Studies on Rubber Nanocomposites based Encapsulants for Underwater Applications

Thesis submitted to

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

in partial fulfillment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

IN THE
FACULTY OF TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI – 682022, KERALA, INDIA

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August 2016

CERTIFICATE

This is to certify that the Ph. D. Thesis entitled **“Studies on Rubber Nanocomposites based Encapsulants for Underwater Applications”** submitted by **Shri. Annadurai P.** in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi -22 is an authentic record of the bonafide research work carried out by him under our supervision and guidance, at Naval Physical and Oceanographic Laboratory, Kochi-21 and in the Department of Polymer Science and Rubber Technology, CUSAT, Kochi - 22 and no part of the work reported in this thesis has been submitted earlier for the award of any other degree from any other institution.

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DECLARATION

I do hereby declare that the thesis entitled "**Studies on Rubber Nanocomposites based Encapsulants for Underwater Applications**" is an authentic record of the original research work carried out by me under the joint supervision and guidance of Dr. T. Santhanakrishnan, Scientist 'E', Naval Physical and Oceanographic Laboratory, Kochi-21 and Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22 in partial fulfillment of the requirements for the award of Degree of Doctor of Philosophy and that no part of the work reported in this thesis has been submitted earlier for the award of any other degree from any other institution.

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ACKNOWLEDGEMENTS

It is with profound joy that I express my heartfelt gratitude to my supervising guides Dr. T. Santhanakrishnan, Scientist 'E' and Prof. (Dr.) Rani Joseph, Department of Polymer Science and Rubber Technology (CUSAT) for their inspiring and excellent guidance, valuable suggestions and intellectual support throughout the period of my thesis research work. I record my deep sense of gratitude to Prof. (Dr.) Rani Joseph for inculcating research ideas, providing necessary facilities at CUSAT, untiring support and constructive criticism. The moral support and freedom provided by both guides needs special mention for the successful completion of my thesis.

I sincerely express my gratefulness to Shri. S. Kedarnath Shenoy, Outstanding Scientist and Director, NPOL for giving me an opportunity to pursue my Ph. D. research work and for providing all the nessary facilities at NPOL.

I feel extremely privileged to place on record my sincere gratitude and respect to Dr. Sudarsan, Scientist 'G', Associate Director, Chairman, HRD Council for the valuable suggestion, encouragement and constant support rendered. I am deeply indebted to him throughout my carrier for being instrumental in providing the opportunity to commence my Doctoral programme at Cochin University of Science and Technology.

I take this opportunity to thank Dr. V. Natarajan, Scientist 'G', Group Head, Materials Science and Engineering for providing all the necessary facilities and encouragement for the successful completion of this research work.

I am grateful to Dr. T. Mukundan, Scientist 'G for his guidance, timely help and constant inspiration throughout the investigation and am deeply obliged to him.

I take this opportunity to thank the doctoral committee member Dr. N.R. Manoj, Scientist 'F', NPOL and Departmental Research Committee members Dr. P.V. Hareesh Kumar, Scientist 'G' and Dr. K.P.B. Moosad, Scientist 'G for sparing a lot of their valuable time and providing proper direction, suggestion, conducting examination and revision etc, without which, this thesis would not have taken this shape.

I feel happy to express special thanks to my colleagues Shri. P. Jayesh and Mrs. R. Rajeswari, Technical Officers, NPOL for their timely assistance in sample preparation and analysis that has aided in the smooth and successful completion of many experiments.

I am extremely privileged to have the care and support of Dr. Santanu Chattopadhyay, Associate Professor and Ph. D. Scholars Shri.S. Kumar and Shri. M. Partheban from Rubber Technology Centre of Indian Institute of Technology, Kharagpur for providing all the necessary facilities in TEM analysis and technical literatures.

I express my deep sense of gratitude to my parents for their dream, encouragement and moral support extended.

Last but not the least, thanks are due to my beloved wife Mrs. Rani and children Aswathy and Naresh for their unreserved and unconditional love, prayers at all stage of my work.

ANNADURAI P.

PREFACE

Polymers and composites have become an indispensable material in the field of underwater acoustic sensor applications such as hydrophone housing, hoses, coatings, sealants, and adhesive, etc. Rubber materials have been widely used in the underwater acoustic sensor scenario. The application includes encapsulants, baffles, hose, shock and vibration isolators, seals, ‘O’ rings etc. The range of versatile applications has been possible due to the large scope for tailor making of properties in rubber compounds. In general, rubbers that are used for acoustic sensors can be termed as passive acoustic materials, which have a definite influence in determining the performance of the device. When we look sensor for underwater application, the most critical subsystem is transducer. Transducers are type of sensors widely used in underwater surveillance and detection. Elastomers or Rubbers employed for encapsulating transducers must have both electrical and acoustic properties optimum. The primary function of encapsulation material is to protect the active sensing material from water without affecting the performance. Ideal encapsulation thus acts as an acoustic window, enabling reflection free transmission of sound between water medium and acoustic sensing material of the hydrophone.

In all underwater applications, rubber materials are critical to the performance and reliability of sensors. The materials are designed to possess the following characteristics: resistance to water ingression, specific mechanical, acoustic and electrical properties and long-term durability in marine environment. Synthetic rubbers such as Polychloroprene (CR), Butyl (IIR), Nitrile (NBR), polyurethane and thermoplastic elastomers are some of the candidates currently used for these potential applications. Each rubber has its own merits and demerits. However, it will operate moderately well according to their functional parameters. One of the key concerns of these materials is their higher percentage of water absorption. With continuous exposure to sea environments, these materials can take considerable amount of water in and make related changes in electro-acoustic parameters. These effects are become cumulative coupled with ageing factors. Ocean environment combined with specific performance requirements, conventional engineering rubbers can hardly meet the performance standards foreseen. One way to improve mechanical and water resistant properties of these systems while maintaining other desirable properties is by adding high modulus reinforcing fillers to make polymer composites. The dispersion of the nanopowders with carbon black within a polymer matrix must be large enough to effect a sufficient reduction in the rate of diffusion of water and to have compromise between preserving acoustic transparency and reducing permeability. These reasons inspired to investigate or study synergistic effect of nano and micro hybrid filler on polymer composites. The present work is to study the effect of carbon black (CB) and nanoclay fillers on physico-mechanical, electrical, dynamic mechanical and water absorption properties of CR and NBR vulcansizates for underwater transducer encapsulation application.

The thesis is divided into seven chapters including summary, conclusion and references.

Chapter 1 presents a comprehensive introduction on rubbers as passive acoustic materials for encapsulation of acoustic transducers and review of literatures pertains to reinforcement of rubber using organoclay, synergistic effect of hybrid fillers and preparation of rubber nanocomposite. The scope and objectives of the study are also included in this chapter.

Chapter 2 describes the specifications of the materials, preparation method and details of the characterization techniques.

Chapter 3 deals with the preparation, optimization and characterization of carbon black and nanoclay filled polychloroprene. The effect of addition of nanoclay on physico-mechanical, electrical and water absorption properties have been presented in **Section 3.1**. The synergistic effect of carbon black and nanoclay is then investigated in CR samples. Influence of carbon black in polychloroprene organoclay nanocomposite with improved mechanical, electrical and morphology characteristics has also been studied and presented in **Section 3.2**. Studies on comparative performance of curing agents on physico-mechanical and dynamic mechanical properties of CR compositions have been presented in **Section 3.3**. A detailed study on the effect of two stages mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/Nanoclay compositions is given in **Section 3.4.**

Chapter 4 deals with the preparation, optimization and characterization of CB and nanoclay filled NBR. Synergistic effect of CB and nanoclay on physio-mechanical, electrical and morphology characteristics is investigated in NBR samples. Dynamic mechanical and dielectric properties have been also been presented in this chapter.

Chapter 5 discusses the details of development of adhesive for bonding dissimilar substrates. Evaluation of adhesive for bonding rubber and metal substrates and its ageing characteristics are presented.

Chapter 6 presents extensive evaluation of nanocomposite properties in comparison with presently used conventional rubber vulcanizate. This chapter covers consolidation of experimental study in terms of mechanical, electrical, dynamic mechanical properties, ageing and acoustic characteristics.

Chapter 7 summarizes and concludes the present work with a brief outlook of future.

ABSTRACT

Rubbers are reinforced with fillers to improve their performance by incorporating conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate *etc*. Among all conventional fillers, carbon black (CB) and silica are the most important reinforcing filler used in the rubber industry. Nevertheless, higher loading of carbon black or silica fillers in rubber compounds lead to the formation of larger filler-filler clusters or even filler networks, which in turn results deterioration of properties. In the past two decades, research was aimed to develop alternate reinforcing agents to replace CB partially or completely in rubber compounds. On the other hand, the layered silicates such as nanoclay with very small amount could reinforce the polymer matrix and enhance the critical performance properties of polymer–clay composites due to their high surface area, platy morphology and exceptionally stable oxide network. Nanocomposite is a composite in which inorganic filler is dispersed within the polymer matrix in nanometer scale. Several benefits of these nanocomposites based on rubber and other polymers are efficient reinforcement lead to new and improved properties when compared to conventional micro composites that are made using conventional fillers. Improved water barrier properties, higher mechanical properties, improved flame retardancy and increased dimensional stability have been achieved in polymer nanocomposites.

Rubbers are widely used as passive acoustic materials in the construction of underwater sonar transducers and operating conditions of these may vary over large ranges of frequency, temperature and pressure. The performance of sonar transducers are critically dependent on encapsulation material used for their construction. The functional property requirement of encapsulant used in underwater transducer is not only depend on the polymer systems but also largely depend on the fillers systems. As compared with the conventional type of fillers like CB and silica the amount of nano-particles which are nowadays being incorporated in the rubber matrix is considerably smaller. Since nanoclay rubber composite alone is not sufficient to provide required mechanical strength in an underwater environment, two different fillers are planned to incorporate in rubber matrix to develop hybrid structures where effects of the different components are combined. Nanoclay was used as reinforcing filler in combination with carbon black in a CR and NBR matrix. The main idea of this work is to replace some parts of carbon black in a transducer encapsulant formulation by few parts

of layered silicate in order to improve mechanical and water resistant characteristics without sacrificing other properties. Hence, the present work is directed towards the development of CR and NBR based nanocomposites for encapsulation of acoustic sensors. CR and NBR rubber nanocomposites have been prepared by incorporating various parts per hundred rubbers (phr) of nanoclay and carbon black using two roll mills.

The design of organic-inorganic nanocomposites is a fascinating topic for science and technology and many applications are expected in the field of optics, electronics, membranes and acoustic sensors etc. The unique properties, imparted by nanoclay (NC) to rubber composites, have opened up a new prospect in developing CB–NC hybrid nanocomposites via facilitating the possible partial replacement of CB with NC in rubber products without affecting the critical performance properties. Several studies have described in literatures that use of CB-NC hybrid filler in rubber matrix resulted in dramatic improvement of technical properties. In our present work, Chloroprene (CR) and Nitirle (NBR) based nanocomposites were prepared by incorporation of a hybrid filler system, organoclay and carbon black (CB), through melt compounding. The synergistic reinforcement effect of NC and CB in CR and NBR matrix has not been studied in detail. Studies on carbon black and nanoclay on properties like physico-mechanical, electrical, dynamic mechanical and water absorption properties of chloroprene and nitrile rubber vulcansizates have been investigated. The effect of addition of two-stage mixing and dispersion agent on morphology and dynamic mechanical properties on CR has been studied. Formation of nano-unit structures with improvement in tensile and tear properties were observed by synergistic filler effect in CR and NBR rubber matrix. Wide-angle X-ray diffraction and transmission electron microscopy were used to study the microstructure of CR and NBR nanocomposites. DMA studies proved that optimised CR and NBR composition shows higher modulus and lower tan delta values for operating frequency requirement of underwater sensors. The findings suggest that the reinforcement is due to a more developed filler network formation in hybrid filler system than that in single-phase filler. The process of encapsulation includes bonding of rubber with metal substrates where suitable adhesive is selected and subsequently, evaluated for bonding characteristics. Pulse tube measurement was done for characterization of acoustic property of the materials. A detailed experimental study has been conducted to evaluate nanocomposite properties in comparison with presently used conventional rubber compound. The results obtained for various properties indicate that the rubber nanocomposites offers significant improvement in mechanical, electrical, dynamic mechanical and ageing characteristics

compared to that of microcomposites. The present work revealed that the rubber nanocomposite reinforced with a mixture of organoclay and carbon black in right proportion could be a better substitute for microcomposite in terms of mechanical, electrical and water resistant properties and therefore found useful as better encapsulation materials for underwater transducer applications.

