MECHANICAL CHARACTERIZATION OF FUNCTIONALIZED CNT REINFORCED NATURAL RUBBER POLYMER

Dissertation-2

Submitted in partial fulfillment of the requirement for the award of degree

Of

Master of Technology

IN

MECHANICAL ENGINEERING

By

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Under the guidance of

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DEPARTMENT OF MECHANICAL ENGINEERING
LOVELY PROFESSIONAL UNIVERSITY
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TOPIC APPROVAL PERFORMA

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Qualitative Assessment of Proposed Topic by PAC		
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2	Project Feasibility: Project can be timely carried out in-house with low-cost and available resources in the University by the students.	7.00
3	Project Academic Inputs: Project topic is relevant and makes extensive use of academic inputs in UG program and serves as a culminating effort for core study area of the degree program.	7.00
4	Project Supervision: Project supervisor's is technically competent to guide students, resolve any issues, and impart necessary skills.	7.00
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DAA Nominee Name: Kamal Hassan	UID: 17469	Recommended (Y/N): Yes

Final Topic Approved by PAC: **Mechanical characterization of the functionalized CNT reinforced natural rubber polymer**

Overall Remarks: Approved (with minor changes)

PAC CHAIRPERSON Name: 12174::Gurpreet Singh Phull **Approval Date:** 29 Nov 2017

CERTIFICATE

I hereby certify that the work being presented in the dissertation entitled "Mechanical characterization of functionalized CNT reinforced natural rubber polymer" in partial fulfillment of the requirement of the award of the Degree of master of technology and submitted to the Department of Mechanical Engineering of Lovely Professional University, Phagwara, is an authentic record of my own work carried out under the supervision of Manish Dhawan, Assistant Professor, Department of Mechanical Engineering, Lovely Professional University. The matter embodied in this dissertation has not been submitted in part or full to any other University or Institute for the award of any degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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The external viva-voce examination of the student was held on successfully _______________

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Thanks to all.

Deepak Sharma

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List of abbreviations:

1. CNT = Carbon nanotube
2. SWNT = Single walled carbon nanotube
3. MWNT = Multiwalled carbon nanotube
4. NR = Natural Rubber
5. UTM = Universal testing machine
6. CVD = Chemical vapour deposition
7. MD = Molecular Dynamics
8. PVC = Polyvinyl chloride
9. TEM = Transmission electron microscopy
10. AFM = Atomic force microscopy
11. SEM = scanning electron microscopy
12. XPS = X-ray photoelectron spectroscopy
13. IGC = Inverse gas chromatography
14. TGA = Thermal gravimetric analysis

Chapter 1

INTRODUCTION

Carbon nanotube(CNT) can simply be described as sheet of graphene transformed into a cylinder. In structural form, CNT is constructed from hexagonal rings of carbon. They can be single layered or multi layered, and from this layering we derive its types i.e. if CNT is single layered it is called as Single walled carbon nanotube(SWNT), or if it is multi layered it is called as Multi walled carbon nanotube(MWNT). A simple classification of CNT is depicted in Fig.1.[1] By now, CNTs have already attracted a lot of researchers because of their eminent physical properties that includes mechanical, thermal as well as electrical properties. CNTs were unknown three decades ago. It was year 1991 when CNTs were discovered by Iijima [2]. In recent years, more excitement has been sparked for their understanding and a large amount of study has been performed. Currently, the physical properties are still being discovered and disputed. A broad range of thermal, structural and electronic properties have been shown by the CNT. These properties vary with the nanotube types which are not just confined to SWNT or MWNT, but types are numerous based on their length, aspect ratio, functional group attached or angle of twist etc. In most of the cases, even steel and Kevlar have a lower tensile strength than the Carbon nanotubes. Since many researchers have done a great job with respect to CNTs, there is a hidden zone and that is composites based on CNTs. Although numerous researches are done in this case also with varying resins but much more can be done here. Researchers in the pursuit of better physical properties have tested and tried many composites like epoxy or polypropylene etc. Quite an untouched area is functionalization of CNTs, in which very less research has been done. So, this study is more focused on functionalization of CNT based composites and the resin chosen is natural rubber. This study is based on SWNT type of CNT, mixed with natural rubber as reinforcement, and Functionalization of CNT based composites.

