and 2932.48 cm^{-1} decreased in C-O, C=O and C-H bonding. Appearance of sharp peak at 2356.73cm^{-1} suggests stronger covalent bonding: either -C ≡ C- or –Si-O-C. Figure 4.11 shows stack comparison FTIR spectrum for all three specimen neat resin (0% carbon black) cured in room temperature for 7 days with 12% DETA curing agent. Unmodified carbon black nanocomposite cured specimen in room temperature after 7 days with 12% DETA curing agent. 4% modified (silanized) carbon black nanocomposite cured specimen in room temperature after 7 days with 12% DETA curing agent.



Decrease sharp peak suggests weaker C-O bonding

Decrease in hydrogen streching

Appearace of a sharp peak suggests a strong covalent bonding in SP region

Figure 4.11: Neat resin cured in room temperature for 7 days with 12% DETA curing agent (bottom). 4%Unmodified carbon black nanocomposite cured specimen in room temperature for 7 days with 12% DETA curing agent (middle). 4% modified carbon black nanocomposite cured specimen in room temperature for 7 days with 12% DETA curing agent (top).

Comparing results to other studies for FTIR confimed consistancy of silanization of carbon black. FTIR results for this study were similar to silanized carbon black results because of the change in covalent bonding in SP region. Also, another significant change was observed in 2932.48 cm^{-1} region; wavelength showed the confirmation of decrease in hydrogen stretching region and perhaps addition of silicon to the region. FTIR in this study agreed with some other studied such as Kathi et al. [36] showed Silicon and O-H bonding, and the difference between two studies were mainly on different wave number regions. As long as existence of bonding between two Si and O-H were confirmed for any wavelength region, silanization of carbon black was confirmed.

4.4 Isothermal Curing Kinetics of Carbon Black Nanocomposites by DSC Measurment

Results from Differential Scanning Calorimetry (DSC) were heat flow versus weight; in another words, DSC measured heat realized during the curing of nanocomposite, unit was W/g. EPON resin 828 at 110ºF was used to find a base line and to find the heat of reaction area under the curve. DOC was calcualted by using an integral, and its unit was J/g.There are different ways to calculate DOC; the caculation used came from Huhn [49]. Where α (t) is degree of cure at time (t); H(t) is area under curve with respect to time (t); and Hu is ultimate heat of reaction. Equation 2 was used to find degree of cure, α [49]. Hres is the residual heat of reaction. The ultimate heat of reaction is the sum of the total heat of reaction and residual heat of reaction. Caculation 3 was used to find the degree of cure equilibrium [49].

$$\alpha(t) = \frac{H(t)}{H_U} \tag{1}$$

$$\alpha = 1 - \frac{H_{res}}{H_U} \tag{2}$$

$$\alpha_{ie} = \frac{H_{T^\circ C}}{H_{T^\circ C} + H_{res}} \tag{3}$$

The software, TA instrument and Universal Analysis 2000 version 4.5 A, were used for modeling and analyzing all of collected data.To find the base line for this study, 12% DETA was added to EPON 828; and the mixture was cured in DSC at temperatures of 110ºF, 122ºF, 140ºF, 180ºF, 220ºF, 300ºF, 320ºF, 330ºF, and 350ºF. As temperature was increased, DOC increased as well; this was expected. Figure 4.12 shows degree of cure for different temperatures as well as the base temperature. 110ºF was chosen to be the base line for all other measurements. DOC for EPON 828 without any nanoparticles was 0.7.

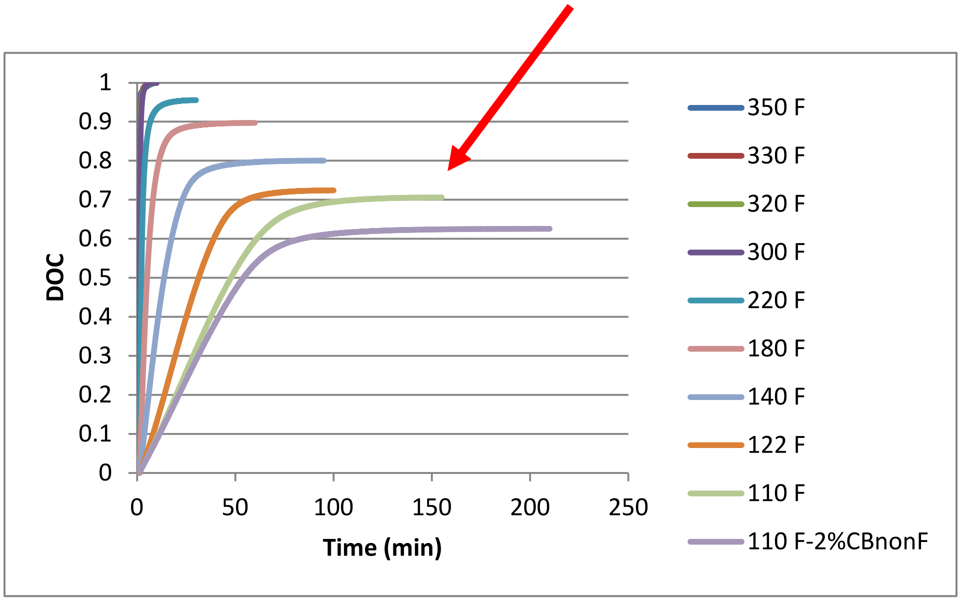

110ºF Base line for DOC

Figure 4.12: Isotermal DOC vs. cure time for EPON resin 828 and 12% DETA at different temperature to find a base line.