GLOSSARY OF TERMS

Al	Aluminium
ACN	Acrylonitrile
ASTM	American Society for Testing and Materials
CB	Carbon Black
CR	Chloroprene Rubber
$CaCO_3$	Precipitated Calcium Carbonate
CBS	N- cyclohexyl-2-benzothiazole sulphonamide
CEC	Cation Exchange Capacity
Cloisite® 15A	Nanoclay
CM	Compound Mix
cP	Centi Poise
CNT	Carbon Nanotube
CNBR	Carboxylated Nitrile Rubber
DMA	Dynamic Mechanical Analysis
dB	decibel
DCP	Dicumyl Peroxide
EB	Elongation at Break
ER	Echo Reduction
FEF	Fast Extrusion Furnace
GPF	General Purpose Furnace
HNBR	Hydrogenated Nitrile Rubber
IL	Insertion Loss
POSS	Polyhedral Oligomeric Silsesquioxanes
MB	Master Batch
MgO	Magnesium oxide
MBTS	Dibenzothiazyl disulfide
MWNT	Multiwall carbon nanotubes
MMT	Montmorillonite
MDR	Moving Die Rheometer
MPa	Mega Pascal

NC	Nanoclay
NR	Natural Rubber
NBR	Acrylonitrile Butadiene Rubber
NA22	Ethylene thiourea
NaCl	Sodium Chloride
OCT	Optimum Cure Time
PCN	Polymer Clay Nanocomposites
Pb_3O_4	Red Lead
Phr	Parts per hundred rubbers
PF	Phenol Formaldehyde
PVC	Polyvinyl Chloride
RPA	Rubber Process Analyzer
SWNT	Single wall carbon nanotubes
SBR	Styrene Butadiene Rubber
SS	Stainless Steel
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TMTD	Tetramethyl thiuram disulphide
Ti	Titanium
TTS	Time Temperature Superposition
UTM	Universal Testing Machine
UTS	Ultimate Tensile Strength
Vulcanox HS	Polymerized 2,2,4 trimethyl 1.2-dihydroquinoline
Vulcanox 4020	N(I ,3-dimethyl butyl)N' -phenyl-p-phenylenediamine
WXRD	Wide angle X-Ray Diffraction
ZDC	Zinc diethyldithio carbamate
ZnO	Zinc Oxide

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CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 UNDERWATER ACOUSTIC TRANSDUCERS

Electrostriction and Magnetostriction are the two phenomena through which under water electro acoustic transduction is accomplished. Electrostriction refers to the conversion of energy between acoustical and electrical forms by means of dependence between electrical fields and particle displacements in both Piezoelectric and Ferromagnetic materials but in case of Magnetostriction, the same conversion occurs by means of dependence between magnetic fields and particle displacements only in ferromagnetic materials. In the electrostriction phenomenon, there is a distinction between piezoelectric effect and ferroelectric effect. Piezoelectric transducers use crystals in which the dimension changes arise according to the applied electric field. If the field is alternating, the crystals may pulsate and give an acoustic radiation.

Transducers are devices that transform one form of energy into another. The types of transducer used in underwater communication are called electroacoustic transducers. They are classified as either projector or transmitter that converts electricity to sound, or receivers that change acoustic energy into electrical signals. Underwater electro-acoustic transducers are used for transmitting and receiving acoustic signal. After World War II, new types of electroacoustic transducers designed to operate in the ultrasonic frequency range were developed for a wide variety of new industrial applications, such as non-contact distance or level measurement, collision avoidance, communication, intrusion alarms, ultrasonic cleaning, ultrasonic welding, ultrasonic flow detection, and ultrasonic imaging. Transducers can be designed to operate at frequencies from as low as 20 Hz to several thousand Mega Hertz, the upper frequency limit of human hearing, to 10 MHz and higher. The frequency between 20 Hz and 20 kHz is known as audio frequencies and those between 16 kHz and109 kHz is called as ultra sonic frequencies.

Electro acoustic transducers are widely used in the area of geographical mapping, oil exploration, doppler navigation, fish finding, fisheries aid, diver’s aid, communication and telemetry, defence applications like detection and ranging of underwater targets etc. In defence sector, underwater sensors are widely used for the detection, localization, tracking and classification of underwater objects. The effective functioning of these sensors is dependent on a verity of acoustic structures like acoustic reflectors, absorbers and transmitters.

1.2 TRANSDUCER MATERIALS

Transducer’s materials are classified into two main categories namely active transduction materials and passive acoustic materials. Both are correspondingly important in the efficacy and reliability of the transducer system performance. A brief discussion of these materials will be pertinent in the context.

1.2.1 Active Materials

Piezoelectricity is the property possessed by certain materials becomes electrically charged when subjected to a mechanical stress. Piezoelectric materials are the actual energy converters used in the construction of underwater acoustic transducers. Polycrystalline Ferroelectric material has been extensively used for fabricating transducer elements. Most favored transduction material for underwater electro acoustic transducers are polarized ferroelectric ceramics like Barium Titanate and Lead Zirconate Titanate. New materials such as piezo polymers and composites are also being employed for applications where they provide benefit to transducer and system performance.

1.2.2 Passive Materials

Passive materials comprise a range of metallic and non-metallic materials with distinct and carefully controlled acoustic properties. The vital parts in the construction of the transducer are diverse, like sounder absorbers, acoustic baffles, window materials, acoustic reflectors, decouplers, encapsulant material etc. Elastomers can be termed as passive acoustic materials, which have a definite influence in determining the performance of the transducer device. These are materials used in transmitting or receiving the elastic waves, or for encapsulation, or materials used in directing the waves or absorb/isolate unwanted signals etc. Rubbers show unique combination of stiffness and damping capability. A major consideration is the constant modulus over a wide range of the operating frequency.

1.3 RUBBERS IN UNDERWATER APPLICATIONS

Rubber components play a vital role in underwater application. Rubber components in underwater electro acoustic transducers is well thrived in usage and one of the most aesthetic applications due to the additional functional prerequisite namely propagation of acoustic waves. In passive acoustic materials, rubber fills the major area of usage. The application of rubbers includes encapsulants, baffles, hose, shock and vibration isolators, seals, ‘O’ rings etc [1]. The range of versatile applications has been possible due to the large scope for tailor making of properties in rubber compounds. Rubbers that are used for acoustic sensors can be termed as passive acoustic materials, which have a definite influence in determining the performance of the device. Performance requirements are specific to each component. For example, for a seal and O-ring materials retention of sealing efficiency demands compression stress relaxation to be minimum. On the other hand, for baffle and anti vibration applications damping behavior is paramount. For rubbers used in acoustic applications, wave propagation characteristics assume greater significance. Ocean environment combined with specific performance requirements, conventional engineering rubbers can hardly meet the performance standards foreseen. The present study pays attention to such acute technologies. When we look sensor for underwater application, the most critical component is transducer. Rubbers are some of the widely used passive acoustic materials in the construction of underwater sonar transducers and operating conditions of these may vary over large ranges of frequency, temperature and pressure [2]. Before underwater usage, these transducers are to be encapsulated with an acoustically transparent material [3]. Rubbers employed for encapsulating electro acoustic transducers must have both electrical and acoustic properties and to protect the underlying sensors and electronics from physical damage and water ingression, while allowing the passage of acoustical energy without significant reflection, loss, or distortion. The primary function of an encapsulation material is to protect the electro acoustic transduction devices from heat, oil, weather, seawater and mechanical breakage and works as an electrical insulator. The important properties considered in the design of encapsulation materials for underwater transducers are low water absorption, high electrical resistivity, better acoustic transparency, optimum static and dynamic mechanical properties and permanence of properties. The service life of transducers is determined by consequent changes in the above parameter. However, rubbers are the most favored material for this application, performance improvement demand extensive research in advancement of materials for balance of properties and extended service life of existing encapsulant materials.

1.4 CURRENT STATUS OF ENCAPSULANT MATERIALS

Elastomers or Rubbers are important polymeric materials because of their unique elastic properties. However, the reinforcement of these soft matrices is essential to realize the required properties for the many different practical applications [4, 5]. Fillers are extensively used in the rubber industry, not only to reinforce the polymer matrix but also to improve the rubber processing and, in some cases, to reduce the price of the final material. Rubber reinforcement is considered as one of the most important topics in rubber science and technology. Carbon black is the most widely used filler in rubber technology [6, 7]. Today, carbon black is increasingly substituted by cheaper and more environmentally friendly inorganic particles such as silica. Contrary to carbon black, inorganic fillers have a much reduced affinity toward the elastomer components and thus tend to form large aggregates, leading to drawbacks in processing and poor reinforcement [8]. Elastomer nanocomposite represents one-step forward in this field, as they hold promise for properties that cannot be realized with their micro composite counterparts [9, 10]. The qualitative difference is caused by distinct characteristics arising from the nanoscopic dimensions and high aspect ratio of the nanofillers, and potential confinement effects on the polymer properties.

Rubber is extensively used in the acoustic sensor scenario. The major use of rubbers is for packaging underwater electronic sensors, which cannot function if directly exposed to seawater environments. Electro acoustic transducers form the primary element in the acoustic projectors and hydrophones used in underwater communication, detection and navigation systems as well as in oceanographic research [11]. Almost all acoustic projectors and hydrophones are encapsulated in polymeric materials to protect the underlying sensors and electronics from physical damage and water ingression, while allowing the passage of acoustical energy without significant reflection, loss, or distortion [12].

Different rubbers are used in transducers manufacturing to meet specific requirements. Polychloroprene, Halogenated Butyl, Nitrile, polyurethane, rubber blend and thermoplastic elastomers are some of the candidates currently used for these applications. Polychloroprene and Nitrile rubbers are found maximum use in underwater transducer encapsulation application due to easy processability and tunability. The details of material and grades are presented in experimental section.

1.4.1 Chloroprene Rubber

Polychloroprene or chloroprene rubber is a versatile material with a wide spectrum of properties. CR is considered to make acoustically transparent material as it has superior chemical and physical response to adverse environment. These properties include excellent weather and abrasion resistance, very good resistance to flame, fuel, water, heat, ozone and oxidation and since it is a polar rubber, it offers very good dielectric properties. W-type neoprene rubber is preferred for the development of encapsulant materials as it has high tensile properties with better storage stability and cure adjustment can be made to suit a wide range of processing conditions. This good balance of properties has made chloroprene rubber useful to large divergent list of applications.

Properties of Chloroprene rubber based encapsulant (presently used)

Hardness, Shore A : 70 ± 5
Tensile strength, MPa : 9 (minimum)
Elongation at break, % : 400 ± 25
Tear strength (N/cm) : 300 (minimum)
Water absorption, % wt gain at 40 ^{o}C : 0.5 (maximum)
Volume resistivity, (Ωcm) : 10^{11}
Damping constant, Tan δ at 5 kHz : 0.2

1.4.2 Nitrile Rubber

There are some applications where underwater sensors use a large array of hydrophones. Transducers are housed in lubricating oil filled long length polyurethane tube. Encapsulation material has been designed for long-term deployment in the fill fluid. Nitrile Rubber is a right candidate because it offers high resistance to marine environment, good acoustic transparency and mechanical properties and excellent resistance to oils and hydrocarbon solvents.

Properties of Nitrile rubber based encapsulant (presently used)

Hardness, Shore A	:	53± 3
Tensile strength, MPa	:	7± 2
Elongation at break, %	:	275± 25
Tear strength (N/cm)	:	225
Oil absorption, 40 °C 168 hrs in Prime-32 oil	:	1 % (Max)
Volume resistivity, (Ωcm)	:	10^{10}
Damping constant, Tan δ at 5 kHz	:	0.4

1.5 POLYMER NANOCOMPOSITE

Although the terms nanomaterial and nanocomposite represent new and exciting fields in materials science, such materials have actually been used for centuries and have always existed in nature. However, it is only recently that the means to characterize and control structure at the nanoscale have stimulated rational investigation and exploitation. A nanocomposite is defined as a composite material where at least one of the dimensions of one of its constituents is on the nanometer size scale. In nanocomposites, at least one dimension of the dispersed particles is in the nanometer range. One can distinguish three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range. When the three dimensions are in the order of nanometers, we are dealing with isodimensional nanoparticles (or simply nanoparticles). Carbon black, silica, aluminum oxide, titanium dioxide, zinc oxide (ZnO), silicon carbide, polyhedral oligomeric sislesquioxanes (POSS) are examples for nanoparticle fillers. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or whiskers or nanofibers. Examples are Carbon nanotubes, carbon nanofibers, cellulose whiskers, boron nitride tubes, boron carbon nitride tubes, gold or silver nanotubes and cellulose whiskers. The third type of nanocomposites is characterized by only one dimension in the nanometer range. In this case the filler is present in the form of sheets of one to a few nanometer thick to hundreds to thousands nanometers long. This family of composites can be gathered under the name of nanoplatelet based nanocomposites. Layered silicates, layered graphite flakes and layered double hydroxides are examples for layered nanofillers.