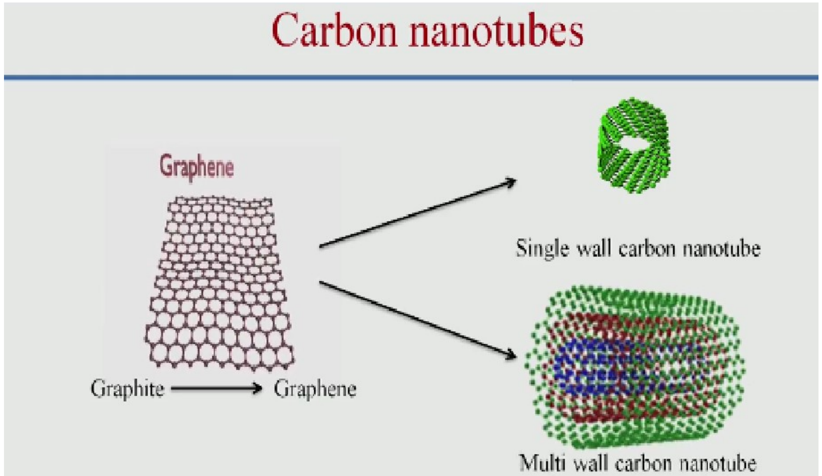


Figure 1 : Types of CNT

1.1. Types of CNT

1.1.1. Single walled carbon nanotube (SWNT)

By rolling a sheet of graphite along chiral axis we can get single walled nanotube. SWNT carries very large density of current without heating because of its ballistic nature of conduction of electrons and photons. Carbon materials have excellent thermal conductivity, electrical conductivity, specific heat capacity. Its structure is 1-dimensional axial symmetry. SWNT can be produced by placing a small amount of iron a dimple in a cathode and mixture of benzene and argon atmosphere is very necessary in this method. This method is called arc discharge method. SWNT can also be produced by evaporation of hot transition metal containing carbon and followed by condensation cold finger. Single-walled carbon nanotubes can be created in different design such as Chiral, Zigzag and Armchair. The CNT design depends on the method of wrapping graphene into a cylinder. For example, one design can be formed by rolling the paper from its corner and other design can be created by rolling the sheet of paper from its edge.

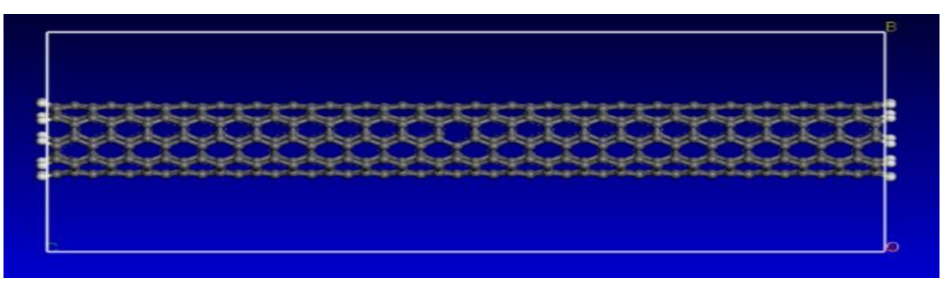


Figure 2 : Molecular model of SWNT (5,5)

Nanotube's electrical properties can be directly affected by its design. The nanotube will be called as metallic (highly conducting) when n - m is a multiple of 3, otherwise the nanotube is a semiconductor. The Armchair design is always metallic while other designs can make the nanotube a semiconductor. SWNT can be categorized as- Armchair type, Zigzag type and chiral type. It has been discussed below-

(i) Armchair Type CNT

The type of CNT as shown in Fig.3. is an achiral nanotube and it has been decided on basis of "Symmetric classification", achiral means the nanotube structure is symmetrical; When chiral vector becomes n = m, then Chiral = (n, n). The value of chiral angle (θ) is 30°, we call it as armchair.

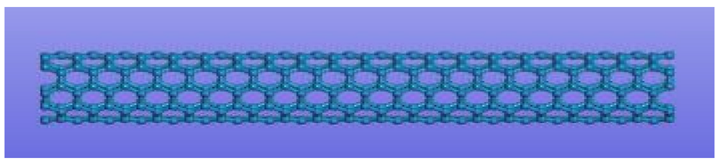


Figure 3 : Armchair SWNT

(ii) Zigzag Type CNT

When chiral vector becomes, m = 0, then Chiral = (n, 0). The angle of chirality (θ) is 0°, We term it as Zig-Zag type of CNT, and it is shown in Fig.4.

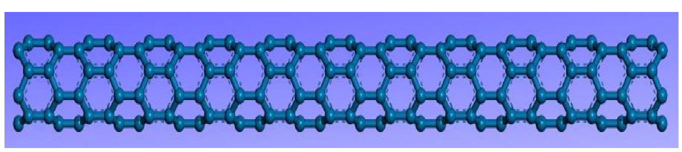


Figure 4 : Zigzag SWNT

(iii) Chiral Type CNT

The nanotube is with a spiral symmetry is called as chiral and it does not give it a mirror image. A chiral nanotube has general n and m values, therefore Chiral = (n, m). The angle of chirality (θ) lies in between 0 and 30, therefore $0° < θ < 30°$, it is depicted in fig.5.

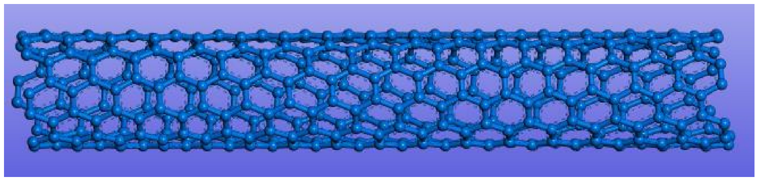


Figure 5 : Chiral CNT

1.1.2. Multi-Walled Carbon Nanotube Structure

Multi-walled CNT can be produced by evaporation of carbon from anode and deposition at cathode. CVD grown carbon nanotube is impure in comparison to arc discharge carbon nanotube. It happens due to the presence of Nano catalyst particles. MWNT structures grown by the CVD process are high defect densities prone and this is the major drawback of this CVD technique. MWNT is five times stronger than carbon fiber.

