

# **NANO COMPOSITES**

## **STUDY ON THE PROPERTY ENHANCEMENT OF NATURAL RUBBER , CARBON NANOTUBE COMPOSITES WITH IONIC LIQUID AS COMPATIBILIZER**

### **MINOR RESEARCH PROJECT (XI<sup>th</sup> PLAN)**



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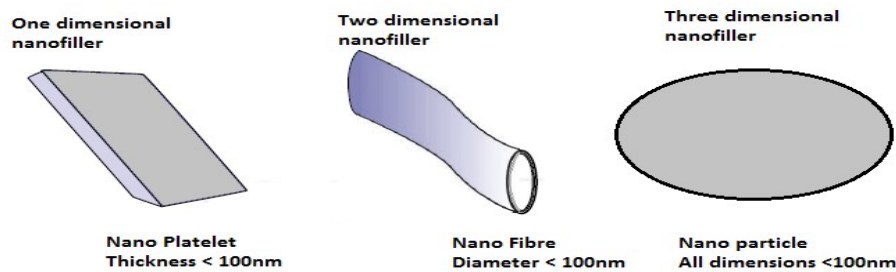
## **Section 1**

### **INTRODUCTION**

A composite material is an engineered or a naturally occurring material made from two or more constituent materials, with significantly different physical or chemical properties, which remains separated and distinct at a macroscopic or microscopic scale within the finished structure. Now a days, nanoparticle filled polymer composites have emerged as one of the important materials that have attracted more attention because they usually exhibit much better performance properties than traditional composites. The usual methods to synthesize nanocomposite are sol-gel, in situ polymerization, intercalation polymerization, blending as well as other methods. An organic/inorganic hybrid nanocomposite provides strong, lightweight and inexpensive polymers for automotive and packing applications.

Polymer is the most widely used matrix material in composites due to their light weight and they are easier to be shaped than metals or ceramics. Polymers materials are soft, have low strength, low electrical conductivity and low thermal stability. Polymers have wide industrial applications. The use of fillers for enhancement of polymer properties dates back to the earliest years of the polymer industry. Initially they are considered as the extending agents to reduce the cost of polymer based products, fillers were soon recognized as an integral component in many applications involving polymers, particularly in reinforcement. Polymer nanocomposites are composites which consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix.<sup>2-9</sup> It has been expected that nanocomposites could provide superior physical properties, because of the high surface-to-volume ratio of nanometer scale reinforcing fillers embedded in the

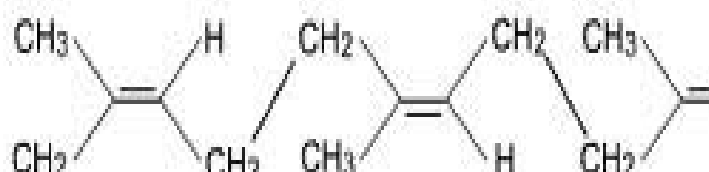
matrix, compared to the conventional fiber or particle reinforced composites. These materials are of great interest and they are rapidly growing new class of materials alternative to conventional filled polymers and polymer blends. The importance of polymer nanocomposites is not only based on the mechanical property enhancement but also due to the value-added properties without losing the inherent properties of the polymer material. Three types of fillers can be distinguished, depending on how many dimensions are in the nanometric range



## Natural rubber

Natural rubber (NR) is a high molecular weight polymer of isoprene (2-methyl,3-butadiene). It is commonly obtained from the latex of the *Hevea brasiliensis* tree and is the oldest known rubber and the most versatile one for fabrication into rubber products [1]. According to the survey of 2006, the worldwide consumption of rubber rose to 21.5 million tones. This statistical report explored the inevitability of rubber goods in the day to day life of human beings. The dominant market for rubber is the automotive industry, in the manufacture of tires and inner tubes. Other industrial rubber goods include various belts, hoses, oil seals, and gaskets and so on. Due to high and reversible deformability of natural rubber is of great industrial importance. However, its initial modulus and durability are low, and an additional reinforcing phase is required for practical use [2–4]. Carbon black and silica particles have been extensively used for this purpose [5–8].

Natural rubber is a high molecular weight polymeric substance with viscoelastic properties. Chemically it is cis 1,4-polyisoprene. Isoprene is a diene and 1, 4 addition leaves a double bond in each of the isoprene unit in the polymer. Due to this feature, natural rubber shows all the reactions of an unsaturated polymer. It gives addition compounds with halogens, ozone, hydrogen chloride and several other reactants that react with olefins. An interesting reaction of natural rubber is its combination with sulphur. This is known as vulcanization. This reaction converts the plastic and viscous nature of raw rubber into elastic. Vulcanized rubber will have very high tensile strength, hardness, abrasion resistance and low elongation properties compared to natural rubber. Because of the unique combination of these properties, natural rubber finds application in biological, economic and industrial fields. The structure of natural rubber can be represented in figure below.



**Structure of Natural rubber**

#### **Characteristics of Natural rubber**

Specific gravity	0.92
Refractive index	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 Cal/cc.
Heat of combustion	10547.084 Cal/g

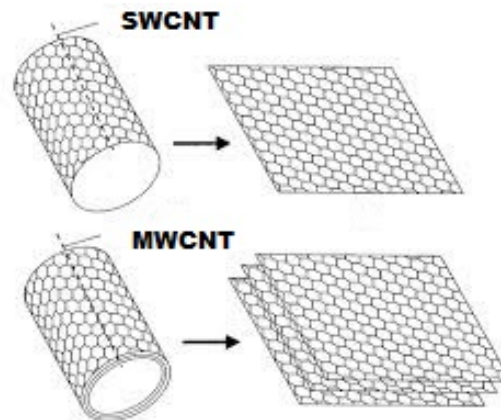
Thermal conductivity	0.00032 Cal/sec/cm/°C
Dielectric constant	2.37
Power factor (at 1000 cycles)	0.15-0.2
Volume resistivity	1015 ohm.cm
Dielectric strength	3937 V/mm

## Carbon Nano tube

Owing to the high modulus, aspect ratio and excellent thermal and electrical properties of carbon nanotubes have been used as reinforcing filler in elastomers instead of conventional fillers such as carbon black and silica. CNTs are also interesting because of their nano-sized diameter and micrometer length in combination with extraordinary thermal and mechanical properties, and high electrical conductivity.

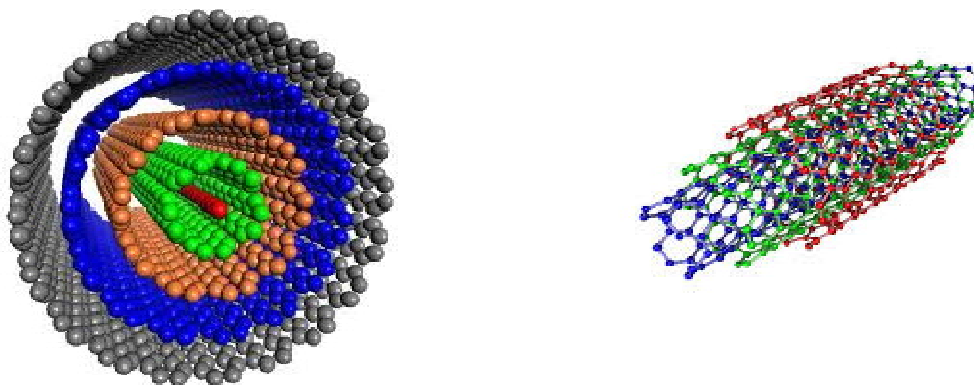
Carbon can exist in several allotropic forms at room temperature like graphite, diamond, carbon clusters (e.g., C<sub>60</sub>-buckminster fullerene) and nanotubes. Carbon nanotubes (CNTs) were discovered by Iijima as an electron microscopic marvel in 1991<sup>11</sup>. Since then, there has been intense activity related to the synthesis, structure, properties and applications of CNTs. A carbon nanotube is a graphene sheet rolled into a cylindrical structure typically several nanometers in diameter and the ends are capped with half fullerene balls. They are unique nanostructures with interesting electrical and mechanical properties which is a result of their close relation between the carbon nanotube and graphite and due to their one-dimensional aspect. The strength of the sp<sup>2</sup> carbon-carbon bonds in the nanotubes gives them amazing mechanical properties. The formation of CNT by rolling up the graphene layer can be schematically represented as shown in figure 1.3. The properties of the nanotubes depend on the