Temperature of 110ºF was used for the base line; then unmodified 2% CB, 4% CB and 8% CB nanocomposites were cured in DSC to find DOC for each sample. Figure 4.13 shows effects of adding CB to the EPON resin 828. 2% unmodified CB nanocomposite decreased the DOC from 0.705 to 0.626. Then by increasing concentration of CB from 2% CB to 4% CB, DOC increased to 0.648. Addition of concentration from 4% CB to 8% CB increased the DOC to 0.710. Basically, at a lower concentration of carbon to EPON resin 828 , DOC decreased; then by increasing the concentration of CB, DOC gradually increased.

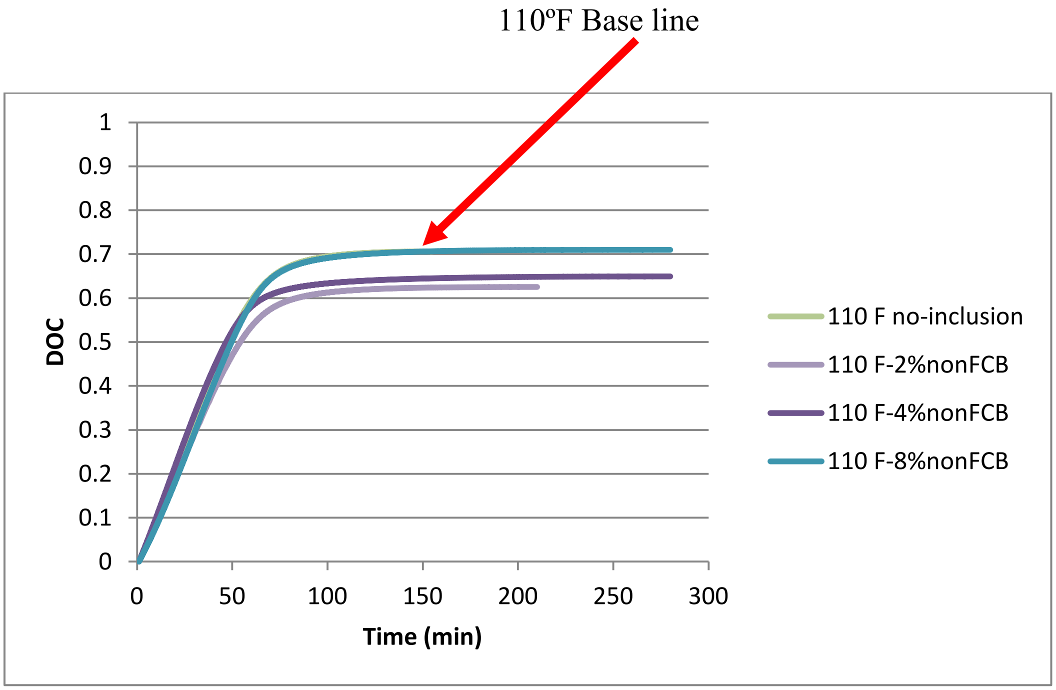
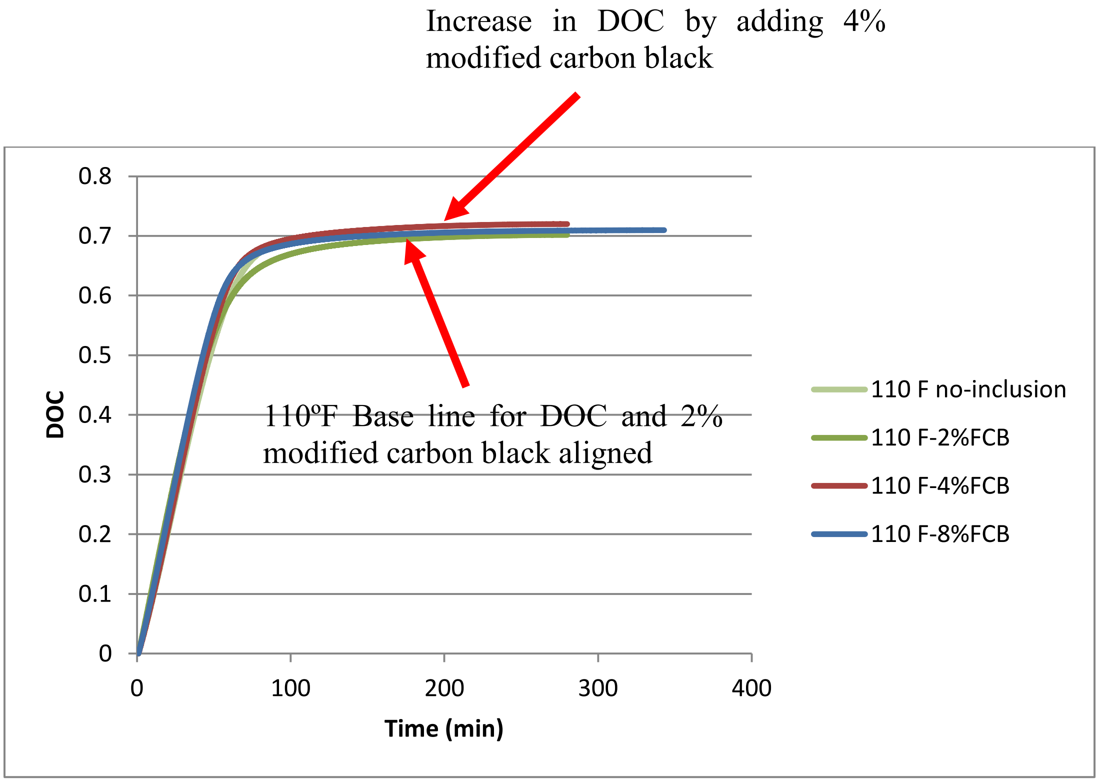