1.2. Production of CNT

There are many methods available which is being used for producing carbon nanotube, some of them are discussed here:

1.2.1. Arc Discharge Method

Carbon arc discharge method is most commonly used method for producing CNT in easy way. By using this method, CNT can be separated from catalytic metals and soot by the help of produced complex components. CNT are produced by using Arc vaporization and in this method two carbon atoms will be placed in an enclosure from end to end and will be separated by 1 mm. Usually Inert gas is filled in the enclosure at low pressure. A direct current of 50 to 100 A between two electrodes is applied for creating a high temperature discharge. By the high temperature discharge carbon electrodes surface gets vaporized and thus a small electrode (rod-shaped) gets formed. In high yield the CNT production is fully dependent on plasma arc uniformity. CNT can also be produced with liquid nitrogen by arc discharge method.

1.2.2. Laser Method

In 1996, for producing CNT a technique was used called as a dual-pulsed laser. This synthesizing technique was produced CNT with purity of 70 %. Nowadays, for producing CNT laser vaporization process is being used. In this process produced CNT are having diameter 10–20 nm more and 100 µm or more in length. Average diameter and size distribution for CNT depends on catalyst composition, growth temperature and other process parameters. For producing high quality CNT in small amount laser vaporization and arc discharge methods are used in recent years. These two methods are also having some drawbacks like:

(1) Evaporation of carbon source is being used in this method and for scale up the production with industrial standard it follows an unclear approach.

(2) The produced CNT get mixed with residues of carbon in the arc discharge method. Therefore, purification, manipulation and assembling of CNT for building nanotube device architectures for practical applications is quite difficult.

1.2.3. Chemical Vapour Deposition

In this process, by catalytic CVD of acetylene CNT in large amount can be produced over cobalt and iron. Along with the MWNT fullerenes and bundles of SWNT can be produced by the carbon/zeolite catalyst. At 1000ºC high yields of SWNT can be obtained by Catalytic decomposition of H_2/CH_4 mixture over nickel, iron and cobalt. In this method by using the decomposition of CH_4 over the newly formed nanoparticles lower proportions of MWNT and higher proportions of SWNT can be achieved.

1.2.4. Ball Milling

Ball milling is one of the simple methods for producing the CNT followed by subsequent annealing. From boron nitride powder and carbon CNT can be produced by thermal milling. In this method, in a stainless-steel container which consists of four hardened steel balls the graphite powder will be placed. At room temperature, for milling process argon is introduced for up to 150h and the steel container is purged using the milling process, under an inert gas flow at 1400ºC for 6h the graphite powder is annealed. More MWNT and few SWNT can be produced by this method.

1.2.5. Other Methods

CNT can also be produced using flame synthesis, electrolysis, synthesis from bulk polymer, use of solar energy and low-temperature solid pyrolysis. In electrolysis method, an electric current is being in molten ionic salt between graphite electrodes for producing CNT. As a cathode high purity carbon rod is used. By consuming the cathode at high melting point, a broad range of CNT are produced. In the flame synthesis method, for functioning the hydrocarbon reagents at an elevated temperature a portion of the hydrocarbon gas.

1.3. Properties of CNT

CNT have extra ordinary mechanical, thermal and electrical properties and only carbon atoms rearrangement are responsible for these unique properties. Some of the properties are as follows:

1.3.1. Electrical Conductivity

Metallic CNT are highly electrical conductive material. Conductivity of CNT can be determined by chirality. Depending upon chiral axis, both the metallic as well as semiconducting properties can be exhibited by CNT. In case of MWNT, its electrical conductivity is very complex due to non-uniform distribution of current by inter-wall interaction over the individual tube. However, in case of metallic SWNT, it has been observed that current is uniformly distributed across different parts of metallic SWNT.

1.3.2. Strength and Elasticity

CNT acts as an ultimate high strength fiber. SWNT has higher modulus of elasticity than steel and it makes it as a highly resistant fiber. Although CNT can bend on pressing on the tip and it retains its original state when forces will remove. It has been reported that SWNTs are having young's modulus of elasticity is about 1Tpa.

1.3.3. Thermal Conductivity and Expansion

In graphene sheet carbon atoms are strongly bonded with three carbon atoms and due this strong in-plane bonding properties CNT can show properties like superconductivity below 20K. CNT are having extraordinary strength and stiffness against axial strains only due the strong C-C chemical bonding. Moreover, SWNT exhibit high flexibility against non-axial strains due to zero in-plane thermal-expansion and the greater inter-plane.

1.3.4. Field Emission

Field emission phenomenon can be observed when from metal tip to vacuum tunneling of electrons occurs by the strong electric field. It results from small diameter of nanotubes and the high aspect ratio. The field emitters are best for flat-panel displays application. Due to the emission of light and electrons the properties of field emission occur in MWNT.

1.3.5. Aspect Ratio

For CNTs, high aspect ratio is unique and exciting properties, inferring that similar electrical conductivity of other conductive additives can be achieved by applying a lower load of CNT. It has been observed that unique electrical conductivity has been possessed by high aspect ratio of CNT in comparison to the conventional additive materials such as chopped carbon fiber, carbon black, or stainless-steel fiber.

1.3.6. Absorbent

Due to the unique properties like superior electrical properties, extraordinary mechanical strength, larger flexibility and light weight, CNT and CNT composites have been emerging as perspective absorbing materials. Therefore, for using in water, gas and air filtration only CNT will be an ideal candidate.