Composite materials nowadays have displaced many traditional ones in a variety of applications. Their lightweight and enhanced properties are the main reasons for their growth. Optimization of the performance of these materials is a worldwide challenge. The reinforcing particle/matrix adhesion is of great importance, as it controls the final properties of the composite. Nanocomposite technology is a new era in polymeric materials. Polymer nanocomposites are a unique new class of materials with an ultrafine dispersion of nanomaterials in a polymeric matrix. They have recently gained a great deal of attention because of the much superior properties in terms of increased strength and modulus, improved heat resistance, decreased gas permeability and flame retardance at very low loadings of nanofillers (< 5% wt). With these improved set of properties, they show a lot of promise in developing a range of advanced plastic and textile products. The competition of polymer nanocomposites with traditional materials can be related to the following:

a) Effective reinforcement,
b) Thermal persistence,
c) Flame resistance,
d) Good barrier properties,
e) Improved abrasion resistance,
f) Reduced shrinkage and residual stress and
g) Stability in electrical and optical properties.

1.6 RUBBER NANOCOMPOSITE

Elastomers are filled with small and hard particles to improve the mechanical properties like elastic modulus or resistance to abrasion. A fine dispersion of filler resulting in good adhesion at the polymer/filler interface is the basic requirement for attaining optimum reinforcement and low hysteresis in elastomers. In rubbers, fillers are used to achieve products with improved properties for end use applications. It is well known that for most of the applications, rubber must be reinforced with certain fillers such as carbon blacks, silica, and clay and so on. However, due to the high structure of carbon black strong shear fields or filler modification needed to ensure fine dispersion. In micro composites or conventional composites, the particles exist as aggregates with no insertion of polymer matrix and hence it cannot impart any enhancement in properties. Rubber nanocomposites have attracted many researchers due to their unique properties. As compared with micron size filler-reinforced rubber, nano size filler reinforced rubber exhibits high hardness, modulus, anti-aging and gas barrier properties. This is due to nanofillers occupy greater number of sites in the polymer matrix and contribute enhanced physical properties increasing specific area of the filler particles. Therefore, the nanoconcept is highly relevant for rubber compounds since their applications require filler reinforcement.

Nanoparticles are of interest in many applications due to their unique properties, the following sections will review the unique properties of specific nanomaterials used for preparation of rubber nanocomposites. The properties of traditional polymer matrix composites can be altered with the addition of nanoparticles such as clay nanoparticles, carbon nanotubes, carbon black, and carbon nanofibers, etc. This literature survey presents a brief but concise review of the current research efforts on elastomeric nanocomposites and their characterization. Review focuses on nanocomposites based on all three types of multifunctional fillers: nanotube/fiber-reinforced composites, nanoplatelet-reinforced composites and nanoparticle-reinforced composites. However, special emphasis is given for nanoplatelet and nanoparticle reinforced nanocomposites. Different processing techniques for manufacturing the nanocomposites and their mechanical, thermal, electrical, barrier and flammability properties are discussed in detail.

1.6.1 Nanotube Reinforced Rubber Nanocomposite

Carbon nanotubes (CNTs) were first discovered by Japanese scientist Sumio Iijima. In 1991, Iijima discovered multiwall carbon nanotubes (MWNTs) in carbon-soot produced by the arc-discharge method [13]. A few years later, he observed single wall carbon nanotubes (SWNTs), which were long, slender fullerenes with hexagonal carbon (graphite structure) tube walls that were often capped at either end. High aspect ratio in combination with low density, exceptionally high strength and stiffness make CNTs an excellent candidate as reinforcement for polymer matrix composites. The preparation of CNT-reinforced polymer nanocomposite is generally performed by different methods, including direct mixing, solution mixing, melt-mixing and in-situ polymerization [14, 15].

Gojny et al. [16] conducted an experiment, using double-wall carbon nanotubes and carbon black, to study the effects of the addition of nanoparticles on the fracture toughness of epoxy resins. It was shown that the nanocomposites had significantly higher fracture toughness when compared to the neat epoxy. Liao et al. [17], conducted studies to investigate the dispersion SWNTs into SC-15 epoxy resin. They conducted dynamic mechanical analysis (DMA) on the nanocomposites produced during their experiments. It was shown that with low nanotube loading, 0.5 wt% SWNT, there was an increase of up to 50.8% in the storage modulus of the SC-15 epoxy resin system.

Dongmei Yue et al. [18] studied the effect of CNT using two type of curing agents on Hydrogenated Nitrile (HNBR) and silicone rubber. They found that mechanical properties of composites cross-linked by Dicumyl Peroxide (DCP) apparently increased with increasing of the content of CNTs in HNBR rubber. H. Lorenz et al. [19] studied the different technique for dispersion of CNT in elastomer. They observed significantly steeper stress–strain curves by addition of 1.6 vol.% CNT to the systems with conventional fillers. Lopez-Manchado et al. [20] studied the effect of CNT in NR rubber composites. They observed a noticeable decrease of the height of tan δ peak with increase in glass transition temperature (Tg) for SWNT reinforced rubber composite. They compared the storage modulus of CB filled compound with SWNT in Natural Rubber (NR) nanocomposite and found that the modulus increases in the presence of both fillers, which is attributed to the hydrodynamic reinforcement upon introducing the filler [21].

1.6.2 Nanoparticle Reinforced Rubber Nanocomposite

One of the most important phenomena in material science is the reinforcement of rubber by rigid entities, such as carbon black, clays, silicate, calcium carbonate, zinc oxide, metal halide and metal oxide [22]. Carbon black is largely reinforced in polymer and rubber engineering as filler since many decades. Wu and Wang [23] studied that the interaction between carbon black and rubber macromolecules is better than that of nanoclay and rubber macromolecules. Sahoo and Bhowmick [24] have reported improvement in mechanical and dynamic mechanical properties in Carboxylated Nitrile (CNBR) and CR rubber using ZnO nanoparticles of average particle diameter of 50 nm. Zheng et al. [25] reported Polyurethane-nano-ZnO hybrid system. Mishra et al. [26] reported the use of $CaCo_3$ on Styrene Butadiene Rubber (SBR) noticing marginal improvement of modulus up to 8% wt filler. Zhang et al. [27] discussed that the properties of rubber composites improved with decreasing particle size of magnesium hydroxide powder but it requires large amounts of metal halides to achieve the desired degree of flame retardancy, which would increase the agglomeration of particles and affect the mechanical properties. Nanocomposite [28, 29] based on polyurethane is prepared using silica, clay and POSS and characterized for mechanical and barrier properties. Sahoo and Bhowmick [30] synthesized hydroxyl terminated POSS and used as curative in carboxylated nitrile rubber. The nanofiller simultaneously cure the rubber and promote solvent resistance, as well as mechanical and dynamic mechanical properties.

1.6.3 Nanoclay Reinforced Rubber Nanocomposite

Rubber-clay nanocomposites have attracted, in recent years, the attention and interest of many industrial and academic researchers, since they often exhibit at low loading levels of clay outstanding properties compared with unfilled rubber compounds or conventional filled composites. Amongst all the potential nanofillers, layered silicates have been more widely investigated probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time. Owing to the nanometer-size particles obtained by dispersion, these nanocomposites exhibit markedly improved mechanical, thermal, optical and physico-chemical properties when compared with the pure polymer or conventional (microscale) composites as firstly demonstrated by Kojima and coworkers [31] for nylon/clay nanocomposites. Improvements can include, for example, increased moduli, strength and heat resistance, decreased gas permeability and flammability.

Polymer–clay nanocomposites are of great interest for both scientific challenges and industrial applications [32–34]. In the open literatures, the polymer–clay nanocomposites are generally classified into three groups according to their structures, i.e., nanocomposites with intercalated, exfoliated, or both of intercalated and exfoliated structures. Among them, the completely exfoliated nanocomposites are desired because the exfoliated layers exhibit the greatest reinforcement. Therefore, many efforts have been made to investigate this type of nanocomposites. Although clay nanocomposites have been prepared and tested for many thermoplastic and thermosetting polymers, rubber nanocomposites constitute only a minor proportion [35–40]. In general, rubber clay nanocomposite preparation methods can be divided into four major groups according to the processing techniques [41].

- In-situ polymerization.
- Intercalation of rubber via solution blending.
- Direct melt intercalation method.
- Intercalation of rubber via latex compounding.

According to the strength of the interfacial interaction between rubber matrix and layer silicate, three different types of rubber-clay composites [42] are evolved depending on the chemistry and processing conditions. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite is obtained (conventional composite). When a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers, intercalated nanocomposite is obtained. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated nanocomposite is obtained. These structures are shown in Figure 1.1.

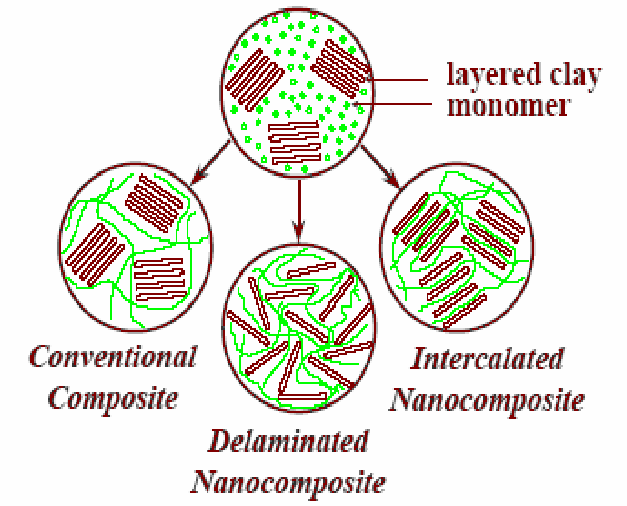


Figure 1.1 Different types of layered silicate/polymer composites [41].

Many different rubbers have already been used to synthesis rubber-clay nanocomposite. The following section describes the work involving rubber nanocomposite filled with nanoclay especially for CR and NBR matrix in addition to few general-purpose rubber. Some of the work carried out on these rubber matrixes are mentioned below.

1.6.3.1 General Purpose Rubbers (NR and SBR)

Rubber nanocomposites based on natural rubber reinforced with organic-modified layered silicate reinforcement have been studied by many authors using different technique [43, 44]. In fact, Intercalated and partially exfoliated structures have been successfully prepared by several processing techniques, such as vulcanization curing process, solution blending or latex compounding. A natural rubber–organoclay nanocomposite with a fully exfoliated structure was reported by many authors [45]. SBR-clay nanocomposites have been synthesized, in most cases, by mixing the organically modified clay in an industrial mixer (2-roll mill and/or Brabender mixer) followed by vulcanization [46, 47]. Many authors reported an increase in tensile strength by 5 times with 5–10 phr (parts per hundred rubber) of clay content and prepared intercalated and partially exfoliated SBR-clay nanocomposites.

1.6.3.2 NBR

Acrylonitrile-butadiene rubber, also known as nitrile or NBR, is a specialty rubber mostly used in automotive components (e.g. belts, O-rings). Many authors studied nitrile rubber as matrices in organoclay-filled systems [48, 49]. They presented for NBR/organoclay nanocomposites (in 10 phr organoclay) that the relative vapor permeability for water and methanol was reduced up to 85% and 42%, respectively, compared to the neat matrix. They also observed for the same type of rubber that water vapour permeability decreases not only with the organoclay content but also with the amount of silane coupling agent used. The latter effect was attributed to the enhanced silicate dispersion owing to the increased chain interactions between the silane and the rubber molecules. Toyota group synthesized intercalated NBR-clay nanocomposites (4% clay by volume) which had hydrogen and water vapor permeability 30% lower than pure rubber [50]. A similar better barrier property was also observed for nanocomposite compared to silica filled nitrile compound by Wu et al. [51] with 10% clay by volume, nitrogen permeability decreased by almost 50%. Nanocomposites also showed enhanced tensile strength and modulus [52].