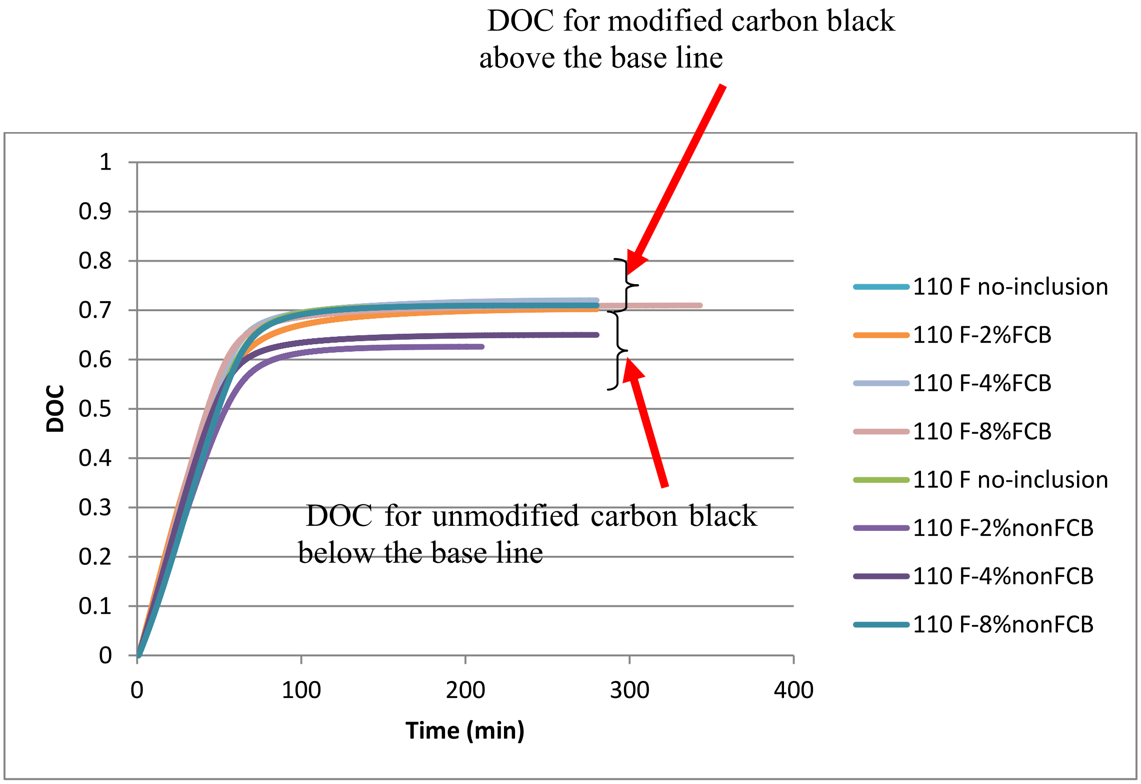
Figure 4.13: Isothermal DOC vs. cure time at 110ºF for base line, 2%, 4% and 8% unmodified CB.

Same procedures were used but with modified carbon black. At 110ºF , base line was compared to 2%, 4% and 8% modified CB nanocomposite. Figure 4.14 shows the DOC vs. curing time. Modified CB made a significant change in DOC for 2% modified CB started at base line, 0.705 . Increasing the concentration of CB increased the DOC for 4% modified CB to 0.720 and decreased the DOC for 8% modified CB to 0.710. This result showed that silanization process on carbon black affected the curing kinetics of nanocomposites and accelarated the curing process. Figure 4.15 illustrates the difference between modified and unmodified carbon black nanocomposite DOC at 110ºF. Graphs show unmodified CB are below the baseline and modified CB are above the baseline.


Increase in DOC by adding 4% modified carbon black

110ºF Base line for DOC and 2% modified carbon black aligned

Figure 4.14: Isothermal DOC vs. cure time at 110ºF for base line, 2%, 4% and 8% modified CB.


DOC for modified carbon black above the base line

DOC for unmodified carbon black below the base line

Figure 4.15: Isothermal DOC vs. cure time at 110ºF for base line, 2%, 4% and 8% modified and unmodified CB nanocomposite.

DOC increased due to increase in temperature from 110ºF to 140ºF. At 140ºF, the DOC trend was different when compared to 110ºF; and as the concentrations of unmodified CB were increased, DOC decreased. Also, since temperature was higher and curing time was shorter, curves were closer. After 30 minutes of curing at 140ºF, 2% unmodified CB showed a greater difference in DOC. 4% and 8% unmodified CB almost overlapped each other meaning by increasing the temperate, concentration does not have a significant effect on DOC. Figure 4.16 shows the baseline and different concentrations of unmodified carbon black at 140ºF.