1.4. Applications of CNT

The outstanding properties of CNTs make then very useful and thus expand its application area from thermal conductivity, field emission, conductive properties, energy storage, conductive adhesive, molecular electronics based on CNTs, thermal materials, structural applications, fibers & Fabrics, catalyst supports, biomedical applications, air & water filtration and some other applications.

1.5. Polymer

A polymer is defined as a macromolecule which is formed by the repeated combination of several simple molecules called monomers through covalent bonds. Polyester, Polyethylene, Teflon, PVC, Bakelite, Nylon, are the examples of polymer. Polymerization has been defined as “the chemical reaction in which monomer is converted into polymer”. Monomer needs the initiator, but it can’t undergo polymerization. In this study natural rubber has been taken as a polymer and has been created using material studio 8.0. Repeat unit has been taken as 10 and it is of a single chain. “Diene” library has been used for creating natural rubber in MD simulation.

1.5.1. Classification of polymers

a) Based on their origin polymer:

(i) Natural polymers: the polymers which are obtained from natural sources like plants and animal called natural rubbers. Starch, Protein, Cotton, Silk, Wool, Cellulose and Glycogen are the natural

(ii) Synthetic polymers: the polymers which are synthesized from simple molecule is called synthetic polymers. Polyethylene, polyester, Teflon, PVC and Nylon are the synthetic polymers.

b) Based on their thermal behavior:

(i) Thermoplastics polymer: The polymer which becomes soft on heating and hard on cooling are called Thermoplastics. Teflon, Polyethylene, PVC and Plexiglas are the thermosetting polymer.

(ii) Thermosetting polymer: The polymers which undergo chemical changes and cross likings on heating and become permanently rigid, hard and infusible are known as Thermosetting. Urea-formaldehyde resin, Phenol-formaldehyde resins and epoxy resin are the thermosetting polymers.

c) Based on their methods of polymerization:

(i) Addition polymers: The polymers which are formed by addition polymerization reaction in which self-addition of several olefin monomers to each other takes place without elimination of by products are called addition polymers. PVC, Polystyrene, Teflon and polyethylene are the addition polymers.

(ii) Condensation polymers: The polymers which are formed by intermolecular condensation reaction through functional groups of monomers with continuous elimination of by products are called condensation polymers. Nylons, polyesters and phenol-formaldehyde resins are condensation polymers.

1.6. Natural Rubber

Natural rubber consists of polymers of the organic compound isoprene, with minor impurities of some other organic compounds, and some water. Presently, rubber is harvested mainly in the form of the latex from the rubber tree or others. Forms of poly-isoprene that are used as natural rubbers are called as elastomers. Natural rubber is used in many products and application, either alone or in combination with other materials. In most of its useful forms, it has a high stretch ratio and high resilience, and is highly waterproof. The earliest use of natural rubber was by the civilization of Mesoamerica. Natural Rubber exhibits unique chemical and physical properties. Natural Rubber's stress–strain behavior shows the Mullins effect and the Payne effect and is often considered as hyper-elastic. The presence of a double bond in each repeating monomeric unit makes natural rubber sensitive to ozone cracking and susceptible to vulcanization. The two major solvents for rubber are naphtha and turpentine. Since rubber does not dissolve easily, the material is divided finely by shredding prior to its immersion. An ammonia solution is generally used to prevent the coagulation of raw latex. Natural Rubber begins to melt at approximately 180°C or 356°F.The modelling model of natural rubber is shown in fig.6.

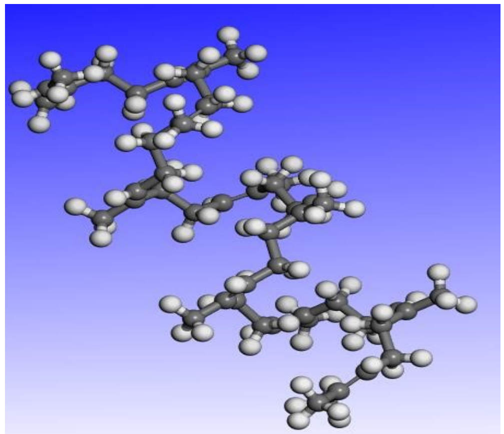


Figure 6 : Molecular model of 10 repeat units of 1 NR chain consisting of 132 atoms.

1.7. Properties of Natural Rubber

The bulk mechanical and thermal properties for continuum scale analysis are highly dependent on experimental study. Molecular simulations provide an excellent opportunity to easily study the influence of nanoparticles on the structure and dynamics of polymers, for detailed information on the properties near a nanoparticle surface is difficult to obtain experimentally. Natural rubber possesses excellent abrasion resistance, tear resistance and resilience properties.

1.8. Functionalised CNT polymer composites

Addition of additional functional groups to the surface of any material is called functionalization. In other words, it is the process of adding new features, functions, properties, or capabilities to a material by changing the surface properties of the material. It is a basic technique used throughout materials science, chemistry, biological engineering, and nanotechnology. A pre-functionalized CNT, is to be mixed with polymer matrix by any of the composite forming methods.