1.6.3.3 CR

Polychloroprene, also known as neoprene, is an elastomer widely used in the electrical and automobile industries. There has been several research reports published in recent years related to elastomeric nanocomposites based on natural and other synthetic rubbers. However, the reports on chloroprene rubber are rare. The durability of chloroprene rubber components is largely dependent on the tear and tensile strength of the matrix. Incorporation of layered silicate into the CR rubber was reported to show an improvement of tear strength of such composites [53]. Nanoclay was found to enhance crystallization tendency of chains and storage modulus of CR based vulcanizates [54].

1.6.3.4 Carbon black and Nanoclay Reinforced Hybrid Rubber Composites

Elastomers are reinforced with fillers to improve their performance by incorporating conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate *etc*. Among all, carbon black is considered to be one of the cost-effective fillers used to improve the physicomechanical properties of rubber compounds such as hardness, tensile properties, tear strength, and a cluster of other properties. However, poor dispersions and lack of polymer filler interaction with higher loading of micron size fillers often lead to failure of finished product [55]. On the other hand, layered-silicates are found recently to be a good candidate for strengthening of rubbers due to their high surface area, platy morphology and exceptionally stable oxide network. The conventional fillers most highly used in the rubber industry include carbon black and silicone dioxide (silica), while organically modified layered clays and carbon nanotubes are opening up new points of access [56].

There is still interest in utilizing their potential by synergistic blending with carbon black that is more conventional or with silica reinforcements to cost effectively extend the “magic triangle” of tread performance. Thus, using nano-fillers in small amounts, which do not lead to the formation of larger filler clusters or even filler networks, opens new prospects in tyre tread formulations. The main idea of this work is to replace some parts of carbon black in a truck tyre formulation by few parts of layered silicate in order to control over the heat build-up without sacrificing other properties.

Many authors have reported recently that two or more different filler types are used in case of multi-component compounding, which produces so-called hybrid structures where effects of the different components are combined. Synergistic effect is achieved in nanoscale–microscale hybrid composites by combination of these two or more fillers and results in superior mechanical and dynamic mechanical properties [57, 58]. Acrylonitrile butadiene (NBR) rubber / Polyvinyl chloride (PVC) composites having carbon black and mica fillers in different compositions as hybrid fillers were investigated by Nugay and Erman [59]. Micro composites containing conventional isotropic fillers have limited barrier action even at high filler contents [60]. However, other sealing applications might require a combined action of spherical and platelet-like fillers. This has been proved for melt blended NBR, containing both CB and organoclay, in respect to the nitrogen permeability [61].

1.7 MOTIVATION FOR THE PRESENT WORK

Electro acoustic transducers form the primary element in the acoustic projectors and hydrophones used in underwater communication, detection and navigation systems as well as in oceanographic research. Almost all acoustic projectors and hydrophones are encapsulated in polymeric materials to protect the underlying sensors and electronics from physical damage and water ingression, while allowing the passage of acoustical energy without significant reflection, loss, or distortion. The rubber encapsulants used for the protection of the sensor element should also be able to sustain various mechanical rigors of the marine situations in addition to withstand temperature extremes, ozone and chemicals attack like oil and other marine pollutants. Presently used rubbers such as polychloroprene and nitrile rubber are not useful especially for deep sea applications due to low compressive modulus/strength and limited life. The failure of many units has been due to a direct result of water ingress through the rubber housing, thereby giving rise to an unacceptably low value of insulation resistance. These effects are become cumulative coupled with ageing factors. Hence, it becomes important to develop new polymeric systems with improved mechanical strength, water resistant and longer life. Ocean environment combined with specific performance requirements, conventional engineering rubbers can hardly meet the performance standards foreseen. In addition, use of conventional synthetic rubbers restricts life of the product in case of water diffusion and to think of other polymers to have better mechanical, electrical, improved life and water resistant properties. Considering the life of the transducers, development of new materials and process with improved performance over existing encapsulant are planned to investigate in this present work. With the view to meeting the above requirements, the major intention of this study has been to upgrade the performance of rubbers like polychloroprene rubber, and acrylonitrile butadiene rubber by modifying with nanoclay and carbon black.

1.8 SCOPE AND OBJECTIVES

Rubber components reinforced with various fillers play a vital role in underwater acoustic application. Conventional rubber compound based on chloroprene and nitrile rubbers filled with high loading of fillers like carbon block (CB), talc and calcium carbonate etc are used at present for encapsulation of underwater sensors. The conventional composite during their service absorb substantial amount of water significantly and alter the performance characteristics leading often to product failures. It is reported that nanoclay (NC) reinforced rubber compound are found to exhibit remarkable property enhancements particularly mechanical strength, flammability and barrier performance compared to conventional micro composites. The primary goal of the work is to replace carbon black partially and to investigate synergistic effect of nanoclay and carbon black to derive chloroprene and nitrile rubber compound having better performance properties particularly for encapsulation of underwater transducer applications. Since nanoclay filled elastomers are well known to improve gas and water impermeability, the effect of different loading of nanoclay and carbon black and using the right processing techniques on the properties of the composites are investigated. Though much research has been reported on conventional rubber composites, no systematic study has been done to analyze the synergistic effect of fillers, curing agent effect, process method and the resulting changes in the properties of the nanocomposites for development of better encapsulant materials. The scope of the present work is to develop CR and NBR based nanocomposites with improved mechanical and water resistant characteristics for the encapsulation of acoustic transducers used in underwater application.

1.8.1 Objectives

The objectives of the study are to investigate the synergistic effect of carbon black and nanoclay on physico-mechanical, electrical, dynamic mechanical, water absorption and morphology characteristics of chloroprene and nitrile rubber composites for underwater transducer’s encapsulation applications.

The following approaches are envisaged to meet the above objective.

- To prepare and characterise chloroprene rubber – clay nanocomposite.
- To investigate synergistic effect of hybrid filler system in CR matrix.

- To study the comparative effect of curing agents on dual filler filled CR nanocomposite.
- To study effect of two stage mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/Nanoclay compositions.
- To prepare and characterize hybrid filler systems (CB–NC) on NBR compound with emphasis on morphology, mechanical and electrical properties.
- To develop an adhesive and study adhesion of rubber nanocomposite to rubber and metal substrates.
- To investigate comparative performance of CR and NBR based nanocomposites with existing conventional rubber compound.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

The materials and the experimental techniques employed for characterisation of the rubber composites are discussed in this chapter.

2.1 MATERIALS

2.1.1 Nanoclay

Nanoclay has layer silicate structure and organically modified nanoclay is known as organoclay. This is natural montmorillonite modified with a quaternary ammonium salt and its trade name is Cloisite® 15A produced by Southern Clay Products, USA. Cloisite® 15A is off white powder material. Basal spacing of this organoclay is reported to be 3.15 nm. The chemical structure of quaternary ammonium salt used to modify nanoclay is shown in Figure 2.1.

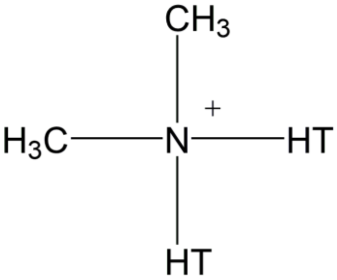


Figure 2.1 Chemical structure of organoclay.

The typical properties of Cloisite® 15A is given in Table 2.1. The organic modifier 2M2HT is dimethyl, dihydrogenatedtallow, quaternary ammonium; where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14) and anion is chloride. Clay minerals are alumino silicates with a 2:1 structure as shown in Figure 2.2; a central alumina octahedral sheet is sandwiched in between two silica tetrahedral sheets. Eg.: Montmorillonite.

Table 2.1 Properties of nanoclay

Treatment/Properties	**Organic Modifier**	**Modifier Concentration**	**% Moisture**	**% Weight Loss on Ignition**	**Specific Gravity (g/cc)**
Cloisite® 15A	2M2HT	125 meq/100g clay	< 2%	43%	1.66

Some of the Al^{3+} and Si^{4+} ions are usually replaced by lower valence ions such as magnesium, iron, manganese and occasionally lithium. This creates a charge imbalance on the surface of each layer platelet.

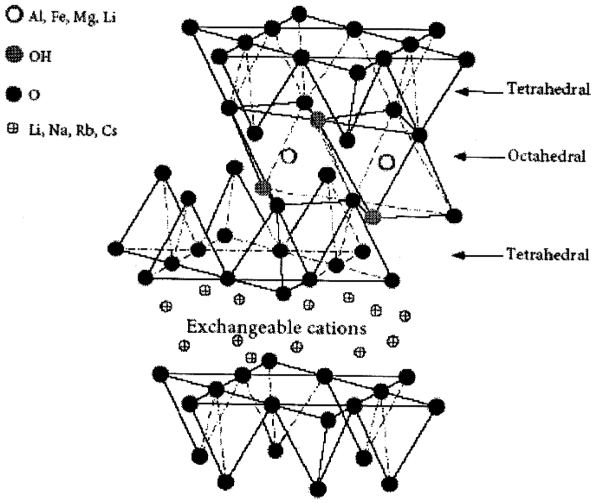


Figure 2.2 Structure of Montmorillonite.

The negative charge imbalance is neutralized by adsorption of hydratable cations, usually sodium and calcium between the clay layer platelets and these cations held the alumino silicate layers together [62].

2.1.2 Carbon Black

A wide range of fillers are used in rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvements in processing. In most applications, carbon black has been used for many years as the main reinforcing fillers that increase the usefulness of rubbers [63]. Carbon black is a colloidal form of elemental carbon. They are prepared by partial combustion or thermal decomposition of oil or natural gases. The particles of carbon black are not discrete but are fused clusters of individual particles. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The furnace process manufactures the major types of rubber reinforcing carbon blacks. The predominant purpose of furnace type carbon blacks in elastomers is the reinforcement they impart to the vulcanisates. Addition of carbon black into rubber enhances modulus, tensile properties and overall improvement in technological properties. Fast extrusion furnace black (FEF) received from M/S Philips carbon chemicals Ltd, Kochi was used and its physical property is given in Table 2.2.

Table 2.2 Physical properties of carbon black

Name	**Abbreviation**	**ASTM Design**	**Particle Dia (nm)**	**Iodine No.**	**Structure (cm^3 DBP/100 g)**
Fast Extrusion Furnace	FEF	N-550	47	42	120

2.1.3 Calcium Stearate

There are different types of metallic stearates used in rubber compound as an effective elastomer processing aid and release agent. Typically, they are zinc, calcium and magnesium stearate, which allows for complete product dispersion in elastomers [64]**.** Zinc stearate has been the most commonly used one to date, but government environmental regulations have limited its use and control its working range. This has caused greater interest in the calcium stearate by the rubber companies. There is also increased interest in the magnesium stearate as well. Calcium stearates, which are recognized as physiologically safe, have become increasingly important in the last few years. They are insoluble in most solvents. The combination of the metallic's, zinc, calcium and magnesium would, therefore, yield a stearate formula as shown in Figure 2.3.

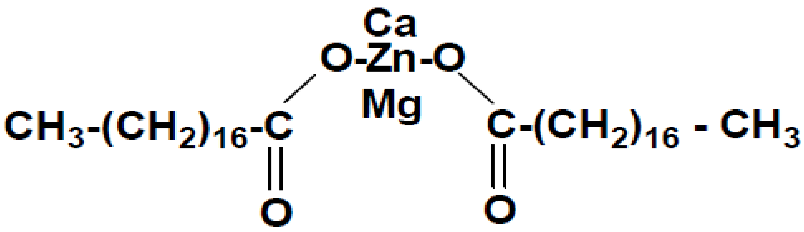


Figure 2.3 Chemical Structures of Metallic Stearates**.**

The chemical structure of metallic stearates consists of a very long stable hydrocarbon chain. The long-chain hydrocarbon structure is insoluble in water and, thus, provides the hydrophobic nature of metallic stearates [65].

2.1.4 Chloroprene rubber

Polychloroprene is an emulsion polymer of 2-chlorobutadiene and has a T_g of about –50 ^oC. Neoprene is the popular name for polymers of chloroprene, 2 chloro-1, and 3-butadiene as shown in Figure 2.4. This is one of the favored materials for underwater application. Neoprene W (for composite) and Neoprene AD20 (for Adhesive) grades obtained from Dupont were used for the present study. Polychloroprene or chloroprene rubber, introduced by DuPont in 1931, was the first synthetic rubber developed that exhibited the elastomeric properties of natural rubber [66].