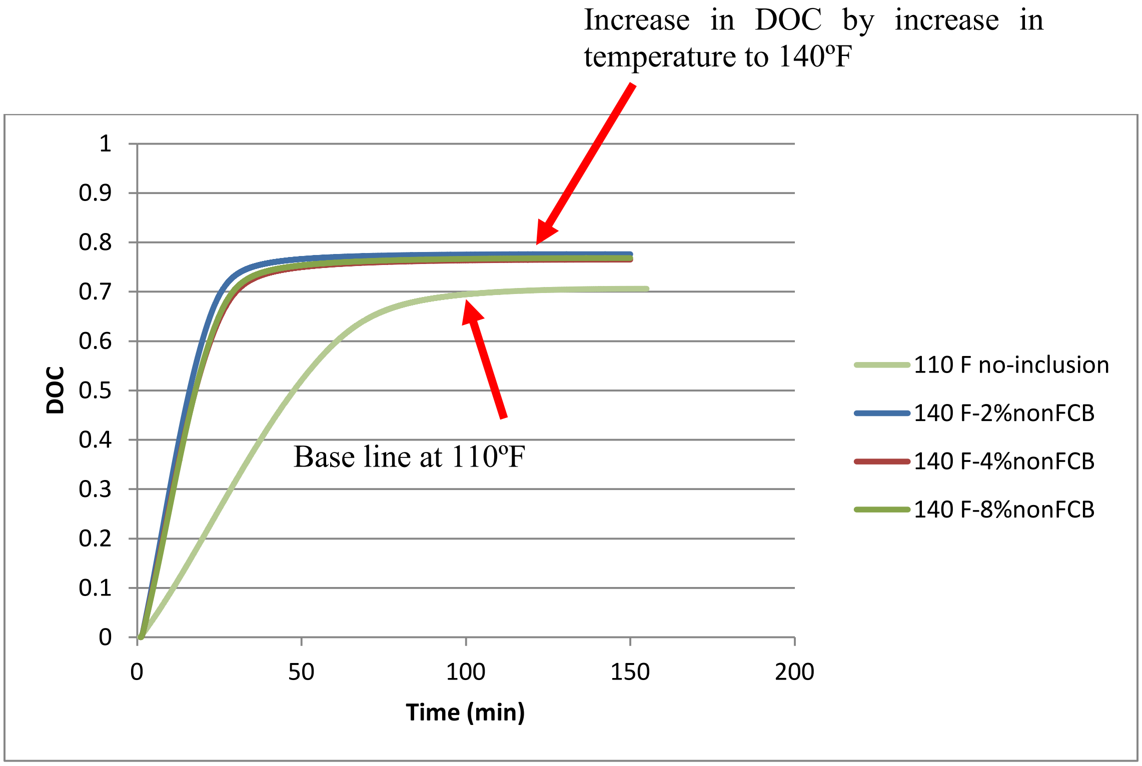
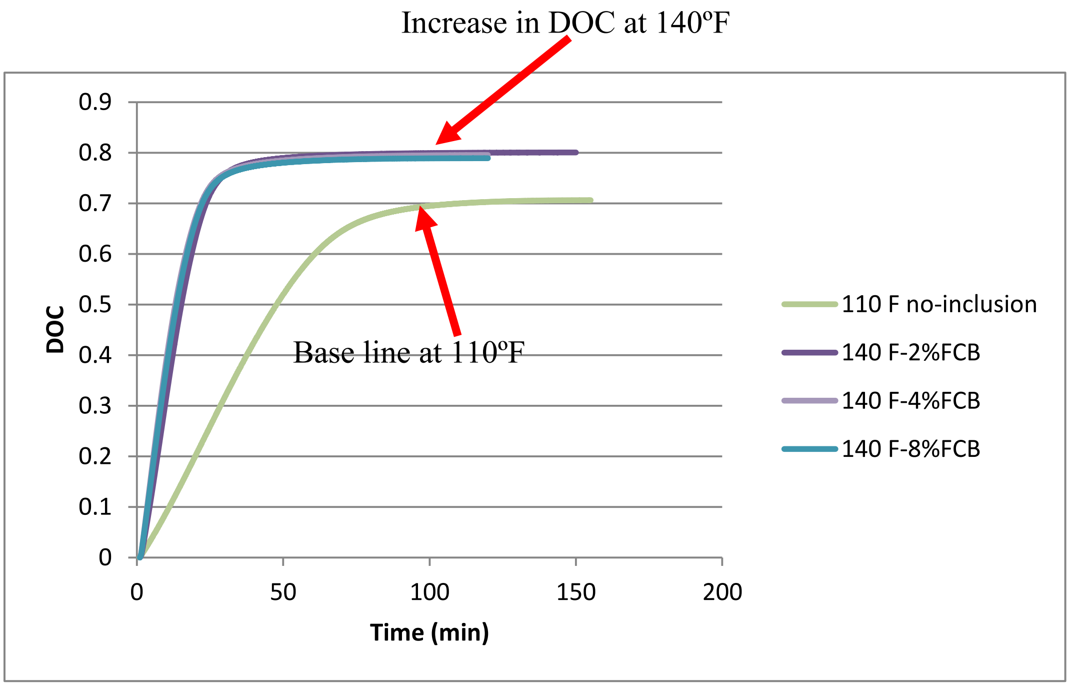


