Development of High Performance Materials based on Smart Elastomer Nanocomposites

by

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MSc

Submitted in fulfilment of the requirements for the degree of

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Deakin University
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I am the author of the thesis entitled

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Development of High Performance Materials based on Smart Elastomer Nanocomposites

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Dedicated to my Mother who gave her youth to me
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Structure & Content of the Thesis-Introduction to the Problem
Introduction

In realizing the new generation materials, polymer nanocomposite systems have a key role and this special topic is one of the most important branches of current nanotechnology and composite science. Nanocomposites with superior properties and multi functionalities are extensively studied in both fundamental and applied research aspects due to their advantageous applications. A polymer nanocomposite system is composed of a matrix polymer part and fillers in nano dimensions. Elastomers, an important class of polymers have been strengthened by adding nanofillers like carbon black (CB), silica, titanium dioxide (TiO₂), organo clay, carbon nanotube (CNT), graphene and graphite intercalation compounds in recent times in order to attain superior functional properties. Of the various filler materials, carbon family has gained extreme importance from the last two decades as there was a great innovation in the field of nanotubes and graphene. It is undoubtedly established that nanofillers such as clay, CNTs and graphene derivatives can improve flexibility, mechanical properties, thermal stability, electrical and thermal conductivities, dielectric performances and gas barrier properties of almost all elastomer matrices.

Among the elastomers, natural rubber (NR) is remarkably important in its technological applications. This rubber is widely used in manufacturing tyre components, rubber hoses, sensing devices, electrical shielding and electrical heating devices. Due to its high significance, this elastomer has been selected as one of the base matrices in this study. Apart from NR, three more elastomers were also found to be useful in fabricating smart
materials. These were poly(isobutylene-co-isoprene) or butyl rubber (IIR), styrene-isoprene-styrene block co-polymer (SIS) and polyurethane (PU). The properties of these rubbers can be further enhanced to great extent when nanoparticles are incorporated in to it. When the two dimensional (2D) fillers such as graphene can impart better sensing properties to NR, IIR and SIS, on the other side, it impart dielectric and shape memory properties to PU. CNT also has tremendous importance in regulating electrical and sensing properties to it. Efforts are being done to get promising applications by increasing the electrical conductivity, mechanical stiffness and strength with low concentration of fillers.

The tremendous advantages of the rubber nanocomposites are often limited by two main problems that come across during the composite fabrication. These are the difficulties in achieving a homogeneous dispersion of fillers in the matrix and maximum compatibility at the filler-elastomer interface. Both these problems are related to the filler-filler and filler-polymer interfacial interactions and the success of a study lies in the extent of minimising these issues. The present thesis mainly focuses on the fundamental as well as the application orientated research work on NR, PU, SIS and IIR nanocomposites. In this work, the various properties of nanocomposites containing different fillers like graphene, CNTs and polyaniline (PAni) are thoroughly examined. We could derive special applications such as sensing (solvent, oil and water), shape memory, dielectric property etc. for the synthesized composites. And a detailed molecular level study on the materials has been carried out to address the filler-filler and filler-polymer interactions and to maximize the filler homogeneity in the matrix and its compatibility with rubber.

The survey is subdivided into five chapters:
• **Chapter I** describes the general introduction on elastomer materials and their significance on account of the wide range of potential applications in many areas. A detailed survey of literature on elastomer composites with different fillers such as CNT, and graphene based fillers is done. The influence of fillers on rheological, electrical, mechanical and dielectric properties of elastomers is discussed. An overview of the composite applications and current challenges in the field are provided with special emphasis on the need of this work and the future perspectives towards the development of such promising materials.

• **Chapter II** is dedicated to the description of the materials and techniques used in this experimental work, including a detailed presentation of the sample preparation methods. The principle of the major characterizations used in this survey is explained here in detail.

• In **chapter III**, a comparison of mechanical, rheological and sensing properties of NR, IIR and SIS with graphene and CNT nanocomposites is done. In the case of NR/CNT better sensing properties is not observed whereas for NR/CNT/reduced graphene oxide (RGO) composites solvent sensing was excellent. The filler-elastomer and filler-filler interactions were deduced from rheology, stress relaxation, swelling index and Mullins effect experiments. X-Ray diffraction (XRD) studies and tunnelling electron microscopy (TEM) results further substantiate the formation of intercalated/exfoliated structures in the nanocomposites. As subsequent sections of this chapter, oil sensing properties of NR/IIR/SIS/CNT composites as well as dual phase sensing of SIS/PAni composites are discussed. These were also correlated with swelling studies and molecular interactions.
• **Chapter IV** deals with the shape memory behaviour of graphene oxide (GO) filled PU composites. Here also the shape memory is related with filler-matrix molecular interactions and it is quantitatively measured in terms of recovery and fixity ratios. The structure of the polymer composites investigated by scanning electron microscopy (SEM) and XRD revealed highly dispersed morphology of GOs in PU. The improvement in shape memory obtained for the nanocomposites was then quantitatively analysed using Payne effect. A nice correlation was established between the temperature dependence of shape memory and the crosslink density.

• **Chapter V** is a brief study on the electrical and dielectric properties of the PU/GO nanocomposites. GOs and modified GOs (mGOs) incorporated in the PU matrix improved their dielectric strength significantly. Broadband dielectric spectroscopy studies reveal the applicability of the prepared composite materials in supercapacitors as dielectrics. The mGOs facilitate interfacial interactions and the properties are correlated with the molecular level interactions. Finally the study is summarised in overall conclusions and the anticipations towards the future. The current work explains several applications for the obtained composites. The extension of these ideas towards more application oriented research is expected.
Chapter I: Elastomer Nanocomposites: Literature Survey & Trends

ABSTRACT
The one dimensional tubes and two-dimensional sheets of sp\(^2\)-hybridized carbon atoms remarkably influence the properties of polymers. CNTs, graphene mono-layers, GOs, graphite oxides, exfoliated graphite, and other related materials are derived from a parental fullerene structure. Here in this chapter, we focus primarily on the impact of these fillers in regulating the mechanical, electrical, viscoelastic and sensing properties of elastomer composites. First, we introduce the different types of fillers as well as various fabrication methods for elastomer nanocomposites and steps for enhancing the filler polymer interactions at the interface. It has been demonstrated that the addition of an optimized amount of nanocarbon fillers to various elastomers produces a record-high enhancement of the electrical conductivity at small filler loading, making it suitable for flexible electronics.
1.1. Introduction

New generation materials, including smart materials, exhibiting high performance and multifunctionality have become a topic of interest of this era. As one of the most important branches of current nanotechnology and composite science, the fabrication of elastomer nanocomposites has much significance in producing such materials. Their advantageous applications have triggered out detailed studies in theoretical as well as in applied research areas. In order to synthesise elastomer nanocomposites, nanofillers such as CB, silica, TiO₂, layered silicates, CNT, polyhedral oligomeric silsesquioxane (POSS), graphene and graphite intercalation compounds have been incorporated into various elastomer matrices which provide efficient reinforcement and functional properties. It is undoubtedly established that the nano carbon derived fillers can improve mechanical and tribological properties, thermal stability, microwave absorption, electrical and thermal conductivities, dielectric performances and gas barrier properties of all elastomer matrices. In addition to exhibiting outstanding transport properties and ambipolar conduction, non-metallic carbon and its derivative materials are flexible, transparent, ultimately scalable, and easily transferable to any surface, thus offering new possibilities for advanced electronics. Here we are analyzing two carbon based fillers-CNTs and graphene and their elastomer composites as an opening towards this current proposal.

CNTs are long cylindrical graphene sheets with or without hemi-fullerene end caps and composed of covalently bonded carbon atoms. They are found to be more reactive than graphene because of the presence of misaligned unhybridized p-orbitals of carbon atoms in them. Since their discovery in 1990’s by Iijima [1], a lot of investigations on the fabrication
of functional nanotube composites have come out. This is mainly because of their extremely high Young’s modulus \([2]\), electrical and thermal conductivity \([3]\), flexibility \([4]\), bending strength, aspect ratio \((300-1000)\), and chemical inertness. Their mechanical properties, together with relatively low density \([5]\), make CNTs ideal candidates for weight-efficient structures and so they are considered to be the ultimate reinforcements in elastomer composites. These extremely light weight materials are much stronger when compared to steel and better conductors compared to copper. Their high tensile strength \((150-180\text{ GPa})\) and tensile modulus \((640 \text{ GPa-1TPa})\) make CNTs the unique fillers in the nano world. Their one dimensional structure allows metallic nanotubes to transport electrons through the entire tube without scattering. This transport behavior and CNT’s large phonon mean free path length are responsible for their high electrical and thermal conductivity \([6]\). All these superior properties of CNTs offer great opportunities towards the synthesis of new composites. High performance light weight structural materials made of CNT/elastomer composites used in space exploration is one example among the tremendous possibilities of CNT composites \([7]\).

Even a single nanotube is hundred times stronger and six times lighter than steel with excellent conductivity. This means a group of CNTs can make wonders, provided it should be uniformly distributed. Thus the future of CNT’s application lies mainly in the fabrication of technologically important materials ranging from reinforced composites to electrical sensors \([8]\). But, the large number of applications of CNT composites as in electronics, optics and bio medical fields has been limited to a certain extent by a few factors. The low level of dispersion of CNTs in polar liquids arising from the tendency of CNTs to aggregate because of the hydrophobic-hydrophobic interactions existing in them is one important aspect to be considered in this scenario. The uneven distribution of fillers in elastomer matrix definitely
causes the composite properties to decrease since it affects the filler uniformity in each phase and the chemical interaction between the filler and the polymer [9, 10]. In order to effectively transfer the stress from one phase to the other, strong bonding between fillers and polymer chains are necessary. Hence the effective dispersion and the long term stability of CNTs in matrix is the most significant, yet challenging part in composite fabrication [11]. In short, the difficulty in dispersing CNTs homogeneously throughout the matrix without destroying their integrity (highly polarisable smooth sided nature of CNTs cause for its bundling tendency), provided a good interfacial interaction with the elastomer matrix is achieved and their inconsistency (all known preparation methods give mixtures of nanotube chiralities, diameters and lengths along with different amount of impurities and structural defects) are considered to be the disadvantages with this filler [12].

Of the several allotropic forms of carbon, conducting graphite is the most thermodynamically stable. Its structure consists of sp²-hybridized carbon atoms in the form of stacked two-dimensional layers, with the planes held together by vander Waals forces. The carbon atoms in this material are crystalline. The presence of large number of π electrons contributes these sheets their conductive property. Their high thermal and electrical conductivity, lubricating action, refractory ability, difficulty in ignition, etc. make these materials useful in many industrial applications such as refractory uses, lubricants, paints, crucibles, electrodes, pencils, etc. [13]. Expanded graphite (EG) is another form of graphite in which the atoms are more weakly bonded in the perpendicular plane (to hexagonal plane) than in natural graphite. This material is also used in brake linings, foundry facings and lubricants. In addition, their conductive properties impart low resistivity to composites when incorporated into polymers [14]. The separation of these sheets/layers down to nanometer
thicknesses results in the formation of high-aspect-ratio (200–1500) and high-modulus (1 TPa) graphite nanosheets (GNs) [14, 15]. These nanosheets are characterized by enormous surface area (up to 2630 m²/g), high optical transmittance, quantum Hall effect at room temperature [16, 17], and a tunable band gap [18] and play a key role in regulating polymer properties [19]. The potential applications of all electrically conductive polymeric composites include light-emitting devices, batteries, electromagnetic shielding, antistatics, field-effect transistors (FET), sensors, super-capacitors and corrosion-resistant coatings [20].

As the shape and size of the conductive fillers influence the formation of the conductive network and thus the final composite conductivity [19, 21], complete exfoliation and good dispersion of filler particles in the matrix are maintained using particular synthesis and processing techniques [22]. The natural abundance, less cost and multi-functionality of graphitic fillers gave rise to the keen interest to manufacture large numbers of elastomer composites. The two research groups Hamed et al. [23] and Zhang et al. [24] explained the importance of graphite derivatives (particularly graphene) over other kinds of nanofillers to impart mechanical and other functional properties to rubber matrix especially when the filler was finely dispersed in the matrix with improved interfacial interaction. Generally, the elastomer/graphene and graphite derived composite fabrication can be done by melt blending, solution mixing and in situ polymerisation methods. For all the preparation methods discussed, the dispersion of platelets in the composite is ensured by the level of exfoliation of the platelets prior to, or during, mixing. In this aspect, solution mixing offers the simplest route to disperse graphite derivatives and graphene platelets into an elastomer matrix, even if some restacking of the platelets is possible. A large number of surfactants also facilitate graphene dispersion [25-29]. The modification of graphitic fillers usually enhances
their interfacial interaction with elastomer chains thereby leading to better properties. Evidence supports the synergistic effect of nitrile rubber (NBR)/expanded graphite (EG)/CB systems and the mechanical and tribological properties are compared among their micro- as well as their nano- composites [30]. The nanodimension and aspect ratio of graphene make its elastomer nanocomposites superior to all other graphitic derived composites, provided better dispersion of the filler is achieved. Significant property improvement is obtained for NR/graphene composites synthesised by Zhan et al. [31].

Elastomers are characterized by low electrical (<10\(^{-11}\) S/m) and thermal conductivities (\(\approx 0.2\) W/m K) which improve upon the incorporation of nanoscale conducting fillers like nanotubes, graphene etc. [32]. The modified CNTs reinforced elastomer composites are reported for having high tensile modulus (over the native elastomer) without much reduction in their strain-at-break [33] values. Recent efforts to use multi walled carbon nanotube (MWCNT) as filler material in elastomers has shown promising results in increasing the electrical conductivity, mechanical stiffness and strength [34]. Graphite derivatives and graphene/elastomeric compounds are widely used in various fields such as automotive, electronics, packaging, aerospace, biomedical and shape memory applications [35-38]. Since the composite properties are highly influenced by the filler-elastomer interactions, making well exfoliated systems by chemical as well as physical modifications of filler particles has a critical role in material fabrication. This thesis entirely focusses on the electrical and sensing properties of CNT and graphene and their elastomer composites used in such applications. This investigation underlines the importance of carefully considering the properties of such fillers in the process of designing sensors, capacitors and shape memory materials. We try to bring out the amazing properties of CNTs and graphene and
their elastomer composites in detail by giving special emphasis to the application side. Before proceeding towards the composite part, let us discuss about the properties of fillers in detail.

1.2. Introduction to fillers

1.2.1. Carbon nanotubes

There are mainly two types of CNTs- single walled carbon nanotubes (SWCNTs) and MWCNTs. SWCNTs have diameter of about 1.2-1.4 nm which may vary due to strain and different mode of wrappings. As radius of the tube decreases, the partial sp$^3$ character of carbon atoms increases and thus leads to more reactivity. SWCNTs can be named by a chiral vector denotation (n, m) which describes how to roll up a graphene layer to make CNTs in an infinite graphene sheet (n and m denote unit vectors along two different directions in the graphene crystal lattice) [39, 40]. Depending upon these chiral vectors, SWCNTs show difference in their properties such as optical activity, mechanical strength and electrical conductivity. When n=m, it is called armchair form, when n-m=0, it is zigzag and all the others, chiral.

In MWCNTs, the interlayer distance is 3.4 Å especially in the case of armchair tubes and is about 3.52 Å for zig zag tubes. For both SWCNTs and MWCNTs the length varies from nm-cm. Also in MWCNT, it is possible for the inner nanotube core to slide within the outer shell without friction, thus improving its kinetic properties. CNTs show thermal conduction along the tube axis and also exhibit ballistic conduction (unimpeded flow of charge or energy carrying particles over high distances) [6]. However they are insulators laterally to the tube axis. This helps in tuning the properties. CNTs are the strongest and stiffest in terms of tensile structure and elastic modulus due to sp$^2$ bonds, but there are some
points which they cannot satisfy. For instance, upon excessive strain, they usually undergo plastic deformation. The high aspect ratio and hollow structure of CNTs also result in buckling (a failure mode characterized for a structure when subjected to high compressive stress) when they are compressed, because of this reason they are not considered to be strong upon compression. Moreover, its mechanical and electronic properties vary remarkably depending on the tube radius and the type.

CNTs are mainly synthesized by three methods including arc discharge, laser ablation and chemical vapor deposition (CVD) of which CVD is the most convenient and common method providing maximum yield. Since the various synthesis methods particularly CVD technique induces certain impurities in the obtained nanotubes, the purification is rather important and necessary. Depending on the reactivity of impurities and the stability of CNT samples, the contaminants can be removed by chemical, physical or by combined methods. The chemical methods include oxidation or dehydrogenation (for removing carbon nanoparticles), acidic treatment (for removing metal catalyst) and other chemical reactions (for removing the catalyst support). The physical methods of purification of CNTs involve mechanical separation of different kind. This includes strong sonication of suspension of the impure material (Snooker effect) \[41\] and collection of magnetic particles with a permanent magnet, thus separating the purified CNTs. Combinations of physical and chemical methods can also be used for better yield.

1.2.2. Graphene and graphitic derivatives

Graphite is available in large quantities from both natural and synthetic sources and is rather inexpensive \[42\]. As noted previously, the main graphite derivatives include EG, graphite oxide, GO, RGO, graphene nanoplatelet (GNP) and graphene. The GO and RGO
derivatives are usually synthesized by solution-based oxidation and reduction, whereas
graphene layers with superior electron transport characteristics are always synthesized using
dry methods such as CVD and surface segregation [16, 17, 44-48]. Because the electronic,
photonic, mechanical, and thermal properties of graphene depend on the number of layers
[49] and its crystalline structure, the controlled synthesis of graphene with defined layers is
rather significant. The major precursor for all graphene-based materials is GO, which is
easily produced by chemical oxidation and subsequent exfoliation of graphite. Generally, GO
is synthesized by oxidization of graphite using the methods developed by Brodie,
Staudenmaier, or Hummers [50, 51]. The Brodie method involves oxidization of graphite
using potassium chlorate (KClO₃) and nitric acid (HNO₃). The Staudenmaier method is a
modification of Brodie method in which a mixture of sulfuric acid (H₂SO₄) and HNO₃ with
KClO₃ is used as the oxidizing agent. A less hazardous and more efficient method is that of
Hummers in which oxidation of graphite occurs in the presence of a mixture of sodium
nitrate (NaNO₃), potassium permanganate (KMnO₄), and concentrated H₂SO₄. The GO is
hydrophilic since its chemical structure contains oxygen-containing functionalities, including
epoxide and hydroxyl groups on the basal plane and carbonyl and carboxyl groups at the
edges [52, 53] of the graphene sheets. These functional groups aid the complete dispersion of
GO in polar solvents, such as water, alcohol and dimethylformamide (DMF) [54]. Due to the
presence of functional groups, GO sheets are susceptible to many chemical reactions and thus
form functionalized GOs [56, 57]. Treatment of GOs with organic isocyanates to form
amides and carbamate esters from the carboxyl and hydroxyl groups in GO was reported by
Stankovich et al. [48]. This isocyanate functionalized GO exfoliates in polar aprotic solvents
such as DMF, facilitating the formation of composites [20].
1.2.3. PolyAniline (PAni)

The conductive polymer PAni is widely investigated for its electronic and optical applications [43]. The simple and reversible acid/base doping/dedoping chemistry of this polymer controls its characteristic properties like freevolume, solubility, electrical conductivity and optical activity [55, 58]. Polymers like PAni possess the advantages of both low-dimensional systems and organic conductors and are therefore applied in wide varieties of technologies. The high sensitivity, fast response, low cost, ease of synthesis, environmental stability and operation at roomtemperature of PAni allows it to be useful in making chemical sensors [235]. The electrically conducting PAni filled polymer composites enhance the sensing characteristics [236, 237] more specifically thermoplastics and elastomers. Such conductive nanocomposites based on PAni particles monitor the sensitivity (to various stimulants like organic solvents) by the varying their electrical resistance. Also, conductive PAni filled elastomer composites show very good sensing properties for the detection of other physical parameters [169] such as temperature, pressure and strain.

1.2.4. Dispersion of fillers in matrices

Once the fillers have been processed and purified to an acceptable level, the next stage in the production of a composite is to homogeneously disperse the fillers in the polymer matrix. The most important problem to be solved during composite manufacture is regarding the dispersion of fillers in the matrix. The nanotube aggregation within a polymer system would certainly have a negative impact on its stiffening ability [59]. So effective separation is required for overcoming the existing inter-tube van der Waal attraction, which is anomalously strong in CNTs due to their high polarizability. Many applications of CNT
composites require the preservation of neat and highly electronically active surface of CNTs (not covered by a surfactant). Also if the tubes are closely packed, an initial formation of a temporary (partial) exfoliation state is required in order to have better interaction with the polymer or the dispersant to adsorb on the surface [59]. Mechanical stirring/mixing and the common ultrasonication process are employed for this purpose; both providing the local shear stress that can break down the bundles. The manufacturing techniques such as melt blending [60-63], in situ polymerization or polycondensation in the presence of nanotubes, [64-66] and solution mixing [67, 68] are also useful in improving the dispersion of CNTs in a polymer matrix. Ultrasonication method cannot produce thermodynamically stable CNT solutions in water since aqueous CNT/surfactant suspensions are metastable colloidal suspensions. After sonication, CNTs individualize but still the reaggregation possibility to form bundles exists as this is their thermodynamically stable state. So true water soluble solutions are those solutions that entropically favor segregated CNTs where the reaggregation in a solvent is less favoured.

In general, to improve the CNT dispersion, two methods are often used: formation of covalent bonds or the establishment of non-covalent interactions between the matrix and nanotube’s surface [69]. Surface and tip functionalization of CNTs and in situ polymerization of monomers can improve the quality of nanotubes dispersion through covalent interaction. The major approaches grafting to and grafting from involving (functionalized) CNTs also cause effective nanofiller dispersion by forming covalent bonds between the tubes and the polymer chains [70-73]. As mentioned, surfactants can provide physical adsorptions on long chain polymers with CNTs, which prevent CNT agglomeration. The surfactant or the polymer can either thread to or wrap themselves around the surface of
CNTs and can disrupt the van der Waals interaction resulting in CNT bundle segregation [74]. In addition to homogeneous dispersion, controllable alignments of CNTs in the matrices are also crucial to achieve improvement in composite properties. In order to ensure better CNT/elastomer compatibility ionic liquids are also used in the dispersion process [75-78].

It is found that functionalization influences the properties of CNT/elastomer composites. Shanmugharaj et al. [79] described the influence of acid/silane treatment on CNT surface due to oxidation/surface interaction and thereby leading to lattice distortions. They also demonstrated that the thermal stability of the composite was increased when silane modified CNTs were incorporated into NR. On comparison, NR composites filled with silane functionalized CNTs prepared by melt processing showed better enhancement for almost all properties than pure CNT/NR composites [79]. Functionalization can also be done during the purification process of CNTs by exposing them to strong oxidizing acids. The functional groups such as oxygenated and nitrogenated groups grafted on the CNT’s surface induce electron donor–acceptor interactions with the unsaturated bonds in the elastomer matrix. Perez et al. [80] proposed the same kind of interaction between the functional groups on CNTs and the nitrile groups of NBR chains. Such filler-matrix interaction results in improved properties. Tour et al. [33] made stable suspensions of sodium dodecyl sulphate (SDS) wrapped SWCNTs and functionalised with diazonium salts yielding heavily functionalised CNTs, which greatly enhanced the interaction with the elastomer matrix.

1.3. Elastomer nanocomposites

Elastomers are widely used—from the small-scale biomaterials to the large-scale earthquake damping devices—because of their highly reversible deformation properties depending on curing. However, the initial modulus and durability of the elastomers are very poor. Also
elastomeric applications generally require and make use of the large deformation extensibility and resilience of the elastomer [80]. Therefore various kinds of fillers such as metal oxides, CB, silica particles and CNTs are usually employed for their effective reinforcement. Upon the incorporation of stiff fillers into elastomers, the stiffness enhances (i.e., enhance the initial stiffness and retain this stiffness enhancement for overall large strain deformation behavior) while retaining the important attributes of large strain resilient behavior and large strain-to break. Fillers are added to rubber products as in vehicle tyres and shock mounts to enhance their stiffness and toughness properties. They also improve the processability, increase the toughness, fracture resistance and stress transfer in elastomers. Filler reinforcement provides fabrication of stronger, lighter or less expensive composites than their traditional neat counterparts. The most commonly available elastomeric composites are reinforced with CB particles which ranges in size from 100-1000Å [81-83].

The unique behaviour of CB filled elastomer composites is attributed to the presence of a rigid particulate phase and the interaction of the elastomer chains with this phase. But the main problem with these fillers is that a substantial improvement in properties is obtained only at higher filler loadings. As there is a demand for modern technological application for superior elastomeric composites, innovative reinforcements having better properties should be introduced [84]. Due to very small size and large surface area and hence surface properties, nanoparticles play an important role as fillers in this regard. By adding only a very small amount of nanoparticles into rubber, excellent enhancement in properties can be achieved. In the case of CNTs, a stronger filler/matrix interaction at the interface leads to a more immobilized rubber shell compared with filler particles of micro dimensions [80, 85]. Incorporation of nanotubes in elastomers like silicone rubber (SR) dramatically improves the
properties of the resultant composites [81, 86]. CNTs act as effective crosslinks even in unvulcanized rubber at low filler loading [87]. Additive effects of the physical and chemical crosslinks of the chains play an important role at the beginning of the deformation and gives higher modulus than pure elastomer. Though rubbers are thermal and electrical insulators, incorporation of conductive fillers could produce conducting composite materials.

The development of CNT based elastomeric composites could demonstrate both the excellent energy absorption characteristics of the matrix components as well as the advanced structural properties of the CNTs. Recent experiments show that significant improvement in the mechanical properties of polymeric materials can be achieved by using even small volume fractions of CNTs as reinforcements [81]. Potential applications of CNT filled elastomer composites could vary from industrial materials such as rubber hoses, tyre components, sensing devices to electrical shielding and electrical heating equipments. If the percentage of reinforcement is very low or if it is well dispersed there are more strong interfaces that slow down the progress of the crack, thus making it applicable in light weight aerospace materials. However there are some critical issues concerned with such composites like the non uniform dispersion of nanotubes in the matrix (as discussed previously), increase in viscosity due to high aspect ratio and lack of control of the alignment or orientation of CNTs. Another problem to be addressed is the lack of a strong chemical bond between the nanotube and the elastomer matrix. This is due to the absence of an electrostatic force between the CNTs and the elastomer and the stress/deformation arising from the mismatch in the matrix-nanotube thermal expansion coefficients. Most of these issues can be solved by modifying CNTs and also during the preparation of the composites [77, 78, 88-91].
1.3.1. Preparation

The major composite manufacturing methods usually employed are explained here in detail.

1.3.1.1. Solvent casting

This method involves dispersion of both filler and matrix in separate suitable solvents and thereafter mixing the two. The solvent evaporates to get dry samples of the composite. Following this method, Bokobza and Belin [92] formulated CNT/styrene butadiene rubber (SBR) composites and achieved a 45% increase in modulus and a 70% increase in the tensile strength with 1 phr (per hundred rubber) MWCNT. Khalid et al. [83] also dispersed CNTs in NR by solvent casting using toluene. Even though this method is effective, the use of organic solvents like toluene cannot be welcomed. Bai et al. compounded hydrogenated carboxylated nitrile butadiene rubber (HXNBR) with exfoliated GO by a solution-blending method using THF as solvent with the aid of ultrasonication [93] and obtained better dispersion [94]. Zhan et al. prepared NR/graphene composites by ultrasonically-assisted latex mixing and an in situ reduction process [95]. However, they couldn’t avoid degradation of polymer during the in situ reduction step. Kim et al. also prepared TPU/FGS (functionalized graphene sheets)/GO composites via solvent blending. They dispersed thermally reduced GO, Phenyl modified GO, and neat GO into TPU using the solvent DMF [96].