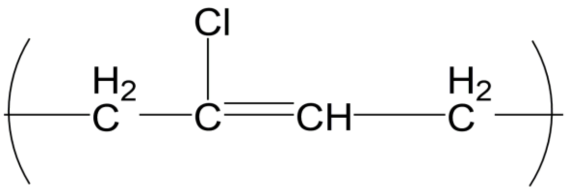


Figure 2.4 Chemical Structures of Chloroprene Rubber.

Neoprene is a true multipurpose elastomer thanks to its balance of inherent properties, which include:

- Outstanding physical toughness.
- Extensive short- and long-term operating temperature range than general purpose hydrocarbon elastomers.

- Resistance to hydrocarbon oils and heat (ASTM D2000 categories BC/BE).
- Resistance to ozone, sun and weather.
- Better flame retardant/self-extinguishing characteristics than exclusively hydrocarbon-based elastomers.
- Excellent bondabilitiy with dissimilar substrates.

This distinctive combination of properties poised neoprene for solving many of the potential problems besetting the automotive, construction, transportation, wire and cable industry. It has made useful in a massive number of applications including aircraft, automotive, bridge pad, chemical-resistant clothing, home furnishings, machinery, mining and oil field belting, underground and undersea cables, recreation, and tires. Among different grades of neoprene, W and GRT grades are generally used in underwater applications. Neoprene-W is more crystallization resistant. It is mercaptan modified to give C–C link in the polymer. W grade has better storage stability and heat resistance. While paralleling with other neoprene grades, W-grades have superior vulcanizate heat and compression set resistance. It also accepts higher levels of filler for a given level of compression set or tensile strength. Hence neoprene W grade rubber is considered to be more agile in research. In addition to molding grade Neoprene AC or AD is selected for preparation of adhesive due to fast crystallization effect. Though CR remains one of the most important specialty elastomers enhancing the tear strength of this synthetic material is challenging. Consequently, although various polymer-Montmorillonite (MMT) composites have been prepared, the polychloroprene-MMT composite has less to be investigated [67]**.**

2.1.5 Acrylonitrile butadiene rubber

Acrylonitrile-butadiene copolymer is a copolymer of butadiene and acrylonitrile as shown in Figure 2.5. It is a special purpose elastomer that is used in applications, which require oil resistance. NBR is produced by an emulsion polymerization process. The acrylonitrile (ACN) content is one of two primary criteria defining each specific NBR grade. Acrylonitrile content may range from 18–50% by weight. The ACN level, because of polarity, determines several basic properties, such as oil and solvent resistance [68, 69], low temperature flexibility/glass transition temperature, and abrasion resistance. Higher ACN content provides improved solvent, oil and abrasion resistance, along with higher glass transition temperature. The NBR grade used in the present study is KOSYN KNB 35L obtained from Korean synthetic rubber company, Korea. It contains 35% ACN content. The chemical structure of Nitrile rubber is shown in Figure 2.5.

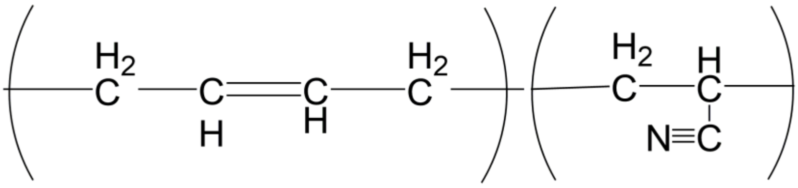


Figure 2.5 Chemical structure of NBR.

2.1.6 Other Rubber Chemicals

The other compounding ingredients with specification and supplier details used for preparation of rubber composite are detailed below.

Zinc oxide

Grade : White seal
Particle size, Max. : 4 µm
Specific gravity : 5.6
Assay %, min. : 95

MgO

Grade : AR
Physical form : white powder
Density : 3.2
Make : SD Fine chemicals, Mumbai, India

Stearic acid

Manufacturer : M/s. Godrej Soaps Pvt. Ltd.
Melting point, ^{o}C : 68–70
Purity % : 95

Vulcanox HS

Manufacturer : M/s. Bayer India

Softening point, °C : > 75

Specific gravity : 1.1

Vulcanox 4020

Manufacturer : M/s. Bayer India

Melting point, °C : > 45

Specific gravity : 1.1

Lead oxide

Manufacturer : M/s. Qualigens / Glaxo, Mumbai, India

Grade : Red lead, Pb_3O_4

Assay %, min. : 94

MBTS (Benzothiazole Disulphide)

Make : M/s. ICI India Ltd.

Specific gravity (25°C) : 1.5

Melting Point, °C, Minimum : 174

NA 22 (Ethylene Thiourea)

Make : M/s. Fluka

Melting Point, °C, Minimum : 150–153°C

2.2 EXPERIMENTAL METHODS

Cure characteristics and other physical properties like tensile, tear, volume resistivity and water-resistant are carried out as per respective American Society for Testing and Materials (ASTM) standards [70–72]. The morphology and dispersion are investigated using XRD and TEM instruments. DMA was used for determination of viscoelastic parameters like dynamic modulus and damping constant. The details of instruments used for characterisation are explained below.

2.2.1 Cure characteristics

Cure characteristic of the rubber nanocomposites were studied using a moving die rheometer (MDR 2000, Alpha Technology, USA) as per ASTM D 2084. MDR consists of a heated, sealed and rotorless moving die system as shown in Figure 2.6. In this rheometer the rubber compound is sealed in a cavity formed by directly heated dies. The lower die moves at 100 cpm. The reaction torque measured at the upper die correlates with the degree of vulcanization varying with time. This rheometer is capable of measuring rubber compound cure under isothermal test conditions at constant strain and frequency. Temperature range is ambient to 200 ^{o}C. The oscillation frequency is 1.6 Hz and strain 0.5, 1.0 or 3.0 degrees (2.8%, 7%, 14% or 42%). The cure curves can be obtained as real time plot. The advantage of the instrument over R100 is that it has better heat transfer capacity and data analysis facilities. The time to attain 90% of the maximum rheometric torque was taken as the optimum cure time (t90). Scorch time (t2), minimum torque and maximum torque also were evaluated.

Figure 2.6 Moving Die Rheometer.

2.2.2 Mechanical property measurements

Mechanical properties can be measured using an Universal Testing Machine (UTM) as shown in Figure 2.7. This machine can be operated in tensile, compression, flexural and cyclic modes. Mechanical properties of rubber vulcanisates like tensile strength, modulus at different elongations, elongation at break etc can be determined using this machine. UTM consists of a fixed upper and lower cross heads and a moving cross head in between (Figure 2.7). The speed of cross head can be varied from 0.001 mm/min to 1000 mm/min. The machine has a microprocessor controller. The load range of the machine can be selected depending on the plug in type electronic load cell. Two load cells of capacity 500 N and 50 kN are used with this machine.

Figure 2.7 Universal Testing Machine.

The test environment can be varied from 80 ^{o}C to 200 ^{o}C with the help of the chamber attached to the machine. For sub-ambient temperature, liquid Nitrogen is used. ZWICK UTM 1476 uses one of the most advanced control electronics module- Dups. Through a set of operator-selected parameter set, complete testing programme can be run, data collected, processed and output generated. To evaluate the stress–strain characteristics, ultimate strength, modulus and elongation at break dumbbell specimens were punched out from the 2 mm thick moulded sheets and tested as per ASTM D412 method on a UTM at a crosshead speed 500 mm/min. Five specimens were tested in each case and the average values were reported. Shore hardness was measured with a Durometer as per ASTM D 2240 and the value was expressed in Shore-A. Tear strength was measured using the same UTM as per ASTM D 624 and tested at a rate of 500 mm per min of cross head speed.

2.2.3 Water absorbance, Diffusion and Permeability

The amount of water absorbed by different polymer nanocomposite and polymer composites is determined according to ASTM D 570-81 and can be described as follows. One-inch square test specimens are cut from the molded sheet and their dry weights are taken in an electronic balance. Then 3.5% salt water is prepared in a beaker and specimens are placed in it. Then the beaker containing the specimens are kept in an air oven maintained at a temperature of 70 °C. After 24 hours, the specimens are taken out and water on the surface of samples is wiped with a tissue paper. Then they are kept at room temperature for one hour.

The conditioned test specimens are then weighed to the nearest 0.0001 g. Weighing is repeated at 3rd, 6th and 7th day**.** Water absorption is calculated using the equation

$$\text{Water absorption} = (W_2 - W_1) / W_1 \times 100,$$

where W_1 and W_2 are the initial and final weights of the samples.

Diffusion properties were studied using rectangular samples of size 20 mm × 20 mm × 2 mm, prepared from the rubber vulcanizates. The edges of the samples were slightly curved to obtain uniform absorption. The thickness and initial weight of samples were measured. The samples were completely immersed in water in glass diffusion bottles kept at uniform temperature. The samples were removed from the water at specific time intervals, excess solvent at the surface removed using filter paper and weighed. The samples were returned to the solvent in the diffusion bottle immediately. The process was continued until equilibrium swelling is reached. At time *t* of immersion, the mole percent uptake Qt for solvent was determined using the formula

$$Q_t = \frac{(M_t - M_0)/M_w}{M_0} \times 100,$$

where M_t is the mass of sample after time *t* of immersion, M_0 the initial mass of the sample and M_W is the molecular weight of the solvent. The sorption isotherms were plotted with the mole percentage uptake of solvents for the nanocomposite versus square root of time. The diffusion coefficient was then calculated. The experiments were conducted at room temperature and the values reported here is the average of three experiments.

Permeation rates were measured using the gravimetric cup method (ASTM D1653-72) with an area of exposure 25 cm^2. These cups were then placed in desiccators over silica gel, and the whole assembly was kept in an oven maintained at the desired constant temperature (40 °C). The weight loss (in mg) was noted until equilibrium was reached. Permeability (*P*), was calculated from a least-squares analysis of the steady-state portion of a plot of weight loss (in mg) *versus* time (in days) using:

Permeability = $P = qL / At$.

Here, L and A represent the thickness (in cm) and area (in cm^2) of the membrane exposed to water; q is the amount of liquid (in mg) permeating through the membrane, t is the time (in seconds) and P is called the permeability coefficient, usually expressed in $gcm^{-1} s^{-1}$.

2.2.4 Salt-water ageing

Short term ageing was conducted in salt water environment and retention of properties such as mechanical strength, electrical properties and dynamic mechanical parameters are measured. Salt-water ageing evaluates the resistance of the polymer nanocomposites to the ageing resulting from the exposure of it to the seawater conditions. Firstly, 3.5% salt water is prepared in a beaker by dissolving 3.5 g NaCl in 100 ml water. Then the beaker is placed in an oven at a temperature of 70 °C. After fixed period of time, the respective samples are taken out, and the retention of properties are measured and the results are discussed.

2.2.5 Volume resistivity

Volume resistivity is the electrical resistance through a one-centimeter cube of insulating material and is expressed in Ohm centimeters. Volume resistivity of polymer nano composites are measured in accordance to ASTM D 257. A Davenport surface and volume resistivity measuring apparatus used for measurement of electrical resistivity of the rubber composites is shown in Figure 2.8.

Figure 2.8 Resistivity Meter.

2.2.6 Rubber Process Analyser

The strain sweep measurements on green compound were conducted to study the rubber filler interaction. Rubber Process Analyser (D-RPA 3000 By MonTech, Germany) shown in Figure 2.9 is also called as dynamic reheometer. Such instrument for capturing strain and torque signals, through appropriate software. Filled rubber compounds exhibit strong non-linear viscoelastic behaviour, the well-known Payne effect, i.e. the reduction of elastic modulus with increasing strain amplitude. RPA can do strain sweep tests in which the variation of storage modulus (G′) loss modulus (G″) and complex modulus (G*) with change in strain amplitude are measured [73]. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. In agreement with ASTM 5289, the manufacturer recommends to load samples of about 1.14 g/cm^3. Samples for RPA testing were consequently prepared by die cutting 46 mm diameter disks out of around 2 mm thick sheets of materials. The testing temperature was selected as around 100 ^{o}C; a temperature below the curing temperature and the shear strain as varied from 0.5 to 100% keeping the frequency measurements at 0.5 Hz.

Figure 2.9 Rubber Process Analyzer.