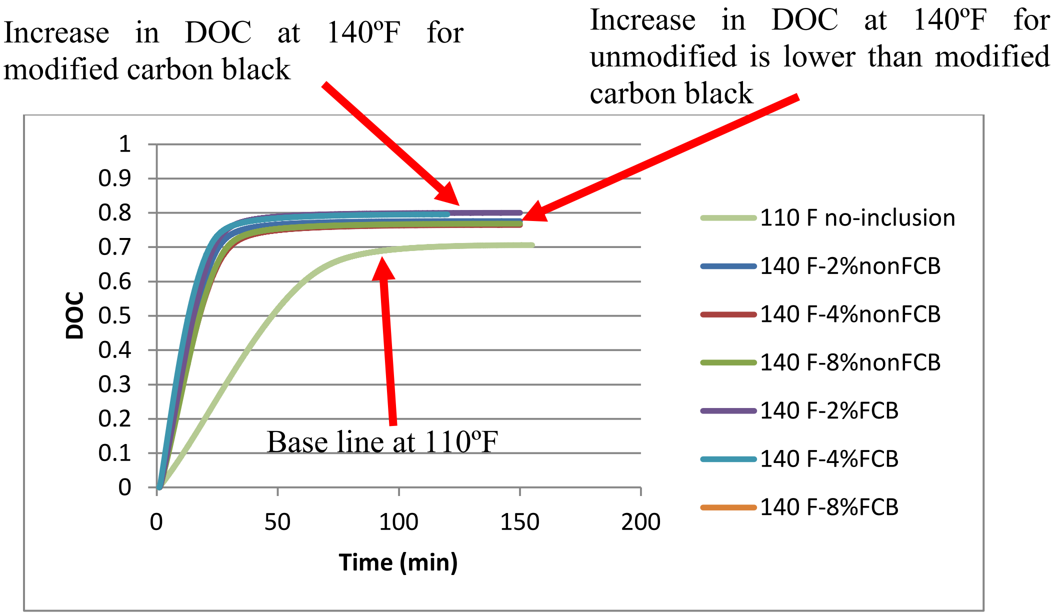
Figure 4.16: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% unmodified CB at 140ºF.

For modified CB nanocomposite at 140ºF, all three concentrations overlapped each other. However, comparing it with unmodifed at the same temperature, results showed that DOC increased to 0.800. Figure 4.17 shows the DOC for baseline and modified CB nanocomposite at different concentrations of modified CB at 140ºF. DOC at 140ºF for modified and unmodified CB nanocomposite showed that DOC of modified CB nanocomposite was 0.800 and for unmodified was 0.776. This suggests that the DOC for higher curing temperature increased, but modified CB had a higher DOC than unmodified CB. Figure 4.18 shows an increase in curing temperature increased the DOC for all concentrations both modified and unmodified.


Increase in DOC at 140ºF

Base line at 110ºF

Figure 4.17: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% modified CB at 140ºF.


Increase in DOC at 140ºF for modified carbon black

Increase in DOC at 140ºF for unmodified is lower than modified carbon black

Base line at 110ºF

Figure 4.18: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% modified and unmodified CB nanocomposite at 140ºF.

All three concentrations were fully cured in about 105min; they showed that an increase in temperature increases the DOC from 0.929-0.954. At 220ºF for 2% CB to 4% CB, DOC slightly increased from 0.929 to 0.954; but for 4% CB to 8% CB, DOC decreased from 0.954 to 0.941. For concentration lower than 4% CB, it increased the DOC; but at higher concentration (8% CB), it reduced the DOC. Figure 4.19 shows the baseline, 2%, 4% and 8% at 220ºF for CB nanocomposite.

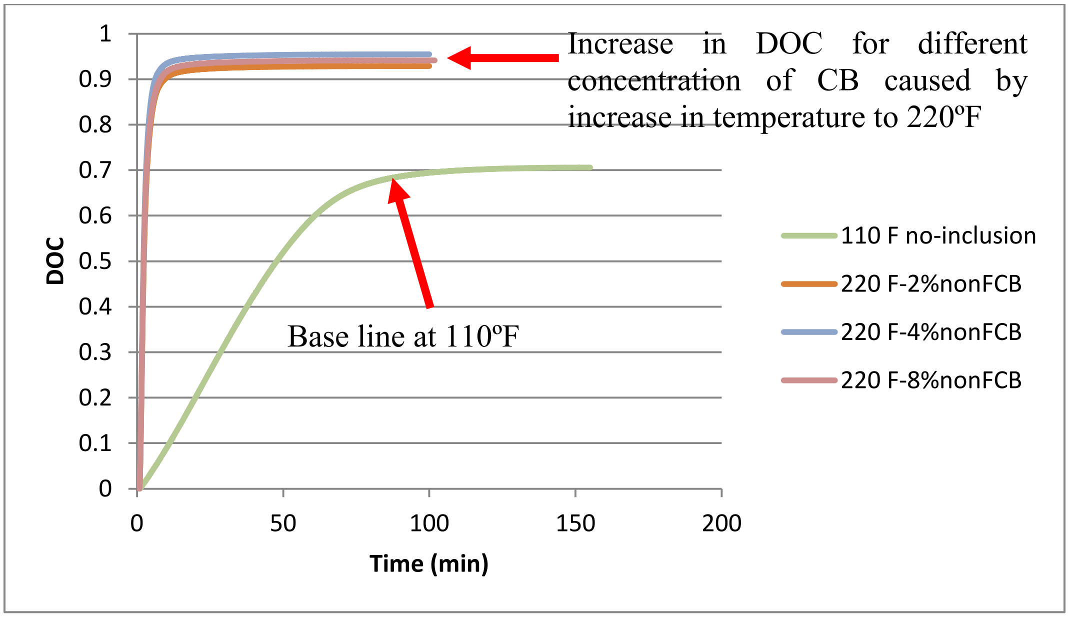


Figure 4.19: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% CB nanocomposite at 220ºF.

DOC at 220ºF, as expected, was much higher than the DOC at 110ºF and 140ºF. Increase in temperature increased the DOC for both modified and unmodified CB nanocomposites. As concentration was increased from 2% CB to 4% CB, DOC increased from 0.92 to 0.95; but from 4%to 8%CB, there is no change in DOC. This suggests increase in lower concentrations (less than 4% CB) increases the DOC but higher concentrations (8% CB) do not change the DOC. Comparing the DOC for modified and unmodified CB nanocomposite at 220ºF, it showed DOC for both modified and unmodified CB was 0.926-0.954. Figure 4.20 shows DOC at 220ºF for both modified and unmodified CB for three concentrations. Figures 4.22, 4.23 and 4.24 show DOC comparison for modified and unmodified CB at 110ºF, 140ºF and 220ºF respectively.