Types of Functionalization:

1.7.1 Non-Covalent Functionalisation
1.7.2 Pi-stacking
1.7.3 Defect Functionalisation
1.7.4 Endohedral Functionalisation
1.7.5 Sidewall Functionalisation

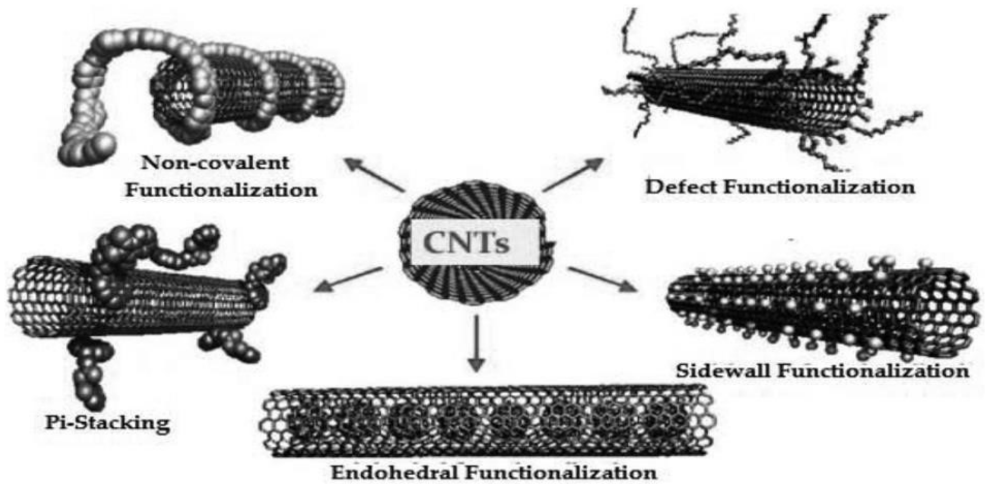


Figure 7 : Types of functionalisation [3]

For this study sidewall functionalization is chosen, as it is very advanced, and a proper care is taken to maintain the structural symmetry as well.

1.8. Molecular Dynamics

By using MD simulation any complex simulation can be performed. In molecular dynamics a molecule is described as a series of charged points linked by springs. There are following methods available for carrying out computation like molecular mechanics, molecular dynamics, Monte Carlo, Free energy and solvation methods, structure/activity relationship and many other established procedures. It is the only method available for solving complex body problems. Hamiltonian is not known to us until we calculate the quantum many-body problem. It requires lots of approximations, so it is not possible in most of the cases. For solving complex many-body systems Molecular simulations are the only method available there. Experiments are expensive and limited in many cases. Experiment can be complemented by the simulations. Even at a single molecule level molecular level understanding can be provided by the molecular dynamic simulation. Molecular dynamics can be performed using following steps:

Step 1. Create molecule like nanostructure, polymer etc.

Step 2. Packing of a composite system using "amorphous cell module".

Step 3: Geometry optimization using forcite tools.

Step 4: Dynamics using forcite tools, Using NPT (Constant pressure, constant temperature), "Nose" as a thermostat and "Berenderson" as a Barostat.

Step 4. Geometry optimization using forcite tools, for minimizing the energy and for stabilization of structure.

Step 5. Dynamics using forcite tools, Using NVT (Constant volume, constant temperature), "Anderson" as a thermostat.

Step 6. Geometry optimization using forcite tools, For stabilization of structure.

Step 7. Mechanical properties, by using forcite tools and constant strain method.

1.9. Universal testing machine (UTM)

UTM is most widely used machine when it comes to test tensile or compressive strength of any material. It is used to test mechanical properties of any material. For compression test, the specimen is just placed in between two jaws and a compressive force is applied, the results can be obtained from the digital machine display. Similar is the case of tensile testing, in which the material is pulled outside i.e. tensile force is applied on the material and similarly results can be obtained from the digital machine display.

Chapter 2

Scope of the Study

This study focuses on CNT-reinforced polymer nanocomposite. CNT can play an excellent role in the polymer nanocomposite and it has been proved by many studies conducted by researchers. So, a SWNT reinforced with natural rubber is taken to form CNT-polymer composites. Analysis of mechanical properties of CNT-NR composites is done when SWNT is not pristine but functionalized with various groups like -OH, -COOH, $-COOCH_3$. By using SWNT as a reinforcing agent, mechanical properties like young's modulus of the polymer nanocomposite can be easily enhanced, which further can be enhanced by using functionalized groups. The most suitable functional group can be applied for practical uses. By adding a few functionalized CNT with natural rubber, we can achieve the strength of composite same as the graphite fiber. So, it will be the best option for removing graphite fiber in coming years because it costs less than graphite fiber and having equal strength. Compared to the other CNT-polymer matrix composite can easily be made because of easy techniques. Very wide application area of both CNTs and natural rubber will expand it further when both used as a composite material.

Chapter 3

Objectives of the Study

Main objectives of this study are:

- To find mechanical properties of SWNT-NR composites, when SWNT is functionalised with various groups like -OH, -COOH, $-COOCH_3$.
- To compare mechanical properties of SWNT-NR polymers with varying functional groups.
- To compare mechanical properties obtained by molecular dynamics simulations to that of experimental observation on UTM.