arrangement of the graphene sheets (how the sheets are “rolled”), the diameter and length of the tubes and the nanostructure. Single-walled carbon nanotubes (SWCNTs) are considered as the simplest member of the family of CNTs, consisting of one graphitic sheet, which has been rolled up into a cylindrical shape. CNT can be metallic or semiconducting depending on the arrangement of the hexagon rings along the tubular surface.



**Figure 1.3: Formation of CNT by rolling up the graphene layer**  
**Multi-walled carbon nanotube (MWNT)**

The concentric arrangement of several SWNTs of slightly varying diameter is termed as Multi-walled nanotubes (MWNTs). They consist of multiple layers of graphite rolled in on them to form a tube shape. A three dimensional model of MWNT is shown in Figure 1.4. The distance between these layers is close to the graphene layer distance in graphite. Thus MWNTs are considered as a coaxial assembly of several SWNTs separated from one another by 0.34 nm, which is slightly more than the interlayer distance in single-crystal graphite.



**Figure 1.4: Three dimensional model of MWNT**

Today natural rubber products fulfill important functions in almost all areas of daily life. Their performances depend on the right combination of rubbers, rubber chemicals and reinforcing filler systems. Various reinforcing fillers are used in rubber industry, e.g. carbon black, silica, kaolin. However, the reinforcement is not so effective for natural rubber due to large dimension and agglomeration of these traditional reinforcing materials. Therefore, it is essential to exploit a new way to enhance the mechanical properties of natural rubber products. Polymer composites based on CNTs show an increase in tensile strength, young's modulus[9]. The change is not remarkable due to poor adhesion weak van der Waals forces, which give rise to lower stress transfer ability in the composite[10]. In order to achieve high stress transfer, strong bonding between CNTs and polymer chain is necessary. Recent reports on the chemical compatibility and dissolution properties of CNTs have promoted a great deal of interest in developing modification or functionalization of their surface [11]. Extensive research has been done by incorporating different types of CNTs as



nano-reinforcements, nano-wires and nano conductors into polymeric materials to form new composites that possess high mechanical strength, electrical and thermal conductivity[12,13,14]. Good interfacial adhesion between CNT and polymer is essential to enhance the mechanical properties of the polymers-CNT composites [14]. In order to ensure better rubber/ carbon nanotube compatibility and to enhance the dispersibility a series of Ionic Liquids can be applied to improve interaction between Natural rubber and carbon nanotubes [16].

In recent times Ionic liquids (IL) in the field of chemical science is drawing attention in many ways. IL is emerging as a class of chemicals and they already have consolidated their status to offer new scope of applications in chemical science. ILs, the **green solvents**, are in the forefront of research activities. They have tendency to act as electrolyte with high conductivity, high electrochemical stability, non volatility, and non flammability. Room temperature ionic liquids (RTILs) have generated interest in recent years because of their unique properties and potential applications in various fields which make them striking substitute to various volatile organic solvents. Recently RTILs can also be employed as solvents in polymerization reactions to replace conventional solvents [17]. ,

## Section 2

## REVIEW

To attain good mechanical properties in accordance with the end use application the elastomers have to be reinforced with particulate fillers such as carbon black and silica. Usually a high percentage, around 20–40 wt% conventional fillers are needed to get adequate reinforcement depends on the application. There are certain drawbacks associated with these traditionally filled rubbers. A higher content of filler: (i) reduces the processability and (ii) increases the weight of the final product. Arroyo et al. [18] have compared the reinforcement imparted on NR upon the addition of organo clay and carbon black. They observed that the mechanical properties of NR with 10 phr organoclay have been comparable to the compound with 40 phr carbon black. Bhattacharyya et al. [19] have reinforced natural rubber using carboxylated multiwalled carbon nanotubes (c-MWCNT) dispersed with sodium dodecyl sulfate. Use of different type of surfactants, especially non-ionic type surfactants, has been reported to facilitate the dispersion of CNT in polymer matrix in aqueous and organic medium by non-covalent adsorption of surfactants and polymers [20]. However, the presence of surfactant might alter the composites properties by different ways. As for example, a non-ionic surfactant was used for the preparation of polycarbonate composites and it was found that the crystallization of polycarbonate was markedly induced and ultimately, the composite lost the transparency and its mechanical properties [21]. Typically in rubbers, the remaining surfactant in the matrix also affects the curing behavior and the vulcanizates properties might be deteriorated. In situ functionalization of CNTs may be one of the alternatives to avoid surfactant in the CNT rubber composites. In the present paper, ionic liquids have been used for in situ modification of CNTs as well as it has been utilized as a coupling agent between CNTs and rubber.

The imidazolium based ILs attracted the attention of wide scientific community because they are moisture and air stable. Because of their unique properties, ILs play a potential role in electrochemical batteries [22], actuators and electrochromic devices[23]. A serendipitous finding of Fukushima et al. provides a new possibility to modify CNTs using ILs [24]. Upon being ground into ILs, CNT bundles are untangled and the resultant fine bundles form a network structure which is due to the specific interaction between the imidazolium ion component and the  $\pi$  – electronic nanotube surface. By using IL modified single-walled carbon nanotubes (SWCNTs), an elastic conductor based on vinylidene fluoride–hexafluoropropylene copolymer coated with PDMS has been developed for the construction of electronic integrated circuits [25]. A study employing ILs as coupling agent between MWCNTs and diene elastomer has been reported[ 26].Subramanian et al [27] reported the influence of Ionic Liquid on carbon nano tube based elastomeric composites. Stenhauser D et al [28] studied the influence of imidazolium type IL on relaxation behavior of CNT based poly chloroprene nano composites.

While CNTs have been widely used with different kinds of polymers, there are rather fewer works dealing with the applications of IL in Natural rubber CNT composites for reinforcement. The motivation of this study is to develop high performance Natural Rubber - carbon nanotube composites with the help of specific ionic liquid.