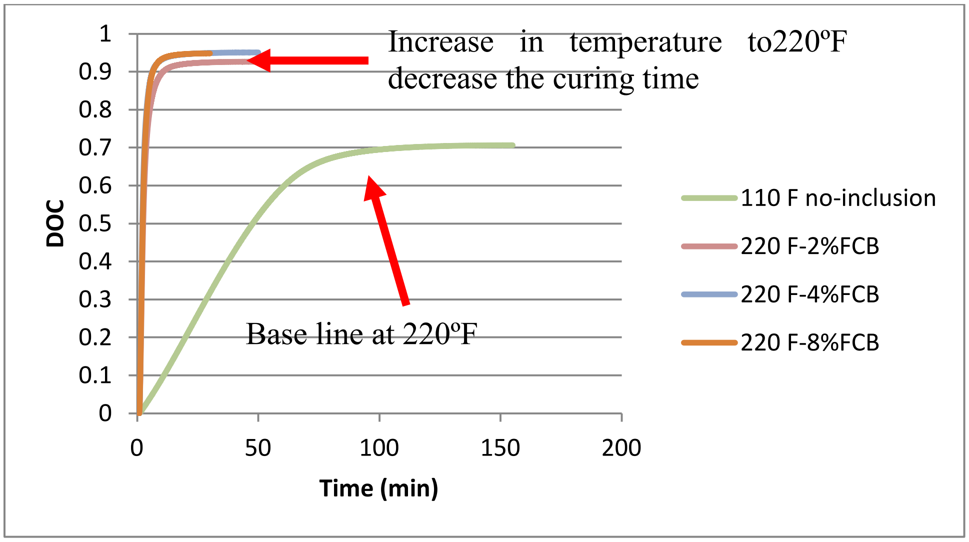


Figure 4.20: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% modified CB nanocomposite at 220ºF.

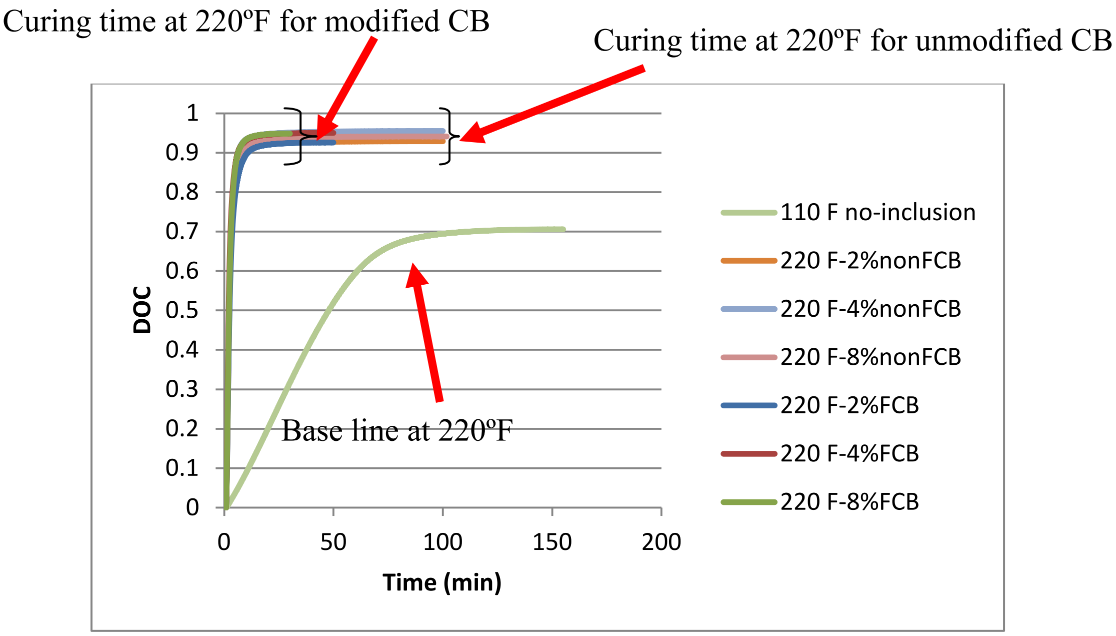


Figure 4.21: Isothermal DOC vs. cure time for base line, 2%, 4% and 8% unmodified and modified CB nanocomposite at 220ºF.