2.2.7 Dielectric Analyzer

The dielectric and electrical properties of the composite films were measured using a computer-controlled impedance analyzer (PSM 1735) on the application of an alternating electric field across the sample cell with a blocking electrode (aluminium foil) in the frequency range of 10Hz –1MHz. The dielectric constant (ε_r) was determined by using the following equation:

$$\varepsilon_r = (C_p \times d) / (\varepsilon_0 \times A),$$

where C_p is the observed capacitance of the sample (in parallel mode), d and A are the thickness and area of the sample, respectively. ε_0 is the dielectric constant of vacuum and the value of ε_0 is 8.854×10^{-12} F/m.

2.2.8 Dynamic Mechanical Analyser

Dynamic mechanical analyser (DMA) is one of the most sensitive single techniques available for characterizing and interpreting the mechanical behaviour of materials. DMA shown in Figure 2.10 measures the response of a material to a cyclic deformation as a function of temperature. Test results are expressed by three main parameters: (i) the storage modulus (E'), corresponding to the elastic response to the deformation; (ii) the loss modulus (E''), corresponding to the plastic response to the deformation, and (iii) the damping factor (tan δ), that is the E'/E'' ratio, which indicates the energy dissipation by the sample, and is useful for determining the occurrence of molecular mobility transitions such as the glass transition. The measurement of the viscoelastic properties of the nanocomposites was performed in single cantilever mode using a DMA (TA Instruments model Q 800). The sample dimensions were 17.5 mm × 12 mm × 2 mm (length × width × thickness). The imposed deformation was chosen that the measurements were in the linear viscoelastic region. The instrument is vital for quantifying the stiffness and damping of the materials. The instrument is supported with various data analysis software, thermal and time–temperature superposition facilities etc.

Figure 2.10 Dynamic Mechanical Analyzer.

2.2.9 Wide angle X-ray diffraction (WAXD)

The structure of nanocomposites in general has been established using WAXD analysis and TEM observation. Both are essential tools for evaluating nanocomposite structure [74]. X-ray diffraction test was conducted using X'Pert PRO X-ray diffractometer of PANalytical shown in Figure 2.11 to measure the change in gallery spacing of organically modified layered silicates. The X-ray beam was produced by nickel-filtered Cu Kα radiation with wavelength of 0.154 nm operated at 40 kV and 30 mA. The diffraction data were obtained within a goniometer angle (2θ) range of 2°–10° (wide angle XRD at lower angular range) at a rate of 0.5° per minute.

Figure 2.11 Wide angle X-ray diffractometer.

This technique allows the determination of the spaces between structural layers of the silicate utilizing Bragg's law: $2d\sin\theta = n\lambda$**,** where λ corresponds to the wavelength of the X-ray radiation used in the diffraction experiment, d the spacing between diffractional lattice planes and θ is the measured diffraction angle or glancing angle and n is the order of reflection (here $n = 1$).

2.2.10 Transmission electron microscopy (TEM)

The formation of nanocomposites and their structure defined by WAXD patterns are only tentative. Conversely, TEM allows a qualitative evaluation of the internal structure, spatial distribution of the various phases and views the defect structures [75]. The rubber composite samples for TEM analysis were prepared by ultra cryo-microtomy using Leica UltracutEM FCS, Gmbh, Austria. Freshly sharpened glass knives with cutting edge of 45°

were used to get cryo-sections of 50 nm thickness. The sample temperature during cryo-microtomy was kept around 45 °C, which was well below the glass transition temperature of NBR composites. The cryo-sections were collected and directly supported on a copper grid by 300-mesh size. The microscopy was performed later using a transmission electron microscope (JEOL JEM-2100, Japan) operated at an acceleration voltage of 200 kV.

2.2.11 Pulse Tube set-up for acoustic measurement

Acoustic properties of the samples were measured using a water-filled pulse tube. The experimental set-up for measurement of insertion loss (IL) and echo reduction (ER) is explained in detail [76, 77]. The impedance tube with instrumentation set-up is illustrated in Figure 2.12. The tube is made up of stainless steel tube 1800 mm length and the thickness of the wall is 25 mm. For studying Insertion loss and Echo reduction cylindrical specimens of 50mm diameter and 200mm diameter with a height of 20mm were made by compression moulding. An impulse of acoustic pressure is generated by the transducer and reflected back by the sample kept at top of the tube. The reflected signal is recorded using the same transducer via trans-receiver switch. The sample is removed and the reflection from the water air interface is measured. The ratio of the reflected signal by the sample to that of air is the echo reduction. For all practical purposes echo reduction (ER) is expressed in decibel.

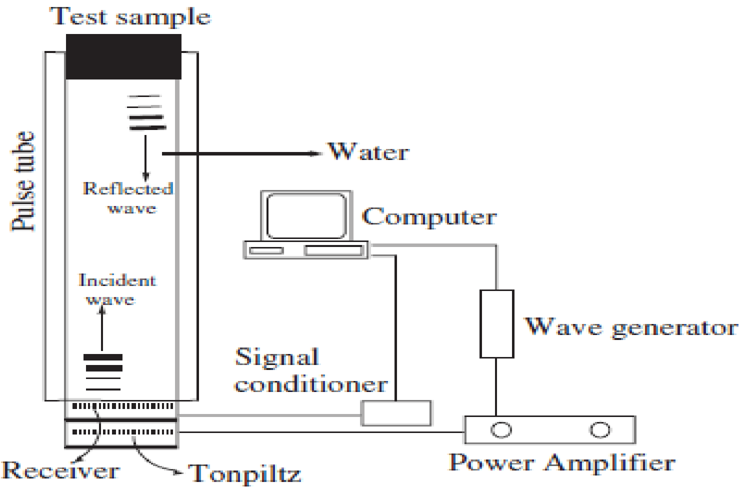


Figure 2.12 Experimental set-up for acoustic measurements.

Echo reduction behavior for 3 kHz to 15 kHz was studied using 50 mm diameter specimen in vertical pulse tube with standard projectors and hydrophone at bottom.

Echo reduction and insertion loss behavior for the frequency range 1 kHz to 4 kHz was studied in vertical low frequency pulse tube using 200 mm diameter specimen. For insertion loss, specimen was submerged in water in the pulse tube with projector and hydrophone located opposite sides of specimen.

CHAPTER 3

CHLOROPRENE RUBBER NANOCOMPOSITES

This chapter deals with the preparation, optimization and characterization of carbon black and nanoclay filled polychloroprene. This chapter is divided into four sections to study the effect of ingredients like nanoclay, synergistic effect of nanoclay and carbon black and curing agent on properties change in CR based rubber compound. The mechanical, electrical and functional property requirement of final rubber products used for any applications is influenced by nature and types of materials and process method adopted for preparation of composites. In order to see materials and process effect on rubber nanocomposite and to distinguish from micro composite, a detailed study is carried out to prepare and optimize CR based rubber composite for development of improved encapsulation materials for underwater sensors applications. The investigation of following four sections will help to design better rubber compound for sensor encapsulation application to work in underwater environment.

Section 3.1 Preparation and characterization of chloroprene organoclay nanocomposites.

Section 3.2 Influence of carbon black in polychloroprene organoclay nanocomposite with improved mechanical, electrical and morphology characteristics.

Section 3.3 Comparative performance of curing agents on physico-mechanical and dynamic mechanical properties of CR compositions.

Section 3.4 Effect of two stage mixing and dispersion agent on performance of CR composites.

3.1 PREPARATION AND CHARACTERIZATION OF CHLOROPRENE ORGANOCLAY NANOCOMPOSITES

3.1.1 Introduction

In recent years, nanoclay has attracted considerable attention since it is the most commonly employed nano-structured material in polymer composites [78, 79]. There are several types of nanoclay composites based on both plastics and rubbers reported in many literatures. Brief review of preparation and process of different polymer nanocomposites based on thermoplastics, thermosets, and elastomers are prepared and reported [80]. Polychloroprene, also known as neoprene, is an elastomer widely used in the electrical and automobile industries. Polychloroprene has outstanding physical toughness, a wider operating temperature range than general-purpose hydrocarbon elastomers, superior flame retardant / self-extinguishing characteristics compared to exclusively hydrocarbon based elastomers, and excellent resistance to ozone, sun and general weather conditions [81]. Consequently, although various polymer nanoclay composites have been prepared, the nanoclay-enabled polychloroprene composite has less to be investigated [82]. In the present work, we report the effect of nanoclay loading on the properties of nanocomposites based on chloroprene rubber. The present study attempts to increase the mechanical, electrical and water resistant properties of polychloroprene through the addition of nanoclay.

3.1.2 Preliminary compound formulation

In the preliminary studies, Chloroprene rubber nanocomposites with four different loading of nanoclay were prepared. At first CR was masticated and then nanoclay was added. After achieving a good dispersion, other compounding ingredients from Table 3.1 are added as per sequence of two steps given in Table 3.2. Compounds were prepared in a lab size rubber mixing mill with roll size 150 mm × 300 mm operating at a friction ratio of 1:1.14. The mill temperature was maintained at 60 ^{o}C by circulating cooling water through the drilled holes of the mill rolls. Master batch containing rubber and nanoclay (Step 1) was first mill mixed for better dispersion of nanofiller and other additives are added to the masterbatch as per the order given in Step 2 to prepare for final mixing compound. The mixed compounds were then passed through the two-roll mill 6 times and the prepared sheet kept 5 hrs for maturation before studying for rheometric parameters. The samples were then cured at 150 ^{o}C in an electrically heated hydraulic press to their respective cure times.

Table 3.1 Effect of nanoclay on CR matrix

S. No.	Ingredients	Parts/100 Rubber
1	Neoprene (CR-W)	100.00
2	**Nanoclay**	**Variables***
3	Stearic Acid	1.0
4	Vulcanox HS	1.0
5	Vulcanox 4020	1.0
6	Red Lead, Pb_3O_4	6.0
7	NA 22	0.6
8	MBTS	1.0
	Batch Weight, g	110.6

* Nanoclay effect studied for 4 different loading such as 2.5, 5, 7.5 and 10 phr

Table 3.2 Preparation of preliminary compound

	Ingredients (phr)					
Step 1	CR-W	100				
	Nanoclay	-	2.5	5	7.5	10
Master Batch		-	102.5	105	107.5	110
Step 2		**GUM**	**N1/1**	**N1/2**	**N1/3**	**N1/4**
	Master batch		102.5	105	107.5	110
	St. acid	1	1	1	1	1
	HS	1	1	1	1	1
	4020	1	1	1	1	1
	Pb_3O_4	6	6	6	6	6
	NA 22	0.6	0.6	0.6	0.6	0.6
	MBTS	1.5	1.5	1.5	1.5	1.5

3.1.3 Evaluation of cure characteristics

Rheometry of the compounds was carried out with moving die rheometer (MDR 2000) at 150 ^{o}C. The parameters such as maximum torque (M_H), minimum torque (M_L), scorch time

(t_{s2}), cure time (t_{90}) etc. are calculated and given in Table 3.3, it was evident that the addition of layered silicate to the CR matrix altered its cure characteristics.

Table 3.3 Cure characteristics

S. No.	Properties	Test Standard	Sample Description				
			GUM	N1/1	N1/2	N1/3	N1/4
1.	Minimum Torque (M_L) (lb.in)	ASTM D 2084	0.47	0.38	0.46	0.48	0.49
2.	Maximum Torque (M_H) (lb.in)		5.88	5.72	5.48	5.54	5.81
3.	Scorch Time (t_{s2}) Minute,		4.67	4.63	4.61	4.89	5.17
4.	Cure Time (t_{90}), Minute		25.67	20.89	19.17	19.98	21.04

It is evident from the results that the scorch time and optimum cure time reduced considerably on addition of nanoclay. The cure time is reduced by almost six minutes for compounds containing 5 phr of nanoclay as compared with the unfilled CR (GUM). This effect is attributed to the ammonium groups of the organic cations present on nanoclay. The reason also support for nanoclay filled natural rubber nanocomposite [83, 84].

3.1.4 Evaluation for Physico-mechnical properties

Mixed compounds were molded by compression molding techniques according to the optimum cure time obtained in Rheometric studies to obtain test slabs. Dumb bell specimens were punched out from the molded sheets using a hollow cutting die and the mechanical properties were determined using a universal testing machine, with a cross head separation of 500 mm/min. The tensile parameters such as, Ultimate Tensile strength (UTS), elongation at break (EB) and modulus etc. and other physical properties are evaluated and are given in Table 3.4. The results indicated that the addition of nanoclay enhances the mechanical properties of neoprene significantly. Tensile strength increases above 22% until 7.5 phr and then it decreases but tear strength improves for all loading considerably. The durability of rubber components is largely dependent on the tear and tensile strength of the neoprene. However, enhancing the tear strength of synthetic rubber is challenging especially neoprene. It is evident from the above table that addition of nanoclay improves tear strength of neoprene considerably [85].