1.3.1.2. Spray drying

A suspension of CNTs in elastomer can be converted to CNT/elastomer powder composites by spray drying process. For this, the suspension of CNTs (with or without functionalization)/elastomer/vulcanizing reagents is homogeneously mixed, atomized and dried by means of spray drying to obtain powders of composites. By means of spray drying,
uniform globules of polymers (diameter less than 10 μm) could be fabricated in which CNTs are well dispersed. Zhou et al. [84, 97] synthesized SBR powders containing CNTs with uniform diameters of about 5-10μm using spray drying process. Compared with those of pure SBR composites, the hardness and tear strength of the composites filled with 60phr CNTs are enhanced by 70 and 250% respectively, and the tensile strength of the composites with 50phr CNTs improved remarkably by 600%.

1.3.1.3. Latex stage compounding

Rubber latex can be compounded with fillers along with curing agents. The main crosslinking method is using sulphur in the presence of ZnO, stearic acid, tetramethyl thiuram disulfide (TMTD), 2,2’-dithiobis(benzothiazole) (MBTS) etc. This process improves crosslinking between the elastomer chains in the composites. In this process, at first the curing agents are mixed well with the latex by milling methods, which is called compounding and then the compounded latex is mixed with the filler [98]. This method is successfully utilised by Anand et al. [74] for preparing MWCNT/NR latex composites. They compounded the NR latex using ball milling and thereafter composites are formulated using mechanical mixing and noticed good improvement in mechanical, rheological and electrical properties.

1.3.1.4. Heterocoagulation approach

The typical heterocoagulation process is based on depositing small charged particles on the surface of larger particles of opposite charge. The method is based on ion exchange between cationic latex particles and anionic (oxidized) nanoparticles [99]. The electrostatic interaction between the filler and polymer is believed to enhance the filler–polymer adhesion
Heterocoagulation method was also successfully used to prepare exfoliated clay filled polymer composites [101, 102]. This technique is employed by Peng et al. [103] while preparing functionalized MWCNT/NR composites. The interaction between the charged particles binds them together to give well dispersed composite materials. A modified solution process is used by Kim et al. for preparing multi-layered graphene sheet/SBR nanocomposites. They used heterocoagulation between negatively charged SBR latex particles and positive surface modified multi-layered graphene in aqueous medium using flocculant, polyaluminium chloride [104]. The hexadecyltrimethylammonium bromide (HTAB) and cetyl trimethyl ammonium bromide (CTAB) surfactants impart positive charge to the filler, and this helps in the improved reinforcement effect between the filler and the elastomer.

1.3.1.5. In situ polymerization

In situ polymerization to fabricate composites involves the polymerization of corresponding monomers in situ within the filler suspensions. This offers an easy and efficient method to disperse fillers uniformly in the polymer matrix. The type of polymerization reaction, nature of solvents used, reaction conditions etc. may vary based on the type of composite required. Curing of elastomers can be done by directly adding curing agents also in situ. When the monomers polymerize in the presence of fillers, covalent bonds can be formed between the monomer units as well as with the functionalized filler particles. These strong matrix-filler bonds enhance the interfacial interaction and lead to highly improved properties like mechanical strength of the composites [105-107]. This method is particularly used for polymers that cannot be prepared by solution processing (insoluble
polymers) and melt mixing (thermally unstable polymers). Macosko and co-workers reported the synthesis of TPU/graphene derived composites following in situ polymerisation [96]. Polyisoprene/graphene and graphite intercalation compound (GIC) composites are produced by the polymerisation of isoprene monomers initiated by the negatively charged fillers in the presence of alkali metals [104]. In situ polymerisation method is quite useful for the fabrication of elastomer composites, but it is not free from limitations. It is found that this method is not suitable if the polymerisation takes place at the surface of the GICs or between the layers [108]. This method also requires monomer units as well as lot of reagents for the polymerisation procedure, and thus less applicable in the case of naturally existing polymers.

1.3.1.6. Melt blending/Extrusion

As the name indicates melt blending offers a high temperature shear mixing for composite fabrication. In this method, elastomers are melted in internal mixers or two roll mills by adding fillers. This is the most industrially preferred method of composite manufacturing since it avoids the usage of solvents. The machines used for this purpose are designed such a way that the screws inside it can move at high speeds which in turn results in efficient dispersion of filler particles inside the elastomer matrix. Even though this method is the best suited one for commercial scale, it has two disadvantages. One is the high possibility of efficient filler dispersion only at higher concentration inside the elastomer matrix [109] and the second is the difficulty to add curing agents to elastomers at high processing temperatures. So this method is more concentrated on thermoplastics reinforced composites. However there are a few works reported on fabrication of elastomer composites also. For instance, Das et al. obtained good dispersion of CNTs in SBR and butadiene rubber (BR)
blend following melt mixing [34]. They also fabricated [82] MWCNT/ chloroprene rubber (CR) composites by adding the CNT dispersion using ethanol as dispersion agent in to mill mixed CR and obtained excellent mechanical properties. Among all graphitic filler-reinforced composites, most researchers reported melt mixing process with thermally reduced graphene (TRG), when compared to chemically reduced graphene (CRG) because of its thermal stability. Prud’homme et al. observed the enhanced properties for NR/graphene nanocomposites prepared by the melt compounding technique [110] over the solution mixing process, and patented the results. Kim et al. prepared TPU/FGS/GO composites following the same technique [96]. Composites of SBR with graphite powder having different sizes are also reported using melt mixing [111].

1.3.2. Orientation of fillers

The orientation and alignment of fillers can influence the properties of composites to a great extent. Orientation effects are mainly due to their high aspect ratio. The degree of alignment of nanotubes is rather important than the graphene flakes due to their one dimensional structure and can be determined by X-ray diffraction and polarized Raman spectroscopy. The alignment of CNTs can be done during composite formation or aligned nanotubes can be incorporated into the polymer matrix [112]. If the composites are manufactured by extrusion or injection molding, there is a chance of tuning the alignment degree. This can be done by regulating the shear rate as well as the pressure applied [113]. In situ polymerization is also possible in which, viscosity of the nanotube monomer suspension affects the degree of alignment. The tubes can be aligned after composite formation also. This is done by mechanical stretching, electrospinning etc. Other methods of alignment also include filtration, plasma-enhanced chemical vapor deposition (PECVD), template, force
field-induced alignment, magnetic field-induced alignment and liquid crystalline phase-induced alignment. Among all methods, the spinning technique offers the greatest degree of alignment [113] due to the extrusion of the composite through a very small orifice during the process. The alignment depends on the fiber diameter and the amount and type of CNTs. SWCNTs can align more than MWCNTs. As the amount of nanotubes increases, motions of the tubes are restricted because of agglomeration and thereby the alignment decreases [114]. Functionalisation also can affect nanotube alignment. For instance, when CNTs are oxidized, carboxyl or hydroxyl functional groups get attached on the terminals and forms COOH-terminated self-assembled monolayers. The tubes having lengths greater than the dimensions of such a monolayer, can align along the inter layer boundaries and these patterns are used for fabricating thin films and continuous ropes of CNTs with sophisticated structures. The orientation depends on the nanotube chirality too [115]. Thus the orientations of nanotubes in composites are functions of nanotube properties. In *ex situ* method CNTs are aligned in advance and then compounded with the polymer matrix by *in situ* polymerization of some monomers.

Filler orientation can influence the electrical conductivity of composites. The anisotropic conductivity of composites has been predicted by orientation of rods or fibres [115, 116]. Wood et al. showed that the radial shear flow during manufacture removes the initial isotropy present in the system [117], but the resulting film has SWCNTs distributed on the plane of the film. Since SWCNTs are randomly oriented in the resulting film, the direction in which sample strips are taken for characterization does not make any difference in the results. To utilize their novel properties, many researchers have focused on the dispersion and orientation of CNTs, and fabricated various CNT/elastomer composites [118-
Deng et al. [126] demonstrated that persistence length and reorientation of MWCNTs during stretch have a significant impact on mechanical properties, such as the modulus of the rubber composite. Hudziak et al. proposed a phenomenological model for magneto resistive effects in an above-percolation-threshold loaded Fe-filled MWCNT/elastomer composite by interpretation of resistance relaxation for a range of axial strain [127]. They observed a large instantaneous magnetoresistance at low axial strain as a result of conduction pathway breaking caused by preferential orientation of the conducting nanotubes perpendicular to the axial current flow as a result of the magnetic torque experienced by the ferromagnetic Fe-MWCNT [127]. The reorientation of nanotubes under strain in the samples may be responsible for the initial increase in modulus under strain and this is quantified in the Raman experiments by Frogley et al. [81]. The Raman measurements provide extra insight into the nature and efficiency of the interface in the composites as well as quantification of the strain induced reorientation of the nanotubes towards the axis of tensile strain. The reason is in composites the polymer chains are more oriented than that of the pure matrix, the orientation being induced by the high alignment of the CNTs upon application of the uniaxial deformation. Summing up, highly ordered CNTs are useful for many applications, such as field emission displays and sensors, data storage, and light-emitters. This also provides superior applications to the obtained well-aligned CNT/polymer composites.

1.4. Characterization of elastomer nanocomposites

1.4.1. Mechanical properties

The fiber like structure of CNTs, their low density and high aspect ratio make them very useful for the reinforcement of elastomers. When such fillers are added to an elastomer its tensile modulus, tensile strength and hardness increase. These properties are found to be
increasing with nanotube loading, their dispersion and alignment in the matrix. The tensile strength increases with CNT content due to high surface area of CNTs in contact with the elastomer molecules. The elongation at break is also expected to increase with nanotube addition; however this trend varies in different systems. The interfacial interaction between the polymer and the filler and also the homogeneous dispersion of filler in the matrix increases the stiffness and ductility of the composites and cause elongation at break also to improve. Adedigba et al. [128] demonstrated a linear relationship between the Young’s modulus of the CNT/NR composites and percentage of CNT addition. They reinforced NR latex with MWCNTs and noticed an increment of about 124% in Young’s modulus at 10 phr CNT loading. The improvement in modulus as well as stress-strain behavior is attributed to the effectiveness of CNTs to uniformly transfer the applied stress through the matrix, which is related to the large surface area of CNTs.

![Figure 1.1](image.png)

**Figure 1.1** (a) Stress–strain curves for pure NR latex and its composites (b) variation in the value of modulus with filler volume fraction [129]
The stress–strain curves for CNT/NR composites are represented in Figure 1.1a. Bhattacharyya et al. [129] observed the typical non-linear “S curve” described in the kinetic theory of rubber elasticity. It is useful in that case to plot the so called reduced (or Mooney) stress as a function of the extension ratio as shown in Figure 1.1b. The plot (Figure 1.1b) of reduced stress vs 1/α illustrates the elastic behavior of rubber-like materials. It shows that the modulus is increasing with the increase of filler volume fraction, which is in qualitative agreement with the Mooney–Rivlin equation (Equation (1.1)), at least in the moderately large deformation regime.

\[ \sigma = 2C_1(\alpha - 1/\alpha^2) + 2C_2(1-1/\alpha^3) \]  \hspace{1cm} (1.1)

where \( C_1 \) and \( C_2 \) are constants, \( \sigma \) is the retractive stress and \( \alpha \) is the extension ratio.

The upturn observed at low inverse extension ratio is related to the stress-induced crystallization of NR [130, 131]. And this can be better explained on the basis of modified Mooney Rivlin equation [132].

\[ \sigma = 2 \left( C_1 + \frac{C_2}{\alpha} \right) F(\alpha) \]  \hspace{1cm} (1.2)

where \( C_1 \) and \( C_2 \) are dependents of \( \alpha \) and the function \( F(\alpha) \) is

\[ F(\alpha) = \frac{1}{\alpha} + \frac{\alpha}{3} \left( \frac{\alpha}{\alpha_m} \right)^3 + \ldots \]

\( \alpha_m \) is the maximum extension ratio. When \( \alpha < \alpha_m \) this equation becomes Mooney Rivlin equation (Equation (1.1)).

A similar behavior although in low magnitude has been reported by Bokobza and Chauvin [133] with silica nanoparticles filled rubber in the unvulcanized state due to a rigid network formation. This ensures a similar type of networking behavior in CNTs also. This as
well as the hydrodynamic effect contributes towards the more significant reinforcement and network formation in CNT/elastomer composites. Cantournet et al. [134] thoroughly investigated the mechanical behaviour of CNT elastomer composites and proposed a constitutive model for explaining their behaviour. They observed an increase in the initial stiffness and the subsequent strain-induced stiffening at large strains with MWCNT content. The weight percentage of CNTs is also found to be influencing the tensile strength and the tensile stretch at break. The strain to failure also increased with the CNT amount. They noticed a 2.5 times increase in the modulus for a 12.2wt% MWCNT/elastomer composite when compared to the neat elastomer. Comparatively, a similar weight fraction of CB filler provides a modulus 1.3 times that of the neat elastomer [135]. Figure 1.2a and 1.2b represent [136] the uniaxial tension load-unload true stress vs true strain plots. These data show an ability to substantially increase the tensile stiffness and retain the stiffness enhancement during large strain deformation as well as the ability to increase the tensile strength and the tensile strain-at-break. The developed hyper elastic constitutive model for composite materials is based on the volume fraction of matrix and MWCNT content. The model is capable of predicting the effects of MWCNT content on the large deformation stress strain behavior of the composite materials in tension and compression modes and it is in agreement with experimental observation.
Chemical modifications of CNTs enable the interaction of the functional groups on the CNTs with the polymer matrix and helps in the homogenous dispersion of the nanotube fillers and consequently, the interfacial bonding and load transfer could be enhanced which increases the elastic modulus and ultimate tensile strength when compared to the unfunctionalised CNTs. This was shown by Park and Bandaru [136]. They used functionalized and unfunctionalized SWCNTs in the polymer matrix. It was also observed that a larger aspect ratio was imperative in enhancing the strength through comparison with functionalized MWCNT reinforced composite. A maximum in the work of fracture was indicated at low nanotube volume fractions, which could be facilitated through bridging effect by the CNTs. This implies that the toughness of the composite could be diminished at increased CNT loading due to network formation of the nanotubes. The mechanical improvement is better explained by Wang et al. [137] by a cellular structure for the obtained
CNT/NR composites. They made the composites by mill mixing with high shear stress and investigated the topography, modulus, and adhesive energy distribution maps of the resulting composites in terms of CNT loading. Due to the three-dimensional structure of CNTs and the mechanical interfacial regions formed within the composite, the mechanical properties were greatly enhanced.

The promising mechanical strength of all graphitic fillers offers great potential towards the development of affordable, high quality composites [110]. Modulus improvement in elastomer/graphene composite is more significant than other polymer/filler nanocomposites, which indicates the better elastomer-graphene interaction [96]. Even though the modulus increases significantly, the ductility of elastomers is compromised by the incorporation of rigid fillers and the graphene-filled elastomers often show a decline in tensile strength. The properties vary significantly with the nature of fillers and elastomers, size and content of fillers, mode of dispersion, influence of coupling agents and composite fabrication methods. Latex compounding results in fine dispersion of fillers in the matrices, more filler-elastomer interfacial interaction and thus better reinforcement. Ozbas et al. observed almost the same level of reinforcement by functionalised graphene sheets (FGSs) for NR and PDMS elastomers, generalising the effect of property enhancement [138]. The relative enhancement in the modulus value is much lower for CB filled composites, as observed from Figure 1.3(b). In this case of CB-filled NR and SBR composites, filler loading of about 16 wt % produces the same modulus enhancement as achieved with 1 wt % FGS addition. Moreover it is clear that better reinforcement for elastomers can be obtained by FGSs rather than CNTs and clay platelets, as demonstrated in Figure 1.3(b). In the case of NR composites, the strain induced crystallisation also contributes towards enhancement in
modulus. Synthesis of NBR/EG nanocomposites following melt mixing [139] also increased the tensile strength by 78% and storage modulus by 90% at a loading of 5 wt% below glass transition temperature.

Figure 1.3 Tensile stress vs. strain curves for (a) composites with different fillers like CB and silica at 10 phr loading. (b) Normalized modulus values with respect to neat rubber for FGS-filled NR, SBR, and PDMS and CB-filled NR and SBR (c) Stress strain curves for Modified Graphene-IIR nanocomposites(1-10wt%) [138, 141, 149]

Zhan et al. [95] obtained an increase of 47 and 50% in the tensile strength and tear strength respectively for the NR Latex/CRG composites with 2 wt % filler content. In contrast, the tensile strength of NR/CB and NR/MWCNT composites was increased by only 6 and 9%, respectively. The reasons for the better reinforcing effect or adhesion between graphene and NR matrix are assigned to their higher specific surface area, high strength and excellent tensile modulus [140]. The greater level of dispersion in MG (modified graphene with surfactant)-IIR nanocomposites causes for its higher mechanical strength compared to NG (natural graphite)-IIR composites [141] as illustrated in Figure 1.3 (c). The highest value for Young’s modulus (3.4 MPa) is shown by 10 wt% MG nanocomposites, which is about 16 times higher than that of pure IIR (0.21 MPa).
Since the mode of dispersion of fillers in the matrix is directly related to fabrication methods of nanocomposites, mechanical properties are strongly influenced by the manufacturing techniques. Macosko and co-workers [96] compared mechanical properties of thermoplastic polyurethane (TPU)/functionalized graphene composites by varying mixing methods, and concluded that solvent mixing is better than melt mixing to enhance TPU properties. Melt mixing shows lower modulus for composite due to the possibility of reaggregation of graphene flakes during compounding. Thermally exfoliated GO (TEGO)/PU composites made via in situ polymerisation showed less improvement in modulus as compared with solution mixed composites despite good dispersion [96][29]. Increase in modulus of over two orders of magnitude (from approximately 10 MPa to 1.5 GPa) at 55 wt% GNP [181] have been reported for PU. Bai et al. [93] observed an increase of 50 and 100% in tensile strength and in the modulus at 200% elongation of the HXNBR when the GO content was 0.44 vol %. The modulus value of HXNBR consistently increased from 1.7 to 6.5 MPa as GO content increased at the expense of elongation at break. The tensile strength also enhanced from 14.8 to 22.4 MPa, by the addition of 0.44 vol.% GO and thereafter decreased to 10 MPa when the GO content was 1.3 vol.%. [93]. GO/HXNBR composites showed higher tensile strength (22.4 MPa) than their CNT counterparts (15.7 MPa) at 0.44 vol.% filler loading indicating better reinforcement effect of GO. The authors correlated the experimental observation with Halpin Tsai model, which is helpful in determining the orientation of fillers in matrices.
Figure 1.4 Young’s moduli of the composites and Halpin–Tsai theoretical models for both random orientation and unidirectional distribution of GO sheets in the HXNBR matrix [93].

From Figure 1.4 it is clear [142, 144] that the experimental results are close to the theoretical modelling results for the composite with random distribution of GO sheets, and thus their random dispersion throughout the HXNBR matrix is confirmed. Pott et al. also explored the influence of orientation of GO platelets in NR matrix by applying modelling [145]. They could draw a correlation between the morphology, mechanical and processing of the nanocomposites. However well explanation of the equations used for the modelling studies is not represented in their survey. In short, the mechanical analyses give not only the information about the tensile properties, but also the factors influencing the properties and physical aspects of composites.

Dynamic mechanical measurements also have a significant role in determining the composite properties. Chen et al. [146] investigated the mechanical properties of SR nanocomposites with various GNP content. The dynamic mechanical properties such as elastic and viscous modulus also vary with the mechanical property improvement. Here, the
elastic modulus of the nanocomposite enhances apparently with increasing GNPs, and further by the addition of Al₂O₃ nanoparticles. The mechanical strength also improves with nano alumina addition even at a very low loading level. Mu et al. [147] observed higher storage modulus (log G’) value for silicone/EG composites prepared by solution intercalation than their melt mixing counterparts at 10 phr EG content as a function of temperature. This is because of the more dramatic reinforcement effect obtained in the solution mixing process. In general when the filler particles are incorporated in the elastomer matrices, the storage modulus at a given temperature above glass transition temperature (T_g) increases resulting in an increased G’ compared to the neat matrix [148]. The value further increases as the filler concentration increases. Also the T_g will be shifted strongly towards the higher temperature as the filler can impart crystallinity to the matrix. The remarkable reduction in the molecular mobility of elastomer chains around the graphitic filler sheets also causes for the T_g shift. In addition, the area under the tan δ peak is greatly reduced with the filler concentration indicating the reduction in damping properties [149].

1.4.2. Viscoelastic properties

Viscoelasticity is not specific to elastomers only, but all macromolecules exhibit viscoelasticity above their softening temperatures [150]. Because of the coiled structure, both the movement of chain segments within one coil and the movement of entire coils with respect to each other are possible for macromolecules. Near the softening point, the chain segments become mobile and the material slowly changes its shape under the influence of a deformation force [151]. Further temperature increase removes the segmental contacts within and between the coils more and more, and the segments become more and more mobile. Thus, a considerable deformation, such as stretching of the polymeric material, is possible
even with a relatively small deformation force. Because of the presence of both the inter as well as intra molecular links in the polymer chains, even if the elastomer chains undergo deformation at higher temperature, they cannot move apart from each other. So the stretched elastomer returns to its original shape as soon as the deforming force is removed (Figure 1.5).

Figure 1.5 A model of the viscoelastic deformation of polymers in the rubber elastic state [61].

As the thermally induced macromolecular motion described above is responsible for viscoelasticity, the viscoelastic properties of elastomers are inherently temperature-dependent [152, 153, 82]. Dynamic mechanical and rheological analysis is often carried out for the rubber composites in order to find out the variation in the storage modulus value with respect to temperature, strain rate and frequency. Bhattacharyya et al. [129] demonstrated variation in storage modulus with temperature and strain amplitude very clearly. Figure 1.6a [129] shows the variation of storage modulus (log E’) as a function of temperature for the various nanotube compositions. It is observed from the figure that the storage modulus of neat rubber depends on the frequency and temperature, but is independent of the strain amplitude. However in the case of rubber composites it strongly depends on the dynamic deformation especially at higher concentration of fillers (Figure 1.6b). In this case, the value of storage
modulus decreases with increase in strain amplitude. This non linear behavior of filled rubbers is known as Payne effect and can be explained by the existence of a filler network in the rubber matrix above the percolation threshold [34, 129].

When the shear amplitude is increased, these filler networks break down leading to the lowering of storage modulus. At low temperature the polymer, NR is in the glassy state with a modulus around 0.6 GPa. With increasing temperature the elastic tensile modulus suddenly drops down by 3 orders of magnitude corresponding to the glass-rubber transition. This modulus drop can be ascribed to an energy dissipation phenomenon involving cooperative motions of long chain sequences. Above \( T_g \), the composite films exhibit a huge increase in the storage modulus with increase in the filler wt\%, for example in case of composite with 8.3 wt\% of CNT the relaxed modulus at \( T_g + 70 \) K is 75 times higher than that of the pure matrix. Also the initial tensile modulus determined from tensile tests is lower than the storage modulus for CNT/NR composites where as they are equal for pure NR films.

**Figure 1.6** Variation of storage modulus (a) with temperature (b) with strain amplitude [129]
This could be related to the observed Payne effect when the dynamic strain amplitude is increased. It is clear from the figure that the initial storage modulus is increasing with the filler content and decreasing with the strain amplitude (Figure 1.6b). This strong Payne effect is consistent with the strong Mullins effect observed when the sample underwent cyclic tensile tests, and the reasons for both effects are explained to be the same. The dynamic mechanical analyses are quite useful in finding out the interactions occurring in the molecular level, for instance, the filler-filler and filler-polymer chains interactions. More detailed explanations of Mullins and Payne effects can be seen from the works of Klueppel and co-workers as well as Lang et al. [154-156]

![Graph showing storage modulus vs time](image)

**Figure 1.7** Depressive effect of CNTs with 2% PTSA (p-toluenesulfonic acid) on EPDM vulcanization at 160°C. Comparison of the vulcanization kinetic of EPDM, 5CNT–EPDM and 5S/CNT–EPDM [80]

Figure 1.7 shows the relative increase in the modulus determined from dynamic mechanical analysis [80]. In fact the storage modulus reflects the elastic modulus of the rubber materials, which measures the recoverable strain energy in a deformed specimen. It is also reported that the Guth model and the Halpin–Tsai (Equation (1.3) [10]) model fit very
well (both models depends on filler aspect ratios) with the experimental data after considering the aspect ratio of 40-45 for MWCNTs in SBR.

\[ E = E_0 \frac{(1 + 2 f\phi\sigma)}{(1 - \phi\sigma)} \] ................................. (1.3)

Where \( \sigma \) is given by

\[
\sigma = \left[ \frac{E_f/(E_a - 1)}{E_f/(E_a + 2f)} \right]
\]

\( E_f \) is the modulus of the filler. In elastomeric composites, \( E_f \gg E_0 \), so Equation (1.3) reduces to Equation (1.4).

\[ E = E_0 \frac{(1 + 2 f\phi)}{(1 - \phi)} \] ................................. (1.4)

In the case of CNT/rubber composites, the high specific surface areas and essential modulus of CNTs enhance the stiffness of rubber which results in an increment in the storage modulus values. In the case of CNT/NR composite, the modulus is increased after the addition of CNTs [80]. With the increase of temperature, the stiffness of NR is also enhanced due to the influence of CNTs. The storage modulus of CNT/NR composites is also high due to the improved dispersion of CNTs in the NR matrix and good interfacial bonding between them. The addition of CNTs reduces the volume percentage of NR in composites, which lowers hysteresis loss of the composites under a dynamic condition. This can be beneficial for some of the applications of rubber products, such as tyres. The presence of CNTs also affects the cure kinetics of rubber due to the increase in activation energy of NR and thus more energy is needed for the curing of the composites.
1.4.3. Electrical properties

Conducting particles have clearly demonstrated their capability as fillers to make insulating polymers conductive. To transfer the composite from the insulating state into the conductive state, a critical filler loading must be required [157]. This critical concentration, known as the percolation threshold is marked by a sudden increase in composite electrical conductivity by several orders of magnitude. This observation of an enhancement in electrical conductivity by several orders of magnitude at very low percolation thresholds (<0.1 wt%) of CNTs in polymer matrices without compromising other performance aspects of the polymers such as their low weight, optical clarity, low melt viscosities etc., has triggered an enormous interest in this specific area. Among various composites, nanotube-filled polymers could be used potentially for transparent conductive coatings, electrostatic dissipation, electrostatic painting and electromagnetic induction (EMI) shielding applications [157, 158]. Often, at the percolation threshold, the filler forms a continuous network inside the polymer matrix, and increase in the filler loading further usually has little effect on the composite electrical resistivity i.e. this interconnecting filler network formed results in a sharp drop of the electrical resistance of the composites. When the concentration of these particles increases above percolation threshold, the formed network like structure will be responsible for the conduction [92].