### **Section 3**

## SCOPE

The filler dispersion and the rubber/filler interfacial bonding are two critical factors in determining the performance of the filled rubber composites. Conventionally, the surface treatments with various modifiers such as Ionic liquid have been used to improve the filler dispersion and strength the rubber/CNT interfacial bonding. Ionic liquid (IL), a kind of fascinating molten salt with nearly zero vapor pressure and high thermal stability, has demonstrated high affinity toward various kinds of solid, such as carbon nanotubes, silica and clays. Ionic liquid not require any other solvent for the dispersion of CNTs at the same time processing of taking CNTs become very simple. Ionic liquids are non volatile, non flammable and environment friendly dispersant for Multiwalled carbon nanotubes in rubber matrix. By taking Ionic liquid as dispersant no structural disruption of CNTs. Various interactions, including cation- $\pi$  interaction, van der Waal force, delocalized electron interaction, hydrogen bonding have been well acknowledged and therefore subjected to a plenty of applications. ILs with specific structure can be employed as possible interfacial modifiers for various filled polymer composites. With rapid advancement of nanotechnology in rubber industry leading to high-performance nanocomposites to meet the increasing demand of aerospace industry for extremely high operating temperatures and extended material service lifetime, improved thermal stability and air/water/oil resistance, this NR-CNT-IL composites can apply for the above application. An enhanced surface area of CNTs, given by the high dispersion with ionic liquids, is not only beneficial for electrochemical applications, such as sensors, capacitors, and actuators, but also allows for the efficient covalent modifications of CNTs. Because ionic liquids are ion conductive, their composites with electro conductive

CNTs are expected to be promising components for electrochemical devices, including solar cells. IL NR-CNT composites have been utilized in catalytic reaction in nano-scale catalyses, membranes for water treatment, super capacitors, sensor applications and many other applications.

## Section 4

## Analytical Techniques

Over the past decade, studies utilizing organoclay nanoplatelets in polymers to create nanocomposites having properties greater than their parent constituents have been accelerated. It has been demonstrated that both thermoplastic and thermoset nanocomposites reinforced by organoclay nanoplatelets lead to an excellent increase of elastic modulus. The clay nanoplatelets in their natural state exist as agglomerated tactoids; although an aspect ratio of each silicate nanolayers is extremely large ( $\sim 1000$ ). The reinforcing effect of the nanoplatelets on the elastic modulus of nanocomposites is maximized when each individual nanoplatelet is completely separated and homogeneously dispersed in the matrix. Additionally carbon nanotubes (CNT) are another major nanoreinforcement for polymers after CNT were discovered by Iijima in 1991, due to their splendid elastic modulus and strength,. Regardless of either clay nanoplatelets or CNT, the nanocomposites with heterogeneously dispersed nanoscale reinforcements possess a lower elastic modulus than a homogeneously dispersed system. The usefulness of rubber ranges widely from household applications to various industrial products; interestingly, the production of tires and tubes are rubber's highest applications. These rubbers are often reinforced by various reinforcements to substantially improve their mechanical properties . For example, it is known that carbon black (CB) and inorganic fillers are used as additives to rubbers to improve the strength of vehicle tires. Rubbers have a high molecular weight, thus rubber compounds show high viscosity. The volume loading of these reinforcements in highly viscous rubber compounds is extremely high in general, due to the low aspect ratio of the reinforcements. This fact reduces the processability of rubber composite compounds [10]. Considering that the homogeneous dispersion of nanoscale reinforcements having a high aspect ratio in

a much smaller volume loading result in the significant improvement of mechanical properties for polymers, nanoscale reinforcements having a high aspect ratio can replace conventional reinforcements for rubber matrix and significantly improve the mechanical properties of rubbers. This chapter discusses reported recent efforts in observing the morphologies of various rubber nanocomposites using wide range of microscopy techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Morphological observations using various microscopies are extremely important to understand the relation between processing methods and properties of rubber nanocomposites, since the mechanical and electrical properties of the rubber nanocomposites strongly depend on the dispersion level of nanoscale reinforcements. The observed morphological information needs to be used for feedback to improve processing methods that will lead to optimize various properties of rubber nanocomposites.

## **4.1 MORPHOLOGICAL STUDIES**

### **4.1.1 Scanning Electron Microscopy**

SEM provides images while a finely focused high-energy electron beam scans across the specimen surface in a raster scan pattern. When the electron beam strikes the specimen surface, it generates secondary electrons and backscattered electrons at or near the specimen surface. The primary detection mode is secondary electron imaging, which can produce high-resolution images of the specimen's surface with topographic features in about 1–5 nm resolution. SEM has a deep focal depth, resulting in a characteristic 3-D appearance useful for understanding the surface structure of the specimens. SEM specimens need to be electrically conductive for the electron beam to scan the surface and to have a path to ground.

An advantage is that the sample preparation for SEM is minimal, comparing with TEM sample preparation. Fractography conducted by SEM is the observation of fracture and failure surfaces of specimens. The fracture and failure surfaces of rubber nanocomposite specimens need to be cut into a smaller size to fit into the SEM specimen chamber, firmly be mounted on the specimen holder and then be sputter-coated with a ultrathin layer of electrically conductive material, such as Au, Au/Pd or Ir. The dispersed nanoscale reinforcements can often be observed on the fracture and failure surfaces of rubber nanocomposites. However, the disadvantage of the SEM is that only the specimen surface, not the inside of the specimen, can be observed. When nanoscale reinforcements are aggregated in the rubber matrix or when the reinforcement–rubber interaction is poor and interfacial debonding happens on the reinforcement–rubber interfaces, it is easy to recognize nanoscale reinforcements on the fracture and failure surfaces. However, when nanoscale reinforcements are uniformly dispersed and these are well coated with rubber matrix due to a cohesive failure in rubber matrix instead of interfacial debonding on the reinforcement–rubber interface, it is often difficult to distinguish between rubber matrix and nanoscale reinforcements. SEM was utilized to observe rubber nanocomposites reinforced by organoclay nanoplatelets, polyaniline-treated clay nanoplatelets, graphite nanoplatelets, starchnanocrystals, vapor-grown carbon nanofibers (VGCNF), and multiwalled carbon nanotubes (MWCNT).

### **SEM Imaging Process**

Electron gun generates high energy electrons which are focused into a fine beam, which is scanned across the surface of the specimen. Elastically and inelastic interactions of the beam electrons with the atoms of the specimen produce a wide variety of radiation products like backscattered electrons, secondary electrons, absorbed electrons, characteristic and continuum x-rays,



etc. A sample of this radiation is collected by a detector, most commonly the Everhart—Thornley detector and the collected signal is amplified and displayed on the computer

### **Image Formation**

The SEM image is a 2D intensity map in the analog or digital domain. Each image pixel on the display corresponds to a point on the sample, which is proportional to the signal intensity captured by the detector at each specific point. In an analog scanning system, the beam is moved continuously; with a rapid scan along the X-axis (line scan) supplemented by a stepwise slow scan along the Y-axis at predefined number of lines. In digital scanning system, only discrete beam locations are allowed. The beam is positioned in a particular location remains there for a fixed time, called dwell time, and then it is moved to the next point.

### **Microtomy of Polymers**

It is a sectioning method which allows the cutting of extremely thin sections of material. The 3 forms of microtomy are useful for polymers which are *simple peel-back methods, thin sectioning, and ultrathin sectioning*. Methods are useful for direct examination of the bulk of fibers and films and for the formation of flat surfaces for x-ray microanalysis of embedded specimens or sections of larger samples. In peel-back method the sample is held onto a glass slide or SEM stub with an adhesive or tape, and a scalpel or razor used to nick the surface. Fine forceps are used to peel back the cut either near the central or surface part of the

specimen. Pieces of molded or extruded plastics are trimmed using small saws and razor blades. Glass knives are best used to prepare flat block faces. Thin sections ( $>5\mu\text{m}$ ) are prepared with the aid of a microtome device. Semi-thin ( $0.2\text{--}3\mu\text{m}$ ) as well as ultrathin ( $<0.2\mu\text{m}$ ) sections are prepared with the aid of an ultramicrotome device.