Chapter 4

Literature Review

E. T. Mickelson et al. (1999) [4] formed "fluorotubes" by fluorinating the pristine SWNT. Fluorotubes were then solvated in alcohol solvents using "ultrasonication". Atomic force microscopy (AFM) was used for the examination. Elemental analysis and number of microscopy and spectroscopies were used for accurate results. It was observed that SWNTs can be fluorinated or functionalized with fluorine and sonicated in alcohol to give highly stable fluorotubes. This solvation technique allows us to manipulate functionalized SWNTs in numerous ways. Important point is that alcohol solvent was used in this research which itself help in further functionalization, and stability of Fluro tubes.

Ya-Ping Sun et al. (2002) [5] attempted to identify and analyze properties as well as applications of functionalized CNTs. It was observed that CNTs can be functionalized through esterification and amidation of the nanotube-bound carboxylic acids. The dissolvability of the functionalized CNTs makes it conceivable to describe and contemplate the properties of carbon nanotubes utilizing arrangement based strategies. Agent comes about concerning the solvency, de-functionalization, scattering, and optical properties of the functionalized carbon nanotubes were displayed. Functionality and solubility of functionalized CNTs were found to be up to the mark.

Haiqing Peng et al. (2003) [6] reacted SWNTs with glutaric acid acyl peroxides with o-dichlorobenzene at a temperature of around 80-90 degree centigrade, to get three carboxy-propyl groups on the side walls of SWNT. FTR, Raman spectroscopy, and transmission electron microscopy (TEM) was done for better results. In examination with the perfect or pure SWNTs, the functionalized SWNTs were found to be demonstrating an enhanced dissolvability in polar solvents, for instance, alcohols and water, which empowers their preparing for joining into polymer composite structures and additionally for an assortment of biomedical applications.

N.O.V. Plank et al. (2004) [7] functionalized SWNTs using traditional Reactive Ion Etching to get fluorinated SWNTs when reacted with CF_4 and SF_6. The functionalized SWNTs were then examined with X-ray photoelectron spectroscopy. Microscopic plasma parameters including ion current density and fluorine pressure within the plasma were also studied using a Langmuir probe and optical emission spectroscopy. This process of making functionalized SWNT is found to be reliable as fluorine was attached to SWNT for a longer period.

Bumsu Kim et al. (2004) [8] oxidized MWNTs using nitric and sulfuric acid (in in ratio of 1:3) that is ultrasonication of MWNTs. Complex development of charged gold nanoparticles and negative MWNTs was accomplished of and without polyelectrolyte coatings by electrostatic collaboration. The perplexing arrangement was described by high-determination transmission electron microscopy and dispersive X-ray spectroscopy. This technique is more of a fault detection than a composite formation.

M.C. Paiva et al. (2004) [9] functionalized CNTs with vinyl group were reinforced into PVA matrix and mechanical as well as morphological properties were observed. Both Pristine as well as functionalized SWNTs were tested under tension, it was observed that functionalized SWNT is superior to pristine SWNT in every aspect of mechanical properties. CNTs were wetted well by PVA matrix, in case of functionalized SWNT, as per SEM results.

Ramanathan et al. (2005) [10] Single-walled carbon nanotubes (SWCNT) functionalized with amino groups were readied through chemical adjustment of carboxyl groups presented on the carbon nanotube surface. Two varying methodologies (amide and amine-moieties) were utilized to create the amino-functionalized nanotubes. The amino-end permits promote science of the functionalized SWCNTs and makes conceivable covalent bonding to polymers and natural frameworks, for example, DNA and sugars. The functionalization of the SWCNTs was also portrayed in detail utilizing FTIR and XPS.

L.Liu et al. (2005) [11] observed mechanical properties of nanocomposites of functionalized SWNTs -polyvinyl alcohol. Absorption spectroscopy was used, and sidewall functionalization was obtained via chemisorption. It was observed that functionalized CNTs produce comparatively better young's modulus than pristine CNTs for the composite case with PVA matrix. Hydroxyl groups were found to increase interfacial properties to a significant extent.

Jie Liu et al. (2006) [12] used free radical addition using aryl to do sidewall functionalization of SWNTs. They reported another SWNT functionalization technique using 4-methoxyphenyl free radical expansion. The 4-methoxyphenyl radicals were produced via air oxidation of 4-methoxyphenylhydrazine hydrochloride. Raman spectroscopy demonstrate the covalent idea of the bond among the nanotubes and the functional groups. The XPS and TGA information outfit quantitative data on the level of functionalization.

Prabhjeet singh et al. (2009) [13] did Esterification and fluorination at different conditions to obtain functional groups as ester and fluorine on the surface of CNT, Organic functionalization process were used for this research and results obtained says that process-ability and capability is more in the case of functionalized CNTs.

Robert Menzel et al. (2010) [14] used a solvent-free, versatile methodology to functionalize CNTs. The conveyance of the functionalized destinations was researched at the infinitesimal scale utilizing labelling responses. The joined items have been described by electron microscopy, thermal analysis (TGA), inverse gas chromatography (IGC), and Raman spectroscopy.

Ailin Liu et al. (2011) [15] observed the impact of functionalization SWNTs on the damping attributes of SWNT-based epoxy composites by means of multiscale analysis. Carboxylic (-COOH) group was used to functionalize the SWNT, and epoxy was used as matrix. Results were obtained using molecular simulations. It was observed that as the number of functional groups increases, the interfacial shear strength also increases. Though, the damping properties did not follow any general trend, unpredictability was observed in case of damping properties.