Anand et al. [74] found very good improvement in the conductivity values of NR even at small loadings of SWCNTs. When CNTs are added to an elastomer, it will be dispersed in the elastomer and this will increase the electrical conductivity due to the presence of free electrons. CNTs show very good enhancement in the conductivity value at smaller filler loading also [159]. The very high aspect ratio of the nanotubes is mainly
responsible for this percolation behavior at very low concentrations. Above the percolation threshold, the material behaves as an ohmic conductor with conductivity almost independent of frequency. Even if Anand et al. [74] succeeded in describing the phenomenon, they didn’t get a much higher improvement in the conductivity value. Verge et al. [160] produced vulcanized CNT/NBR composites by melt blending in the Brabender internal mixer. It was shown that during the blending process, the polymer chains are grafted onto the CNT surface via a free-radical mechanism. Indeed, NBR generates free-radicals from its acrylonitrile (ACN) units upon heating and/or shearing. As a result of the high inherent affinity between the CNTs and ACN units, and due to the formation of ACN-based free-radicals leading to NBR-grafting on CNTs, increasing the ACN relative content along NBR chains triggers higher polymer-grafting on the nanotube surface. The higher rate of disentanglement of CNT bundles and their dispersion in NBR matrices with higher ACN relative content should favor the formation of a percolation network and likely reduce the electrical percolation threshold. They noticed an increase in the percolation threshold even with lower acrylonitrile NBR. Das et al. [82] illustrated the variation in electrical conductivity of SBR and BR blends by preparing the composites from two methods-wet chemical method and dry mix method. The CNTs formed very good network even at very small concentrations when they were dispersed by wet chemical method. This is clearly indicated in Figure 1.8a and 1.8b. The authors could explain well the conduction mechanism occurring in CNTs along with the morphology of the CNT network.
Bokobza [10] studied the effect of filler loading on the volume resistivity of CB and MWCNT filled composites based on insulating SBR. A continuous network is formed at lower filler loading with MWCNT bundles compared with CB. The higher aspect ratio of the nanotube bundles which increases the probability of particle-particle contacts explains this low percolation threshold. Their results are in agreement with those of Flandin et al. [161] and of Thongruang et al. [162] who showed that the percolation threshold concentration in composites is around 10-15 wt\% for carbon fiber and high structure CB and around 40-50 wt\% for graphite and low structure CB. Since the resistivity of the unfilled elastomer is several orders of magnitude larger than that of the filled vulcanizate, any rearrangement of the filler particle distribution induced, for example a deformation, leads to a change in the vulcanizate conductivity. Significant changes in electrical resistivity against deformation in CB filled composites have already been reported in the literature [10,163-167].
The important uses of electrically conducting composites (volume conductivity $>10^{-10}$ S/cm) are shown in Figure 1.9a. As already discussed the electrical conduction mechanism depends on percolation theory which explains an insulator-to-conductor transition, on increasing the conducting filler concentration. Below the percolation region, conductive network does not exist and the electrical properties are only contributed by the polymer matrix. In contrast, above the percolation range, conductive filler networks and multiple electron paths exist and so the electrical conductivity of the composite shows a saturation plateau, as shown in Figure 1.9b [151]. The electrical percolation threshold is found to decrease by using ethanol as dispersion agent, compared to dry mixing, correlating with improved optical dispersion. However, different studies of CNT-filled elastomers have shown that this is not the case always. In previous investigations, the reason for the missing direct correlation between thermal and electrical conductivity has been related to the contact resistance between adjacent CNTs in the composite [34]. The mechanism of charge carrier transport in composites with conductive carbon particles has been analyzed extensively by
Sheng et al., showing the conductivity is limited by the tunneling of charge carriers over nanoscopic gaps between neighboring particles with potential-barrier modulation by thermal fluctuations [168]. The morphological properties of these gaps can be characterized by dielectric spectroscopy, where typical gap distances between 3 and 8 nm have been found for CB-filled elastomers. The dielectric data show that similar gaps are also present in CNT-elastomer composites [34]. The electronic contribution is about 15 times higher than the thermal conductivity of rubber. But, this is too small, in comparison with many magnitudes of order between the electrical conductivities of CNT and rubber, to allow for a percolation behavior of the electron thermal conductivity.

Dependence of conductivity of the MWCNTs/rubber composites on the surfactants, CTAB and silane coupling agent (KH550) is demonstrated by Jiang et al. [85] as in Figure 1.10c. They proposed two main factors that can affect the conductivity of the composites with different modifiers- good dispersion, which is helpful to improve the conduction due to the formation of conductive network and the interfacial interaction that produces energy barrier and blocks the transport of electrons. In the case of KH550, most of the MWCNTs are tightly combined with the rubber and relatively thick rubber layers exist among the CNTs, which cause a high transport barrier of electrons by tunneling mechanism. This factor results in a low conductivity of the MWCNTs/rubber composites. The composites with MWCNTs modified with CTAB display a relatively high conductivity because of physical interfacial action. In this case, it produces a considerable lower transport barrier for electron among the CNTs. In addition, the NH$_3^+$ in CTAB is also helpful to the transport of electrons because the amine salt can decrease the energy barrier for the charge transport. In case of the combination of both surfactants, KH550 and CTAB, the composites not only exhibited stronger interfacial
interaction but also offered better dispersion. It is reasonable that the conductivity of this kind of composites is intermediate.

![Figure 1.10](image)

**Figure 1.10** Dependence of the conductivity of the m-MWCNT/VMQ composites on the (a) m-MWCNT volume fraction, fm-MWCNT, at room temperature and 100 Hz and the inset shows the best fits of the conductivity (b) on frequency at room temperature [85] (c) Dependence of conductivities of the MWCNT/VMQ composites with the modified MWCNTs at two concentrations (0.9 vol% and 1.6 vol%) on the modifiers at 10^5 Hz [170].

A series of polymer-based composites with various modified CNT (m-MWCNT) volume fractions were prepared in order to address the percolation threshold as closely as possible. Figure 1.10a clearly shows a metal-insulator transition at the volume fraction, \( \Phi_{m-MWCNT} = 0.01 \). Percolation theory helps to describe the conductivity of the composite near the metal-insulator transition with power laws as indicated in **Equation (1.5)** [170, 171].

\[
\sigma(\phi_{m-MWCNT}) \propto \phi^{t}_{m-MWCNT} \text{ for } \phi_{m-MWCNT} > \phi_c \quad (1.5)
\]

where \( \Phi_c \) is the percolation threshold and \( t \) is the critical exponent in the conducting region.

The best fits of the conductivity data to the log-log plots of the power laws give \( \Phi_c = 0.01 \) and \( t = 3.45 \) (inset in Figure 1.10a). This small \( \Phi_c \) indicates the good dispersion of m-MWCNT in the rubber host, its high aspect ratio (about 100) and the unique physical properties, so that little content of m-MWCNT in the composites could form a percolation
cluster. A plot of the AC conductivity as a function of the frequency in Figure 1.10b tells about the conductivity dependence on frequency. Chemically modified nanotube, m-MWCNT/methyl vinyl silicone rubber (VMQ) composites were prepared [172] by treating the surface of MWCNT using c-aminopropyl triethoxy silane. Based on the percolation threshold, two kinds of electrical behavior are possible, namely the insulators with conductivity dependent on the frequency (for composites at $\Phi_{m-MWCNT} < 0.01$) and the conductors with conductivity independent of frequency (for composites at $\Phi_{m-MWCNT} > 0.01$).

Compared to the MWCNT/VMQ composite, m-MWCNT/VMQ composite has better interface compatibility due to a strong interaction between m-MWCNT and VMQ. The conductivity is as high as $10^{-2}$ (S m$^{-1}$) in the m-MWCNT/VMQ composite at $0.03 \Phi_{m-MWCNT}$ value, which is a 7-order of magnitude larger than that of rubber matrix. However, Skakalova and coworkers [173] have obtained a better improvement in electrical conductivity (14-order of magnitude) for the modified nanotubes/polymer composites. The effect of CNTs on the stability of the mechanical and electrical properties of recycled waste rubber was better investigated by Mahmoud et al. [174]. Their results indicate that the addition of CNTs to the recycled rubber improves its electrical conductivity by more than two orders of magnitude. The stiffness of the recycled rubber also increased by 6, 15, and 28 times as a result of the addition of different concentrations of the CNTs to it. This piece of work is found to be useful as it involves recycling mechanism of polymer too. The recent work on CNT/rubber by Bokobza also showed a correlation between the mechanical and electrical behaviour of the composite [159]. The electrical conductivity is reported to be depending on the processing condition and is found to be very sensitive. They obtained the percolation at very lower content of CNTs, 0.5 phr for all the three composite systems studied NR, SBR and
EPDM. Raman spectroscopy revealed the penetration of elastomer chains into the filler agglomerates and the decreased filler-filler interactions. The CNT orientation influences the electrical conductivity even above the percolation threshold. When the filled composite is stretched uniaxially, both polymeric chains and anisotropic filler particles align and this is evidenced from the increased electrical resistivity of the composites with strain. This also points towards the decrease in the number of nanotube contacts and thus better dispersion. An interesting property of drastic increase in electric resistance of MWCN/PU conducting composite was observed by Shang et al., in the presence of organic vapors. They explained the reason as the matrix swelling induced by the solvent absorption that expands the gap between the fillers and found that the electrical response behavior of the composite depends on solvent-polymer interaction, temperature and vapor pressure [175].

By combining the ionic liquid assisted better dispersion of CNTs with the electrical conductivity requirement, Kim et al. prepared SWCNT/SR composite useful in making electrodes [176]. The sheet resistance of the obtained stretchable composite is significantly decreased by the imidazolium-based ionic liquid assisted dispersion. The obtained material is useful as stretchable conductor that requires a constant conductivity when a high tensile strain up to 200% is applied. Thus the dispersion of nanotubes in the matrix has a key role in enhancing the elastomer conductivities.
Addition of graphite derivatives to insulated elastomer matrices can change them into electrical conductors with high level of electron delocalization at significantly lower loading [176], compared to CNTs. This is mainly due to the larger surface area of graphite sheets than nanotubes. Kim et al. also studied the change in electrical conductivity of multi-layer graphite (MLGS) containing SBR nanocomposites fabricated by heterocoagulation, and the data obtained are shown in Figure 1.11 (c) [104]. The conductivity of the composite increased from $4.52 \times 10^{-13}$ to $4.56 \times 10^{-7}$ S/cm when the MLGS concentration changed from 0.1 to 5 wt%. It is also noted that the concentration of the filler that is required to achieve the same electrical conductivity from CB is lower because of the high aspect ratio and electrical conductivity of MLGS [177]. The reasons for the observed low electrical percolation threshold were attributed to the efficient mixing process, without damaging fillers and effective network formation in the matrix [178], and the authors have explained this by the segregated network concept [179].

Al-solamy et al. [180] obtained the best electrical property for NBR/graphite nanoplatelets composite at 0.5 phr level much less than the usual percolation range of 5 phr.
EG. Similar to MLGS, EG also enhances the conductivity to a great extent compared to the conventional CB [181, 182]. EG imparts very good electrical conductivity at 10 phr loading [27] to a similar system (carboxylated acrylonitrile butadiene rubber (xNBR)/EG nanocomposites). The influence of graphite and TRG on the electrical conductivity of TPU was reported by Kim et al. [96]. The DC surface resistance of graphite and TRG composites prepared via different methods are compared in Figure 1.12. Both graphite and TRG effectively reduce the resistance, but they differ greatly in the percolation concentration (>2.7 vol% for untreated graphite and <0.5 vol % for TRG) [96]. Among the TRG composites, the resistance decreases even at <0.3 vol % of TRG in the case of solvent-mixed samples, whereas it requires >0.5 vol % for melt intercalation because of the possibility of platelet reaggregation in the latter.

Figure 1.12 DC surface resistance of melt-blended graphite/TPU composites (closed symbols, also in inset) and melt-blended, solution-mixed, and in situ polymerized TRG/TPU composites (open symbols) [96]
1.4.4. Dielectric properties

Conducting polymer composites with high dielectric constant are increasing attention in many technological fields. But, though there is an increase in dielectric constant, these composites show an increase in dielectric loss and a significant decrease in dielectric strength, which are undesirable for many practical applications. To increase the dielectric constant by minimizing the increase in dielectric loss in the composites is a matter of great importance. It should also be noted that covalent functionalization on CNT surface can damage their intrinsic properties like electrical conductivity [183]. The study of dielectric constant becomes important in this context. Ryan et al. [184] compared the electric and dielectric properties of MWCNT/PDMS composites based on pristine and functionalised nanotubes. They succeeded in demonstrating the feasibility of using core-shell MWCNTs to increase the dielectric constant by reducing the dielectric loss of the composites for the first time. Hydroxylated MWCNTs (MWCNTs-OH) represent one of the simplest types of core-shell MWCNTs. In core-shell MWCNTs, the outer graphene layer is covalently functionalized to become non-conducting, whereas the unmodified inner layers remain conducting. This leads to increase the dielectric constant while lessening the increase in electrical conductivity and dielectric loss of the CNT-polymer composites. The room temperature dielectric loss of composites as a function of MWCNT mass fraction (wt %) at 10 kHz is shown in Figure 1.13a. It is clear that the dielectric loss (~0.63) of the 9 wt % MWCNT-OH/PDMS composite is much lower than that (~1.25) of the 6 wt % pristine MWCNT/PDMS composite. It is also found that the dielectric constant and dielectric loss of the 9 wt % MWCNT pristine-PDMS composite are ~1631 and 10 (obtained from Figure 1.13a which indicates that the dielectric loss either reaches or exceeds the instrument’s
maximum measurement limit, that is 10) respectively. Whereas the dielectric constant of the 9 wt% MWCNT-OH/PDMS composite (~1249) is close to that of the 9 wt % MWCNT pristine-PDMS composite (~1382), but its dielectric loss (~0.80) is much lower than that (~2.31) of the same pristine CNT composite. Yet the impact of covalent functionalization of CNT surfaces on the values of dielectric constant and the dielectric loss of the composites compared with pristine CNTs remains essentially unclear. Seok et al. [185] determined the dielectric constant of the MWCNT/SR composite within room temperature to 180°C range at 50 Hz and 100 kHz of frequency. They observed a similar range in permittivity (ɛ’) values (3-5), in both frequencies, and it is found to be increasing with increase in the CNT content. Fritzsche et al. [186] synthesised CNT/NR hybrid composites and noticed a significant increase in dielectric properties up to ɛ’=103 with increase in CNT. They interpreted this large permittivity value as a combined effect of nanoscopic gaps between adjacent nanotubes and a percolation network with bottle-necks and dead ends of the CNTs on various length-scales. Since the permittivity is a measure of the polarization in the sample, the amount of interfaces between CNTs and polymer is more pronounced. They observed a relaxation process at low frequencies for the sample containing less amount of CNT (about 3 phr). Also this relaxation process is increasing in strength and is more shifted to higher frequencies with increase in CNT. This behavior is similar to CB filled composites [187-188]. In such cases the bound rubber between CB particles, obstructs the electrical contact between them. When the gaps between the filler particles are of nanometer size, free electrons tunnel between the particles. This movement of electrons by tunnelling over the gaps is referred as the relaxation process. The characteristic frequency of the relaxation transition observed at high frequencies can be related to the distance between adjacent filler particles [189, 190]. The dependence of
frequency on dielectric properties of the CNT/ blend composites in the presence of different ionic liquids has been explored by Das and co-workers (Figure 1.13b). For the CNT/(S-SBR/BR) composite, the permittivity value is a constant throughout the frequency range whereas for the compounds containing ionic liquids a different behavior is observed [82]. The composite comprised with AMIC ionic liquid shows the highest $\varepsilon'$ value (~$2\times10^4$) compared to the other composites. For the samples containing other ionic liquids the relaxation process is seen at low frequencies indicating a large gap between the nanotubes whereas for AMIC containing sample, the relaxation process is shifted to very high frequencies (1–10 MHz). So the smallest gap size is achieved with AMIC resulting in the best contact between the tubes and therefore in a high conductivity. All these factors point out to the formation of an effective percolation network in the presence of the reactive ionic liquid AMIC.

![Figure 1.13](image)

**Figure 1.13** a) Room temperature dielectric loss of both MWCNT/PDMS composites as a function of MWCNT mass fraction (wt %) at 10 kHz [184] b) Dependence of permittivity of 3 phr CNTs loaded SSBR/BR matrix in presence of different ionic liquids at 20 °C [82].

The frequency independence on the dielectric permittivity of CNT/PU composites was explained by Barick and Tripathy [191]. The magnitude of $\varepsilon_r$ does not vary significantly
with the concentration of MWCNT as well. This is because the relaxation time for realignment of interfacial dipoles along the direction of external electric field is reduced with increase in frequency. It is also observed that the loss tangent values of both neat TPU and its composites exponentially decay with increase in frequency at lower region (up to $10^5$ Hz), and it rapidly increases thereafter. With increase in CNT loading the tan $\delta$ of the composites enhances up to $10^5$ Hz but above which it reduces than that of the neat TPU. The significant increment of loss tangent with MWCNT concentration is due to the high electrical conductivity of CNTs. The authors pointed out that the composite system is suitable for developing capacitors [191]. In short, the low dielectric loss and high permittivity which are often necessary for making good dielectric materials for capacitors are satisfied with CNT based systems provided a good dispersion is achieved.

![Figure 1.14](image)

**Figure 1.14** Variation of $\varepsilon'$ of the SBR vulcanisates with the graphite loading for different particle sizes (53–150 $\mu$m) at 100 Hz [111].

The dielectric properties are also notable for the graphene based composites. Ismail and Khalaf [111] measured $\varepsilon'$ values of SBR composites filled with graphite particles of
different sizes at different concentrations. Measurements were done at room temperature and at 100 Hz, and the obtained result is depicted in Figure 1.14. The values of $\varepsilon'$ increased with increasing graphite content. This increase in $\varepsilon'$ is a typical response of all heterogeneous systems where the conductivity and relative $\varepsilon'$ of the constituent phases differ as a result of an interfacial polarization phenomenon that occurs at the interfaces of dissimilar materials at low frequency. Moreover, it is interesting to observe that, for samples containing up to 70 phr graphite, $\varepsilon'$ was inversely proportional to the particle size as evidenced in the figure (Figure 1.14). Recently Romasanta et al. compared the dielectric permittivity of PDMS/FGS and PDMS/CNT nanocomposites at room temperature (Figure 1.15). The dielectric permittivity spectra of PDMS/FGS with 0.5-1 wt.% FGS loading shows the values of composites to be twice as much compared to the PDMS matrix, thereby suggesting its smooth and frequency independent behavior. At 2 wt.% of FGS, the permittivity constant is increased ($\varepsilon' = 23$) to about ten times higher than the pure matrix at low frequencies, whereas only a six fold increase is observed for CNT composites at the same concentration [192]. The reason for this behavior is explained in terms of compatibilisation. The functional groups present on the graphene sheet surface reduced the polarisation process and, thus, improved the compatibility of nanofiller/polymer at the interface [193]. Also, not much variation is found in the loss tangent values with frequency, again attributed to the homogeneous dispersion of FGS in the matrix and the presence of functional groups on the filler surface. The functional groups can interrupt the $\pi$-conjugation occurring in the graphene layers and, thus, can favour enhanced filler/polymer compatibility [194]. The authors also compared the figure of merit (FoM) values of PDMS composites with different fillers. The composites containing FGS show the
highest permittivity enhancement (1 or even 2 orders of magnitude) with the lowest amount of filler when compared to all other composites.

Figure 1.15 Dielectric permittivity as a function of frequency at room temperature, for (left) CNT/PDMS and (right) FGS/PDMS composites at various filler concentrations [192].

1.5. Applications

1.5.1. Overview

Elastomer composites containing conducting fillers such as CB, carbon fiber, and metal fiber have been extensively investigated for multi-functional applications such as structural reinforcement [195], EMI shielding, electronic packaging, radar absorbing materials and high charge storage capacitors. Addition of CNTs and graphene is promising in improving the flame retardancy of elastomers as well [77, 196]. These nanofillers have the unique ability to delay ignition, reduce smoke emissions and eliminate slumping and dripping of the molten polymer by formation of a strong, stable char. Some applications such as flame retardant material include wire and cable covers, battery jars and electrical enclosures, small appliances and home interior decoration materials. The CNT composites have potential applications in automotive industry that could lead to better quality, lower cost, less fuel consumption and lower environmental emissions. Those applications include
electrostatic painting of exterior panels, shielding of automotive electronics and addition of nanofibers to tyres to improve stiffness. Recent researches developed a high performance rubber sealing material resisting 260°C/240 MPa using a special composite of surface controlled MWCNT, which can act as a sealing material. This composite material can be used at low temperatures in a real oil field, which can avoid the energy crisis. Upon increasing the CNT concentration, the tensile strength, stiffness and electrical conductivity of the composites increased significantly but the elongation at break decreased in MWCNT/EPDM [197]. Sui et al. found out enhanced performance for the CNT/NR composites compared to neat NR and CB/NR composites by the incorporation of acidic treated and ball-milled CNTs [198]. Kim et al. reported that rubber composite sheets filled with highly aligned MWCNTs showing significant improvement in their elastic modulus and thermal and electrical conductivities [121].

Recently, Hata and co-workers [199] developed a new viscoelastic material from CNTs that is similar to SR, but maintains temperature independent viscoelasticity at a range of temperatures from -196 to 1000°C in an oxygen-free environment, unlike the traditional composites. Among many other applications, temperature-invariant rubbery material made from CNTs could be used as dampeners (antivibration mounts) for high-vacuum furnaces and even aerospace vehicles that travel to the cold interstellar space. These composites remain flexible over the entire temperature range. This CNT rubber can be stretched in the direction of applied stress up to 5% strain before an irreversible process of straightening, slipping, and bundling of CNTs occurs at the failure strain of 100%. The porous network structure, coupled with excellent thermal transport properties intrinsically associated with graphitic fillers allows their rubber composite for rapid and efficient heat dissipation to prevent
significant heat accumulation. Such composite materials with exotic viscoelastic properties can outperform the existing elastomers. Even though it is difficult to picturise all the applications of conducting elastomer composites, a few of them are illustrated in Figure 1.16.

![Figure 1.16 Major application of conducting elastomer composites a) Home appliances b) switches c) pressure sensing skin in robotics d) strain sensor attached to tyre engineering e) energy storage application as capacitors and f) cables.](image)

In addition, conducting rubber composite consisting of EPDM matrix, MWCNT and clay is used as strain sensitive material [128]. The piezoresistance of MWCNT/SR composite give a positive piezoresistance both parallel and perpendicular to the direction of applied pressure [200]. Conductive thermoplastic elastomer composites of PP/EPDM and three kinds of carbon fillers including CB, MWCNT and hybrid CNT-CB show piezo resistive properties depending on the nature of filler, concentration and percolation threshold [201]. At low filler concentration high pressure-resistance sensitivity and at high concentration low pressure-
resistance sensitivity is observed. The composites are well suited for fabricating pressure sensors, the detailed study of which is given in the next section. There are certain kinds of sensors useful for health monitoring [202] and for detecting dangerous deformations and vibrations of vehicle parts. CNTs having high dielectric constant are very effective for synthesising composite dielectrics. Such composites are very beneficial as actuators for artificial muscles, capacitors for energy storage, sensors for mechanical strain, humidity, and gases and in flexible electronics [203-208]. CNTs can act as the electric or light induced heating sources for liquid crystalline elastomers. They are efficient heat absorbers and can convert heat energy to light energy [209]. This is really important in the field of electronics specifically in solar cells or light emitting diodes. The three dimensional network structure formed by boron doping of CNTs by CVD behaves like elastomer solid and these materials have unique properties. These oil absorbing sponge-like solids possess multi functionalities such as ultra-light weight, super-hydrophobicity, high porosity, thermal stability and mechanical flexibility [210]. Incorporation of this kind of systems in elastomers creates blend morphology and such kinds of applications are anticipated. Photo-actuating materials based on the commercial elastomer EVA filled with well-dispersed MWCNTs were developed as potential materials for the fabrication of smart actuators [211].

1.5.2. Sensing

Recently electrically conducting flexible rubber composites (CRC) containing CNTs and graphitic fillers have received much attention as potential materials for vapour, strain and pressure sensors [212-214]. Upon external forces, CRC deformation takes place with the micro scale change of inter-electrical conduction in rubber matrices due to the change of
contact resistance, and CRC exhibits macro scale piezoresistivity. This effect can be more explained as follows. The electrical conductivity of graphene composites depends on the resistance of conducting particles and contacts between them at junction points based on the stress applied to the material. The stress is transferred to the junction points via the stiff nanotubes causing the resistance change sensitive to small material deformations [215]. Extensive studies on this resistance-strain sensitivity reveal interesting results and corresponding models were reported [216]. The effect of strain on the electrical resistance of RGO/IIR composites by solution mixing [214] has been reported by Sadasivuni et al. Zhang et al. also described simultaneously existing giant effects -strain sensing and gas sensing- based on CNT/polyisoprene composites [217]. Conducting rubber composites of EPDM has been prepared with MWCNTs and organo-clay to develop flexible strain sensitive materials [197]. The composites were prepared by adding various amounts of MWCNTs to a fixed amount of organo-clay. It is found that the organo-clay has the ability to better exfoliate the MWCNT bundles inside the rubber matrix and this led to enhancement in properties. Figure 1.17 describes the strain sensing properties of MWCNT/EPDM composite due to piezoresistivity of the rubber composites containing 20 wt% of MWCNTs during extension and compression. When the MWCNT/EPDM composite sheet was extended from 0 to 4000 micro strain, the resistance increased significantly as expected (Figure 1.17a). However, there are still some problems that must be resolved to get composites exhibiting significantly improved properties like mechanical strength and conductivity.
Figure 1.17 (a) Strain response of the MWCNT/EPDM composite containing 20 wt % of MWCNT during compression and extension (b) Changes of electrical resistance under various pressures for the samples A–C (Sample A = Unmodified-MWCNTs, Sample B= Carboxylated-MWCNTs, Sample C=Silicon Rubber) [197]

For predicting the piezoresponse of the MWCNT/polymer composite films Park et al. [215] proposed the Equation (1.6).

$$\frac{\Delta R}{R_0} \approx \begin{cases} ke \rightarrow (0 \leq \varepsilon \leq \varepsilon^c) \\ ke + u(\varepsilon - \varepsilon^c)N \rightarrow (\varepsilon > \varepsilon^c) \end{cases} \quad \text{................. (1.6)}$$

where $\Delta R$ is the change in resistance, $R_0$ is the initial resistance, $k$ is the slope of the linear region, $\varepsilon$ is the strain of film, $\varepsilon^c$ is the critical strain at which the number of contacting MWCNTs begins to decrease significantly, and $N$ is the tunneling resistance between adjacent MWCNTs.

The piezoresponse of MWCNT/SR composite under uniaxial pressure was studied by Wang et al. [200] and they found that the carboxyl radical (-COOH) on MWCNT avoids the second aggregation and improve the degree of homogeneous dispersion of MWCNT in rubber, thus enhancing the piezoresistive properties. They studied the variation of electrical resistance with pressure for three samples A, B and C. Sample A is of unmodified CNTs,
sample B, the carboxylated CNTs and sample C the neat SR. Figure 1.17b shows an increase in electrical resistance for samples with unmodified and carboxylated MWCNTs with pressure, showing positive piezoresistance. Also a sharper and more linear increase of sample B than sample A is found because of homogeneous dispersion of MWCNTs under 0-2.86 MPa uniaxial pressure.