#### **4.1.2 Transmission Electron Microscopy**

Transmission electron microscopy (TEM) provides images, when an electron beam is transmitted through an ultrathin specimen and interacts with the specimen. Therefore, it can be thought that TEM images contain information inside the specimen. Comparing with SEM, the resolution of TEM is better than that of SEM in general. However, TEM sample preparation is more difficult and often tedious. Observations of rubber nanocomposites using TEM are impossible in general without sample preparation and samples need to be thinned for TEM observations. Importantly, the quality of obtained TEM micrographs strongly depends on the uniformity and thickness (preferably approximately 100 nm) of thinned TEM samples. TEM samples from the rubber nanocomposites can be prepared using either cryomicrotomy or the focused ion beam (FIB) technique. Cryomicrotomy is a method for preparing samples for examination using TEM. Since rubber samples are soft at room temperature, they need to be cooled at cryogenic temperature which is below the glass transition temperature of the rubber matrix of nanocomposites. The general procedure is as follows. First, the sample block of rubber nanocomposite is first trimmed to create a block face. Second, thin sections are cut using a diamond or glass knife. The thin cut sections

stay on the knife. Finally these thin sections are placed on a TEM grid for TEM observation. The ideal thickness of the thin sections is approximately 100 nm.



### **Principles of operation:**

The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of  $0.025\text{\AA}$ . However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2  $\text{\AA}$ .

Because even for very thin samples one is looking through many atoms, one does not usually see individual atoms. Rather the high resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The

brightfield/darkfield imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material. Finally the microscope is equipped with a special imaging lens allowing for the observation of micromagnetic domain structures in a field-free environment.

The TEM is also capable of forming a focused electron probe, as small as 20 Å, which can be positioned on very fine features in the sample for microdiffraction information or analysis of x-rays for compositional information. The latter is the same signal as that used for EMPA and SEM composition analysis (see EMPA facility), where the resolution is on the order of one micron due to beam spreading in the bulk sample. The spatial resolution for this compositional analysis in TEM is much higher, on the order of the probe size, because the sample is so thin. Conversely the signal is much smaller and therefore less quantitative. The high brightness field-emission gun improves the sensitivity and resolution of x-ray compositional analysis over that available with more traditional thermionic sources.

### **Restrictions on Samples:**

Sample preparation for TEM generally requires more time and experience than for most other characterization techniques. A TEM specimen must be approximately 1000 Å or less in thickness in the area of interest. The entire specimen must fit into a 3mm diameter cup and be less than about 100 microns in thickness. A thin, disc shaped sample with a hole in the middle, the edges of the hole being thin enough for TEM viewing, is typical. The initial disk is usually formed by cutting and grinding from bulk or thin film/substrate material, and the final thinning done by ion milling. Other specimen preparation possibilities include direct deposition onto a TEM-thin substrate (Si<sub>3</sub>N<sub>4</sub>, carbon); direct dispersion of powders on such a substrate; grinding and polishing using special devices (t-tool, tripod); chemical etching and electropolishing; lithographic patterning of walls and pillars for cross-section viewing; and focused ion beam (FIB) sectioning for site specific samples.

### **4.3 Atomic Force Microscopy**

AFM consists of a micro scale cantilever with a sharp tip (called as a probe) at its end that is used to scan the specimen surface. The cantilever is typically made of silicon or silicon nitride with a tip radius of curvature on the order of nanometers. In general, AFM can be operated in either contact (static) mode or tapping (dynamic) mode. In contact mode operation, the probe is essentially dragged across the sample surface. The tip of the cantilever probe is always in contact with the specimen surface during scanning, while the force between the tip and the surface is maintained as constant in order to maintain a constant deflection. A bend in the cantilever corresponds to a displacement of the probe tip along the z-axis relative to an undeflected cantilever. As the topography of the sample changes, the z-scanner must move the relative position of the tip with respect to the sample to maintain the constant deflection. Using this feedback mechanism, the topography of the sample is thus mapped during scanning by assuming that the motion of the z-scanner directly corresponds to the sample topography. Low stiffness probes are normally used to minimize the amount of applied force for scanning the sample and to boost the deflection signal. However, significant deformation and damage of rubber samples may often occur during this contact mode imaging in air, since significant force is applied to overcome the effects of contamination, including adsorbed moisture, on the specimen surface. In contrast, tapping mode operation is more applicable particularly to obtain images of rubber-related samples. The resolution is similar to that in contact mode operation. Additionally, the forces applied to the specimens are lower, thus this causes less damage to the specimens. In tapping mode operation, the cantilever is externally oscillated close to its first bending mode resonance frequency by a small piezoelectric element mounted in the AFM tip holder. The amplitude of this oscillation is greater than 10 nm, typically in the range 20–200 nm. The tip makes

contact with the sample for a short duration in each oscillation cycle. When the probe tip approaches the specimen surface, the tip-sample interactions alter the amplitude, resonance frequency and phase angle of the oscillating cantilever due to, for example, van der Waals force or electrostatic forces. This change in oscillation with respect to the external reference oscillation provides information for the characteristics of each AFM specimen. Especially, a later development in tapping mode is the use of the changes in phase angle of the cantilever probe to produce a phase contrast image. In general, changes in phase angle of the cantilever probe during scanning are related to energy dissipation by the interaction between the probe tip and the specimen surface. The phase contrast image obtained by the tapping mode often provides significantly more contrast than the topographic image and has been shown to be sensitive to material surface properties, such as elastic modulus and topographic image, and this concurrent imaging is another benefit of tapping mode operation in contrast to contact mode operation. The disadvantages of tapping mode operation, relative to contact mode operation, are that the scan speeds are slightly lower and the operation may also be a little more complex; however, more information from tapping mode operation can certainly cancel such small disadvantages. An advantage of AFM over SEM is that AFM can provide a true 3-D surface profiles, while SEM provides only 2-D micrographs. Although the surfaces of SEM specimens need to be coated with metal or graphite and this coating process as a sample preparation is irreversible and may cause artifacts, such a coating process is not required for AFM. Additionally, most AFM modes can work perfectly in ambient air or even a liquid environment, whereas SEM needs an expensive vacuum environment for proper operation. However, a disadvantage of AFM compared to SEM may be the limited focal depth. AFM has a shallow focal depth on the order of only microns,

while SEM has a deeper focal depth on the order of millimeters. AFM cannot scan images as fast as SEM, thus it is necessary to spend several minutes in a typical scan for an entire image. AFM was utilized to observe rubber nanocomposites reinforced by montmorillonite clay nanoplatelets, silica nanoparticles, graphite nanoplatelets, MWCNT, metal nanoparticles and magnetic nanoparticles.

#### 4.4 Mechanical Properties

Many types of nanofillers can be incorporated in rubber for reinforcement issue. One of their most important characteristic is their specific surface (generally of the order of several hundreds of square meters per gram) which is directly related to their size, and which controls (at given filler content) the characteristic inter-filler distance. Another important parameter which has to be considered to describe these reinforcing elements is the average length/diameter ratio, known as the “aspect ratio”. This aspect ratio may change from one to values as high as several thousands. Carbon blacks and precipitated silica are the most common nanofillers used for reinforcing elastomers. Recent years have seen an increased interest for rod-shaped nanofillers. Carbon nanotubes, long and thin cylinders of carbons, were discovered in 1991 by the electron microscopist Iijima who was studying the arc-evaporation synthesis of fullerenes. Just few nanometres across, the cylinder can be tens of micron long, and each end is “capped” with half of a fullerene molecule. Nanotubes can have either a unique cylindrical wall (SWNTs) or multiple walls (MWNTs). Their structural properties depend on the diameter, length, and chirality, or twist of the nanotubes. Their predicted mechanical characteristics are remarkable (Young’s Modulus  $\sim 1$  TPa, maximum tensile strength  $\sim 30$  GPa). They have excellent thermal conductivity, are chemically inert and, depending on the details of their atomic arrangement

(chirality), behave as metals or semiconductors. Therefore, combined to a low density, these characteristics make them particularly attractive for reinforcement.