Table 3.4 Physical properties of different rubber compound

S. No.	Properties	Test Standard	Sample Description				
			GUM	N1/1	N1/2	N1/3	N1/4
1.	Specific gravity	Wallace Specific gravity balance	1.29	1.29	1.29	1.29	1.30
2.	Hardness (Shore A)	ASTM D 2240	35–36	38–39	40–41	41–42	44–45
3.	Water absorption, % wt gain, Max 40°C 24 hrs, 3.5 % NaCl solution	ASTM D 471	0.38	0.38	0.31	0.32	0.30
4.	Volume resistivity (Ωcm)	ASTM D 257	3×10^{10}	3×10^{10}	3×10^{10}	3×10^{10}	3×10^{10}
5.	Tensile strength (MPa), Minimum	ASTM D 412	11.93	13.01	15.30	15.48	14.64
6.	Tensile stress at 300% , (MPa) Minimum	,,	1.39	1.55	1.76	1.89	2.30
7.	Elongation at Break % , Minimum	”	1097	1102	1067	1073	1060
8.	Tear strength (N/cm), Minimum	ASTM D 624	183	192	218	242	258

It is found that the addition of 5 phr nanoclay in chloroprene rubber enhances tensile, tear and water resistant properties without compromise in electrical resistivity. However, this particular compound cannot be used for underwater application due to lower value of hardness. A material of higher hardness and strength is required to withstand temperature and pressure conditions of marine environment. Hence, further investigation is necessary to improve performance characteristics of compound. This has led to focus on understanding the synergistic effect of nanoclay and carbon black in more detail.

3.1.5 Conclusion

In this study, the effect of nanoclay on property of chloroprene rubber has been investigated. It is evident from the cure studies that the scorch time and optimum cure time reduced considerably on addition of nanoclay. The cure time is reduced by almost six minutes for compounds containing 5 phr of nanoclay as compared with the unfilled CR.

Furthermore, test results of physical properties indicate that the addition of nanoclay enhances the mechanical properties significantly. It is concluded that the addition of 5 phr nanoclay in chloroprene rubber enhances overall tensile, tear and water resistant properties without compromise in electrical resistivity.

3.2 INFLUENCE OF CARBON BLACK IN POLYCHLOROPRENE ORGANOCLAY NANOCOMPOSITE

3.2.1 Introduction

Polychloroprene or Chloroprene rubbers are widely used in electrical and marine application and have outstanding physical toughness, good bonding with different substrates and aging resistance. Chloroprene rubber composites usually contain carbon black and other inorganic fillers and requires a high content (>30%) in order to impart the desired mechanical properties. Such high filler loading increase the density of the product and can cause deterioration in properties through interfacial incompatibility between the filler and the organic matrix. Among many types of fillers, carbon black is the most important reinforcing filler used in the rubber industry. About 90% of the worldwide production of carbon black is used in the tire industry in which the carbon black improves tear strength, modulus, and wear characteristics of the tires. In the past two decades, research was aimed to develop other reinforcing agents to replace carbon black partially or completely in rubber compounds such as sepiolite, kaolin, and precipitated silica. The application of organophilic clay in elastomers provides a new technology of rubber/clay nanocomposites with enhanced properties. Arroyo et al. [86] prepared natural rubber nanocomposites with 10 phr organoclay with similar modulus, tensile strength and hardness as natural rubber with 40 phr carbon black. Varghese and Karger-Kocsis [87] also prepared natural rubber nanocomposites with 7 phr of nanoclay functionalized with octadecylamine which presented higher tensile strength and elongation than NR with 20 phr carbon black.

Polymers are increasingly used in a variety of underwater applications, for example, as cable sheathing and transducer encapsulation, because of their high resistance to abrasion and tear and excellent electrical properties. Rubber is an excellent material usable for underwater applications because of its easy fabrication. The successful long-term operation of the sensors was found to be dependent on the correct choice of material for an elastomeric membrane intended to prevent moisture ingress into the underwater transducer system [88, 89]. Conventional rubber composite filled with carbon black fillers are in use; however, the effect of nanoclay and carbon black for underwater rubber encapsulation has not been reported much in the literatures. In this chapter, polychloroprene (CR) filled with nanoclay and carbon black was prepared and characterised. The synergistic behaviour of organoclay and carbon black was investigated in CR samples, which contained constant loading of nanoclay (5 Phr) and carbon black at different concentrations. In addition, the effect of carbon black on the cure behaviour, mechanical and electrical properties and morphology changes in polychloroprene clay nanocomposites have been examined.

3.2.2 Materials

The elastomers used were CR (Neoprene W of Dupont Dow Elastomers, USA) purchased from their Indian distributor M/s. Pollmann India Limited, Mumbai. Organically modified montmorillonite containing 90 mequiv./100 g clay of quaternary ammonium ions (Cloisite15A) was purchased from the Southern Clay, USA. Fast extrusion furnace black, FEF (N550) with a specification of mean size 30–50 nm and surface area 40-70 m^2/g was procured from Philips Carbon Black, India. All other compounding ingredients such as antidegradents and vulcanising agents were obtained from local rubber chemical suppliers and used as such.

3.2.3 Compounding and Sample preparation

The compounding of CR with fillers and other ingredients was done by laboratory two roll mixing mill. All the weights were taken in parts per hundreds of rubber and the formulation is given in Table 3.5. Master batch blending both rubber and nanoclay (5 Phr) was mixed at first in order to disperse the organo-clay in the rubber matrix. After 3 minutes of mixing for master batch preparation, other ingredients are added as per the order given in the recipe. This technique of mixing is followed for all compounds except the conventional CB compound (CB in Table 3B.1). In these recipes, the contents of carbon black were varied as 5, 10, 15, and 20 phr whereas nanoclay and other ingredients were kept constant. For improved water resistance, a lead oxide cure system is selected instead of conventional magnesia/zinc oxide combination. The following mixing sequence was followed in each case in order to disperse the nanoclay in a rubber matrix—prepare master batch containing rubber and nanoclay and pass under tight nip 3–4 times (5 minutes) —addition of activator followed by addition of antidegradents—addition of carbon black followed by addition of curatives. Final sheet can be prepared from the mixed compound by passing end wise through the tight rolls six times.

Table 3.5 Recipe of rubber compounds

Ingredients	**Gum**	**CB**	**NC**	**NB1**	**NB2**	**NB3**	**NB4**
Neoprene W	**100**	**100**	**100**	**100**	**100**	**100**	**100**
Nanoclay	---	---	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
HS[a]	1	1	1	1	1	1	1
4020[b]	1	1	1	1	1	1	1
FEF N550 Carbon Black	---	5	----	5	10	15	20
Red lead (Pb_3O_4)	6	6	6	6	6	6	6
NA 22[c]	0.6	0.6	0.6	0.6	0.6	0.6	0.6
MBTS[d]	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total	111.1	116.1	116.1	121.1	126.1	131.1	136.1

[a] 1,2-dihydro-2,2,4-trimethyl quinoline, polymerized.
[b] N-(1,3-dimethylbutyl)-N'-phenyl- p-phenylenediamine.
[c] ethylene thiourea.
[d] Benzothiazyl disulfide.

3.2.4 Results and discussion

3.2.4. 1 Cure Characterisation

Compound cure characteristics were measured using a Moving Die Rheometer (MDR 2000) at 150 ^{o}C. The effect of organoclay and organoclay/carbon black on neoprene rubber composite is given in Table 3.6. M_L and M_H decreases slightly with the addition of 5 phr nanoclay compared to gum rubber vulcanizate. However, addition of increasing carbon black loading on nanoclay filled rubber composite increases both these values. It is observed that the viscosity increases with increase in carbon black loading. The incorporation of carbon black stiffens the rubber composite. A similar trend observed for torque difference (M_H–M_L), which indicates the extent of cross linking and rubber-filler interaction of the composite. It is seen from the table that faster scorch time and increase in maximum torque obtained for the NC/CB incorporated CR compounds compared to gum and over that with CB or NC as single phase filler. It is found from the Table 3.6 that cure time t90 reduced considerably with the addition of NC and CB on gum compound but increases with CB loading. This may be attributed to the presence of functional group on NC and basic nature of CB, which facilitate the curing reaction of CR stocks.

Table 3.6 Cure characteristics of different rubber compound

S. No.	Properties	Sample Description						
		Gum	**CB**	**NC**	**NB1**	**NB2**	**NB3**	**NB4**
1.	Minimum Torque (M_L) (lb.in)	0.47	0.49	0.46	0.66	0.66	0.74	0.95
2.	Maximum Torque (M_H) (lb.in)	5.88	5.93	5.48	6.33	7.29	8.36	10.74
3.	Scorch Time (t_2) Minute,	4.67	4.58	4.70	4.72	4.24	3.78	3.15
4.	Cure Time (t_{90}), Minute	25.67	16.08	19.17	22.13	22.18	21.24	21.81
5.	M_H–M_L	5.41	5.44	5.02	5.67	6.63	7.62	9.79

3.2.4. 2. Physico-Mechanical properties

Low water absorption and retention of electrical resistivity is important parameter for rubber components used in underwater environment apart from mechanical strength and acoustic transparency. Water absorption behaviour of all composites has been studied on rubber samples cut from moulded sheet of dimension (25×25×2mm). The absorption of water for filled composite reduced considerably compared to gum vulcanizate. Electrical properties were determined as per ASTM D 257 standard in a DavenPort electrical resistivity meter. Volume resistivity of the rubber filled with nanoclay and carbon black has been determined after 1 min of continuous electrification at 1000 V. It is observed that addition of fillers with good dispersion improves electrical resistivity properties. Test results of physical properties for all formulated compound are given in Table 3.7. Tensile and tear tests were performed on a universal testing machine (Zwick 1476) at a cross-head speed of 500 mm/min at room temperature. Test specimens for the tensile and tear tests were punched out from the vulcanized sheets. Addition of 5 parts naoclay to the gum CR improves tensile strength from 11.93 to 15.79 MPa (> 30% increase) and tear strength from 183 to 260 N/cm (> 50% increase). Similar improvement was noted for 5 parts CB as single filler but when these two fillers are combined, mechanical properties are improved enormously, as it is seen in NB1 sample.

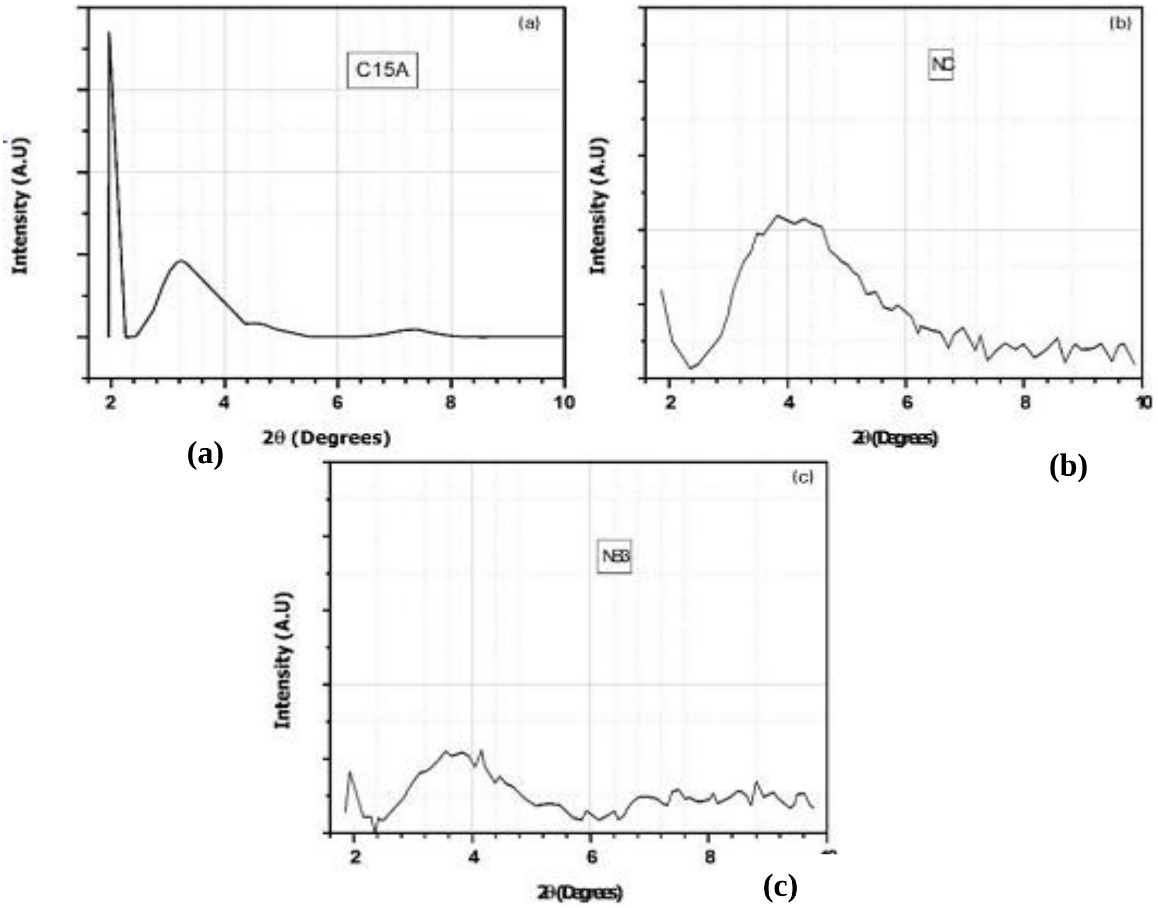
Table 3.7 Physical properties of different rubber compound