**Figure 1.18** A schematic model for the change of conductive structure in the composites under pressing: the conductive fillers disperse randomly in the composite [215].

Elastomer/graphite derivatives have extensive possibilities as piezoresistive materials where the electrical resistance depends on both the resistance of each conducting particle and of the polymer matrix [216]. When an external pressure is applied (compression), the inner conducting network of electrically conductive composites changes and this results in resistance variation. During the compression process, destruction and formation of conductive networks simultaneously occur in the composites (Figure 1.18). If the compression is small, the experimental data are consistent with the tunnelling conductance model. But for larger deformations, destruction of the conductive network and decrease of the number of conducting pathways have to be considered [217]. But, for the composite with aggregating filler particles, the aggregations are treated as particles, and their piezoresistivity is different from that of homogeneous particles filled composites. When the composite is
subjected to stress, the volume is compressed and the particle’s fraction increases, with a resulting decrease in resistivity. However, the thickness of the sample also decreases, that result in an increase in the resistance between two electrodes. In short the conducting elastomer finds application in sensor bending, such as electronic textiles.

1.5.3. Shape memory

Some polymers possess the unique ability of shape memory by which the polymers restore their original shape after a structural deformation by an external stimulus such as heat, light and/or chemicals [218, 219]. Such shape memory polymers (SMPs) exhibit superior properties like large rate of shape recovery, easy processing, lightweight and low cost compared to shape memory alloys and thus have great significance in technology and industry [220]. Commonly thermal stimulation is used to deform the material which is done by heating the polymers above their transition temperature (either the glass transition or melting temperature). Polyurethanes (PUs) are the most relevant examples of shape memory polymers. PU possesses hard and soft segments in their structure and the physical crosslinks present in their hard segments helps in their easy processing [221]. The shape memory property of segmented PU block copolymers has been extensively addressed because of its superior material properties, arising from the phase-separated structure of its hard and soft segments. PUs show higher recovery ratio and fixity and shorter recovery time based on the molecular weight of the polyol precursor used to synthesize it. Thus the glassy and rubbery properties of PU and its composites depend on the urethane content and its crosslink density [222]. Various fillers such as CNTs and graphitic derivatives enhance the shape memory properties of PU [223, 224]. In addition the soft segments containing PU exhibit better shape
memory than their hard segmented counterparts [222]. Using a two step synthesis method Kim et al. derived the dependence of graphene on the shape memory nature of PU containing 30% hard segments. Here the shape recovery was monitored using a tensile machine equipped with a thermal chamber and the composite containing 1.5 phr graphene showed the best recovery [224].

1.5.4. MEMS and MAMS

MEMS or microelectromechanical systems form the basics of several industrially significant devices such as sensors, actuators, displays, optical switches, energy harvesting devices, transducers etc. Since nanotechnology joins hand with this field it can also be called nanoelectromechanical systems or NEMS. Using the low-cost MEMS technology, CNT/PDMS composite is applied in fabricating piezoresistors by Kim et al. They have observed good mechanical, electrical and pressure sensing properties for the composites at various filler loadings. The gauge factor of the CNT/PDMS composites showed values 1.38 - 12.4 according to the CNT concentration. In addition to nanosensors such materials are useful in microfluidic systems as well [225]. By aligning CNTs on the polymer surface CNT/PDMS composites were formulated [226]. Such composite showed excellent electrical properties, rheological properties, room temperature micropatternability and elasticity. Surface potential measurements reveal the increased charge storage capacity and stability of the CNT/PDMS composite when compared to neat PDMS and CNTs over a measurement period of 280 h. The authors have illustrated the power generation in this corona-charged composite by ball drop experiment and the composite is proposed to be suitable as elastic electrets.
The polymer PDMS is widely used in MEMS because of its structural applications. In another work conducting MWCNT/PDMS composites were fabricated by monolithic integration. Fabrication processes including PDMS patterning, micromolding, and bonding techniques were employed. Such composites are applicable in elastomeric strain gauges, capacitive pressure sensors, microfluidic channels with heaters, electrodes and sensors [227]. Buckling is another phenomenon addressed using MEMS technology. In the case of SWCNTs filled elastomer composites, the buckle wavelength is proportional to ¾th power of the CNT radius whereas for MWCNTs, it linearly increases with the number of walls. When two parallel nanotubes on the elastomer surface are considered, they interact and buckle together at the same wavelength below a critical spacing. For the coupled buckling, the larger tube dominates as the cobuckling wavelength is close to the wavelength of larger CNTs [228].

Microwave-absorbing materials (MAMS) made from CNT/elastomer composites are widely applied in wireless communication. CNTs are capable of absorbing microwave radiation and this capability is found to increase with their functionalization and rate of dispersion. A layered and porous structured RGO filled NBR composite was reported for improved microwave absorption and used in shielding applications [229]. The property of microwave absorption of the composite varies with the thickness of the material, working frequency, complex permittivity and permeability. Zhang et al. investigated the effect of fabrication method on the microwave absorption property of MWCNT/PVC/NBR composites. The composite made by premixing with PVC had a higher dielectric loss and thus better microwave absorbing performance than that made by premixing with NBR at the same MWCNT concentration. The former had a minimum reflection loss of 49.5 dB at the
optimum composite thickness of 1.96 mm due to a high dielectric loss and moderate permittivity. Upon the addition of SiC to the composite the reflection loss decreased to 34.9 dB at 3 mm thickness due to an impedance mismatch at the air–material interface since the permittivity increased [222]. Researchers made it possible to produce graphene nanosheets decorated with PANi nanocomposites with high charge storage capacity in lithium ion batteries useful as electrochemical capacitors [230]. Very recently IIR-SWCNT composites prepared by solution mixing have shown to exhibit high shielding efficiency in the X and Ku band (8.2–18 GHz) frequency range [231]. A shielding effectiveness of about 9–13 dB was obtained for the composite with 8 phr of SWCNT and here the absorption was the dominating shielding mechanism. The dielectric properties, conductivity and skin depth of the composites depend on the SWCNT loading and influence the shielding effectiveness.

In another case the effect of CNTs and GNPs on the microwave (reflection coefficient, attenuation coefficient, shielding effectiveness) properties of NR nanocomposites has been investigated in the wide frequency range (1–12 GHz) [232]. Liu et al. used in situ reduction process to prepare binary composite of graphene/poly(ethylene oxide) (PEO) with excellent microwave absorption property at low graphene content. The minimum reflection loss of the composite is up to −20.0 dB at 1 wt% graphene loading [233]. The graphene/PEO has better thermal stability attributed to the graphene restoration of sp² bonded carbon structure. Annealing self-assembly of block copolymer thin films on silicon substrate using a microwave oven is very fast and the key steps that taking place during this process is addressed by Jin et al. They found the silicon substrate is the dominant source and the doping, sample size, and polymer composition influence annealing [234].
In short the applicability of graphene derivative fillers as well as CNTs on elastomer nanocomposites is many, and this thesis is aimed at exploring a few of them.

1.6. Conclusions
This chapter summarizes the various kinds of fillers (specifically CNTs and graphitic fillers) and their elastomer nanocomposites mainly used in this study. Various characterization techniques reveal the improved properties for the nano carbon filled composites. The mode of dispersion, alignment and interfacial interaction play key roles in regulating the composite behavior. Apart from these aspects the main application of such conducting nanocomposites in electronics is also dealt with.

1.7. References


Chapter II: Materials and Methods

ABSTRACT

In this chapter we discuss about the materials used in this work and the main synthesis methods followed in detail. The fillers RGO and PANi have been synthesized by various means. Graphene is synthesized from graphite, by following the improved graphene oxide synthesis method. The preparation of composites, characterization techniques etc. are elaborated. Theoretical background for the major studies used in this survey is also dealt with.
2.1. Introduction

The objective of this chapter is to describe the various materials, sample preparation methods and techniques used in this thesis. First part describes the various materials used in this work and their sample preparation techniques. We describe the composite fabrication method and the major characterization techniques used in this study as the second part along with the principle of major properties studied here. The dynamic mechanical property of rubber, the “Payne Effect” and the models used to interpret the results are also addressed in this section.

2.2. Materials

2.2.1. Elastomers
NR with antioxidant (%) 1.400, organic acid (%) 0.250, soap (%) 0.004, Mooney viscosity (ML1+4 100°C) 40.000, bound acrylonitrile (%) 34.000 and intrinsic viscosity (dl/g) 1.527 was purchased from Rubber Board, Kottayam, India and curing ingredients from Apollo tyres, India. The commercially available elastomer poly(isobutylene(98%)-co-isoprene(2%)), IIR(density 0.9 g/cm³) was purchased from Exxon Company. The tri block polymer SIS obtained from KRATON D1165 PT, Kraton Polymers, USA consists of 30 wt% of polystyrene. The monomers, MDI and 1,4-Butanediol (1,4-BD) for PU synthesis were purchased from Interchemol S.A., Poland and BASF, Germany respectively. The polyol, poly(tetramethylene ether) glycol (PTMG, 1889 g/mol) was obtained from BASF, Hungary.

2.2.2. Fillers
MWCNTs with high aspect ratio (>150) was obtained from Nanocyl-NC7000. Natural flake graphite (molecular weight 12.01 g/mol), maleic anhydride, curing agents and
all other minor reagents (solvents) were procured from Sigma Aldrich. Graphite, dibutyltindilaurate (DBTL), N,N-dimethyl formamide (DMF) and other reagents such as H₂SO₄, HNO₃, HCl, KMnO₄ and H₂O₂ were also procured from Sigma–Aldrich. PTMG and 1,4-BD were dried separately at 100°C with stirring under reduced pressure. MDI was melted at 46°C and filtered before use. All other reagents were used as received. Aniline, dodecyl benzenesulfonic acid (DBSA), ABS, chloroform etc. are obtained from Aldrich, Qatar. Hydric oil for the sensing experiments was obtained from ADNOC company (grade – FOD, H-68).

2.3. Methods
2.3.1. Synthesis of RGO
TRG is prepared from graphite by following a chemical approach. This technique involves two key steps, (i) oxidation of graphite to GO and (ii) thermal reduction of the prepared GO to TRG. A schematic representation of the whole process is given in Figure 2.1. Firstly, GO is prepared by the so-called improved graphene oxide synthesis method [1]. A 9:1 mixture of concentrated H₂SO₄/ H₃PO₄ (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and KMnO₄ (18.0 g, 6 wt equiv). The mixture was then heated to 50 °C with stirring for 12 h. The reaction was cooled and poured onto ice (400 mL) with 30% H₂O₂ (3 mL). Unreacted large graphite plates were separated by using metallic U.S. standard testing sieve (size 300 μm) and then filtered. The filtrate was centrifuged and solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol (repeated twice). Finally the material remaining was washed with 200 mL of ether to obtain GO. For the reduction of GO, thermal method was preferred rather than chemical method as thermal reduction leads to nearly complete exfoliation [1, 2]. Hence the dispersion of TRG becomes easier where as stacked layers of CRG have to be
exfoliated by applying mechanical stress prior to dispersion. For thermal reduction, nitrogen gas was passed through GO for 30min in sealed container to create an inert atmosphere on GO surface and the resulting product was placed in pre-heated muffle furnace at 1000 °C for 30s. The thermal reduction at two different temperatures 200°C for 30 min and 600 °C [3] for 30 min gives different deoxygenation degrees for GO and at 200 and 600 °C respectively produces G200 and G600.

Figure 2.1 Schematic representation: preparation of thermally reduced graphene oxide (in site shows fillers dispersed in THF and water).

The morphology of the synthesized GOs was examined by AFM. Figure 2.2 shows the tapping mode AFM image of GO sheets that was taken by coating it on the oxidized silicon wafer. The smooth surface indicates the defect free layers, the thicknesses of which were calculated [4] to be about 1.5nm.
Figure 2.2 AFM images of GO platelets deposited on a smooth silica surface.

2.3.2. Synthesis of PAni/DBSA

The polymerization of aniline to PAni was carried out by chemical oxidative polymerization of aniline (2.07g) in the presence of DBSA (10.9g) using APS (5.1g) as oxidant at <2°C. For this aniline with 100ml distilled water was magnetically stirred in ice bath to form a homogeneous milky suspension and then APS dissolved in 50ml water was added to the aniline/DBSA mixture. The stirring was carried out for 24 h and the dark green PAni/DBSA was precipitated using acetone. The precipitate was filtered and washed continuously with water and finally dried to obtain the PAni doped with DBSA [5]. The SEM image of the PAni/DBSA showed in Figure 2.3 confirms the flat fibrous circular morphology of the particles. The molecular weight of PAni/DBSA obtained from the chromatographic technique was 391.94 g/mol.
2.3.3. Preparation of SIS-PAni composites

SIS-PAni composites were synthesized by following in situ polymerization of aniline in presence of SIS. For this 4 g of SIS was dissolved in 50 ml toluene in an RB flask using magnetic stirring. Required amount of aniline was mixed with specific amount of DBSA and 100 ml distilled water and added to the above SIS solution. The mixture turned to a white milky emulsion and was continuously stirred by keeping in ice bath. Then specific amount of the APS dissolved in 50 ml distilled water was added to the mixture with vigorous stirring. The solution first appeared to a brownish yellow colour which turned to deep brown and finally green. Stirring was continued for 24 h and finally the composite was precipitated with acetone, filtered, washed with water and dried. The mole ratio of Aniline:DBSA:APS was always maintained as 1:1.4:1. The details of all samples prepared are given in Table 2.1.
Table 2.1. Details of samples prepared

<table>
<thead>
<tr>
<th>Notation</th>
<th>PANi (wt %)</th>
<th>TGA degradation peak (°C)</th>
<th>Glass transition (Tg in °C)</th>
<th>Water Contact angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS</td>
<td>-</td>
<td>377.3±0.1</td>
<td>-60.1±0.06</td>
<td>103 ± 3</td>
</tr>
<tr>
<td>SIS-PAni1</td>
<td>15</td>
<td>347.0±0.3</td>
<td>-61.0±0.04</td>
<td>24 ±11</td>
</tr>
<tr>
<td>SIS-PAni1.5</td>
<td>20</td>
<td>352.0±0.5</td>
<td>-61.2±0.03</td>
<td>23 ± 5</td>
</tr>
<tr>
<td>SIS-PAni2</td>
<td>22.5</td>
<td>345.8±0.4</td>
<td>-61.6±0.03</td>
<td>21 ± 16</td>
</tr>
<tr>
<td>SIS-PAni2.5</td>
<td>25</td>
<td>349.7±0.3</td>
<td>-61.8±0.01</td>
<td>10 ± 4</td>
</tr>
</tbody>
</table>

2.3.4. Synthesis of RGO/CNT

Homogeneous dispersions of MWCNTs separately and together with RGOs were made in THF by sonication followed magnetic stirring. The formation of synergistic MWCNTs/G200 (CG200) and MWCNTs/G600 (CG600) mixtures is schematically represented in Figure 2.4. The filler dispersions were added to the solution of dry NR in THF (1:5), and mechanically stirred for about 3 hours. After completion of the mixing process, the composite dispersion was casted into films and dried. Then it was again melt blended in Haake mixer (at 60 °C, 10 minutes, 30 rpm) with curing agents. The composition of curing agents used were zinc oxide (4.49 wt %), stearic acid (1.80 wt %), MBTS (1.08 wt %), TMTD (0.54 wt %) and sulphur (2.25 wt %) per 89.85 wt % of NR. Curing was done at 150 °C for the respective cure times measured from the moving die rheometer in a preheated hydraulic press mold. The details of the prepared samples are given in Table 2.2.
Figure 2.4 Schematic representation of the preparation of CG200 and CG600 by sonication.

Table 2.2 Details of prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (wt %)</th>
<th>MWCNT (wt %)</th>
<th>G200 (wt %)</th>
<th>G600 (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>89.85</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NR-CNT</td>
<td>85.98</td>
<td>4.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NR-CG600</td>
<td>85.98</td>
<td>2.15</td>
<td>2.15</td>
<td>-</td>
</tr>
<tr>
<td>NR-CG200</td>
<td>85.98</td>
<td>2.15</td>
<td>-</td>
<td>2.15</td>
</tr>
</tbody>
</table>

2.3.5. Preparation of NR/IIR/SIS/CNT

Solution mixing process was employed for synthesizing CNT based nanocomposites of NR, IIR and SIS by varying filler loading of CNT. At first, filler was sonicated in chloroform for 1h and then mixed with polymer/chloroform solution using mechanical stirrer for 3 h. All composites were dried at 80 °C in a vacuum oven till it attained a constant weight. The details of all samples prepared are given in Table 2.3.
Table 2.3: Details of samples analysed and their glass transition values.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Polymer</th>
<th>CNT (wt %)</th>
<th>Glass transition (Tg, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>SIS</td>
<td>-</td>
<td>-60.09±0.01</td>
</tr>
<tr>
<td>SC2</td>
<td>SIS</td>
<td>2</td>
<td>-61.04±0.02</td>
</tr>
<tr>
<td>SC3</td>
<td>SIS</td>
<td>3</td>
<td>-61.17±0.05</td>
</tr>
<tr>
<td>SC4</td>
<td>SIS</td>
<td>4</td>
<td>-61.60±0.03</td>
</tr>
<tr>
<td>BC</td>
<td>IIR</td>
<td>-</td>
<td>-62.12±0.04</td>
</tr>
<tr>
<td>BC3</td>
<td>IIR</td>
<td>3</td>
<td>-61.83±0.07</td>
</tr>
<tr>
<td>BC4</td>
<td>IIR</td>
<td>4</td>
<td>-60.09±0.06</td>
</tr>
<tr>
<td>BC5</td>
<td>IIR</td>
<td>5</td>
<td>-60.02±0.05</td>
</tr>
<tr>
<td>NC</td>
<td>NR</td>
<td>-</td>
<td>-64.12±0.04</td>
</tr>
<tr>
<td>NC4</td>
<td>NR</td>
<td>3</td>
<td>-63.51±0.03</td>
</tr>
<tr>
<td>NC5</td>
<td>NR</td>
<td>4</td>
<td>-62.31±0.02</td>
</tr>
<tr>
<td>NC6</td>
<td>NR</td>
<td>5</td>
<td>-62.12±0.04</td>
</tr>
</tbody>
</table>

2.3.6. Synthesis of Polyurethane

In order to synthesize PU, a calculated amount of MDI was added to the polyol, poly(tetramethylene ether) glycol PTMG, and the mixture was stirred at 80°C for 1 hour to obtain a prepolymer (with a theoretical concentration of 6.6% unreacted NCO groups). The MDI:PTMG ratio was maintained to be 2.6:1. Then, the prepolymer was mixed with 1,4-BD at a NCO/OH molar ratio of 1 while stirring vigorously and was poured into a hot mold (90°C). The reacting mixture was annealed at 100°C for 24 hours to complete the reaction. Finally non-modified soft PU (containing 33.3% of hard segments) was obtained [24]. Due to the low level of hard segments, the PU does not have a sharp melting temperature (Tm). The absence of unreacted NCO groups in the polymer was verified by FTIR spectra. Its $T_g$ was found out to be about 5°C using the differential scanning calorimetry. The molecular weight of PU was determined from chromatography and was about 6791.94 g/mol.
Required amounts of GO and MDI were dissolved in DMF and sonicated for 10 min. The mixture was then refluxed for 48 h at 100°C. The precipitate was filtered and washed several times with DMF to remove the extra phenylisocyanate. The product was dried in a vacuum oven at 60°C to obtain the functionalised GO nanosheet-phenylisocyanate complex [6]. AFM gives the planar morphology of the GO and mGO nanosheets with interplanar distances 1.5 and 3.3nm respectively. The average contact angle values of water droplet on both GO and mGO platelets were also calculated to be 92.5°±6 and 152.5°±6 respectively indicating the comparatively lower hydrophobicity (partial hydrophilicity) of GO and super hydrophobicity of mGO.

2.3.7. Synthesis of mGO
In order to modify GOs, both the GO and MDI dissolved in DMF were mixed by sonication for 10 min and thereafter refluxed for 48 h at 100 °C. The obtained precipitate was filtered and washed several times with DMF to remove the extra phenylisocyanate and then dried in a vacuum oven at 60 °C. The synthesized mGO was analyzed using the FT-IR characterization and its spectrum along with that of GO and MDI is shown in Figure 2.5. The common peaks observed at 3411, 2900 and 1060 cm⁻¹ were respectively assigned to the O-H stretching intramolecular bond vibration, C–H stretching and the C–O–C pyranose ring skeletal vibrations. For GO, the bands at 1063, 1264 and 1385 cm⁻¹ correspond to oxygen containing functionalities like alkoxide, epoxy/ether and hydroxyl groups respectively [25,26]. In mGO, the peaks at around 1620–1644 cm⁻¹ is assigned to carbonyl peak of amide or urethane stretching (Amide I vibrational stretching) which is coming from the coupling reaction of sp²-hybridized carboxyl groups at the edges and sp³–hybridized hydroxyl groups on MDI and GO basal plane with organic diisocyanates. Also in mGO, the signal associated
with asymmetric NCO stretching vibration (2275–2263 cm\(^{-1}\)) is absent pointing all towards the effective modification.

![FTIR spectroscopy of GO and mGO](image)

**Figure 2.5 FTIR spectroscopy of GO and mGO**

### 2.3.8. Preparation of PU/GO Nanocomposites

PU/GO nanocomposites were prepared by solution mixing by dispersing GO in DMF by bath sonication and then mechanically stirring with the PU/DMF solution for 3 h at 3000 rpm at 130°C. Samples were casted on Teflon sheet and dried in the vacuum oven at 110°C. PU represents the neat matrix. PG0.5, PG1.5 and PG3 denotes GO filled PU nanocomposites and PMG0.5, PMG1.5 and PMG3, the mGOfilled PU respectively at 0.5, 1.5 and 3 wt%.

### 2.4. Characterization of fillers and composites

- The microstructures of synthesized GO and RGO sheets were found out by AFM (diCaliber Veeco instrument) and FTIR (spectrum ranging from 4000 to 400 cm\(^{-1}\) region
using JASCO FTIR-5300 spectrophotometer, ATR method, 32 accumulated cycles, 4 accuracy, 2 cm\(^{-1}\) resolution).

- Morphology of the samples was studied with a JEOL SEM-1400 scanning electron microscope (SEM) at an acceleration voltage of 100 kV. Ultra-thin samples were cut using a cryogenic ultramicrotome Leica ultracut UCT at -90°C.

- X-ray diffraction (XRD) measurements were carried out in an expert model of Philips diffractometer with Cu K\(\alpha\) radiation generator (1.5404 Å, 40 kV, 40 mA).

- TEM images of the composites were taken in JEOL JEM 2100 microscope with an accelerating voltage of 200 keV. Ultrathin sections of bulk specimens (~100 nm thickness) were obtained at -85 °C using an ultra microtome diamond fitted with a diamond knife.

- Raman scattering studies using laser beam of wavelength 514 nm at 50 % and for 60 seconds were done by a Ranishaw micro-Raman spectrometer (model-InVia). A 100× objective was used for focusing the laser beam on the sample. The spectrometer resolution for 1800 l/mm grating was ~2 cm\(^{-1}\).

- Mechanical measurements, such as the moduli at 100 and 300% elongation, tensile strength and elongation at break, were carried out in an INSTRON 5566A universal tensile machine at room temperature using dumb bell shaped samples (45 mm × 4 mm × 0.5 mm) at a test speed of 500 mm/min using a 5000N load cell. For Hardness measurement, Zwick Durometer Hardness Tester, ASTM D2240, Zwick/Roell 3130 (force 12.5N, indenter angle 35 degree) was used.
• Stress relaxation measurements were monitored at 40% strain at 100 mm/min rate for 2hr using Instron, universal testing machine (UTM). Mullins effect at 5, 10, 50 and 100% elongations with 5 mm/min rate was also observed with the same instrument.

• Sensing measurements of samples were done by noting the electrical resistance of composite films using a Keithley 2650A electrometer. These measurements were performed under atmospheric pressure, 40–60% RH and at 25–27°C temperature.

• Payne effect was observed from metraviB dynamic mechanical analyser (DMA) using rectangular-shaped samples (4×2.5×0.5 mm³) in tension mode. Measurements were done at a constant frequency of 0.5Hz with strain sweeping from 0.01 to 10% at different temperatures- 25°C, 50°C and 75°C.

• Rheological measurements were performed with the help of stress controlled rheometer (AR2000, ARES), equipped with parallel plates of diameter 25 mm at 160 °C. The samples in the form of disks with approximately 2 mm thickness and 25 mm diameter, were prepared by compression molding at 100 °C for 3 min. The strain sweep at 0.1–100% strain at a constant frequency of 1 rad/s was performed to determine the linear viscoelastic region and the elastic modulus (G₀) was measured in the linear domain at frequency between 0.01 and 100 rad s⁻¹ at a constant strain of 0.05%.

• The thermal stability of all the samples was evaluated by thermogravimetric analysis (TGA) with a Mettler Toledo TGA 50 thermobalance (Mettler Toledo, Greifensee, Switzerland). Experiments were conducted from 25 - 700 °C, at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Thermal properties were also investigated in the temperature range from -170 to 40 °C at 10 °C/min using TA Q200 series DSC.
instrument. The calibration of the DSC is done by using indium with onset of the melting
temperature at 156.6 °C and an accuracy of ±1°C is maintained.

- For the swelling measurements, circular samples of composites (1*1*0.2 cm$^3$) were
  immersed in diffusion bottles containing oil and water and were kept at constant
temperature in a thermostatically controlled oven. Using an electronic balance
(reproducibility within $10^{-4}$ g) the weights of all swollen samples were periodically
determined, until equilibrium swelling was reached. Since the weighing was done within
40 s, the error associated with the evaporation of the solvents was negligible.

- Shape memory property was studied by recovering the original (permanent) shape from a
deformed (temporary) shape under a thermomechanical loading–unloading cycle by the
tensile tester (Instron). For this, rectangular tensile specimens of 45 mm length, 9 mm
width, and 0.5 mm thickness were used. The samples were elongated to 100% 
[deformation ($\varepsilon_m$) =100%] strain at 25°C, 50°C and 75°C respectively at 100 mm min$^{-1}$
rate. While maintaining the strain, each set of samples was cooled to 5°C and unloaded;
the deformation under frozen conditions was denoted as $\varepsilon_u$. The sample was subsequently
heated again to desired temperature, left freely at that temperature for the next 10 min and
allowed to recover the strain; the recovery deformation was termed as $\varepsilon_p$. The shape fixity
($R_f$), measuring the ability of fixing the mechanical deformation and the shape recovery
($R_r$) measuring the ability of retaining the deformation were calculated by using the
following equations:

$$ R_f(\%) = \frac{\varepsilon_u \times 100}{\varepsilon_m} \quad \text{.................................. (2.1)} $$
\[
R_f(\%) = \frac{(\varepsilon_m - \varepsilon_p)}{\varepsilon_m} \times 100
\]

(2.2)

- Contact angles were measured using a Kruss G40 contact angle goniometer employing the sessile drop principle. This instrument is equipped with automatic image acquisition and contact angle computation softwares. The sample compartment was saturated with the test liquid for at least 30 min before measurement commenced. The contact angle was monitored up to 30 min after a drop of the test liquid was placed on the film surface. The water drop volume for the contact angle measurements was 5μl in all cases and the temperature was 25°C. The images were captured by online microscopy (GBX Digidrop intelligent version, France) using Windrop++ software and the measurements were repeated six to ten times for each sample specimen.