The resulting dispersion strongly depends on: (i) the choice of the polymer, which controls the filler/matrix compatibility, (ii) the surface chemistry of the filler, which can change this compatibility, and (iii) the filler morphology, including their shape factor and specific surface area that impacts the amount of interfacial contact area with the polymer, the complex shape of the aggregates and therefore the rheology of the filler/matrix mix. The filler chemical modification is particularly studied, resulting in an impressive increase of the number of nanocomposite systems studied. Moreover, the complex chemistry of cross linking of the host elastomer can also be chosen as a function of the nanofiller/polymer system. Obviously, all these parameters must be taken into account when one wants to understand the role of the filler incorporation in the mechanical properties of the processed nanocomposites, since they influence the microstructure (filler dispersion, crosslinking) and the different type of interaction (filler/filler, filler/Matrix). As reported in all the articles concerning filled elastomers, when stiff fillers are introduced, the material stiffness increases. Obviously, this is also the case for nanofillers. the filler aspect ratio is the main parameter for the reinforcement efficiency, the latter being higher for high aspect ratio filler. Thus, carbon nanotubes have a much higher reinforcing capability than silica or carbon blacks. Literature also suggests that the reinforcement is strongly dependent on the elastomer matrix, the material processing, and the filler surface treatment. Besides a strong reinforcement, the introduction of nanoscopic fillers in a rubbery matrix leads, at intermediate strain level (below 100%) to a nonlinear mechanical behavior

## **4.5 Thermal Analysis**



#### **4.5.1 Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique, DSC. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is especially useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints. TGA measurements provide valuable information that can be used to select materials for certain end-use applications, predict product performance and improve product quality. The technique is particularly useful for the following measurements

- Compositional analysis of multi-component materials or blends, Thermal stabilities, Oxidative stabilities, Estimation of product lifetimes, Decomposition kinetics, Effects of reactive atmospheres on materials, Filler content of materials
- Moisture and volatiles con

#### **4.5.2 Differential scanning calorimetry (DSC)**

Differential scanning calorimetry (DSC) is a thermoanalytical technique used to characterize the difference in the amount of heat as a function of temperature required to increase the temperature of a sample and a reference. The temperature of the sample container is kept the same as that of the reference container by a continuous and adjustable heat power. The

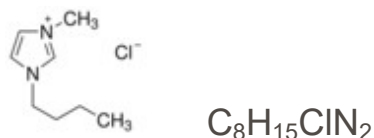
power difference between the sample and reference is recorded. The containers are heated individually and the temperatures are measured by Pt sensors. DSC was applied to evaluate changes in crystallinity and transition behavior of the high pressure treated composites and polymers. The samples were scanned at heating and cooling rates of typically 10°C per min. From the measured DSC signal,  $T_g$ ,  $T_{melt}$ , melting onset temperature ( $T_{onset}$ ), melting enthalpy ( $\Delta H$ ) and  $T_{cry}$  etc. could be obtained.

## Section 5

### Materials and Methods

#### 5.1 Materials

The commercial Multi-Walled Carbon Nanotubes[MWCNT] were procured from NANOSHEL, Intelligent Materials Pvt Lt ,Panchkula . The diameter of the tubes less than 5 nm and the average length is 5-1.5 mm. The carbon content of the material is more than 95% and the rest is amorphous carbon, ash and impurities. The Natural rubber ISNR -5 grade purchased from Rubber Research Institute of India , Kottayam, Kerala and , Ionic liquid 1-butyl 3-methyl imidazolium Chloride [BMIC] were obtained from SigmaAldrich, Chemicals Pvt Ltd, Bangalore. The chemical structure of the Ionic liquid is given below. It's melting point is 70<sup>0</sup>c. The zinc oxide (ZnO), stearic acid, CBS and sulphur used in this study were of industrial grades.



1- Butyl- 3- Methyl Imidazolium Chloride[BMIC]

#### 5.2 Preparation of composites

The natural rubber masticated in a two roll- mixing mill (Santosh) at friction ratio of 1:1.25 as per ASTM standards and it cut in to small pieces. The masticated natural rubber mixed with Ionic liquid by using a internal mixer Brabender at 80<sup>0</sup>c. Composites of NR- CNT-IL are prepared by adding stearic acid and Zinc oxide followed by CNT, C B S and sulphur respectively at room temperature to the NR-IL mixture. Samples are prepared in different categories by varying the concentrations of Ionic Liquid

Table-1.

<u>Sample composition in phr</u>	
Natural Rubber	100
MWCNT	3
Zinc Oxide	5
Stearic Acid	2
Sulphur	2
CBS <sub>a</sub>	1
BMIC <sub>b</sub>	[1-3]mmol

a[N-cyclohexylbenzene thiazole-2-sulphenamide]

b [1-butyl 3-methyl imidazolium Chloride]

Cure Characteristics and rubber filler interaction have been studied using a Rubber Proces Analyzer( model- RPA 2000, Alpha Technologies). The optimum cure time ( $t_{90}$ ) of the sample were determined at 150<sup>0</sup>c at a frequency of 50.0cpm and a strain of 0.2<sup>0</sup>deg. Blanks cut from vulcanized samples at a temperature of 150<sup>0</sup>c and a pressure of 200Kg cm<sup>-2</sup> in a electrically heated hydraulic press(Antosh model SMP-50),to their respective optimum cure times. Rectangular moldings were cooled quickly in water at the end of each curing cycle and were used for subsequent property measurements.

## Section 6

## Result and Discussion

### Morphology of NR-CNT IL composites

The morphology and state of dispersion of the carbon nanotube in a polymer matrix can be investigated using scanning electron microscope[SEM] , Transmission electron microscopy (TEM) and Atomic Force Microscopy(AFM).

#### 6.1 SEM analysis

Generally, it is hard to disperse individually MWCNTs in polymer matrix , due to strong aggregation and high viscosity of the polymer Fig: [1][ a,b, c,and d] shows SEM images of NR-MWCTs composites without IL (a) ,with varying concentration of IL (b,c,&d ). The figures show that the presence of ionic liquid enhances the uniform dispersibility of CNTs in the rubber matrix . It can be seen that CNTs without IL were not dispersed well in the NR matrix, and some aggregations existed. Meanwhile some smooth outcrops of the CNTs on the fracture surface indicated that the interfacial bonding between the CNTs and the rubber matrix needed to be improved. These conditions weakened the reinforcement of CNTs in the rubber matrix. After NT-CNTs treated with Ionic liquid, the dispersion uniformity of CNTs into rubber matrix was improved. Fewer outcrops of the CNTs were found on the surface, which may prove the strong interfacial bonding between the CNTs and the rubber macromolecules in the NR-CNT nano composites.

The main factor which influences the dispersibility is that upon being ground into ionic liquids, carbon nanotube bundles are untangled, and the resultant fine bundles form a network structure. This is due to the possible specific interaction between the imidazolium ion component and the pi-electronic nanotube surface.