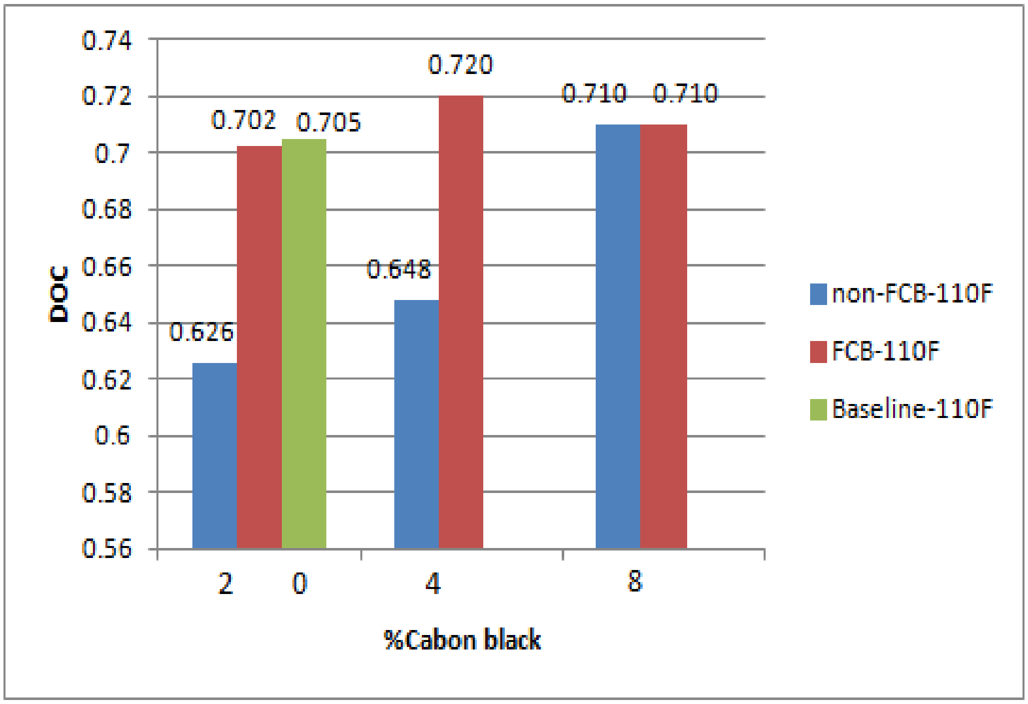


Figure 4.22: DOC Comparison for Modified and Unmodified CB at 110ºF

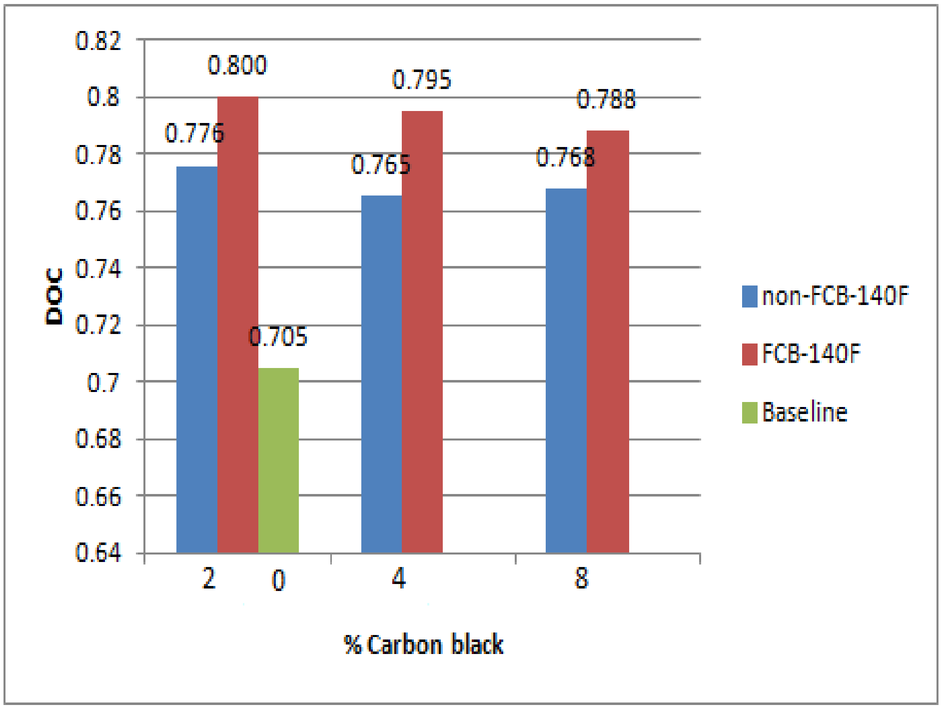


Figure 4.23: DOC Comparison for Modified and Unmodified CB at 140ºF

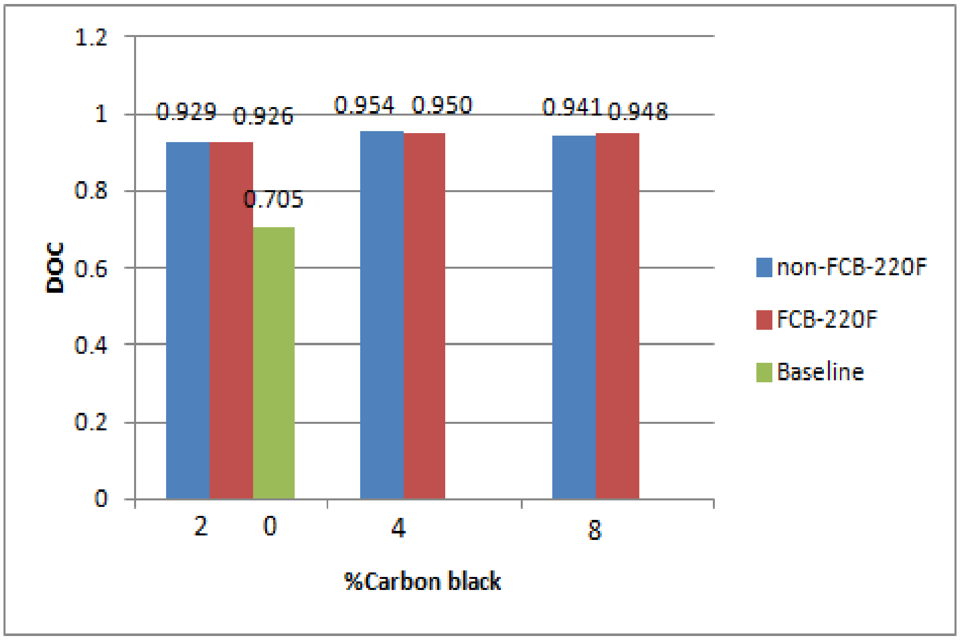


Figure 4.24: DOC Comparison for Modified and Unmodified CB at 220ºF

Table 1 shows the percent comparison of DOC for unmodified CB at different temperatures and wt% of CB. At 110ºF, adding 2% and 4% CB to EPON resin 828 decreased the DOC percent compared to the baseline (70.5%). However, for 2% to 8% CB, DOC percent increased to 71%. At 140ºF, addition of CB at any wt% of CB decreased the DOC percentage; but compared with the baseline (110ºF), DOC percentage increased. At 220ºF, addition of 4% CB did not change the DOC percent; but 2% and 8% modified CB decreased the DOC percent.

TABLE 1

DOC Percent for Unmodified CB

W% CB Tem(ºF)	0	2	4	8
110	70.5	62.6	64.8	71.0
140	79.4	77.6	76.5	76.8
220	95.4	92.9	95.4	94.1

Table 2 shows the DOC percent comparison for modified CB at different temperatures and wt% of modified CB. At 110ºF, adding 2% modified CB decreased the DOC percent whereas 4% and 8% modified CB increased the DOC percentage. At 140ºF, adding 2% and 4% modified CB increased the DOC percent but 8% modified CB decreased the DOC percentage. At 220ºF, adding any wt% of CB decreased DOC percentage.

TABLE 2

DOC Percent for Modified CB

W% CB Tem(°F)	0	2	4	8
110	70.5	70.2	72.0	71.0
140	79.4	80.0	79.5	78.8
220	95.4	92.6	95.0	94.8

Results from DSC agreed with other studies related to curing kinetics of modified and unmodified nanoparticles. Chen et al. [43] study concluded addition of nanoparticles such as CNT. It accelerated curing reaction and lowered the degree of cure, but Chen et al. [43] did not use modified CNT to compare to results of CNT. The curing kinetic results would be different depending on what method was used for calculation. Zhou et al. [27] compared two methods of calculation for curing kinetics, and results showed one method agreed with experimental data more than the other method. One method of calculation of curing kinetics showed differences between model prediction and experimental data observation [44]. Choi et al. [45] compared the curing rate of functionalized MWNT and unfunctionalized MWNT, and results showed increase in curing rate of functionalized MWNT amine functional groups. This study agreed with the results of Choi et al. [45] in that it was observed that the curing rate accelerated due to nanoparticle surface modification. Results from this study along with other studies concluded that functionalization of nanoparticles create a strong interface bonding between nanoparticles and epoxy resin; they eventually result in improvements of nanocomposite properties [45].

In recent years, many nanoparticles have been used for different nanocomposite research; however, there is a degree of risk to both environment and human health. Only the future will determine the tradeoff between benefits of nanocomposite and safety. Many more studies and investigations need to be performed to confirm that nanocomposite and nanotechnology in general is safe to use for any kind of application [50].