- Dielectric measurements were done on samples of ~0.300 mm thickness using an ALPHA dielectric analyzer (Novocontrol Technologies GmbH) in the frequency range \(10^{-2} < \text{Hz} < 10^6\), at 25°C.

2.5. Theoretical background

2.5.1. Payne effect

The dynamic performance characteristics of tyres such as sliding friction and rolling resistance critically depend on the nonlinear dynamic viscoelastic behavior of the tyre material which is a vulcanized elastomer/filler composite. The frictional factors are really important while dealing with driving safety and vehicle fuel consumption and so the dynamic properties have great significance in rubber composite characterization. A quantitative understanding of this property can be given by Payne Effect, which is the
variation of storage modulus (G’) with strain amplitude and plays a very significant role in explaining filler interactions in rubbers. The contributions of both viscous and elastic modulus towards the composite material are illustrated in Figure 2.6. The filled composites show obviously higher G’ and loss modulus (G") in the rubbery region than neat rubber. However, geometric dimension of the filler particles essentially influence the values.

At higher strain rates, the rate of destruction of filler networks [7–10] is higher than their rate of reconstruction which causes the dissipation energy associated with the network breaking to decrease [11, 12]. The maximum amount of energy dissipated comes from the consecutive breaking and reformation of all kinds of networks in the composites (filler-filler, filler-polymer, entanglement, glassy bridges, etc). This phenomenon is assumed to be arising from two factors, one related to the hydrodynamic reinforcement and the other from the filler-filler and filler-elastomer interactions. In the case of neat matrix, molecular disentanglement does not occur at low strain amplitudes and thus the G’ is constant. The mechanism behind Payne effect is explained as an adsorption-desorption process between the elastomer chains and the filler particles [7-10, 13-15]. Phenomenological models have been proposed by Kraus [16], Huber and Vilgis [17] and Maier and Göritz [18] for this effect, respectively based on the filler-filler interactions, filler network with cluster-cluster aggregation and stable (strong) and unstable (weak) filler-rubber interactions.
Figure 2.6 Modulus contributions in filled rubber materials [19]

Kraus [16], proposed a phenomenological model of the Payne effect based on the filler-filler contacts and they assumed that the contacts are continuously broken and reformed under dynamic deformation. Later Huber and Vilgis [17] explained the effect by correlating the filler network formed, fractal dimension $d_f$ and its connectivity $C$. Maier and Göritz [17] proposed another model contrary to the Kraus model, and considered filler-rubber interactions with two types of filler-rubber bonds—stable (strong) and unstable (weak). If the bond is strong the elastomer chains will be adsorbed strongly on the filler surface. Unstable bonds with the filler are formed by the chains adsorbed on the constrained elastomer part. And so the mechanism involved in breakage of filler–elastomer of Payne effect is mostly associated with the weak bonds. The elastic modulus of the filled composite has two contributions, the pure rubber contribution and the filler contribution arising from the filler/rubber interface instead of the filler network. The value of storage modulus is explained by equation (2.3)

$$G' = Nk_B T$$  \hspace{1cm} (2.3)
where $k_B$ is the Boltzmann constant, $T$ is the temperature and $N$ is the crosslink density of the filled network. The crosslink density itself is a combination of a few components (Equation 2.4)

$$N = N_C + N_{st} + N_i \quad \text{(2.4)}$$

where $N_C$ is the chemical crosslink density and bonds from entanglement, $N_{st}$ and $N_i$ are the number of rubber–filler stable and unstable bonds per unit volume of the material. $N_C$ represents the contribution of both the chemical crosslinks and the trapped entanglements and denoted as $N_p$, the number of elastically active rubber chains per volume unit of material. The variation of the storage modulus with strain is represented by Equation 2.5.

$$G'(\gamma) = G'_{st} + G'_i \frac{1}{1 + C\gamma} \quad \text{(2.5)}$$

with $G'_{st} = (N_g + N_{st}) k_B T$ and $G'_i = N_i k_B T$. $G'_{st}$ is the value of $G'$ at high deformations and $G'_i$ the Payne effect amplitude. The value of $G'_i$ is obtained from Equation 2.6.

$$G'_i = G'_0 + G'_{st} \quad \text{(2.6)}$$

With regard to the unfilled rubber, the composite containing 10 phr of MWNT has been shown to display a greater Payne effect probably associated with the breakdown of large agglomerates of carbon nanotubes (Figure 2.7).

The loss modulus values can be explained by Equation 2.7.

$$G''(\gamma) = G''_{st} + G''_i \frac{c\gamma}{(1 + c\gamma)^2} \quad \text{(2.7)}$$

$G''_{st}$ is associated to the internal friction, and $G''_i$ refers to slippage of polymeric chains segments.
2.5.2. Sensing

Sensing responses of the samples were monitored by measuring the change in electric resistance of polymer nanocomposites upon introducing the stimulus. This is the main mechanism behind most of the sensing devices. The electrical resistance variation can be quantitatively expressed by Equation 2.8.

\[ A_R = \frac{{R - R_0}}{R_0} \times 100 \]

where \( A_R \) is relative resistance, \( R_0 \) and \( R \) are the initial and final resistances. Measurements of the samples (3cm×1cm) were done at room temperature by recording their electrical responses to a liquid atmosphere in a closed chamber using a Keithley 2400 series multimeter. Though the sensitivity depends on many factors such as nature of the polymer matrix, filler concentration, initial resistance, solvent molecule characteristics, solubility parameter etc., the chemical nature of the matrix is the most important parameter which determine \( A_R \).
2.5.3. Swelling studies

Knite et al. [21] demonstrated the variation of electrical resistance upon swelling of a composite matrix. This is due to particle separation occurring because of the solvent penetration. Assuming that under swelling of matrix the particle separation changes from \( P_0 \) to \( P \), the relative resistance \( \left( \frac{R}{R_0} \right) \) is given by Equation 2.9.

\[
\frac{R}{R_0} = \left( \frac{P}{P_0} \right) \exp[\gamma(P-P_0)] \quad (2.9)
\]

The particle separation can be calculated by knowing the initial length of the sample, elongation of the composite sample under swelling and the relative elongation of matrix during swelling [21]. The equilibrium swelling for the composites was done in all the solvents benzene, toluene and p-xylene at 25 °C for 24 hours using circular samples of 1.5cm diameter and 0.5cm thickness and the swelling index was calculated using Equation 2.10.

\[
S = \frac{W_2-W_1 \times 100}{W_1} \quad (2.10)
\]

where \( W_1 \) and \( W_2 \) are the weights of the rubber before and after swelling.

The swelling data is used to calculate the diffusion coefficient \( (D) \), which is a measure of the ability of the solvent molecules to move into the polymer. The \( D \) is calculated using the data fitting Equation 2.11 for sorption [22-23] of a penetrant by a polymer film, as described by Crank.

\[
D = \pi \left( \frac{16}{4Q_\infty} \right)^{2} \quad (2.11)
\]
Where \( l \) is the thickness of the dry sample, \( \theta \) is the slope of the initial linear portion of the curve of \( Q_t \) versus \( \sqrt{t} \); and \( Q_\infty \) is the mole percent uptake of the solvent at infinity. The value of \( Q_\infty \) can be obtained from **Equation 2.12**.

\[
Q_t = \frac{M_t \times 100}{M_r \times M_i} \quad \text{(2.12)}
\]

Where \( M_t \) is the mass of the solvent up taken at time interval \( t \), \( M_r \) is the relative molar mass of the solvent and \( M_i \) is the mass of the dry sample. For each experimental run, sorption of solvent by the composite sample was monitored for an additional 24 to 48 h after reaching steady state.

### 2.6. Conclusions

In summary the present chapter gives an idea about the materials used as well as the synthesis methods of RGOs, PANi fillers and their composites of NR, IIR and SIS polymers. The theoretical background of the Payne effect observed for all elastomer composite systems was explained along with the mechanism of sensing and swelling. This chapter acts as an introductory section for the subsequent chapters of this thesis.

### 2.7. References

20 Bokobza L, *Polymer* 2007, **48**, 4907-4920
Chapter III: Elastomer Nanocomposite Sensors

ABSTRACT
Utilizing the electrical property of polymer nanocomposites is an important strategy to develop high performance sensors. This chapter is dedicated to the developed three sensors which can detect solvent, oil and water based on MWCNT, RGO and PANi. It is found that the synergy between CNTs and RGO exfoliated at 200°C imparts maximum sensitivity to NR in recognizing the usually used aromatic laboratory solvents. In the subsequent work, oil sensors made of PANi filled SIS block copolymer composite films with good uniformity and dispersion were developed. The changes in resistivity of the samples in presence of both oil and water media reveal the good sensing ability of SIS-PANi films towards oil in water (dual phase). Swelling studies are performed to correlate the sensing response to the structural variations and based on it a mechanism is derived for the dual phase sensing. The developed oil sensor material is able to withstand extreme temperature condition as well. Moreover CNT based NR, BR and SIS composites were also found to be good for detecting oil in oil spills.
3.1. Introduction

Sensing materials have become very attractive due to their ever increasing applications in technology; in general and in the field of industry, biomedical and environmental; in particular. The importance of organic solvent sensing lies in the fact that it is a quite useful technology in many ways ranging from the common laboratory applications to checking hazardous solvent leakage [1-3]. There have been many studies on the sensors and their ability in detecting vapours, gases and experimental factors like pressure, [2] temperature and strain. The sensing property is usually addressed by noting the electrical resistance variation when the sample is subjected to external factors. Polymer based materials are much used in fabricating low cost sensors; provided either the polymer is conducting or conductive filler particles are embedded in it [4]. Very recently, nanostructured filler particles (graphene, CNTs, metal oxides) are getting much attention in regulating the sensing ability of elastomers [5, 6]. The unique structure (high aspect ratio) and superior properties including exceptionally high electrical conductivity and specific surface area make graphene [7, 8] and CNTs [9, 10] suitable fillers in fabricating polymer composite sensors.

Here in our study, our approach is to derive the influence of structural modification of composites on sensitivity by correlating with common physical experiments like swelling and dynamic mechanical studies. Three composite materials useful in sensing solvent, oil and water are investigated. The NR composite formulated by putting CNTs alone and together with RGO is invented as solvent sensors. For this RGO is synthesized by the reduction of GO, which is obtained through the chemical exfoliation of graphite. Since GO contains large number of functional groups such as hydroxyls, epoxides, carboxyls and
carbonyls on its surface, its conductivity is less than both graphene and RGO. The reduction of GO is done thermally by which RGOs with less agglomeration, higher specific surface area, and higher electrical conductivity [11, 12] are produced. Varying the reduction temperature (usually from 150–900 °C), varies the deoxygenation degree of GO and this can improve the interlayer spacing and the sheet surface area [13] further. The synergy of MWCNTs and RGO produced at different temperatures (200 °C (G200) and 600 °C (G600)) is observed to be affecting the molecular level interactions of NR/CNT/RGO composites. Successful stress transfer and improved mechanical properties of this electrically conductive, mechanically robust and flexible composite are also observed when there is a strong bonding between the rubber matrix and filler [14].

In the second stage, a novel macroporous polymeric material based on IIR was developed as a sorbent compared to the widely used PP sorbents in an oil spill cleanup. As oil is an inevitable natural resource, its processing from mining to refining should be maintained devoid of environmental vulnerability. But oil spills often happen by release of crude oil from tankers, off shore platforms, drilling rigs and wells, spills of refined petroleum products (e.g., gasoline and diesel fuel) and their by-products from heavier fuels used by large ships or from the spill of any oily refuse or waste oil. In this scenario, monitoring oil pollutants in water with the help of sensing devices has great importance [15, 16]. So far a lot of researches on oil sensors have been reported [17]. However, the large size of the devices (e.g., require water to be pumped in), high cost, large energy consumption, low sensitivity etc. prevail to be the problems associated with. Therefore, fabricating an oil sensor which is reliable, inexpensive and able to operate at room temperature is significant for human demand [18-20]. Other than oil, polycyclic aromatic hydrocarbons (PAHs), a large group of
organic compounds with two or more fused aromatic rings also has been discharged from oil spills in large amounts [21, 22] which can affect a variety of biological processes and act as potent cell mutagens and carcinogens [23]. Sorbents generally remove oil and PAHs from waters [24, 25] and PP based materials are most common sorbents in oil spill clean up [26-28] since PP possesses hydrophobicity, high uptake capacity and high rate of uptake, buoyancy, retention over time, durability in aqueous media, reusability or biodegradability, and recoverability of oil. [29-33].

IIR is a low-cost commercial elastomer with many desirable and interesting properties such as low air permeability, a good resistance to aging and weatherability [34]. Although cross-linked IIR exhibits a high sorption capacity for organic solvents, its sorption rate is so slow that it has not been used as oil sorbent [35]. Recently, macroporous IIR able to absorb large volume of organic solvents in a short period of time [36, 37]. Due to the hydrophobicity, fast-responsivity, and reusability, macroporous IIR seems to be suitable sorbent material in oil spill clean up from surface waters as well as for the removal of PAHs from waters. Three different kinds of CNT nanocomposites with elastomers poly(Isoprene), Poly(Isoprene-co-isobutylene) and Poly(styrene-isoprene-styrene) were prepared.

PAni possesses high sensitivity, fast response, low cost, ease of synthesis, environmental stability and operation at room temperature [38-40] and conductive nanocomposites based on PAni particles proved their capability sensing organic solvents. PAni embedded SIS, an unsaturated block copolymer of styrene with good softness, flexibility, excellent tack and adhesive properties has turned out to be a highly sensitive oil sensor. This thermoplastic elastomer is widely used in fabrication of adhesives and sealants. The presence of conjugated pi electrons in both SIS and PAni can lead to strong interfacial
interactions [41]. The SIS-PAni composite is an easy movable, reliable, simple and low price oil detector which can detect oil spill in hardly accessible places such as pipelines. The composite thin films exhibited sensitivity to both hydrophilic and hydrophobic medium on different rates. Based on the film response to the medium one can confirm the presence of oil or water in contact with the sensor. Thus these thin film sensors are anticipated to stick on to the pipes (due to adhesive property of SIS) carrying oil so that oil leakage can be monitored as fast as possible. Ansari et al. prepared a nanocomposite-containing graphene platelets embedded in SIS matrix useful as an optomechanical actuator driven by IR radiation [42]. Gan et al. prepared interpenetrating polymer networks by sequential crosslinking reactions of tetraethyl orthosilicate with silicon-grafted functional SIS triblock copolymer and PAni doped with DBSA [43]. Querelle et al. used SIS composites for synthesizing ultrafiltration membranes [44].

Since the final performance of any composite material depend on two main factors, the filler-polymer interfacial interaction and the nature of dispersion of filler in the matrix, these factors are investigated for the obtained composites. The mechanism of sensing is explained through these filler-filler and filler-polymer interactions derived from the dynamic studies such as stress relaxation, Mullins effect and Payne effect. A mechanism has been proposed and explained through diffusion studies. The thermal properties of the obtained oil sensors were analyzed to test its suitability of usage at ultimate environmental conditions. All the sensors developed in this study had good reproducibility as well. For practical application, oil sensors are required to be with high selectivity and quick response. More efforts are needed on studying the long-term stability and reliability of the CNTs-based sensors, which has been less studied.
3.2. Results and Discussion

3.2.1. Solvent sensing characteristics

Electrical conduction in rubber composites varies with several parameters like processing techniques, content and nature of filler (particle size and structure) as well as the rubber-filler interactions [45]. At percolation threshold, a conductive network of fillers forms within the sample and an insulator–conductor transition takes place rapidly. The conductivities of all nanocomposites synthesized were checked prior to sensing experiments. Figure 3.1 shows the I–V (tunneling current-voltage) characteristics of NR-CNT, NR-CG200 and NR-CG600 nanocomposites. All I–V curves exhibit nonlinearity from the typical metallic linear nature which is an indication of their semi conducting behavior. NR-CNT shows the maximum deviation in the tunneling current among all nanocomposites which indicates its enhanced semi conducting behavior. This is because of the large number of CNT-CNT networks present within the composite, which decrease upon the incorporation of RGOs [46]. For the neat RGOs, the C/O ratio was observed to be less than 6 and this make it poor conducting due to the partial restoration of aromatic graphene structure (disrupted sp² bonding network). Thus the NR filled with RGOs alone does not possess any sensitivity and is not presented here.
In order to conduct the sensing experiments, samples are kept as shown in Figure 3.2a and solvent drops are introduced on to it. This was done by clamping the sample strip at both ends in a closed chamber (connected to Keithley multimeter) and putting the solvent drop from a syringe on the top of it. Three different aromatic solvents, benzene, toluene and para-xylene (p-xylene) were used to measure the electrical responses. The variation in relative electrical resistance observed for all composite samples, upon the introduction of solvents as a function of time is shown in Figure 3.2b, c and d. The sensing was repeated by cyclic means by simultaneously applying the solvent and heating the samples. At first the sensitivity was checked by keeping the solvent drops on the sample with respect to time. Then temperature was applied on the sample to recover the solvent effect. The recovery curve shape depends on the boiling point of the solvent and polymer-solvent interaction parameter. These experiments were done in a closed chamber to prevent solvent
vaporization. The cyclic heating process was done using the hot air from a hair drying system and observed the time to recovery depending on the sample size.

![Experimental setup for solvent sensing](image)

**Figure 3.2** Experimental setup for solvent sensing in closed chamber (a) and the electrical resistance variation with solvents toluene (b) p-xylene (c) and benzene (d) for composites

In NR-CNT, the concentration of CNTs used (4.30 wt %) is above the usual percolation threshold (1.9-2.9 wt %) of other NR-CNT composites, whereas in the case of NR-CG200 and NR-CG600, CNT content is at the range of percolation (2.15 wt %). Also RGOs are less conductive than CNTs due to their partial ionic nature. Because of these
reasons NR-CNT exhibits lower initial resistance than the hybrid composites, NR-CG600 and NR-CG200. At the point of solvent injection, a rapid increase in relative resistance is seen for all samples, and is much pronounced for NR-CG200. After reaching a maximum value it starts decreasing, but does not come back to the exact original position. The decrease in relative resistance observed for NR-CNT in presence of toluene (Figure 3.2b) may be due to the vaporization of the solvent. For all aromatic solvents used, NR-CG200 shows the maximum sensitivity, the mechanism of which can be explained through the swelling studies and filler-polymer molecular level interactions.

Since the resistivity is affected by solvents, it is important to evaluate the degree of swelling of the composites to derive the sensing mechanism [6]. The calculated $S$ values for all samples are shown in Figure 3.3 (for better comparison in Table 3.1 as well) and among the composites the degree of swelling is the highest for NR-CG200.
Figure 3.3 Swelling index of NR and NR composites with different solvents i.e toluene, p-xylene and benzene.

When solvent enters the sample, the matrix swells thereby increasing the distance between the filler particles. Since there are no filler networks inside the neat NR, it exhibits maximum solvent swelling. Whereas in composites, the additional filler–filler and filler–polymer network bonds prevent the solvent molecules from entering to the inner structure and thus cause lower rate of swelling. In CG200 and CG600, RGO provides connecting bridges between CNTs. These conductive networks and the orientation of CNT aggregates and RGOs within the sample break during swelling and the layer between the agglomerates becomes thinner. This causes the quantum mechanical tunneling current between the particles to decrease rapidly and thus the electrical resistance of the composites increases. Thus a nice correlation can be established between the swelling index and maximum
relative resistance. It is considered that the relative resistance is sensitive to change in filler
distribution as well as the nature of solvent. This is because the polymer matrix absorbs the
solvent molecules in different ways and the nanoparticles separate (move) from each other
at different velocities.

In order to substantiate the sensing mechanism, apart from swelling studies, exploring the molecular level orientation of fillers and the filler-rubber interfacial
interactions are also necessary. Such molecular interactions existing within the
nanocomposites are addressed here using the dynamic mechanical studies such as stress
relaxation, hysteresis and Payne effect [47, 48]. The motion and orientation of polymer
chains, disentanglement of chain network strands and deformation and rupture of micro
domains and crosslinks are the main reasons for the relaxation of stress in composites. In a
composite system, due to the filler inextensibility, the strain in the polymer phase is greater
than the overall strain. So the stress relaxes at a higher rate than the neat matrix due to the
breakdown of the filler-filler and filler-polymer interactions occurring in it [47]. This varies
with the nature of filler [49] as well. The stress relaxation curves obtained for the neat NR,
NR-CNT, NR-CG600 and NR-CG200 at 40% elongation is given in Figure 3.4. To explain
the observed behavior, the experimental relaxation curves were fitted to the stretched
exponential Kohlrausch Equation 3.1.

\[
\frac{\sigma_1}{\sigma_0} = \frac{\sigma_{\infty}}{\sigma_0} + \frac{\sigma_1}{\sigma_0} \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right] \quad \text{.................................(3.1)}
\]

where \(\sigma_1/\sigma_0\), \(\sigma_{\infty}/\sigma_0\), \(\tau\), and \(\beta\) are the fitting parameters. \(\tau\) is the relaxation time, \(\beta\) is the
stretching parameter (0<\(\beta\)≤1), \(\sigma_1/\sigma_0\) is the transient stress, \(\sigma_{\infty}/\sigma_0\) the limiting stress and
\([(\sigma - \sigma_0)/\sigma] \times 100\) the relaxation ratio. The experimental curves are in good agreement with
the equation and the best-fit values of the parameters are given in Table 3.1. From the fitting parameters, $\tau$ and $\beta$ were estimated in order to understand the mechanism of the relaxation processes.

Figure 3.4 Time dependence on the normalized stress for neat NR, NR-CNT, NR-CG600 and NR-CG200 nanocomposites (Dotted lines represent the curve fits).

The change in $\left(\frac{\sigma}{\sigma_0}\right)$ with time $t$ (Figure 3.4), indicates the time dependent stress decay until it approaches equilibrium. Since the stress relaxation behavior is mostly attributed to the breakage of filler–NR interactions, a better reinforcement of CNT with NR is observed compared to the other composites. This is observable from the decrease in overall chain flexibility and slow stress relaxation. The higher contribution in the progressive failure in filler–rubber bonding also supports this higher degree of filler-rubber interaction. Whereas in NR-CG200 and NR-CG600, the relaxation time is lower which indicates the existence of filler–filler interactions and is stronger in the former case.
Table 3.1 Fitting parameters of stress relaxation from Equation 3.1.

| Sample codes | $\sigma_0/\sigma'$ | $\sigma_1/\sigma'$ | $\beta$ | $\tau_{(\text{min})}$ | Relaxation ratio $[(\sigma - \sigma_0)/\sigma'] \times 100$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>0.9599</td>
<td>0.9958</td>
<td>0.135</td>
<td>1.4E-05</td>
<td>4.000</td>
</tr>
<tr>
<td>NR-CNT</td>
<td>0.7832</td>
<td>0.9863</td>
<td>0.165</td>
<td>0.01</td>
<td>21.67</td>
</tr>
<tr>
<td>NR-CG600</td>
<td>0.8229</td>
<td>0.9872</td>
<td>0.165</td>
<td>0.0051</td>
<td>17.7</td>
</tr>
<tr>
<td>NR-CG200</td>
<td>0.8238</td>
<td>0.9685</td>
<td>0.165</td>
<td>0.0021</td>
<td>17.61</td>
</tr>
</tbody>
</table>

Mullins effect or stress softening effect is generally observed as lowering in stress at high extensions when the rubber composite is subjected to successive extension cycles. This process has a hysteretic mechanism related to the breakdown of molecular interactions and the energy dissipated by the material during deformation. The unfilled rubbers have less stress softening than filled composites, but it is also observed that when stretched to the same stress, neat and filled rubbers show same level of stress-softening [50, 51]. This indicates the behavior comes from the rubber phase itself. The stress softening behavior for NR, NR-CNT, NR-CG600 and NR-CG200 is monitored by subjecting the samples to a cyclic process at 5, 10, 50, and 100% elongations and the results obtained are illustrated in Figure 3.5. It is found that the magnitude of stress softening significantly increased in all composites and the intensity of the effect strongly depends on the nature of filler. When the rubber is stretched, the adjacent molecular chain segments exert a viscous drag on the chains and this causes it to respond slowly. This kind of behavior is very less in the case of neat NR.
whereas in NR-CNT (Figure 3.5d), NR-CG600 (Figure 3.5c) and NR-CG200 (Figure 3.5b), filler-filler and filler-rubber interactions break and causes more softening.

![Stress-strain response graphs](image)

**Figure 3.5** Stress–strain responses of a) neat NR, b) NR-CG200 c) NR-CG600 and d) NR-CNT, to simple and cyclic uniaxial tension with increasing maximum stretch at every 3 cycles.

The higher softening behavior of NR-CNT compared to NR-CG600 and NR-CG200 is attributed to the strong reinforcement effect of CNTs with NR. The large area under the cyclic deformation curve of NR-CNT also indicates the higher reinforcement as well as the more energy dissipation in this composite. The less pronounced stress softening effect of RGO/CNT hybrid samples is due to the lack of stronger filler-rubber interactions due to the ionic nature of RGO. In addition, the effect is less pronounced in NR-CG200 than NR-
CG600 as the possibility of filler-rubber interactions is higher in the latter. The stretching history of Mullins effect shown in Figure 3.6 also supports these explanations. In short, the softening effect and filler-rubber interactions are in the order of NR<NR-CG200<NR-CG600<NR-CNT. Higher the stress softening, greater the filler-rubber interaction.

Figure 3.6 Stretching history of Mullins effect: a) NR, b) NR-CNT, c) NR-G600 and d) NR-CG200.

Figure 3.7 shows the comparative nonlinear dynamic viscoelastic response of neat NR, NR-CNT, NR-CG600 and NR-CG200 at 0.5 Hz [52] frequency and at 25 °C. The theoretical parameter values were calculated using Equation 2.5 and Equation 2.6 as given in Table 3.2 and are fitted with the experimental data. It is clear from the results that both
the filler surface area and their interactions with the rubber strongly influence the network strength (Table 3.2). The decrease in storage modulus with shear amplitude is highly significant for NR-CNT indicating the order of filler - rubber interaction as NR-CNT>NR-CG600> NR-CG200.

The relatively large size of the stacked graphene flakes compared to the filler volume will lead to possible measurement errors. If the real curve is noisy, extracting information from them directly will introduce errors but in our case we didn’t find any significant noise that makes to find an error. The goodness of fit is shown by the correlations factor value, which is ~0.8 for all samples and was reasonably acceptable.

![Figure 3.7](image)

**Figure 3.7** Strain dependence of the storage modulus (fitted with Maier and Göritz model) for neat NR, NR-CNT, NR-CG600 and NR-CG200.

The high crosslinking density \(N_{\text{total}}=1.3E20/\text{cm}^3\) of NR-CNT (Table 3.2) compared to other composites is considered to be due to the high level filler-polymer interaction. In NR-CG200 and NR-CG600, the interaction between NR and RGO is less due
to the presence of ionic groups on RGO surfaces which causes the storage modulus to decrease. Comparison between NR-CG600 and NR-CG200 shows higher crosslinking density for the former \((N_{\text{total}}=11.35E20/cm^3)\) than the latter \((N_{\text{total}}=10.28E20/cm^3)\). This again confirms the decrease in ionic nature of GOs upon high temperature thermal reduction. The results are quiet similar to that of stress relaxation and Mullins effect studies.