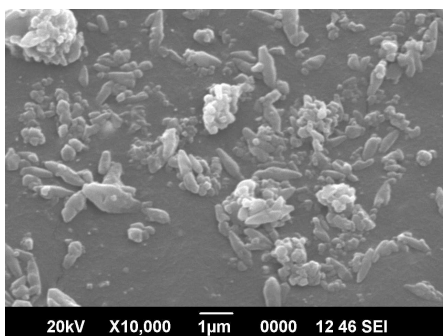


Fig1(a) 3% CNT

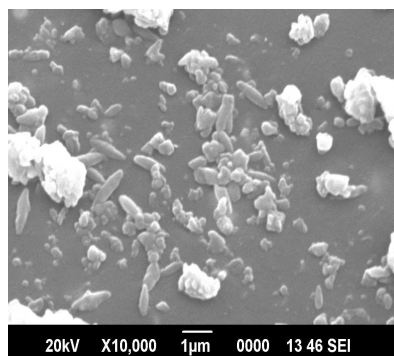


Fig1(b)[ 3%CNT&1mmol IL]

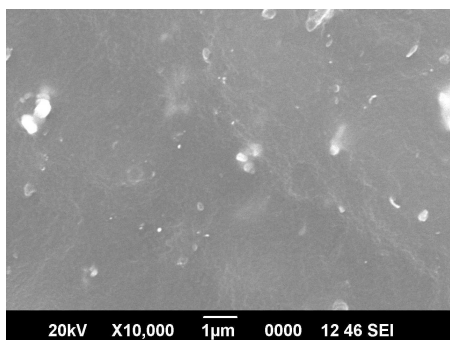


Fig1(C)[3%CNT&2mmolIL]

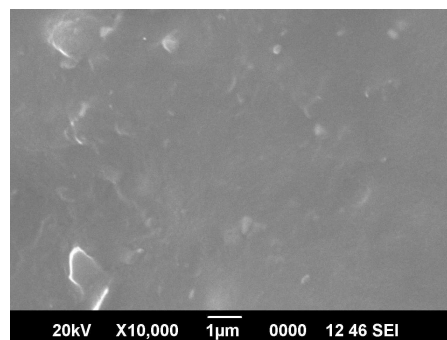


Fig1(d)[3%CNT&3mmol IL]

## 6.2 TEM analysis

As SEM pictures do not provide precise information about the dispersion of tubes in the sample bulk, TEM study was carried out for the same set of samples. As expected, the dispersion and distribution of CNTs within the matrix become more better. The TEM images shows tubes are spaced apart without intertubular connection in many region It also shows a reasonably good tube–tube contact with minimum agglomerates

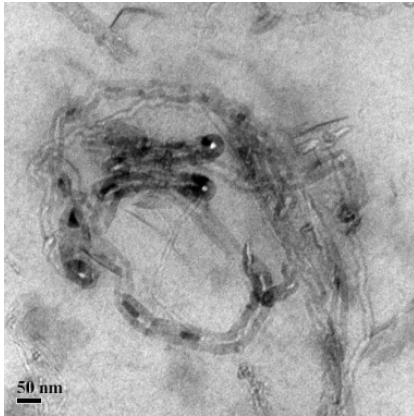


Fig2(a) [ 3% CNT ]

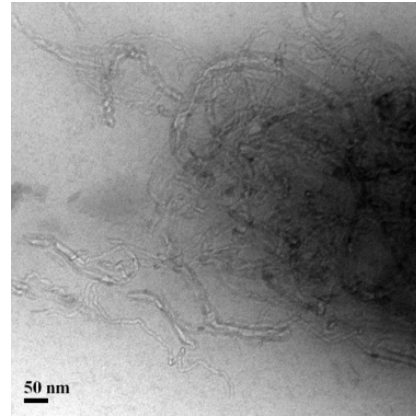


Fig2(b)[3%CNT&1mmolIL}

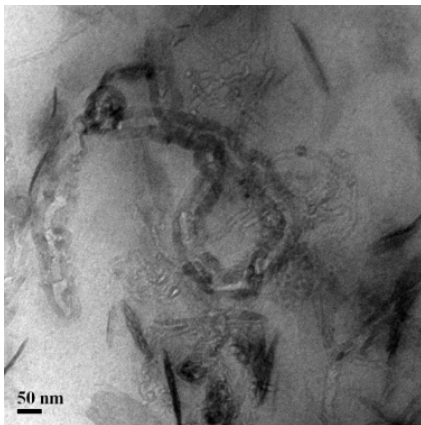


Fig2(c)[3%CNT&2mmolIL]

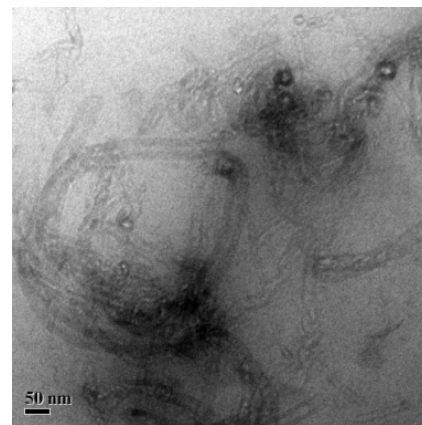


Fig2(d)[3%CNT&3mmol IL]

### 6.3 AFM analysis

Additional information on how the nanotubes are actually being distributed within the polymer matrix can be obtained from Atomic Force Microscopy (AFM). AFM

has been shown to be particularly well suited for the characterization of filled elastomers and more generally of heterogeneous systems with components of different stiffness [22]. AFM images of natural rubber with MWNTs shown in Fig. 3(a) which observed rough surface of the Natural rubber CNT composite. Natural rubber - CNT composites filled with 3 phr of MWNTs and varying IL contents, shown in Fig. 3[a,b,c&d]; give some indication of larger-scale dispersion. The brighter domains easily identified and rather homogeneously distributed in the film, are ascribed to filler structures

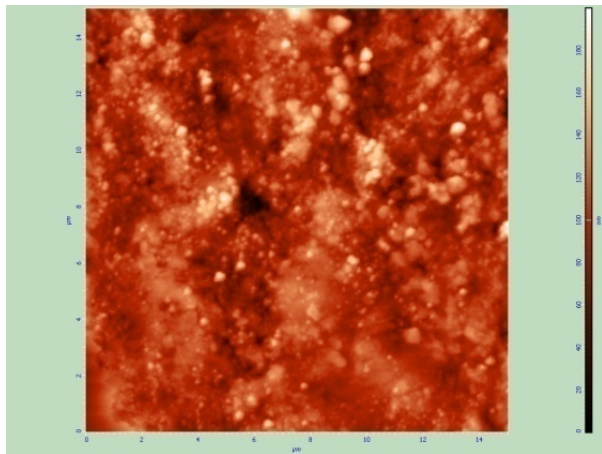


Fig3(a) 3% CNT

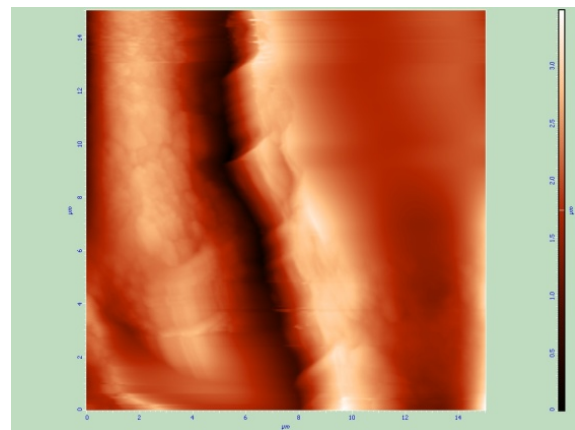


Fig3(b)[3%CNT&1mmolIL}

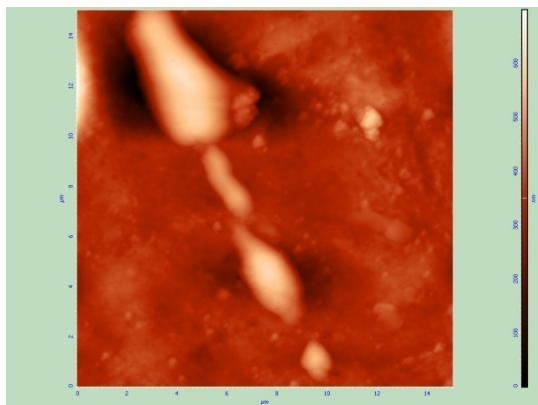


Fig3(c)[3%CNT&2mmolIL]