Hailong Chen et al. (2012) [16] used Methoxy Polyethylene Glycol Amine as functional group and used micro RNA analysis for functionalizing SWNTs. This type of approach to do functionalization find its application in the field of biology, as it makes drug delivery easy.

Valentini Lara et al. (2014) [17] used radial deformation method to functionalize CNT with carboxylic groups. In this research the reliance of the basic and the electronic properties of functionalized (5, 5) SWNTs were examined through ab initio thickness utilitarian simulations when the carboxyl gathering is fortified on the bended or flatter areas. Radial deformations result in measurement diminishing of up to 20 for each penny of the first size of diameter, which was the breaking point decrease that keeps up the SWNT functionalized structure. Changes on the electronic structure were seen because of the symmetry break of the SWNT caused by both the carboxyl group and the C–C bond twists came about by the radial deformation. It was concluded that the functionalization procedure is uncommonly supported by the sp_3 hybridization actuated on the more bended district of the twisted SWNT.

Zahra Mohammadi et al. (2015) [18] did a relative report on non-covalent functionalization of CNTs by chitosan, as functional element, and its subsidiaries for conveyance of doxorubicin. This type of approach to do functionalization find its application in the field of biology, as it makes drug delivery easy. It was observed that applying Carboxymethyl Chitosan rather chitosan for functionalization prompted 10% expansion in stacking productivity.

E.V. Basiuk et al. (2015) [19] used amines to do solvent free functionalization of CNTs. In this study filtration of the MWCNTs-ox scatterings created uniform perfect BP mats, promptly expelled from their fundamental help membranes. The tangle thickness as measured by SEM and HeIM differed in the scope of 35-50µm. The maximum amine content, as examined from

TGA curves, was found for BP-ODA, and the minimum one was found for BP-DAN. Though, it is accurate, but expensive approach for functionalization.

Kong N. et al. (2015) [20] used a different approach for functionalization of CNTs. In outline, they proposed a successful strategy to conjugate carbohydrate structures to perfect SWNTs utilizing microwave-helped response of perfluoro phenyl azides. This was the first case of applying microwave radiation to PFPA actuation, speaking to another approach to integrate carbon nanotube-based glyconanoparticles. This strategy utilized pristine SWNTs rather than oxidized SWNTs, maintaining a strategic distance from broad modification to the cross section and the inherent properties of SWNTs. The subsequent materials were less packaged and very much scattered in water contrasted with pristine SWNTs.

Vinay Deep Punetha et al. (2016) [21] did a comparative analysis between CNT and graphene based on the nanocomposites formed by functionalization of CNTs. Mechanical, electrical, and thermal properties was compared, and it was found that CNT as well as graphene both shows remarkable properties. It was reported that the only different arises with their compatible polymer matrix.

Ge Tian et al. (2016) [22] observed substituent impacts in p-stacking of histidine on graphene and functionalized-SWNT. Molecular simulation was run for SWNT zig-zag (10,0), three varying groups –COOH, –OH and $–NH_2$, were attached directly on the sidewalls of the SWNT structure. The results show that the pi-stacking for functionalized-SWNT is weakened.

Sumit Sharma et al. (2016) [23] used molecular dynamics simulations to analyze functionalized SWNT-polymer nanocomposites; In this research both dynamics as well as mechanical properties of SWNT with varying functional groups were observed. Armchair (4,4) SWNT was chosen and molecular simulation was done with proper consideration of practical environment conditions. Aspect ratio was fixed to 10. It was reported that functionalization reduces the young's modulus of SWNT, the largest reduction was observed in case of carboxylic (-COOH) functional group.

Chapter 5

Materials and Equipment

5.1 SWNT (Single-walled carbon nanotube)

By rolling a sheet of graphite along chiral axis we can get single walled nanotube. SWNT carries very large density of current without heating because of its ballistic nature of conduction of electrons and photons.

SWNT properties:

- High electrical conductivity
- Very elastic
- High tensile strength
- Low coefficient of thermal expansion
- Highly flexible
- High thermal conductivity

5.2 NR (Natural Rubber)

Natural rubber consists of polymers of the organic compound isoprene, with minor impurities of some other organic compounds, and some water. Presently, rubber is harvested mainly in the form of the latex from the rubber tree or others.

NR properties:

- Good elongation
- Good compression strength
- Moderate tensile strength
- High abrasion resistance
- Very high resilience