**Table 3.2** Fitting parameters of Equation (2.5) and (2.6).

<table>
<thead>
<tr>
<th>Samples</th>
<th>(G'_s) (10^7 MPa)</th>
<th>(G''_s) (10^7 MPa)</th>
<th>(N_i) (10^20 cm(^3))</th>
<th>(N_g+N_{st}) (10^20 cm(^3))</th>
<th>(c)</th>
<th>(N_{\text{total}}=N_i+N_g+N_{st}) (10^20 cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>5.5</td>
<td>1.1</td>
<td>3.9</td>
<td>0.19</td>
<td>2.1</td>
<td>4.09</td>
</tr>
<tr>
<td>NR-CNT</td>
<td>21.1</td>
<td>3.8</td>
<td>13.6</td>
<td>0.7</td>
<td>1.4</td>
<td>14.3</td>
</tr>
<tr>
<td>NR-CG600</td>
<td>10.2</td>
<td>3.25</td>
<td>11.0</td>
<td>0.35</td>
<td>1.3</td>
<td>11.35</td>
</tr>
<tr>
<td>NR-CG200</td>
<td>8.3</td>
<td>3.06</td>
<td>10.0</td>
<td>0.28</td>
<td>1.3</td>
<td>10.28</td>
</tr>
</tbody>
</table>

Based on all these points, a mechanism in solvent sensing of composite films is derived emphasising the molecular level interactions, and is schematically demonstrated in Figure 3.8. This explains the large area of confined rubber in NR-CNT than the other NR composites due to higher filler reinforcement as evident from Payne, Mullins, stress relaxation and mechanical properties. Swelling measurements clearly explained the difficulty in penetration of solvent molecule through NR-CNT because of the presence of highly reinforcing confinement regions.

When solvent enters inside, the tunneling gap between filler junctions increases as shown in Figure 3.8 (insets). In NR-CG600 (Figure 3.8b), the confinement region is less...
compared to NR-CNT (Figure 3.8a). This is due to the comparatively less reinforcement between NR and G600 which enables the toluene molecules to penetrate through the sample during swelling. Finally in the case of NR-CG200 (Figure 3.8c), the reduced compatibility of G200-CNT and rubber-G200, results in the easiest penetration of solvent molecules during swelling and this increases the tunneling gap to a great extent. Because of this reason, the relative resistance of NR-CG200 is the highest among all other composite systems when solvent is injected to it. It is also noticed that the obtained sensors exhibit good reliability, but this factor depends highly on the nature of the solvents used. If the solvent degrades the sample, the sensors will not be dependable for a second test. For instance we have observed faster velocity of degradation of the samples for chloroform than toluene or n-hexane. The lifetime of a particular sensor varies with respect to the solvent as well as the temperature i.e. if the temperature increases the sensitivity decreases due to solvent evaporation. In addition the sensitivity of the sensor depends on the solvent purity and thus the present sensor is capable of identifying the purity of the solvent as well. The impure solvents alter the detect ability of the material, the reason behind this behavior being the variation in the interaction parameter between polymer and solvent caused by the impurities and thus changing the diffusion coefficient and finally the solvent sensitivity.
Figure 3.8  Mechanism involved in the change in relative resistance during swelling for a) NR-CNT, b) NR-CG600 and c) NR-CG200.

For verifying the structural change upon the reduction of GOs, X-Ray diffractogram were taken for G200 and G600. The well exfoliation of RGO sheets is clearly understood from XRD as well. Figure 3.9a shows the XRD spectra of G200 and G600. The characteristic sharp peak of graphite at $2\theta = 26.5^\circ$ (shown as an insight to the Figure 3.9a) is more broadened and less intensified in both RGOs. This gives evidence for the loss of regularity in RGOs due to exfoliation of platelets upon reduction. On moving from 200 to 600 °C, the characteristic peak diminishes in intensity, and shifts towards the lower angle side indicating the complete exfoliation of individual GO sheets as the functional groups and interlayer interactions reduce. Both RGOs shows the diffraction peak corresponding to (002) plane [53] of hexagonal carbons.
XRD pattern for the composite samples, NR, NR-CNT, NR-CG600 and NR-CG200 are shown in Figure 3.9b. The amorphous nature of NR contributes towards the obtained halo in the spectrum, which exists in all composites. The absence of characteristic peaks of fillers in the spectrum reveals their well dispersion in the composites.

![XRD spectra](image)

**Figure 3.9** XRD spectra of a) G200 and G600 (insight shows neat graphite peak) b) NR, NR-CNT, NR-CG600 and NR-CG200.

Detailed phase composition and morphology of the nanocomposites were investigated using TEM and Raman spectroscopy. Figure 3.10 displays the TEM micrographs of the cryo cut surfaces of NR-CNT, NR-CG600 and NR-CG200. All images substantiate the uniform dispersion of filler particles within the matrix. Exfoliated RGO sheets are marked in the figure.
Figure 3.11 illustrates the Raman spectra obtained for the NR-CNT, NR-CG600 and NR-CG200 composites. All composites show both D-band and G-band respectively at 1351 and 1572 cm⁻¹ arised from the disorder induced and in plane vibration of the C-C bond in graphitic materials. The presence of D band in nanocomposite indicates the increase in number of defects during composite formation [54]. Broadening of G-band at 1580 cm⁻¹ for graphene along with its decrease in intensity specify the creation of defects on it [55]. The ratio of intensities of D and G band explain the quality of the sample. When this ratio is the lowest, nanocomposites suffer a higher defect level due to grafting of the polymer chain on the high surface area of graphene as well as to the passivation of dangling bonds in the MWCNT. All these results substantiate the uniform distribution of fillers within the NR matrix and thus points towards high property enhancement.
The Young’s modulus of NR-CNT composite is observed to be superior than NR-CG600 and NR-CG200, which is attributed to the stronger polymer–filler interfacial compatibility and the better dispersion of CNTs in the NR matrix. Addition of CNTs also imparts high hardness to rubber due to its high crosslink density. In NR-CG200, strong filler-filler interactions exist and because of that it shows higher tensile strength compared to NR-CG600 and NR-CNT. Between CG200 and CG600, the latter has higher rate of compatibility with NR (the higher reduction rate makes RGO at 600°C better interactive with the CNTs through similar sp2 hybridized carbon atoms) [13]. This increased compatibility with the matrix is assumed to be the reason for the larger Young’s modulus of NR-CG600. For an easy comparison, the values are given in Table 3.3. The elongation at break is the highest in the case of NR-CG200 because of the lesser filler-polymer compatibility thereby enhancing the polymer component behavior and also the lubrication property of filler.
Table 3.3 Mechanical properties and swelling index of neat NR, NR-CNT, NR-CG600 and NR-CG200

<table>
<thead>
<tr>
<th>Sample</th>
<th>Y’ modul us (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Hardness (ShoreA)</th>
<th>E’ break (%)</th>
<th>Swelling Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>NR</td>
<td>0.4±0.1</td>
<td>0.5±0.1</td>
<td>51.2</td>
<td>243±7</td>
<td>3.52±0.02</td>
</tr>
<tr>
<td>NR-CNT</td>
<td>1.9±0.1</td>
<td>0.9±0.1</td>
<td>64.7</td>
<td>144±4</td>
<td>2.57±0.07</td>
</tr>
<tr>
<td>NR-CG600</td>
<td>1.4±0.1</td>
<td>0.9±0.1</td>
<td>58.7</td>
<td>167±9</td>
<td>2.85±0.03</td>
</tr>
<tr>
<td>NR-CG200</td>
<td>0.8±0.1</td>
<td>1.4±0.3</td>
<td>58.2</td>
<td>390±1</td>
<td>2.95±0.08</td>
</tr>
</tbody>
</table>

3.2.2. Oil sensors
In order to investigate the oil sensing three CNT samples of NR, BR and SIS elastomers were prepared at various filler loading. The experimental set up for oil detection is illustrated in Figure 3.12a. Variation in electrical conductivity for the uniformly dispersed films with respect to the filler loading is shown in Figure 3.12b.
Figure 3.12 a) Experimental setup for oil sensing experiment b) Electrical conductivity of NR/BR/SIS rubbers with different filler concentrations

At low CNT loading the film is still an insulating material, afterwards the resistance increased suddenly and becomes constant. The sharp increase in conductivity around 1-3 wt% of CNT indicate the formation of a percolation network in the composite. Figure 3.13 illustrates the oil sensing capability of all samples prepared at different filler concentrations- SIS/CNT with 2, 3 and 4 phr, IIR/CNT with 3, 4, and 5 phr and NR/CNT with 4, 5 and 6 phr respectively. The electrical response characteristics of the samples depend on the diffusion kinetics of the oil in the samples. Thus the relative resistance varied according to the diffusion coefficient of the sample which in turn changing because of the interaction between oil and polymer. The NR composite shows the best performance (Figure 3.13 a, b and c) than the other elastomers due to the better interaction between oil and NR. Out of the NR composites, again NC4 gives good ability to repond with oil (Figure 3.13 c) than that of NC5 and NC6 because of the good percolation network formed in the case of NC4. In the case of NR composites increasing the CNT content decreases the diffusion coefficient as denser
CNT networks represent obstacles for the oil molecules to penetrate. Thus the time dependent relative resistance change is mostly affected by the diffusion coefficient value.

![Graphs](image)

**Figure 3.13** Oil sensing curves for samples a) SIS/CNT b) IIR/CNT c) NR/CNT, Relative Resistance ($\Delta R/R_0$) vs Time (min)

To confirm the surface structure of the CNT/elastomer nanocomposite films, the determination of the surface properties by contact angle measurements is necessary. Figure 3.14 illustrates the corresponding contact angle changes of NR/BR/SIS-CNT nanocomposites. It is observed that the static contact angle for the droplet of NC2 is 110°, whereas it is 95° and 90° in the case of BC2 and SC2 which may be attributed to the relatively high hydrophobicity of NR. The surface hydrophobicity reduces as moving from NR to SIS. NC2 shows very high contact angle, indicating that poly (isoprene) have high...
hydrophobicity due to lack of polar groups in the polymer chains and high molecular weight. Based on the contact angles of the water droplets, hydrophobicity was in the order of NC4>BC4>SC4.

![Contact angle measurements of NR/BR/SIS-CNT elastomer nanocomposites.](image)

**Figure 3.14** Contact angle measurements of NR/BR/SIS-CNT elastomer nanocomposites.

The NR/BR/SIS-CNT composite morphology was monitored using SEM micrographs of the cryo cut surfaces and **Figure 3.15** shows the morphology of NC4, BC4 and SC4. CNTs distribute well in NR, but at low level in SIS due to the enhanced non polar matrix filler interactions in NR/CNT. The bundles of CNTs are more in SIS/CNT as the figure indicates.

![SEM image of sample a) NC4 b) BC4 c) SC4](image)

**Figure 3.15** SEM image of sample a) NC4 b) BC4 c) SC4

### 3.2.3. Dual phase sensors

The electrical conductivity of the SIS/PAni composite samples showed a uniform trend as illustrated in **Figure 3.16**. Here the conductivity of the composites is plotted as a function of filler loading for uniformly dispersed composite films. At low PAni loading the film is still an insulating material but afterwards the resistivity decreased (conductivity
increased) suddenly and becomes constant. This sharp increase in conductivity around 15-22.5 wt% of PANi indicate the formation of a percolation network as represented in the figure.

![Figure 3.16](image)

**Figure 3.16** Electrical conductivity of SIS-PAni composite vs filler loading.

The sensing ability of the composites are noted by dipping the thin films in water and/or oil after connecting the two ends of the strip with a multimeter. A schematic representation of the experimental set up is shown in **Figure 3.17** which illustrates the measurement route. These composite films can work as replaceable sticker type sensors on the surface of oil pipe lines. The conductive path of the PANi particles in the SIS base matrix and the coating of the DBSA doping agent (surfactant) on it are also shown in the figure. The possible interaction between the PANi and SIS through this doping agent can be better understood from **Figure 3.17**.
Figure 3.17 Schematic representation of the experimental set up for oil in water sensing by SIS-PAni composite film.

The resistances of all the SIS-PAni thin film sensors are measured at 25 °C in both water and oil media. The third medium of oil in water was made by sonicating water containing a drop of oil so that the concentration of it in water was maintained in the μL level. As shown in Figure 3.18a, the relative resistance of the SIS-PAni thin film sensors increases slowly when exposed to oil, and then reaches towards a constant value with time. Figure 3.18b shows the variation in relative resistance of the SIS-PAni sensors upon the exposure to water medium. Here the change is rather drastic and the resistance value shows a decrease trend different from the previous case. In both cases the response varies relative to the concentration of PAni. SIS-PAni1.5 exhibits the highest resistance in oil at a particular time whereas the same composite sensor has the least resistance in presence of water. In the presence of oil in water medium the response is again different. This is shown in Figure 3.18c, where the relative resistance first decreases and then increases. These different
behaviors observed finalize the use of SIS-PAni films as ideal candidates in dual phase sensing and in detecting oil in water [56].

Figure 3.18 Relative resistances ($\Delta R/R_0$) vs time (min) for SIS-PAni composite films in different media a) oil b) water and c) oil in water.

All these observations can be explained with the help of percolation theory. During liquid exposure, the polymer matrix absorbs some of the molecules and expands, decreasing the effective filler volume fraction and causing the resistivity to change near the percolation-concentration threshold [57]. Typically on exposure to water, PAni becomes protonated and an increase in conductivity is observed. The water sensing property of PAni can be regarded as due to electron hopping assisted by proton transfer mechanism and capillary condensation of water molecules onto the sample surface [58]. Or in other words the absorbed water acts
as bridge between the filler clusters and used to carry electrons which cause relative resistance to decrease. With increase in weight percentage of PANi in SIS, the decrease in resistance with time was found to be less affected. This could be due to an increase in the heterogeneity of the composite with increasing amount of PANi which is also clear from the SEM. The mechanism of conduction is well pictured in Figure 3.19.

![Figure 3.19](image)

**Figure 3.19** Mechanism involved in (a) oil and (b) water sensing in SIS-PAni composite.

In the case of oil, the continuous conductive pathways break down eventually throughout the polymer matrix [57]. As indicated in the figure, sorption of oil into the polymer causes swelling of the polymer and increases the distance between the PANi particles and as a result the overall resistivity increases [59]. For oil dispersed in water medium, a combination of these two effects is observed. All SIS-PAni composites have shown good response towards oil, water and oil in water sensing; but the composite SIS-
PA ni1.5 exhibits better result, indicating its potential as a duel sensor. The different effects for different solvents can also be explained in terms of the corresponding solubility parameters of the matrix and the different solvents [60, 61].

In order to explain the variation in behavior for the SIS-PA ni composites towards the oil and water media, diffusion measurements were carried out. The data obtained for diffusion experiments are shown in Figure 3.20.

Figure 3.20 Oil and water diffusion curves for SIS-PA ni samples (relative mass change (Δm/m₀) vs time)

For better understanding of the diffusion behaviour, the coefficient values were calculated as tabulated in Table 3.4. Here the Fickian diffusion model was used to quantify the diffusion process and the diffusion coefficients were calculated based on the model for water and oil diffusion. The maximum value of diffusion coefficient for the SIS-PA ni1.5 reveals its highest ability to pass the solvent molecules through it. With increase in PA ni content the coefficient decreases and the sample becomes impermeable to both oil and water. The behaviour of neat SIS was not shown in the graph since it didn’t give any noticeable swelling property in water.
Table 3.4 Diffusion coefficient values for the samples.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Sample</th>
<th>Diffusion coefficient (cm²·sec⁻¹) In oil</th>
<th>Diffusion coefficient (cm²·sec⁻¹) In water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SIS-PAni1.5</td>
<td>1.71E-08±0.71E-08</td>
<td>2.14E-08±0.08E-08</td>
</tr>
<tr>
<td>2</td>
<td>SIS-PAni2</td>
<td>9.80E-09±0.52E-09</td>
<td>6.65E-09±0.19E-09</td>
</tr>
<tr>
<td>3</td>
<td>SIS-PAni2.5</td>
<td>6.99E-09±0.26E-09</td>
<td>3.37E-09±0.24E-09</td>
</tr>
</tbody>
</table>

In order to optimize and predict the sensor response, factors affecting the diffusion of water and oil into the SIS composite films has been examined. A correlation is obtained between the diffusion coefficient values and sensing data as shown in Figure 3.21.

**Figure 3.21** Correlation between diffusion coefficient and max relative resistance for SIS-PAni composites.
The polarity of the solvent and samples with different compositions has a fundamental issue in sensor design. The polarity of the matrix is altered by the addition of different concentrations of PAni. Rate of diffusion is seen to increase with decreasing composite polarity. Initial examination of the diffusion coefficient values in oil shows that the diffusion coefficients have small variation from PAni1 to PAni2.5 but in the case of water, we found significant variation from PAni1 to PAni2.5. This suggests the influence of steric/molecular size effects on diffusion coefficients. Steric effects are found to dominate, followed by molecular size and then polarity effects. Another factor affecting sensitivity stems from the difference in sorption of solvents and swelling ability of the different dispersed phases. In the sorption curves for oil in water the two stages- fast sorption followed by gradual slower sorption- can be observed. Slightly higher sorption levels are observed for water as compared with the oil.

The structural analysis of the SIS-PAni composites was addressed with the help of SEM. The SEM images of the composite samples were taken by scanning through the sample surface.
Figure 3.22 SEM images of a) Neat SIS b) SIS-PAni1 c) SIS-PAni2.5

Figure 3.22a shows the surface of the neat polymer. With the addition of PAni particles the roughness of the surface increases as evident from Figure 3.22b and 3.22c. Both at lower and higher filler concentrations, uniformity in dispersion are clearly seen.

To examine the surface properties of the composite films in terms of compatibility at the interface, contact angle measurement is necessary. Table 3.4 shows the contact angles obtained by water on the surface coated with SIS and its PAni composite films. The measurements were repeated thrice and the results obtained are in accordance with the observations of Zuo et al. [62]. Neat SIS is hydrophobic and its hydrophobicity decreases with the addition of PAni as evidenced by the low contact angle. PAni film alone shows very low contact angle of 13.95°. Addition of surfactants to PAni again decreases the contact angle due to the decrease in hydrophobicity of the PAni/DBSA films. The variation in
contact angle of PANi/DBSA with SIS can be explained on the basis of a phase inversion process occurring in the composite, i.e. the surfactant wrapped PANi migrate to the elastomer composite surface, making it hydrophilic, indicating a bridging action of surfactant in between PANi and SIS [63]. The hydrophobic tail of the surfactant chain has more interaction with SIS and anionic head part has more interaction with the PANi.

The thermal properties of the samples were monitored using TGA and DSC studies in inert nitrogen atmosphere. The DSC thermograms of SIS and its composites at a heating rate 5 °C/min are shown in Figure3.23a.
Figure 3. 23a) DSC b) TGA and c) DTG for amorphous SIS and SIS-PAni composites.

An endotherm at around -60.09 °C in the DSC thermogram of neat SIS corresponds to its glass transition temperature ($T_g$). This $T_g$ is shifted to lower values in SIS-PAni composites. i.e. $T_g$ decreased to -61.0±0.3 °C, -61.1±0.2 °C, -61.6±0.5 °C and -61.8±0.4 °C respectively for the samples PAni1 to PAni2.5, as shown in Table 3.4. However the $T_g$ increased slightly in case of composite samples compared to the neat SIS. This may be due to
the interaction between PANi/DBSA and SIS chains, which could reduce the segmental mobility of the chains. The effect of nanoparticles on T_g values can also be explained by the enthalpic interactions between the polymer and the nanoparticles [64]. The absence of any other exothermal or endothermal signals confirms the amorphous nature of the composites. Finally, the slight decrease observed in the T_g of SIS filled PANi/DBSA composites can be attributed to the plasticization effect of the DBSA modification on PANi. The decrease in T_g could also be attributed to the presence of trapped solvent [65] in the composites. Though the vacuum drying method was applied to remove the solvent trapped inside (for three days), the % trap might decrease the chance of feeble amount of trapped solvents in the samples cannot be ruled out.

The thermal stability of PANi/DBSA and SIS-PANi composites was further illustrated by TGA and DTG (Figure 3.23b and c). It can be deduced that the incorporation of PANi affects the thermal stability of the SIS. This is marked by the significant displacement of the degradation peak to lower temperatures upon adding PANi to SIS. This confirms the formation of a conventional composite on a microscopic scale, where the polymer chains are not much intercalated into the galleries of the PANi. The decomposition rate of the SIS when combined with PANi is found to be very different from the decomposition rate of the bulk polymer as well. The SIS-PANi composites undergo four-step thermal degradation processes. In the first step of degradation, a small fraction of weight loss occurs in the temperature range of 70–190 °C, which is due to the expulsion of the moisture present in the PANi [66]. The second step weight loss in the temperature range of 220–340 °C is due to the loss of unbounded dopant (DBSA). Then, a very significant weight loss occurs in the third and fourth steps in the temperature ranges of 369–566°C and 580–744°C, which are respectively
due to the loss of the dopant bound and thermal oxidative decomposition of the composites [67]. The results show that the thermal stability of the composite is decreased as the amount of PANi enhanced. Also the decomposition of SIS-PAni2.5 starts at 349.65°C and 84.3% weight loss up to 700°C while decomposition onsets of the SIS was 377.26 °C and showed weight loss of 100% up to 520°C. It indicates that SIS-PAni 2.5 is less thermally stable than the SIS and other composites shows similar kind of behaviour as SIS-PAni 2.5. But out of all the composites SIS-PAni1.5 has the highest thermal stability. Thus the SIS-PAni1.5 composite is a useful sensor for oil detection in water and has good thermal stability among all other sample compositions.

3.3. Conclusions

The development of solvent sensing composite films and the mechanism involved in it are demonstrated here by deriving the molecular level interactions. Weaker rubber–filler interactions are observed for NR-CG200 and NR-CG600, compared to the NR-CNT composite due to the presence of polar groups on RGO surfaces. The investigations have shown that the diffusion process and, therefore, the rate of change of relative resistance decrease with increasing molecular size of the solvent (diffusant). The results indicate that the NR-CG200 composites can be used as a novel organic liquid sensor to detect, and discriminate various aromatic solvents.

The NR/BR/SIS/CNT sensor has turned out to be a good oil detector. The SIS-PAni composite has been synthesized by in situ polymerization of aniline in the presence of doping agent and SIS polymer. SIS-PAni thin film sensor exhibits much higher sensitivity towards both oil and water phase. Moreover, the SIS-PAni thin film sensors have fast response and good reproducibility in oil detection. This study provides developing sensors
which are simple in structure, low cost, easily fabricable, stable, easy to handle and able to operate at room temperature. The SIS-PAni1.5 has turned out to be the best composition for oil detection in water and has good thermal stability. This sensor is applicable to find out the presence of oil spill in sea water by sticking on the surface of pipelines.

3.4. References


Chapter IV : Interrelated Shape Memory and Payne Effect in PU/GO Nanocomposites

ABSTRACT
The fabrication of GO based PU nanocomposites by simple method of mixing and its shape memory properties at different temperatures are discussed in this chapter. Both the polymer and the filler were synthesized in the laboratory by simple and easy methods-PU by pre-polymer method and GO by improved graphene oxide synthesis method. The structure of the polymer composites investigated by SEM and X-ray diffraction studies revealed highly dispersed morphology of GOs in PU. The improvement in shape memory obtained for the nanocomposites was then quantitatively analysed using Payne effect. A nice correlation was established between the temperature dependence of shape memory and the crosslink density.
4.1. Introduction

Shape memory polymers (SMPs) have great significance in technology and industry due to their unique ability to restore the original shape after a structural deformation by an external stimulation such as heat, light and chemicals [1, 2]. Their superior properties like large rate of shape recovery, easy processing, lightweight and low cost as compared to shape memory alloys have promoted their rapid development and commercialization [3-5]. Usually, the deformation is induced by thermal stimulation by heating the polymers above their transition temperature, which is either the glass transition or melting temperature. PU belongs to the class of thermoplastic elastomers and possesses excellent shape memory properties. They have hard and soft segments in their structure and since because of the physical crosslinks present in their hard segments, these copolymers are very easy to process [6]. The shape-memory property of segmented PU block copolymers has been extensively addressed because of its superior material properties, arising from the phase-separated structure of its hard and soft segments. Depending on the high molecular weight of polyol precursor, PUs exhibit higher recovery ratio and fixity and shorter recovery time [7]. This can be attributed to the greater rubber elasticity [8]. The glassy and rubbery properties of PU respectively depend on the urethane content and the cross link density as well. It is reported that the soft segments containing PU exhibit better shape memory than their hard segmented counterparts [7].

Even though PU has better melt processability and many physical properties like flame retardancy, despite good deformability, low stiffness and tensile strength can limit its use in structural applications [9]. It’s mechanical and gas barrier properties can be complemented by reinforcing the matrix with rigid, impermeable nanofillers [10]. However,
strain and thermal expansion may lead to the breaking of filler aggregate network and can cause deterioration in modulus [11, 12]. Commonly used fillers such as clay, CNTs, graphitic platelets and bio fillers are renowned in enhancing the shape memory of PU. The shape recovery of SMPs is enhanced when spherical silica particles are embedded in it [13, 14]. Influence of nanoclay on the shape memory nature of PU containing 30% hard segments was addressed by Haghayegh et al. by following a two step synthesis method. The shape recovery was monitored using tensile machine equipped with a thermal chamber and the composite containing 1% clay showed the best recovery [15]. This was followed after the observation of a 20% increase in magnitude of shape recovery at the same concentration of nanoclay, by Cao et al. [16]. However an optimum shape memory was noticed for 3% clay loading in the hyperbranched PU matrix synthesized using the palm oil polyol [17]. The reason for the higher shape recovery of nanocomposites is ascribed to the enhanced polymer-clay interaction [18].

Conductive fillers like CNTs, carbon fibers etc. can generate heat in order to facilitate the heat transfer to initiate the shape recovery of the matrix [19, 20]. By discarding the problem of their requirement in high concentration, composites for electrical actuation were fabricated by incorporating MWCNT carbon nanopapers at lower concentration in to the SMPs [21]. The improved interaction between acid modified MWCNTs and PU in enhancing the electro active shape memory property was illustrated by Cho et al. [22]. Similar kinds of shape memory enhancement i.e. about 95% of shape recovery, was attained on introducing the carboxyl groups at the side walls of CNTs and thereafter cross linking with PU [23]. Thus it is possible to tune the conductivity of the composites fabricated using conductive fillers.
like MWCNTs after modifying with various functionalising agents, and correspondingly, structures having various electro active shape recovery were obtained [24].

The functional groups such as amines and hydroxyls on the basal plane of GOs attach with polymers through either grafting-onto or grafting-from approaches providing chemical bonding with the matrix. This minimizes the irreversible agglomerate formation of graphene fillers through vander Waals interactions and contribute to reinforcement. RGO filled PU composites are widely reported possessing high strength, elastic modulus, thermal conductivity, stability and impermeability [10, 25-27]. Khan et al. fabricated highly stiff PU/graphene (55 wt %) composite with deterioration in elasticity using liquid exfoliated graphene of up to 90% mass fraction and proposed its better performance than CNTs [28]. Kim et al. [10] compared the different mode of dispersion of thermally and chemically expanded graphene on the electrical property of PU and achieved high homogeneity and superior properties for the composite fabricated by solvent assisted mixing. Substantial enhancement in both stiffness and toughness with improved hardness and scratch resistance without deteriorating elasticity is obtained for PU/GO composites by Cai et al. which is attributed to the chemical bonds formed between PU and GO [29]. These molecular interactions occurring within the composites (in addition to the other factors such as crystallinity, cross link density etc.), were supposed to be the reason for the enhanced shape memory of graphitic filler platelets reinforced PUs [10, 30].