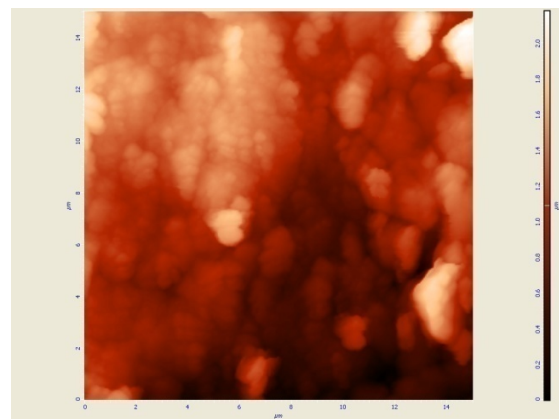
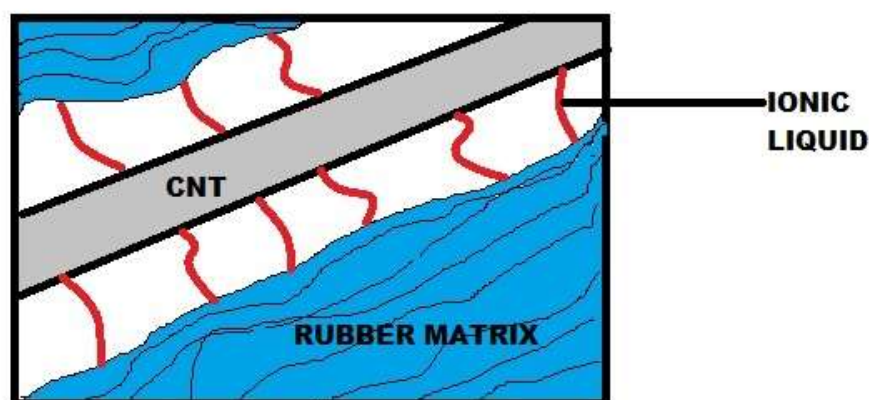


Fig3(d)[3%CNT&3 mmolIL]



## SCHEMATIC ILLUSTRATION OF THE INFLUENCE OF IONIC LIQUID ON THE DISPERSION OF CARBON NANOTUBES IN THE POLYMER MATRIX



Ionic liquid provide a strong level of reinforcing ability to the carbon nanotubes in the natural rubber matrix forming a homogenous dispersion in the polymer matrix .

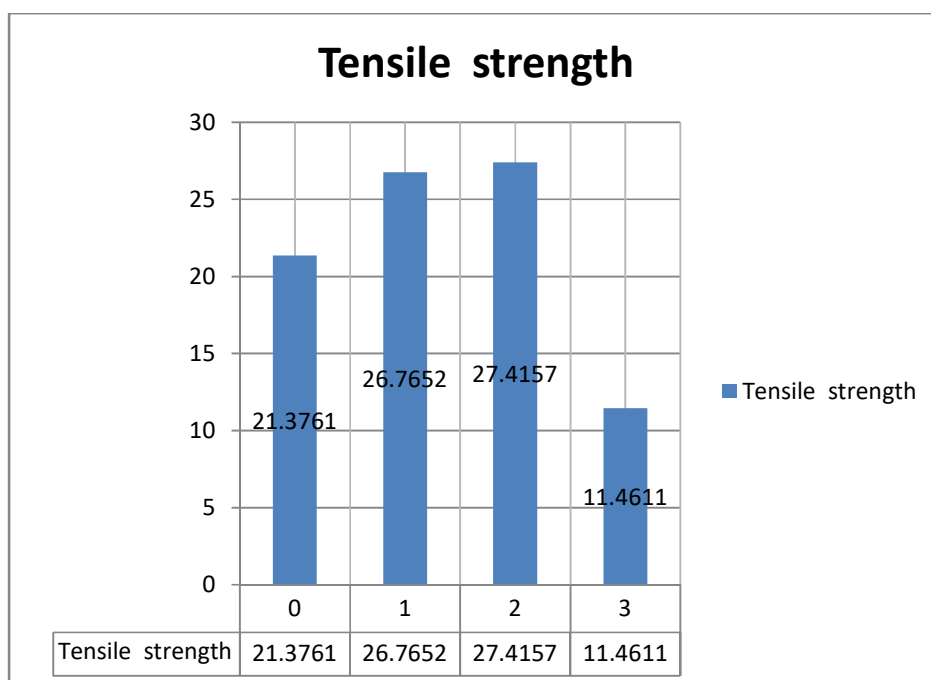
### 6.4 Mechanical Properties

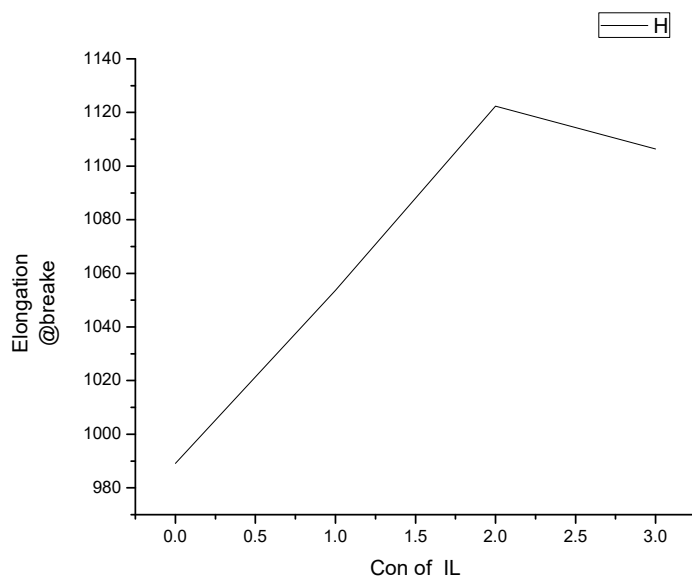
Dumbbell shaped tensile and angle tear specimens were punched out from the vulcanized sheets and the mechanical properties of NR-MWNT nanocomposites were studied using a Shimadzu Universal Testing Machine (UTM, model-AG1) with a load cell of 10kN capacity. The gauge length between the jaws at the start of each test was adjusted to 30mm and the measurements were carried out at a cross-head speed of 500mm=min.

The mechanical properties of the NR- CNT-IL composites are shown in Table 2. Mechanical properties of NR/CNT/IL nanocomposites like tensile strength and elongation at break increased with the increase in IL concentration up to 2mmol, thereafter these properties marginally fall when the IL concentration increased to 3mmol.