CHAPTER 5

CONCLUSIONS

The purpose of this study was to prepare nanocomposites by using silanized carbon black nanoparticles to improve the curing kinetics of nanocomposites. It was found that the silanization process significantly affected the homogeneous dispersion of carbon black in EPON resin 828 without any agglomeration of carbon black. For confirmation of success of the silanization process, FTIR and SEM were used. However, stability dispersion test of unmodified and modified carbon black was a faster method of confirming the success of the dispersion.

Different weight percentages of nanocomposites were prepared with a mechanical stirrer. Modified and unmodified 2wt% CB, 4wt% CB and 8wt% CB were separately mixed for 2hr, and then mixture was placed in ultrasonicator for 30 min. After that, curing agent DETA was added and mixed for 15min. Samples for DSC, FTIR and SEM were collected. DSC test samples were placed in Tzero pans and were immediately placed in the DSC. Curing of nanocomposites took place in DSC at controlled temperatures. For FTIR and SEM, samples were taken and left at room temperature for seven days to cure. The results of DSC indicated that modified CB nanocomposites for the temperature of 110ºF for 2%, 4% and 8wt% CB showed a significant difference in degree of cure (DOC). As temperature increases from110ºF to 140ºF and then to 220ºF, differences in DOC are not as significant because curing time is much faster at higher temperatures. Thus, silanized CB significantly accelerates the curing of nanocomposites at temperatures lower than 140ºF. At temperature below 220ºF, CB dominated the curing kinetics; above 220ºF, heat dominated the curing process of nanocomposites. Heat flow in nanocomposite at higher concentration of CB is slower, which is because more agglomeration for a higher concentration of CB caused a decrease in DOC.

CHAPTER 6

FUTURE WORK

In the future, there are some other mechanical properties such as tensile strength and conductivity that can be tested for modified and unmodified carbon black nanocomposites. Also, future studies are needed to investigate the interaction between carbon black and epoxy resin. Different surface modification methods can be done and compared to the effects of silanization process. Silanization could be used to experiment with different nanoparticles, such as Graphene, CNTs, SWNTs or MWNTs, and compared to the results of carbon black curing kinetics.

Future investigation of mixing procedures can be carried out with different weight percentages of carbon black in epoxy resin. The dispersion of carbon black in the epoxy resin still needs to be improved and investigated further. Also, different curing agents can be added to the nanocomposites to find its effects on curing kinetics. In the future, nanocomposites can be prepared with different types of epoxy resins to compare the results for curing kinetics and other mechanical properties.

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