Here we emphasizes on the shape memory property of PU/GO composites by focussing on its deformed (temporary) shape and recovered original (permanent) shape under a thermo mechanical loading–unloading cycle at different temperatures. The variation in the storage modulus values with strain at different temperatures was fitted with Maier and Göritz
model and using this, the crosslink densities of nanocomposites were determined. Besides the $T_g$, the dependence of crosslink density on the storage modulus variation and shape memory behaviour is well reported, and its quantitative contribution is brought out by this study. The stress relaxation and cyclic hysteresis (Mullins effect) studies on the mechanically strong nanocomposites evidence for the filler polymer molecular level interactions and subsequently support the improved shape memory property. Finally, a correlation has been recognized between the shape memory and crosslink density at different temperatures and at different filler concentrations.

4.2. Results and discussion

The shape memory behavior of the unfilled and filled PU samples was examined and the results showed both qualitative and quantitative features generally observed in most of the nanocomposite systems. It is well known that the main idea behind the shape memory effect is the capability of a material to maintain the temporary shape over long times. As reported, this effect comes from the contribution of two phases existing in the polymer nanocomposite systems—a reversible phase related to the transition temperatures (glass transition and melting) and a fixed phase coming from the crystallites and cross linking points. A reversible phase transition takes place within the polymer upon heating near to its $T_g$ or $T_m$, and its molecular alignment disturbs. At this state, the specimen is cooled followed by applying stimulation in the form of heat or light; and this releases the stress and fixes the polymer chains back to its original random conformation. Since the shape recovery is related to the stress transfer, in nanocomposites, the filler elastomer interactions, chemical cross links existing, crystallinity etc. affect the recovery to a great extent.
Figure 4.1 Stress-strain curves of PU and its nanocomposites containing GO under cyclic loading at 100% strain at different temperatures 298K, 323 K and 348 K

The hard and soft segments present in PUs are much related to the transition between the “fixed phase” and “reversible phase” [31, 32]. And so the shape memory property is a noteworthy topic in case of all PU based systems. The recovery cycles for the neat PU and all
PU/GO composites are shown in Figure 4.1. From these stress strain loading cycles, the calculated shape fixity (Figure 4.2a) and shape recovery (Figure 4.2b) at various filler contents and different temperatures are summarized. On moving from PU to PU/GO composites, the recovery (R_r) shows a gradual increase of ~96.5%, ~97.7%, ~98.3%, ~99.2% respectively for all filler concentration at 348K temperature. The better shape recovery of composites observed must be due to the higher stored elastic strain energy by GOs which in turn helps the composites to gain higher recovery stress by releasing the stored elastic strain [33]. Enhanced PU-GO interfacial interactions contribute to large number of crosslinks resulting in the increase in amount of unlocked oriented chains (soft segments) [34, 35]. The ionic groups on GOs (evident from the FTIR spectrum) are mainly responsible for the enhanced interactions at the interphases and on the phase transition and stress transfer happening during the recovery process.

![Figure 4.2](image.png)

**Figure 4.2** a) Shape fixity and b) Shape recovery ratio of polyurethane and its nanocomposites with graphene oxide under cyclic loading at different temperatures 298K, 323 K and 348 K.
Since the physical crosslinks within the composite act as net points during the shape recovery process [36], the location of such cross-links is one of the most important factors while addressing the memory effect. The number of available physical crosslink points depends on the functional group on filler (-OH,-COOH,-O-) and matrix (-CNO). PU contains hard segments and hydrogen bonding sites which strongly attract the GOs by hydrogen bonding and/or dipole–dipole interaction and forms physical crosslinks [37]. The HS in the matrix form physical crosslinks arising from polar interactions, hydrogen bonding, and crystallization in the hard domain, while the soft segments form a reversible phase because of molecular motion in a rubbery state [38-40].

The shape recovery varies positively with GO concentration. This phenomenon would also be justified by correlating with the increased degree of interfacial bonding. This observation is in agreement with the already reported behavior [41] where the recovery ratio decreased while the shape fixity increased with increasing amount of the filler particles (GO). The presence of crosslink points (within the PU chains and between PU and GOs) prevent [41] the neighbouring chains from slipping when it is subjected to deformation and consequential stress build-up [42]. This kind of crosslinking is purely dependent on temperature and thus temperature is a decisive factor in shape memory property. While analyzing the temperature dependence of shape memory by varying the temperatures 298, 323 and 348 K, for all samples, we observed an increase in Rf and Rr with temperature. The variations in shape memory with temperature are mainly due to structural changes occurring in polymer chains and polymer-filler interactions. At higher temperature, the polymer chains become more labile and upon stimulation they can have a large number of conformational arrangements.
The shape fixity \( (R_f) \) of PU, PG0.5, PG1.5 and PG3 respectively shows values of \(-95.8\), \(-91.8\), \(-75.1\) and \(-69.7\)%. There is a noticeable decrease in the fixity value on moving from PU to PG3. Upon filler addition, the polymer chains are entangled together by the GO sheets. As the filler concentration enhances, the number of filler-polymer bonds also increases and the interfacial interaction facilitates better reinforcement as well. When such nanocomposite samples are heated, large number of crosslinks break compared to the neat polymer lowering their ability to fix mechanical deformation. This can also be attributed to changed crystallization (when stretched) and other secondary interaction between GO and the chains. The shape fixity highly depends on the crystalline phase of the sample and the lack of adequate amount of crystalline phases causes immediate shrinkage of composite upon deforming stress release \([41, 43]\). GOs may disturb the crystallization process as well. In addition, the shape fixity of the composites decreased with temperature. Enhanced mobility of polymer chains and thus better ability to switch bonds is attributed to this trend.

![Figure 4.3](image_url)

**Figure 4.3** a) Stress relaxation curves, time dependence on the normalized stress for neat PU, PG0.5, PG1.5 and PG3 nanocomposites (The dotted lines represent the curve fits). b) Stress softening responses of neat PU, PG0.5, PG1.5 and PG3 systems.
Addressing measurements such as stress relaxation and cyclic hysteresis is essential in order to have a better understanding about the stability of interactions between the elastomer and filler with respect to time. During stress relaxation, a part of the energy stored in the material is dissipated and a part of the deformed chains cannot retract. Therefore, more pronounced stress relaxation results in higher permanent deformation of the material [44, 45]. Figure 4.3a shows the stress relaxation curves for the neat PU, PG0.5, PG1.5 and PG3 composites at 25°C and at a constant elongation of 40%. In neat PU, the fast relaxation in stress is contributed by the chain motion and orientations, rearrangement of broken chains, crosslinks and entanglements. However, in case of PU nanocomposites the stress decay exhibits a controlled pattern. This stress relaxation pattern in a filled system depends on the filler structure and the filler-polymer interactions. The relaxation time coming from the disentanglement of the soft segment chain network in the soft phase increases with the filler addition. Thus for the nanocomposites more time is required for the polymer entanglement network to disentangle as evident from the figure. Longer polymer chains require longer time to disentangle and with increased relaxation of the chains, the less concentration of unrelaxed chains promotes a drop in modulus resulting in a terminal zone. Thus the filler addition has a very strong effect on the crosslink density of PU and the increase in the filler content increases the hard domains in PU, decreases the amount of elastic cross-linked network structure and thus increases the relaxation ratio.

Since the quantification of interactions depends largely on the relaxation time, its determination is rather significant. This can be fulfilled by fitting the experimental relaxation curves of the composites with equation 3.1. The experimental curves are well fitted with the
theoretical values and the calculated relaxation ratio, relaxation time and fitting parameter, β using equation 3.1 are given in Table 4.1. Neat PU has relaxation time in the range of ~4.8 sec whereas at 3 phr filler concentration it is the highest (τ₀~13.8 sec). The highest value of the relaxation time for PG3 owes to its higher crosslink density. This is because at high filler concentration, the number of physical and chemical interactions and the reinforcement between filler and polymer is quite high. The increase in the initial stress for the composites upon GO addition indicates the effect of filler on the crosslink density of PU. The addition of GO affects the degree of micro phase separation (decrease in HS content in the soft phase), increases the soft chain flexibility and elasticity leading to a slow stress relaxation process [46]. In short, the decrease in overall chain flexibility and slow stress relaxation process confirm the reinforcing ability of GO to PU matrix. This higher degree of polymer–filler interactions is further evidenced from the higher contribution in the progressive failure in filler–elastomer bonding [47]. In some cases, reasons for the higher relaxation rates in filled elastomers are associated with breakdown of the filler-filler or filler-polymer interactions in it and the extent of such breakdown depends on the nature of filler [48].

Table 4.1. Mechanical and relaxation properties of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at Break (%)</th>
<th>β</th>
<th>τ (sec)</th>
<th>Relaxation ratio [(σ₀ - σₐ)/σ₀]×100</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>22.1±0.1</td>
<td>5.5±0.1</td>
<td>397±10</td>
<td>0.22</td>
<td>4.8</td>
<td>40.3</td>
</tr>
<tr>
<td>PG0.5</td>
<td>18.5±0.4</td>
<td>6.5±0.1</td>
<td>385±15</td>
<td>0.19</td>
<td>9.0</td>
<td>41.6</td>
</tr>
<tr>
<td>PG1.5</td>
<td>30.5±0.2</td>
<td>8.1±0.1</td>
<td>391±25</td>
<td>0.15</td>
<td>11.4</td>
<td>42.3</td>
</tr>
<tr>
<td>PG3</td>
<td>25.0±0.1</td>
<td>10.5±0.1</td>
<td>307±30</td>
<td>0.15</td>
<td>13.8</td>
<td>44.3</td>
</tr>
</tbody>
</table>
The stress softening behavior also known as Mullins effect [49] for PU, PG0.5, PG1.5 and PG3 subjected to a cyclic process at 10, 50 and 100%, elongations respectively is illustrated in Figure 4.3b. The composite exhibits softening at subsequent cycles during the cyclic tests and it is more pronounced compared to its response during low stretching and it increases with the amount of filler. According to Mullins, the softening of stress in filled elastomers is due to the occurrence of disentanglement, bond rupture, rupture of filler aggregates, molecular slipping, buckling of molecular bundles [50-52], polymer chain network etc. resulting in the breakdown of filler-polymer interactions similar to stress relaxation phenomena. PG3 shows high stress softening due to the high viscous drag exerted by neighboring molecular chain segments, which is very less in the case of neat PU. The entanglement characteristics of polymers and trapping of polymer chains at the filler surface have been suggested as primary factors inducing non-linear viscoelasticity [53, 54]. This effect can be ascribed to the strengthening of the interactions between nanoparticles and polymer chains [54]. The effect is observed here at 5 mm/min but at slower strain rates, the interfacial interactions break more gradually. Owing to the elastomeric nature of the PU and the loss of conformational entropy, the polymer chains will try to retract to their original state. In case of nanocomposites nonlinear behavior can be explained by localized glassy layers of reduced molecular mobility around particles and softening is more pronounced in case of strong interaction between filler and matrix [55, 56]. Finally Mullins effect contributes towards the molecular structure, which is formed by locating the fillers on the polymer and forming a strong network with high filler-polymer interactions.
Figure 4.4 Strain dependence of the storage modulus (fitted with Maier and Göritz model) for a) neat PU, b) PG0.5, c) PG1.5 and d) PG3 at different temperatures 298K, 323 K and 348 K.

The viscoelastic responses of PU/GO composites with strain are addressed by monitoring the Payne effect under finite values of $G'_0$ and $G'_x$ at small and large strain amplitudes and at constant frequency 0.5 Hz with strain sweep at 298, 323 and 348 K. The result obtained is illustrated in Figure 4.4. The decrease in the initial storage modulus of neat PU with increase in temperature is attributed to the loss of entanglements or improvement of soft regions in the matrix at higher temperature. PU/GO nanocomposites also show similar kind of evolution but it has some additional crosslink’s than PU. Fitting with Maier and Göritz model provide a better understanding about the existing filler-polymer interactions.
The dotted lines in the Figure 4.4 represent the model curve fits. The various parameters characterizing the network strength were calculated using equation 2.5 and the modulus variation is observed to be strongly influenced by the amount of the filler and filler polymer interactions (Table 4.2). It can be observed that the dynamic modulus increases significantly but the temperature hardly affects the modulus values. The modulus notably fluctuates with a standard deviation of 3% which is quite acceptable for rheological measurements. We have observed the same for all composites, and sometimes the larger deviation at low frequency was also observed. The deviations in the fitting parameters reflect the fact that filled rubber is not a "perfect" linear response system, but exhibits non-linearly. One source of non-linearity is the so called Payne effect, due to the strain- induced break-up of the filler networks.

Table 4.2 Fitting parameters of Equation 2.5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>$G'_st$ (10^6 MPa)</th>
<th>$G'_i$ (10^7 MPa)</th>
<th>$N_i^0$ (10^27 cm^-3)</th>
<th>$N_g + N_st$ (10^26 cm^-3)</th>
<th>$N_{il} + N_i^0 + N_st$ (10^27 cm^-3)</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>298</td>
<td>0.20</td>
<td>1.3</td>
<td>3.1</td>
<td>0.06</td>
<td>3.10</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.09</td>
<td>0.8</td>
<td>1.8</td>
<td>0.02</td>
<td>1.80</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.09</td>
<td>0.3</td>
<td>0.7</td>
<td>0.02</td>
<td>0.70</td>
<td>12</td>
</tr>
<tr>
<td>PG 0.5</td>
<td>298</td>
<td>1.10</td>
<td>2.1</td>
<td>5.2</td>
<td>0.27</td>
<td>5.23</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.05</td>
<td>1.1</td>
<td>2.6</td>
<td>0.01</td>
<td>2.60</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.05</td>
<td>0.5</td>
<td>1.1</td>
<td>0.01</td>
<td>1.10</td>
<td>12</td>
</tr>
<tr>
<td>PG1.5</td>
<td>298</td>
<td>4.01</td>
<td>2.2</td>
<td>5.6</td>
<td>0.41</td>
<td>5.64</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.05</td>
<td>1.7</td>
<td>3.9</td>
<td>0.01</td>
<td>3.90</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.05</td>
<td>0.7</td>
<td>1.6</td>
<td>0.01</td>
<td>1.60</td>
<td>15</td>
</tr>
<tr>
<td>PG3</td>
<td>298</td>
<td>7.50</td>
<td>3.1</td>
<td>7.3</td>
<td>0.90</td>
<td>7.39</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.05</td>
<td>2.4</td>
<td>5.4</td>
<td>0.01</td>
<td>5.40</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.05</td>
<td>0.9</td>
<td>2.0</td>
<td>0.01</td>
<td>2.00</td>
<td>20</td>
</tr>
</tbody>
</table>
The crosslink density values calculated using equation 2.5 helped in the quantitative estimation of the matrix filler interactions. The higher crosslink density of PG3 ($N_{\text{total}}=7.39\times10^{27}/\text{cm}^3$) compared to the neat PU ($N_{\text{total}}=3.10\times10^{27}/\text{cm}^3$) is explained to be due to the confinement effect and good interaction between GOs and PU. The ionic groups on GO surfaces interact strongly with urethane groups, causing more reinforcement and network formation in PU/GO nanocomposites. The small size and the high specific surface area of nano fillers favor the formation of a three-dimensional network within the polymer matrix. It is observed that the crosslink density of the pure matrix and nanocomposite network is identically reduced by a factor of ~4-5 when the temperature rose from 298 to 348K as given in Table 4.2. There is a significant crosslink density difference between PU and PU nanocomposites at lower temperature and upon temperature increase the difference reduces. Table 4.2 gives a clear idea on the huge variation of the number of stable bonds with
temperature in case of GO filled PU but not in the case of pure matrix. This information is
clear from Figure 4.5 as well, where the influence of both stable and unstable bonds on
temperature is illustrated with former due to the presence of glassy bridges [57, 58]. On the
basis of this analysis, the shape memory property is well described as a key part of the study.

In general shape memory property of pure polymer is dependent on the crystalline
(hard and soft segments) nature, dipole-dipole interactions, hydrogen bonding and molecular
entanglements. On the other hand, for filled polymers, there will be some other factors also
influencing the shape memory. The restricted mobility of the polymer chains, cross link
density, interfacial interaction, glass transition etc. are a few such factors [59]. Other than the
crystallinity, the mechanism involved in the shape memory property of composites is
explained here by quantization effect. As already explained the polymer composites contain
network architecture including flexible chain segments connected by chemical or physical
crosslink’s corresponding to the polymer-filler contacts and phase separation from molecular
interactions, respectively [36]. The dependence of crosslink density (from Payne amplitude)
on the, content was reported to be linear [60] representing its direct influence on interactions
in the composites. Tiwari et al. [61] observed a linear relationship between crosslink density
and the average number of immobilized bridges in elastomer matrix. Even though
crystallinity plays a role in shape memory, in nanocomposites some of the crystallites
generated during fixing may be melted when heated. So in a better way, the shape recovery
ratio could be interpreted by the increased crosslink density, and the possibly increased
amount of the crystallites (survived during the recovery process). Based on a thorough
understanding on the Payne effect, a strong linear correlation between crosslink density
calculated from Payne (from dynamic mode experiment, DMA), and shape memory for PU-
composites, is established as demonstrated in Figure 4.5. In PU/GO system, the GO sheets interfere with soft segment crystallization, and promote phase mixing between the hard and soft PU segments, thus affecting the shape fixity and recovery ratio. It may be justified to correlate the increased degree of crosslink density to this increasing trend of shape recovery property. The increased crosslink density (or amount of crosslink’s) on incorporation of GOs results in enhanced shape recovery (Figure 4.5) with filler addition.

![Figure 4.6](image)

**Figure 4.6** Schematic representation of temperature dependence of shape memory-effect of stable and unstable regions upon heating.

The dependence of shape memory and crosslink density on temperature is also interesting and schematically illustrated in Figure 4.6. At lower temperature, the molecular chains were released from the constraints of soft segment crystals gradually and had enough time for stress relaxation (Figure 4.3a). On the other hand, the higher heating rate provides limited time for molecular chains to rearrange and relax, resulting in rapid recovery and higher recovery stress [61]. At sufficiently high temperature, however, the molecular chains become softer and the relaxation time is shortened, thus, starting the recovery stress after the peak stress to decline. At still higher temperature physical cross-links melts (breaking of
filler-polymer interactions in case of composite) which contribute to the flexibility in shape memory. The rate of desorption is directly proportional to the number of stable and unstable bonds at the filler surface. At higher temperature the rate of desorption is more and most of the bonds on the filler surface are converted into flexible polymer chain (Figure 4.6) which contribute to shape recovery process. Hence it is understood that the number of unstable fixed chains adsorbed on the filler surface is responsible for the improvement in shape recovery with increase in temperature. Thus the key role of shape memory and the consequence in the non linear behavior of PU nanocomposites as well as the quantitative estimation of crosslink density contribution to shape memory are brought out by this study, which is an innovative and novel concept towards the polymer composites field.

The mechanical strength of the fabricated composite materials is investigated in order to get a picture on the composite micro level behaviour. In all nanocomposite systems, the interfacial interactions play a crucial role in determining the mechanical strength. The distribution, orientation and aspect ratio of the nanofillers, domain size and shape and degree of polymer-filler compatibility are some of the factors depending on nanocomposite strength [62]. In order to achieve better mechanical properties, an efficient level of stress transfer between the GOs and elastomer is very essential. We notice a nano reinforcing effect of the GOs in PU/GO, from the improvement in mechanical strength. The values of Young’s modulus, tensile strength and elongation at break are tabulated in Table 4.1. The modulus of pristine PU is 5.5 MPa and it improves 1.2 times at 0.5phr filler loading. In PG3, the modulus almost doubles (10.5 MPa). Since neat PU is not so strong due to the less chain entanglements and viscosity, the modulus improvement obtained here in PU/GO composite is really significant [64]. The well exfoliated GO sheets with high level of confinement in PG3
would cause maximum stress transfer and this explains its highest modulus. Better interfacial bonding between PU and GOs could be the exact reason for this observation. The functional groups like –OH, -C=O, –COOH present on the surface of GOs facilitate hydrogen bonding interaction with the urethane groups of PU. The well dispersed GOs further enhance the interfacial interactions through their bridge, loop and tail linkages with the polymer chains resulting in higher filler-matrix adhesion [63]. It is this increase of molecular restrictions of the polymer chains attributes towards the decrease in elongation at break of the composites compared to that of the neat PU (Table 4.1). The reduction in the values of strain at rupture for the PU composites limits the tensile behaviour at high deformations.

Interpretations of the reinforced GOs on PU soft, hard segments and interface can be observed by different methods. Due to the special morphological arrangement of hard and soft domain segregation, the composite exhibit very interesting thermal and mechanical properties. We interpreted this property enhancement as evidence for the selective insertion of GO sheets in hard segments depending on the surface chemistry of the GO and the chemical structure of the segment. GO based composites tend to maintain their strength and elongation at higher filler loading. At certain concentration of GO in PU, GO become segregated in the hard segments and thus enhance the modulus and tensile strength with significant value of elongation at break. This controlled reinforcement of the hard segment of PU has allowed us to prepare its GO composites.

It has been revealed that the hard segments with glassy or laminar crystalline structure acts as physical crosslinkers for the rubbery soft segment in PU. Furthermore, we note that the interaction with the matrix polymer will be very sensitive to the nature of the functional group (or grafted polymer chain). Here, we interpret the successful grafting of PU
on the GO surface and graphene sheet, became a part of hard segment. Furthermore, it is expected that the functional group present on GO can allow targeted insertion of the GO sheets into specific regions of the matrix. This can allow fine control over the properties of the final composite. The decrease in the elongation at break with increasing GO content in tensile test of the composite is in agreement with DMA results with regards to the increase of rubbery plateau moduli. Hence, the GO affected the PU by two ways. Grafting of MDI on the GO retarded the crystallization of the hard segment of PU and GO itself reinforced the PU matrix to increase the mechanical strength of nanocomposites.

As the fillers are well dispersed in the PU medium (from the SEM as follows), the soft, hard and interfacial PU segments interact well with the filler surfaces. The mode of interaction between the PU and filler is physical in nature and the vander waals forces and dispersion forces play in this regard. Also the functional groups present on the GOs and PUs interact by hydrogen bonding as well which contribute to all sorts of filler-PU interactions as the chains are not arranged in a specific conformation. Thus all kinds of interactions between the filler and polyurethane (hard, soft and interfacial) are present in the composite.
Composite morphology was monitored using SEM micrographs of the cryo cut surfaces of PU/GO samples (Figure 4.7). The influence of filler platelets on the microstructure of PU is very lucid from the series of SEM pictures obtained. The exfoliated GO sheets as evident from its SEM image (Figure 4.7a), are uniformly dispersed in the PU medium as the composite morphology indicates. The fractured surface of pristine PU is smooth (Figure 4.7b); however, it becomes rough in the presence of GO (Figure 2c and 2d). Surface roughness increased from PG0.5 (Figure 4.7b) to PG3 (Figure 4.7c), which is due to the increase in concentration of GO sheets.
To further analyze the mode of dispersion of nano fillers, the structural variation within the filler as well as composites were investigated by XRD. The characteristic sharp peak of graphite at $2\theta = 26.5^\circ$ is more broadened and shifted to $2\theta = 5.3^\circ$ in GO as illustrated in Figure 4.8a. The oxidation process would cause the delamination of individual graphene layers in graphite and this is the reason for the observed downward shift in $2\theta$. In other words, the exfoliation of platelets leads to loss of regularity of GO sheets by enhancing the platelets gap similar in the case of exfoliation of clay platelets [15-18]. In composite samples, the case is rather different. Neat PU is soft in nature (32% HS) and the peak obtained near $2\theta = 21^\circ$ may be an amorphous halo attributed to its elastomeric structure (Figure 4.8b). For PU/GO samples, the peak intensity marginally enhances, though the peak remains at the same position at $2\theta = 21^\circ$. This can be related to the crystallinity imparted to the PU matrix by the GO addition. GOs possess strong nucleating effect [26] within the polymer matrix.

**Figure 4.8** X-Ray Diffraction patterns of a) GO and Graphite b) PU, PG0.5, PG1.5 and PG3
Moreover, GO peak in the XRD pattern of nanocomposites is much diminished, indicating the exfoliated nature of GO sheets in PU [10].

### 4.3. Conclusions

Analysis of the relaxation time and nonlinear viscoelasticity studies from the Mullins effect and Payne effect revealed confinement effects occurring in GO filled PU nanocomposites. The shape memory behaviour addressed by varying the temperature and cyclic loading reveals the maximum shape recovery in PU/GO composites at 3phr filler loading. This is because of the phase mixing between soft and hard segments of PUs when the GO sheets interact with the soft segmented portions. Due to their high specific surface area, GO sheets facilitate larger rate of filler polymer interaction and Maier Goritz model quantified this in terms of cross link density. Stress relaxation and Mullins effect experiments also satisfied the crosslink density measurements and thus support the shape recovery of the nanocomposites. It is concluded that the polymer filler interactions are strongly affected by the temperature variations as the stable and non stable polymer chains within the composite is influenced.

### 4.4. References


Chapter V: Dielectric Properties of PU/modified GO Nanocomposites

ABSTRACT
Here in this chapter we discuss about the dynamic mechanical, dielectric and rheological properties of reinforced PU nanocomposites containing hydrophilic GO and/or hydrophobic mGO sheets. The organic modification of GO was performed with 4,4’-methylenebis (phenyl isocyanate) (MDI) and the samples were prepared by solvent mixing. The addition of mGO provides a more significant increase in the dielectric permittivity as compared to the addition of GO. This qualitative morphology observation is correlated with the quantitative results inferred from the dynamic mechanical analysis, rheology and dielectric studies. The non-linear viscoelastic behaviour of the PU nanocomposites is in good agreement with the Maier and Goritz model, which includes the effects of the adsorption/desorption of PU chains on the filler surface. The observed results underline the possibilities of PU composites with mGO sheets in energy storage applications.
5.1. Introduction

PU is industrially important due to its excellent flexibility, elasticity and damping ability. These properties together with its high melt processability and tunable physical properties make this thermoplastic elastomer applicable in coatings, adhesives, foams, biomimetic materials and various diversified fields of modern technologies [1]. PU also possesses a high tensile strength, abrasion, tear resistance, and solvent resistance and combines properties of elastomers as well as thermoplastics. However, the applicability of PU (especially PUs having a small amount of hard segments) is still limited by its low stiffness, inferior gas barrier properties and poor conductivity [2]. Among various nanofillers employed for composite fabrication with the objective to enhance the physical properties of PU, graphene and GO have utmost importance owing to their unique properties such as stiffness, strength, specific surface area, thermal conductivity and gas impermeability [3].

Since the properties of polymer nanocomposites largely depend on the dispersion of nanofillers in the matrix and the filler-polymer compatibility and interfacial interaction, several modifications of graphene fillers have been employed; often depending on the polymer nature [2]. A number of studies report on GO and functionalised graphene filled PU [4-6]. Khan et al. reported on extremely stiff PU containing 55 wt% graphene [7], but the elasticity of PU was seriously deteriorated. GO consists of polar groups, such as hydroxyl, epoxide, ether and carboxylate groups, as the result of oxidation [8]. Due to its polar nature, GO has only limited solubility in organic solvents and nonpolar polymers and thus surface treatment have been employed to improve the performance of the nanocomposites. Stiffness and scratch resistance of PU significantly enhance by GO addition [9]. However Nguyen et al. disclosed that non-covalent interfaces led to a poor reinforcing effect of GO [10]. The
ideal interface for stress transfer was proposed to be covalent bonds formed between graphene/GO and the PU matrix \([5, 11, 12]\).