Table 2

Concentration of CNT	Tensile strength	Modulus @ 300%	Elongation at Breake	MAX Strain
0	21.3761	2.56291	989.101	1028.3
1	26.7652	2.77864	1053.65	1053.12
2	27.4157	2.57105	1122.39	1122.39
3	11.4611	2.88571	1106.37	858.485





## 6.5 Thermal Analysis.

### 6.5.1 TGA analysis

Since the thermal stability of elastomer based composites is critical as far as their application potential is concerned, we have investigated the effect of IL on the thermal stability of NR-CNT composites. Figure 4 shows TGA curves of the NR-CNT and NR-CNT-IL composites. By comparing the weight loss as a function of temperature, the effect of IL on the thermal stability of NR -CNTs can be analyzed. TGA plots of NR-MWCNT -IL nanocomposites indicate that the presence of IL at low weight fractions has no significant effect on the thermal stability of natural rubber. The reason is that the IL can impose the restriction on

the mobilization of rubber macromolecules and conduct heat homogeneously and avoid the heat concentration.

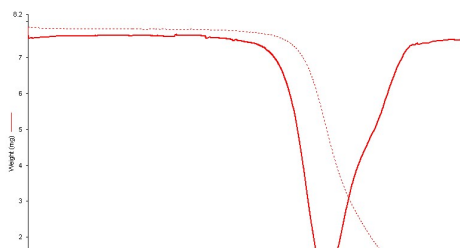


Fig 4(a)[ 3% CNT] 372.42°C

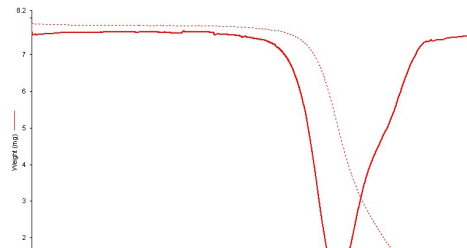


Fig 4(b) [3%CNT&1mmol IL] 370.11°C

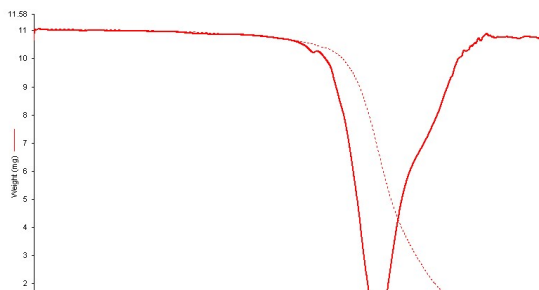


Fig 4 (C)[3%CNT&2mmol IL ]371.45°C

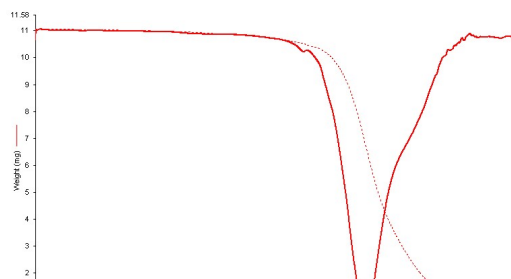


Fig 4(d)[3%CNT&3mmol IL]372.30°C

### 6.5.2 Differential scanning calorimetry (DSC)

DSC (Differential scanning calorimetry) can explore the heterogeneous nature of rubber composites. This will give the  $T_g$  of the polymeric material and the fibre phases. Miscible system will show single, sharp transition peak( $T_g$ ) intermediate between those of the components. Separate peaks will be obtained for heterogeneous phase separated systems. In principle, the glass transition temperature  $T_g$  of a polymer is a manifestation of the chain mobilities reflecting the glassy-rubbery transition in the bulk. According to Lipatov the chain mobility depends on the polymer cohesive forces [23]. In nonpolar elastomers, the cohesive

forces are low and therefore only minor changes in Tg are expected for the NR-CNT composite by the addition of IL. Table 3 gives result of DSC analysis which shows single Tg value for each composite and it hasn't any considerable difference with the other values. The result indicate that NR-CNT composites with IL are homogeneous and due to non polar nature of matrix (NR) there is no considerable change in the Tg values.

Table 3

Sample	Tg
NR+ 3% Cnt	-60.77
NR+ 3% Cnt+1mmol IL	-61.78
NR+3% CNT+2mmol IL	-62.53
NR+3% CNT+3mmol IL	-62.81

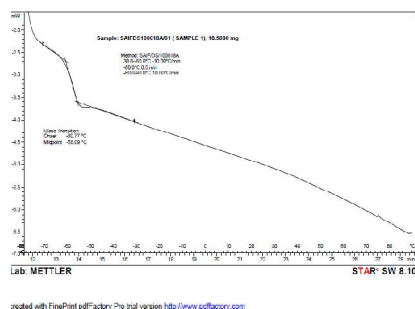


Fig 5(a)[ 3% CNT]

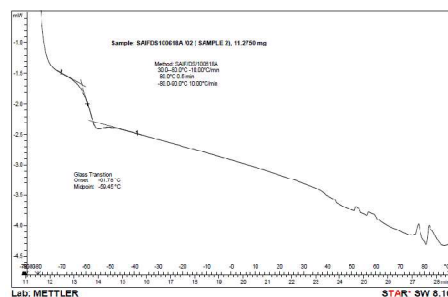


Fig 5(b) [3%CNT&1mmol IL]

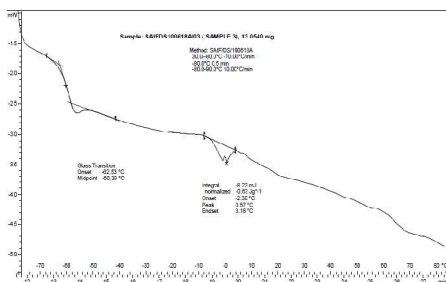


Fig 5(c) [3%CNT&2mmol IL]

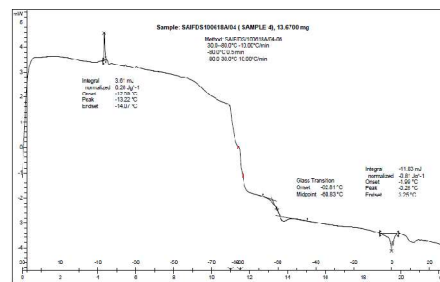


Fig 5(d) [3%CNT&3mmol IL]

## Conclusion

Eco friendly Natural rubber-Multiwalled Carbon nano tube composites with varying concentrations of ionic liquid has been prepared. Ionic liquid (IL), a kind of fascinating molten salt with nearly zero vapor pressure and high thermal stability, has demonstrated high affinity towards carbon nanotubes. Ionic liquid not require any other solvent for the dispersion of CNTs at the same time processing of CNTs become very simple. Ionic liquids are non volatile, non flammable and environment friendly dispersant for Multiwalled carbon nanotubes in rubber matrix. By taking Ionic liquid as dispersant no structural to CNTs. The influence of Ionic Liquid on the morphology, thermal properties and mechanical

performance of NR-CNT nano composites was studied.. The morphology of the nanocomposites were evaluated using scanning electron microscopy( SEM),Transmission electron microscopy(TEM)and Atomic Force Microscopy(AFM)studies. SEM,TEM and AFM results show that with the increase in the Ionic liquid content uniform dispersion of CNTs increases in the NR matrix . There is considerable increase in the mechanical properties of the NR- CNT-IL nano composites compared to the NR- CNT composites. There isn't noticeable change in the thermal stability. From DSC analysis Tg values are derived for different samples which are very much close to each other .Only single Tg results are obtained for different samples which indicate the homogeneous nature of the samples.

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