5.3 Material Studio

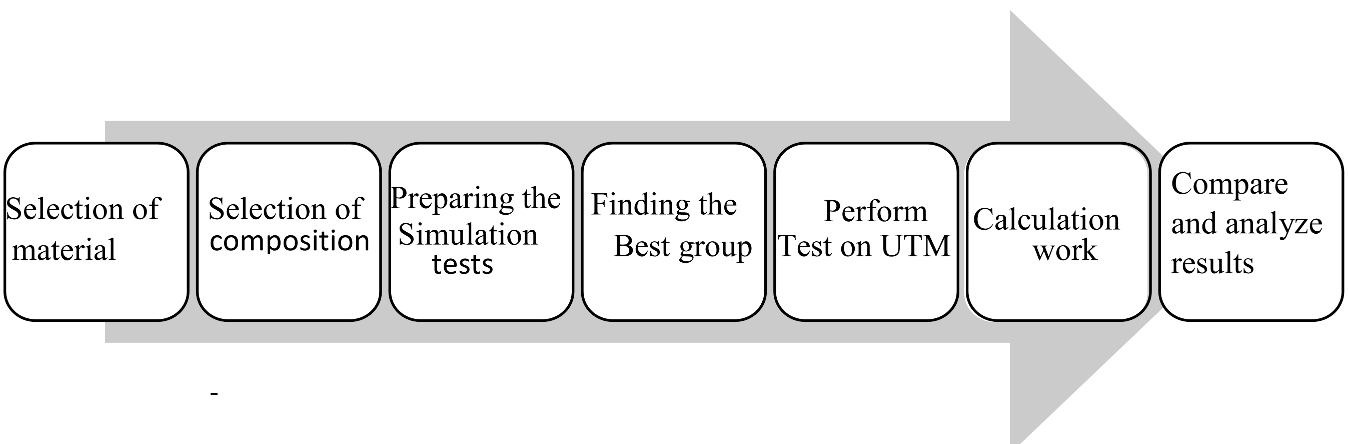
Materials Studio is a software that is used for modelling materials and run simulations. It is developed by BIOVIA. This software is widely used for advanced researches in:

- Computational chemistry
- Bioinformatics
- Molecular dynamics simulation,
- Quantum mechanics.

Chapter 6

Test and methodology

1. Selection of proper material (SWNT, functional groups and NR)
2. Selection of composition (SWNT 8% Volume fraction)
3. Molecular Dynamics simulation (For SWNT reinforced in NR matrix)
4. Choose best functional group for experimental work.
5. Mechanical strength test of functionalised SWNT on UTM.
6. Calculation of mechanical strength as per UTM results.
7. Comparison of experimental and molecular dynamics based work.



Chapter 7

Work plan and timeline

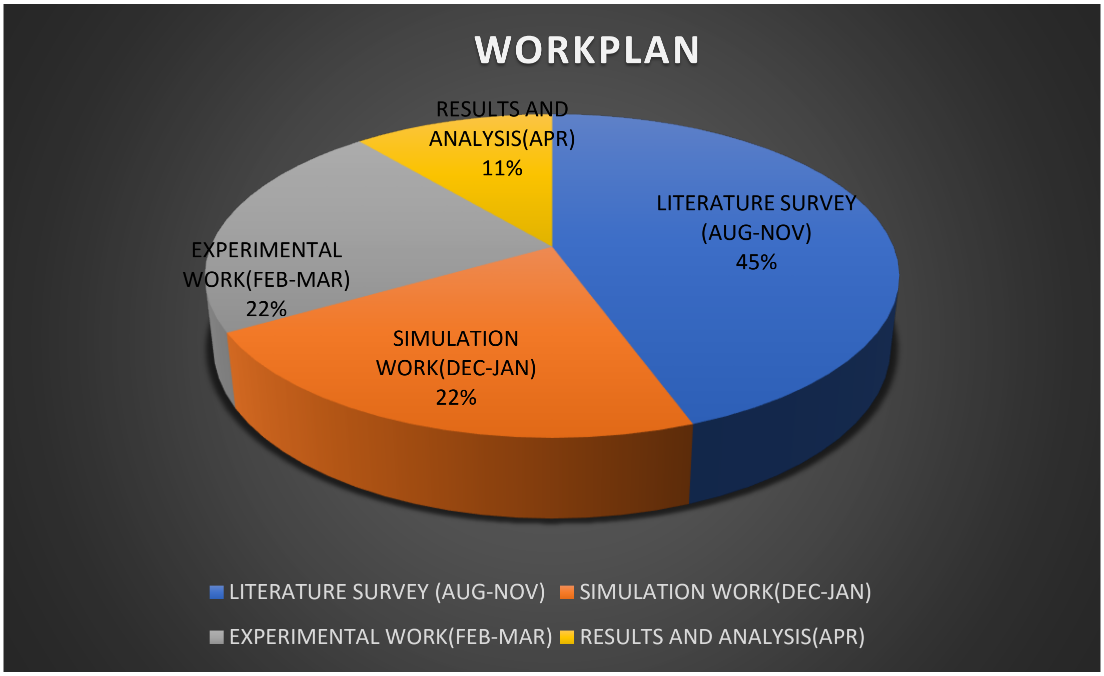


Figure 8 : Work Plan Pie-Chart

The research work started in August and will end by April next year. As clear from the pie chart literature review took most of the time as it is the most crucial work in identifying a research gap and took four months. Experimental and simulation work is supposed to take two months each i.e. the months from December to March. It involves molecular simulation in material studio followed by collection of material and performing the experiment. One more month i.e. April, is supposed to be consumed by result analysis.

Chapter 8

Expected Outcomes

It is expected that the new composite formed will be of high strength, low cost and of wide use. Though the strength of the natural rubber is less than the CNTs, but natural rubber enjoys properties like resilience and elasticity, so composite of the two is expected to be of a greater quality. Also by adding some functional groups, properties of CNT are supposed to be improved. If not all, it is expected that some of the functional groups will add on to the mechanical properties of the SWNT.

Chapter 9

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