Here the quality of dispersion of GO in PU is enhanced by introducing methylene diphenyl diisocyanate (MDI). The isocyanate (NCO) group at the end of the linear PU interacts with the oxygen groups on the GO. Solution mixing is employed in order to achieve a better dispersion of GO in the PU matrix and the filler concentration is varied from 0 to 3 wt\%. Using MDI the GO filler surface is also modified. The dynamic mechanical, dielectric and rheological properties of the PU/GO nanocomposites were determined and compared with those of PU/ isocyanated modified GO (mGO) nanocomposites and neat PU. Here the stiffness and toughness are enhanced without deteriorating the storage modulus. The qualitative information of dispersion from rheology is related with its quantitative assessment from dielectric property and DMA depending on the filler concentration and reinforcement state. The extent of GO exfoliation in the final composites was characterized by X-ray diffraction scattering and electron microscopy.

5.2. Results and discussion

5.2.1. Dielectric measurements

The strong binding of electrons through covalent bonds in the structure makes polymers good insulators and dielectric materials. Polymer nanocomposites exhibit higher values of the dielectric constant than the corresponding traditional polymer matrices. When placed in an electric field, nanocomposites can undergo ionic, interfacial and dipole polarization over different time and length scales. The effective dielectric constant of a nanocomposite system can be represented by Equation 5.1\([15]\).
\[
\frac{\varepsilon_r}{\varepsilon_m} = \left| f_c - f \right|^s
\]  
(5.1)

Here \( \varepsilon_r \) is the effective dielectric constant, \( \varepsilon_m \) is the dielectric constant of the polymer matrix, \( f_c \) is the percolation threshold, \( f \) is the volume fraction of metal or inorganic filler, and \( s \) is a scaling constant (~1). Low \( \varepsilon_r/\varepsilon_m \) values can be attributed to a poor dispersion of the filler in the composites and weak filler-polymer interactions, thus correlating dielectric spectroscopy with the microstructure of the composite.

**Figure 5.1** Variation of a) dielectric permittivity (\( \varepsilon' \)) and b) dielectric loss (\( \varepsilon'' \)) at 25 °C temperature for PU and PU composites. Rheological behaviour of PU, PG and PMG composites by c) \( G' \) and d) \( G'' \) vs frequency curves at 160 °C.

The dielectric constant \( \varepsilon' \) and dielectric loss \( \varepsilon'' \) of PU nanocomposites over a frequency range of \( 10^2 \) to \( 10^6 \) Hz at room temperature are presented in Figure 5.1a and 5.1b.
dielectric constant significantly increased over the whole frequency range by the addition of GO/mGO nanosheets due to the high filler surface area. With the incorporation of GO/mGO, the dielectric constant for filled PU films measured at a frequency of 20-1000Hz increased significantly from PG0.5, PG1.5, PG3, PmG0.5, PmG1.5 and PmG3 films respectively. This abrupt increase in the dielectric permittivity of the nanocomposites is ascribed to the motion of free charge carriers due to the formation of a continuous conductive pathway of GO/mGO nanosheets throughout the medium. Usually the increase in dielectric constant in conductive polymer nanocomposites is accompanied by an increase in the dielectric loss and a decrease in the dielectric strength, and this limits their applicability in energy storage devices. But here in these systems, PMG3 proves to be capable of producing stable nanocomposite films of high dielectric constant and low dielectric loss.

According to the Maxwell-Wagner-Sillars (MWS) process, the presence of a polymer-filler interface can lead to changes in dielectric properties [16]. When current flows across the two-material interface, charges can be accumulated at the interface between two dielectric materials with a different relaxation time (τ = ε/σ, where ε is the dielectric permittivity and σ is the conductivity). The nanocomposites have a huge interfacial area, which in turn provides numerous sites for the reinforced MWS effect as compared to microcomposites [16]. For PU/GO composites, the value of the permittivity constant raised towards low frequencies, which is 3 times that of the pure matrix. The increase in the dielectric permittivity with decreasing frequency suggests that charge accumulation at the filler/polymer interface starts to appear. This might originate from the homogeneous dispersion of the GO in the PU and the facts that the oxide groups on GO prevent electrical conductivity. A high dielectric loss involves an energy cost, heat liberation and thus
instrument problems. When comparing the dielectric losses of the different composites at 100 Hz, mGO composite shows a very high dielectric loss whereas GO composites have a much lower dielectric loss.

5.2.2. Rheology and Payne effect

Rheology can offer insight to the microstructural changes occurring within composite systems, depending on the filler-matrix interactions and the method of preparation. The degree of dispersion and exfoliation of filler particles in the medium and thus the structure of the nanocomposites –intercalated or exfoliated- can be assessed from rheology studies. Here, the rheological behaviour of the PU composites was analysed with frequency and strain sweep experiments. Figure 5.1c and 5.1d illustrates the variation in storage modulus $G'$ (Figure 5.1c) and loss modulus $G''$ (Figure 5.1d) at 160 °C as a function of angular frequency. As reported, the melt rheological properties of filled polymers are sensitive to the structure, particle size, shape and surface characteristics of the fillers. This technique offers original means to assess the state of dispersion in the nanocomposites and to investigate the influence of flow conditions upon nanofiller dispersion itself. Below 160°C, we couldn’t manage to get accurate melt viscosity values, though it is far from the glass transition temperature and this is the reason why this particular temperature was taken to observe the rheological behavior.

On increasing the filler loading from 0.5 to 3 wt% a noticeable qualitative change in the moduli versus frequency curves was observed, particularly significant at low frequencies. At low GO and mGO contents, the exponent of $G'$ versus frequency was high. With concentration it slightly decreased and finally reached a value of approximately zero. This plateau in $G'$ corresponds to a liquid-to-solid transition. The plateau is obviously higher for
G’ than for G” and the filler concentration at which the liquid-solid transition occurs strongly depends on whether GO or mGO was added. The compatibilizing agent, polymer molecular weight, interfacial properties and filler dispersion influence the linear viscoelastic properties [14]. The properties are also affected by the gelation of filler platelets in the entangled matrix.

Figure 5.2 Dynamic mechanical analysis of PU and PU composites

The dynamic mechanical properties of PU/GO and PU/mGO nanocomposites are presented in Figure 5.2 as plots of E’, E” and tan delta against temperature. In DMA, the response of the samples to an applied oscillatory stress is analyzed. From Figure 5.2a it is
clear that the storage modulus (E’) of all nanocomposites (modified and unmodified) is higher than that of neat PU. The increase in the E’ values with increasing GO/mGO content, which shows the ability of the material to store energy, is due to the reinforcement effect and restrictions in the polymer chain mobility upon GO addition. The increase in storage modulus with increase in filler content in the matrix is more pronounced in the case of mGO based PU (PMGs) than PGs, again illustrating the efficient reinforcement effect of mGOs. The loss modulus also follows the same trend indicating a larger amount of energy dissipation for PU/mGO samples as compared to PU/GO (Figure 5.2b). The temperature that corresponds to the maximum value of tan δ provides an estimation of the T_g of the samples. The T_g’s of the nanocomposites, derived from tan δ curves, are slightly higher than that of neat PU. This can be related to the enhanced stiffness and load bearing capability, and restricted chain mobility of the material upon GO incorporation, which also explains the improved mechanical properties of the nanocomposites. Krol et al. also have reported a similar behavior in which the soft segments of GO filled PU shows a transition at -50 to -43 °C and the hard segments at 23–39 °C. The introduction of the filler slightly enhances the glass temperature of soft segments whereas for hard segments, a significant increase of glass temperature is observed [23]. In addition the less reinforced contribution of the low percentage of the filler causes the T_g to decrease in PG0.5 as there is a chance for the PU chains to degrade during the prolonged mechanical mixing process. The peak intensity is inversely proportional to peak broadening and the broadening observed in PMG0.5 causes good reinforcement and thus doesn’t show any enhancement in intensity.

As reported, the melt rheological properties of filled polymers are sensitive to the structure, particle size, shape and surface characteristics of the fillers. Here for this analysis,
the technique of melt rheology has been used. This technique offers original means to assess the state of dispersion in the nanocomposites and to investigate the influence of flow conditions upon nanofiller dispersion itself. Below 160°C, we couldn’t manage to get accurate melt viscosity values, though it is far from the glass transition temperature and this is the reason why this particular temperature was taken to observe the rheological behavior. Generally speaking, both graphene oxide and modified GO filled PU nanocomposites show a solid-like rheological response which includes a non-terminal relaxation zone, an apparent yield stress and strong nonlinearity (Payne effect).

When molecular chains are restricted, the motion or relaxation of the chain segments becomes difficult. However, with increasing temperature, chain motion is facilitated [18]. This is the reason why the tan δ values decrease with temperature (Figure 5.2c). Also, the increase in \( T_g \) can be related to the degree of homogeneous dispersion of the filler in the matrix and the filler-polymer interactions [18]. The high \( E' \) value for PMG3 in the glassy region confirms the presence of highly dispersed mGOs in the PU nanocomposites as evidenced from the SEM analysis. This also suggests the ability of nano mGOs to reduce the domain size and to provide a substantial improvement of the modulus of the PU matrix by reinforcement.

We also have observed a difference in the value of \( T_g \) obtained from DSC (reported in the previous sections) from DMA. Actually the sensitivity to \( T_g \) improves from DSC to DMA. However, temperature accuracy decreases from DMA to DSC due to the challenges related to the proximity of the thermocouple to the sample (sample size, reproducibility of sample placement etc.). Also, with DMA, there are generally three different \( T_g \) numbers that are reported. Some use the onset temperature from the storage modulus, others use values
that come from either the loss modulus or $\tan \delta$. The DMA seems to be an excellent tool to quickly characterize materials for their suitability to be used as backing material in transparent armor applications. Generally the viscoelastic materials perform the best when they are in their glass transition range, more specifically in the region between the maximum of the loss modulus and the maximum of $\tan \delta$. Here for the PU, the glass transition (from DSC) of soft segments is in the range from $-50$ to $-43 \, ^\circ\text{C}$ and that of hard segments in the temperature range of $23$–$39 \, ^\circ\text{C}$. The variation in hard and soft segments is responsible for the change in the values observed.

Non-linear viscoelastic behavior of polymer nanocomposites can shed light on the inter-particle interactions within the system through phenomenological modeling. In case of strain sweep characterizations, these models are mainly based on the concepts of change in microstructure of the composites upon filler cluster breakdown and the reagglomeration - deformation mechanism [19]. In 2002, Heinrich and Kluppel [20] reviewed all such models for the amplitude dependence of the dynamic viscoelastic properties of reinforced elastomers. Breakdown of the particle structure happens on the expense of excess dissipated energy. In the case of elastomer samples, structural variations of the entanglements at the filler-polymer interface can also take place and cause additional energy dissipation [22].
Figure 5.3 Strain dependence of the storage modulus fitted with a) Maier and Göritz model b) strain dependence of loss modulus for neat PU and PU composites.

The dynamic viscoelastic response of neat PU and nanocomposites containing GOs or mGOs at a constant frequency of 0.5 Hz are plotted as a function of strain in Figure 5.3. When polymer-filler interactions dominate, the non-linear viscoelasticity of elastomer composites originates from variations in the topological constraint density at the filler-polymer interface [20], as described by the model of Maier and Göritz [22] in Figure 5.3a. The experimental results of $G'$ obtained for all composites are fitted with the Maier and Goritz model as well (Figure 5.3a). Fitting with the Maier and Göritz model provides a better understanding of the filler-polymer interactions. The dotted lines represent the curve fits. Model parameters calculated using equation (2.5) is given in Table 5.1 which demonstrates the effect of the filler concentration and filler-polymer interactions on the modulus variation.

The cross link density values given in Table 5.1 can assist in providing a quantitative estimation of the matrix filler interactions. There is a significant crosslink density difference between the neat PU and PU nanocomposites at different filler loadings [14]. The higher $N$ value of PMG3 ($N_{\text{total}}=0.27 \times 10^{26}$/cm$^3$) as compared to PG3 ($N_{\text{total}}=0.16 \times 10^{26}$/cm$^3$) can be
explained by the high confinement effect due to the good filler dispersion and effective interaction between mGOs and PU. Both values are much higher than the neat PU ($N_{\text{total}}=0.01 \times 10^{26}/\text{cm}^3$) case indicating the efficiency of GO nanosheets in reinforcing the polymer. The GO surfaces interact strongly with the urethane groups, resulting in the formation of three-dimensional filler networks in all nanocomposites. The small size and the high specific surface area of nano fillers favors this mechanism, which is enhanced in the case of PU with mGO, due to the increased interaction between GO and PU. The variation in loss modulus (Figure 5.3b) with respect to strain is also shown.

Table 5.1 Fitting parameters for Maier and Göritz model according to Equation (2.5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maier and Goritz model fitting parameters</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G'_1$ ($10^6 \times \text{MPa}$)</td>
<td>$N_g + N_{st}$ ($10^{22} \times \text{cm}^3$)</td>
<td>$N_{i0}$ ($10^{24} \times \text{cm}^3$)</td>
<td>$N=N_{i0}+N_g + N_{st}$ ($10^{26} \times \text{cm}^3$)</td>
</tr>
<tr>
<td>PU</td>
<td>0.03</td>
<td>3.5</td>
<td>1.34</td>
<td>0.01</td>
</tr>
<tr>
<td>PG0.5</td>
<td>0.07</td>
<td>8.9</td>
<td>2.78</td>
<td>0.02</td>
</tr>
<tr>
<td>PG1.5</td>
<td>0.14</td>
<td>12.6</td>
<td>5.41</td>
<td>0.05</td>
</tr>
<tr>
<td>PG3</td>
<td>0.42</td>
<td>19.3</td>
<td>15.3</td>
<td>0.16</td>
</tr>
<tr>
<td>PMG0.5</td>
<td>0.18</td>
<td>11.2</td>
<td>6.47</td>
<td>0.07</td>
</tr>
<tr>
<td>PMG1.5</td>
<td>0.5</td>
<td>21.6</td>
<td>17.41</td>
<td>0.19</td>
</tr>
<tr>
<td>PMG3</td>
<td>0.9</td>
<td>35.3</td>
<td>26.90</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Based on the characterization of the nanocomposites, a strong correlation has been observed between the dielectric and rheological properties of the nanocomposites.
Irrespective of the frequency, the dielectric constant and dielectric loss of the GO and mGO filled nanocomposites increased with an increase in filler loading. The fillers are capable of generating continuous networks in the polymer matrix through which charged species move from one end to the other under an applied field. This movement of electrons causes the phenomenon of electric conduction and is the basis of the well-known filler-polymer network theory. At low GO concentration, the composites already show significant improvements in properties as compared to the unfilled PU, which is due to the large filler-polymer interfacial interaction giving rise to network formation. This filler network formation which occurs through physical contacts of particles or their aggregates and enhanced filler-PU interactions were illustrated in rheological measurements combined with Maier Goritz modeling. The dielectric constant of the composites depends on the filler volume fraction since the tunneling of charges takes place through the gaps between filler surfaces. At higher concentrations of the filler, the distance between the aggregates reduces and the gap between the particle aggregates controls the charge transfer between filler aggregates. The sharper increase in both dielectric and rheological properties of PMG3 can be explained on the basis of this point. However, the correlation between the rheological percolation and dielectric mechanism is drawn in the case of PU/mGO samples based on the filler polymer interfacial interaction and the better filler platelet dispersion.
Composite morphology was monitored using SEM micrographs of the cryo cut surfaces of PG3 and PMG3 samples (Figure 5.4). The effect of filler nanosheets on the microstructure of the PU is very lucid from the pictures shown. The smooth fractured surface of pristine PU (Figure 5.4a) became rough due to the presence of GO (Figure 5.4b). Here the exfoliated GO nanosheets are uniformly dispersed in the PU medium as evidenced by the PU/GO composite morphology. For mGO composites, a comparatively better dispersion of the mGO nanosheets is observed, which can be attributed to the increased interaction between PU and mGO as compared to GO (Figure 5.4c).
To further analyze the GO and mGO dispersion in the polymer, the structural variation within the filler as well as the composites was investigated through X-ray diffraction studies. As shown in the XRD pattern (Figure 5.5a), the characteristic sharp peak of graphite at 2\(\theta\) = 26.5° is more broadened (Figure 5.5a, inset) and shifted to 2\(\theta\) = 5.3° in GO. This is due to the delamination of individual GO layers from graphite by the oxidation and sonication processes. This enhances the interlayer distance and causes a partial loss of regularity of the GO sheets. For mGO, the characteristic peak is even less clear, indicating a wider range of interlayer spacings and a more substantial amount of exfoliation due to the surface modification. In the composite samples, the case is rather different (Figure 5.5b). The neat PU is soft in nature (32% HS) and the peak obtained near 2\(\theta\) = 21° is a crystalline halo attributed to its elastomeric structure. For PU/GO and PU/mGO, the peak intensity marginally enhances though it remains at the same position at 2\(\theta\) = 21°. This can be related to the crystallinity imparted to the PU matrix by the GO (or) mGO addition. GOs possess a
strong nucleating effect within the polymer matrix [14]. In addition, the XRD spectrum of the nanocomposites shows no characteristic peak at 5°, originating from loss of regularity or exfoliation of the GO (or) mGO in the PU, which indicates the good dispersion of fillers in the PU matrix.

5.3. Conclusion

PU nanocomposites filled with unmodified and modified GOs prepared by simple solution mixing method are subjected to rheology and dielectric measurements. Both nano fillers –GOs and mGOs- remarkably enhanced the properties of the PU elastomer. Effects were however dependent on the filler volume fractions and filler modification. The methylene diphenyl diisocyanate modified GOs offered better interactions with the urethane skeleton through hydrogen bonding. The various interactions existing in the composites were addressed through nonlinear viscoelastic studies. Correlating this with the dielectric constant showed the significance of these characterization techniques in manufacturing ultracapacitors and electrically applicable materials. Payne effect observed for these thermoplastic elastomer composites explained the confinement effect of filler platelets in immobilized polymer chains.

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Conclusions & Future Outlook
Natural Rubber (NR), Polyisobutylene co isoprene rubber (IIR), styrene-isoprene-styrene (SIS) and PU are typical elastomers used widely in manufacturing various technological materials. The nano carbon fillers are extensively added to those matrices in order to develop conducting and non-conducting smart materials for advanced functional applications. CNT and graphene can offer high electrical and dielectrical properties to elastomers due to the presence of free electrons in it and can make rubber conducting and mechanically strong. A thorough study of these composites is rather necessary since a lot of fields like flexible electronics, wearable electronics, robotics etc. need the composites’ valuable use. In the current survey, the potential of both two dimensional (modified graphene, reduced graphene oxide etc.) and one dimensional (CNT) fillers in rubber industry is established in detail. The thesis covered a systematic and detailed investigation of the preparation, characterization and physicomechanical properties of various elastomer nanocomposites with different fillers. The specific applications of elastomer composite such as high performance mechanically strong dielectrics, shape memory and sensing materials are derived as the final outcome of this study.

In order to examine the effect of filler dispersion, modification has been done for the fillers chemically and also by following hybrid filler addition. Cured samples are prepared by melt mixing and the samples are cured according to their respective cure times. Graphene fillers are synthesized in the laboratory by following improved graphene oxide method and the thickness of the obtained sheet was about ~1.5nm. The fillers as well as their dispersion in the composites were characterized by Wide Angle X-ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy.
Sensing is a developing field of technology and most of the day to day affairs are now utilizing this technique. We have aimed mainly at this aspect of the nanocomposites based on the resistance variation of the samples upon stimulation. Oil sensors were fabricated based on SIS, BR and NR composites using CNTs. NR filled with thermally reduced graphene at 200 °C and CNTs are very good in detecting the presence of aromatic solvents and this ability depends on the molecular weight of the solvent molecules used. In addition to detecting the presence of solvents, the purity of the solvent can also be found out through this sensing analysis. While Polyaniline SIS composite is a good sensor for dual oil and water phase on the other hand NR/CNT exhibits the best oil sensibility compared to BR/CNT and SIS/CNT.

The shape fixity ($R_f$) of PG3 showed an enhancement of ~69.7% when compared to the neat PU (~95.8). This noticeable decrease in the fixity value on moving from PU to PG3 is attributed to the increased crosslinking density upon filler addition. The shape memory behaviour of the PU/GO samples are also analysed by varying the temperature and cyclic loading. When the GO sheets interact with the soft segmented PU portions phase mixing between soft and hard segments of PUs occur. The GOs are further modified using MDI and this helped in manufacturing excellent dielectrics out of PU/mGO nanocomposites.

Molecular level interactions are very important while dealing with the properties of a composite. It is rather interesting to study the effect of micro as well as nano fillers on the molecular chain motion of rubber chains. The filler–filler and filler–polymer network are focused and is correlated with the dynamic viscoelastic behavior of the nanocomposites (Payne effect). This is done by analysing the stress relaxation, hysteresis and dynamic mechanical studies in all the systems studied. The electrical, sensing, shape memory and dielectric properties of nanocomposites are discussed based on the various molecular
interactions and by applying mathematical modelling (Payne effect). It is established that the filler-polymer interfacial interactions regulated by the compatibility, nature and rate of dispersion, mode of bonding etc. determines the various properties of nanocomposites.

In short, the major applications derived from this thesis include superior sensing, shape memory and dielectric properties, simultaneously achieving good mechanical properties. Stronger, lighter and high performance multi-functional materials having tremendous possibilities in technological field are fabricated and the more are anticipated towards the future.

**Future Outlook**

6.1. **Visco elastic Studies- Rheology**

The visco elastic behavior of polymer chains varies to a great extent upon the addition of filler particles in to it. The variation in the flow properties is one of the important steps during composite manufacturing as this is the primary step in regulating the filler dispersion. The elastomer filler interface and the viscolelastic behavior of hybrid composites using two different fillers is another area of interest.

6.2. **Positron Annhiliation Spectroscopic Studies**

Positron Annhiliation spectroscopy has turned out to be an important method to characterize filler dispersion and thus the composite properties. The free volume calculated based on this study enable the researchers to identify the morphology of the nanocomposites. A lot of studies correlate this PALS technique with mechanical, electrical and diffusion studies. In connection with this method, Doppler broadening spectroscopy is also targeted to study in future.
6.3. Energy Harvesters (Piezoelectrics)
Harvesting energy from the naturally occurring mechanical energy sources is the need of the hour and elastomer nanocomposites dielectrics have utmost importance in this growing field. The major advantages of using nanocomposites for this particular application include their low cost and simple way of fabrication combined with high efficiency and energy density. However there are still issues that must be solved to commercialize the concept. For instance, the effective energy conversion in a polymer dielectric takes place only if the material possesses low dielectric and mechanical losses at the same time withstanding large strains over an extended lifetime without any loss in conductivity. Fabrication of soft, flexible and stretchable CNT filled elastomer composite electrodes are expected to be manufactured for use in capacitive energy harvesting and mechanical sensing. It is reported that the voltage generation along with stretching could be either linear for fabrication of sensors or superlinear for energy harvesters.

6.4. Electromagnetic induction shielding
The graphene based electromagnetic shielding materials have attracted wider attention today. Our subsequent study is anticipated to focus on this property of the synthesized materials. Parallelly we have succeeded in evaluating the induction shielding effectiveness of graphene oxide filled polyaniline polycaprolactone blend type composites and this will be extended on the elastomer composite systems as well.

6.5. Developing thermal materials
A lot of studies have reported on the thermal conductivity of nano carbon materials and their usefulness in burners and other conducting materials. The polyurethane based composites will be further proceeded to study this effect and to derive the thermal mechanism based on phonon conduction.
PUBLICATIONS

Journal papers – from the thesis

1) Synergistic effect of reduced graphene oxides and CNTs in natural rubber for sensing application
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3) Graphene and graphitic derivatives filled polymer composites as potential sensors
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   (Physical Chemistry Chemical Physics, 2015, DOI: 10.1039/C4CP04418E)

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   (RSC Advances, 2013; 3: 16068-16079)

5) Dielectric properties of modified graphene oxide filled polyurethane nanocomposites and its correlation with rheology
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   (Material Chemistry and Physics, 2014; 147(3): 1029-1036)

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   (Polymer Engineering & Science 2014, DOI: 10.1002/pen.23992)
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Book Chapters

1) Green Composites Green Methods to Synthesize and Recycle Materials- A promise
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   Deepalekshmi Ponnamma, Sabu Thomas, In Recent Advances in Rubber Recycling
   Edited by Yves Grohens, Kishor Kumar Sadasivuni and Abderrahim Boudenne,
   Apple Press Academy, 2013.ISBN: 9781926895277

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   Challenges and Opportunities.
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Springer Publisher 2014. (in press, Springer)
2) Recent Advances in Material Science- Volume 1. Polymer Processing and Characterization Polymers.
Deepalekshmi Ponnamma, Ajesh K Zachariah, Sabu Thomas.
3) Non-Linear Viscoelasticity of Rubber Composites and Nanocomposites: Influence of Filler Geometry and Size in Different Length Scales

AWARDS
1) Best Oral Presentation Award in “National Conference on Nanostructured materials and Nanocomposites (NCNM) 2012” Sponsored by UGC, at NSS College, Ottapalam, Kerala, India.
2) Best Poster Presentation Award in “International Conference on Recent Trends in Materials Science and Technology (ICMST) 2010”. Organized by: MRSI, Thiruvananthapuram & Indian Institute of Space Science and Technology (IIST), Thiruvananthapuram, India.
3) Best Poster Presentation Award in “National Seminar on Recent Advances in Polymer Science and Technology-2012” Organized by: Society for Polymer Science India and Mar Ivanios College Trivandrum, India.
4) Invited Speaker in “Polymer Conference for Young Researchers-2014” Organized by: Society for Polymer Science Trivandrum, India.

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GLOSSARY, SYMBOLS AND ABBREVIATIONS

List of symbols

G’ – storage modulus
G” – loss modulus
Tg – glass transition temperature
% wt – weight percent
phr – parts per hundred
nm – 10^{-9} m
A° - 10^{-10} m
rad – radians

List of abbreviations

AFM – Atomic force microscopy
CB – Carbon black
CNT – Carbon nanotube
CRG or GE – Chemically reduced graphene
CTAB – Cetyltrimethyl ammonium bromide
CVD – Chemical vapor deposition
DMA – Dynamic mechanical analysis
DMF – Dimethyl formamide
EG – Expanded graphite
FGS – Functionalised graphene sheet
FTIR – Fourier transform infra-red spectroscopy
GIC – Graphite intercalation compounds
GO – Graphene oxide
GNP or GN – Graphite nano platelets
HR-TEM – High resolution- Transmission Electron Microscopy
IIR – poly isobutylene isoprene rubber
MLGS- Multi layer graphene sheets
MG – Modified graphene
NGs – Natural graphite
NR – Natural rubber (Poly isoprene)
RGO – Reduced graphene oxide
SEM – Scanning electron microscopy
SWCNT – Single wall carbon nanotube
TEM – Transmission electron microscopy
TGA – Thermogravimetry analysis
TRG – Thermally reduced graphene
WAXS – Wide angle X-ray scattering