S. No.	**Properties**	**Sample Description**						
		Gum	**CB**	**NC**	**NB1**	**NB2**	**NB3**	**NB4**
1.	Saltwater (3.5 % NaCl solution) absorption, % wt gain, 40 °C 24 hrs	0.38	0.27	0.25	0.24	0.24	0.24	0.24
2.	Volume resistivity @ 1000V (Ωcm)	3.00×10^{11}	1.97×10^{11}	2.70×10^{11}	1.78×10^{12}	1.76×10^{12}	1.64×10^{12}	2.35×10^{12}
3.	Tensile strength (MPa)	11.93	16.46	15.79	19.18	19.78	21.54	21.37
4.	Tensile stress at 300% EB (MPa)	1.39	2.08	1.94	2.66	3.65	4.62	5.69
5.	Elongation at Break %	1097	1014	1047	1105	888	813	712
6.	Tear strength (N/cm)	183	212	260	316	360	410	448

To understand the effect of carbon black loading on the mechanical properties of the nanocomposite, loading of N550 is varied from 5 phr to 20 phr. With increasing filler loading, the tensile strength increases up to 15 phr loading, beyond which the properties are not changed considerably. The incorporation of 15 Phr carbon black into nanoclay filled composite enhances tensile strength by 90% and tear strength by more than 100%, which could be attributed to a synergistic effect between the fillers. These results depict that the carbon black filled nanocomposite (NB3) has outstanding tensile and tear strength when these are compared with the conventional carbon black and inorganic mineral filler filled vulcanizate reported by previous workers. Thus, it can be said that, although with the addition of nanoclay, there is some improvement over carbon black filled samples at every loading, the best improvement in mechanical strength can be seen with 15 phr of carbon black loading.

3.2.4.3 Structural Analysis of Nanocomposites

The XRD results on nanoclay powder, nanoclay filled CR composite (NC) and optimised compound containing both nanoclay and carbon black (NB3) are shown in Figure 3.1. The XRD measurements were carried out in an expert model of Philips diffractometer with a Cu Kα radiation (40 kV, 40 mA). The nanoclay powder (C15A) shows intensity peak at $2\theta = 2.9$ and 7 but addition of nanoclay into the rubber matrix shift the peak towards lower angle.



(a) (b) (c)

Figure 3.1 XRD Graphs for (a) nanoclay (C15A), (b) nanoclay composite (NC) and (c) composites with nanoclay and carbon black (NB3).

In CR having only nanoclay filled composite, there is an evidence regarding presence of intercalated clay structures in the rubber matrix since particular peaks are obtained at relatively lower angles with reduced intensity. Addition of CB particles into nanocomposite improves mechanical properties as seen from Table 3.7. This is due to carbon black structures and good interactions with nanoclay are responsible in increasing the gap amongst the clay platelets. CB might have enhanced the extent of intercalation of CR macromolecules through the clay platelets. It is understood from XRD graphs that carbon black filled nanocomposite does not have ordered exfoliated structures but shown aggregated and intercalated form in rubber matrix. To confirm the aggregate and intercalated structures, morphological investigation was carried out using TEM observation.

3.2.4.4 Morphology using TEM

TEM, unlike XRD, provide the information about the spatial distribution of clay layers or structural heterogeneities in nanocomposites. JEOL JEM-2100 transmission electron microscope equipped with lanthanum hexaborate filament (acceleration voltage of 200 kV and beam current of 116 μA) was used for observing the dispersion of the nanoclay and CB in neoprene rubber. The TEM micrographs of CR nanocomposite and CR nanocomposite filled with carbon black loading is shown in Figure 3.2. The morphology appeared to be intercalated with some partial exfoliation of the silicate layers. Neverthless, addition of carbon black form complex intercalated structure with nanoclay and rubber matrix and there is tendency for CB particles to associate around the NC layers.

On increasing the amount of CB above 15 phr, the nature of layered structures remains almost same along with increased population of intercalated and aggregated structures. The clay layers appear to form long continuous structures in between spherical carbon black particles. The carbon black particles are more uniformly distributed among the intercalated clay layers and these two fillers interaction giving rise to reinforced intercalated structure. This emphasizes the role of matrix-filler interaction. TEM micrographs displayed predominantly intercalated and aggregated structure in presence of both nanoclay and carbon black fillers in rubber matrix. The improvement of tensile and tear strength properties of the rubber composite, as observed from Table 3.7, also confirmed the TEM results. It can be concluded that CB plays a major role in the dispersion, intercalation, and exfoliation of NC in an optimum loading. 5 phr NC in 15 phr FEF loaded CR is found to be the optimum.

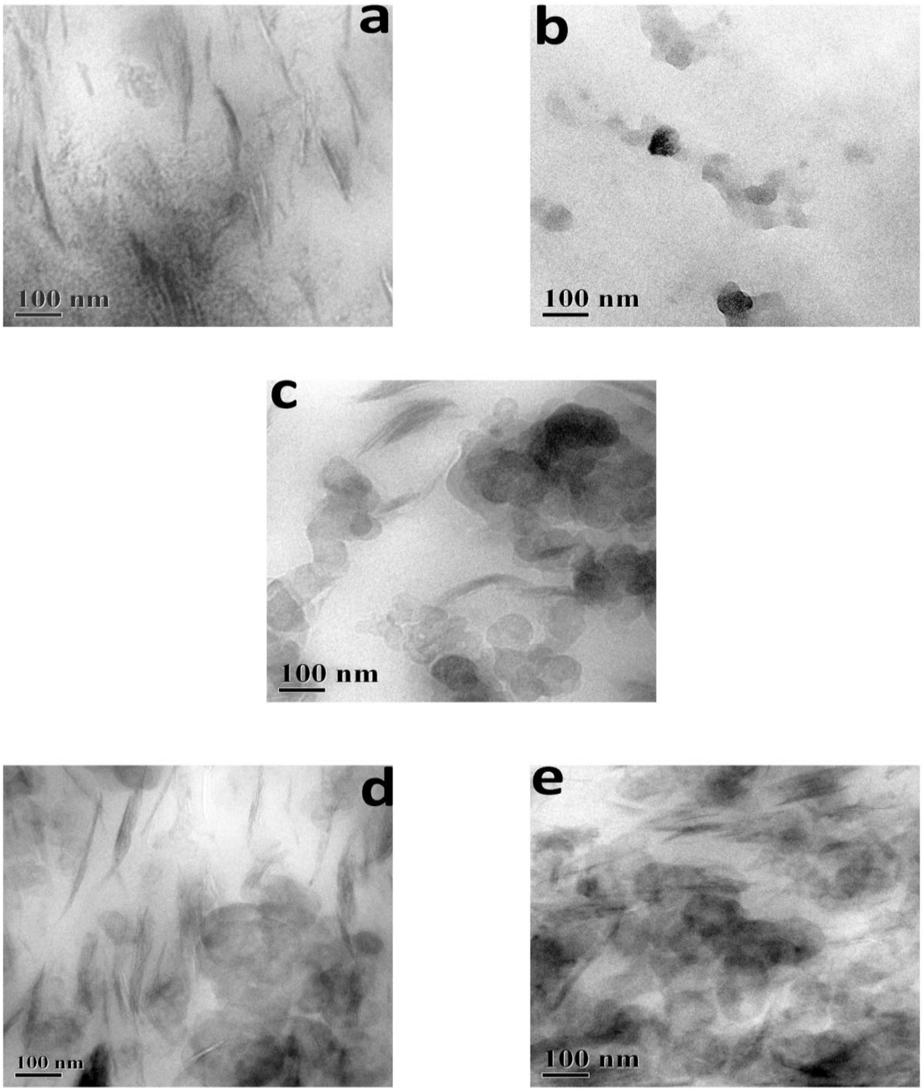


Figure 3.2 TEM photomicrographs of CR composites at 25 KX magnification: (a) CRwith 5 phr nanoclay (NC), (b) CR with 5 phr nanoclay with 5 phr CB (NB1), (c) CR with 5 phr nanoclay with 10 phr CB (NB2), (d) CR with 5 phr nanoclay with 15 phr CB (NB3) and (e) CR with 5 phr nanoclay with 20 phr CB (NB4).

3.2.5 Conclusions

Rubber nanocomposite based on polychloroprene was studied by varying the carbon black loading in rubber filled with 5 phr nanoclay. Master batch blending of rubber and nanoclay is adopted in early mixing cycle for better dispersion. The incorporation of 15 Phr carbon black into nanoclay filled composite enhances tensile strength by 90% and tear strength by more than 100%. Low water absorption and improvement in electrical resistivity is also observed for the optimised vulcanisate (NB3) compared to gum compound. XRD results indicated that carbon black might have enhanced the extent of intercalation of CR macromolecules through the clay platelets. TEM results showed that clay layers appear to form long continuous structures in between spherical carbon black particles leading to the formation of intercalated and aggregated structures. These results indicate that nanocomposite containing a mixture of organoclay and carbon black in right proportion can be a substitute for rubber components used in underwater sensor application.

3.3 COMPARATIVE STUDY OF CURING AGENTS ON NANOCLAY FILLED POLYCHLOROPRENE RUBBER COMPOSITES

3.3.1 Introduction

Polychloroprene is considered to be found maximum use in underwater transducer encapsulation application due to easy processablity, tunability and its balance of properties. The mechanical, electrical, elastic, dynamic properties of the final rubber products are influenced by various factors like the nature of rubbers, types of fillers, curing system and temperature etc [90]. A selection of correct choice of curatives or vulcanizing agent is necessary to obtain rubber products with best possible properties. Chloroprene rubber is generally vulcanized using metallic oxides curing systems [91, 92]. Use of 4 parts magnesium oxide (MgO) and 5 parts zinc oxide generally results in a good balance of processing safety and cure rate. Zinc Oxide is a common curative for chloroprene rubber but in some cases lead oxide is also used. Use of combination of magnesium oxide and zinc oxide generally results in a good balance of processing safety and cure rate. One of the key concerns of these CR is its higher percentage of water absorption for continuous exposure to sea environments and related changes in properties. For improved water resistance, a read lead (Pb_3O_4) is commonly employed in curing chloroprene rubber [93]. Conventional rubber composite filled with carbon black and curing agents are in use; however, the effect of curing agents on NC and NC/CB reinforced chloroprene rubber for underwater rubber encapsulation has not been reported much in the literatures. In this study, influence of curing agents on nanoclay and nanoclay/carbon black reinforced chloroprene rubber compounds are examined in order to evaluate the best possible composition with improved water resistant property for under water acoustic encapsulant. The present work discuss the effect of two types of curing agents on the cure behaviour, rubber filler interaction, mechanical and electrical properties and changes of these properties on salt water ageing to select the improved composite for requirement of encapsulant for underwater sensor applications.

3.3.2 Rubber Formulation and preparation

The compound formulations for both zinc oxide and lead oxide are prepared in a laboratory two roll mill and are given in Table 3.8. Mixing of compound for gum samples is followed as per the order in single stage mixing but for nanoclay filled compound, master batch containing CR and nanoclay is prepared first and then other ingredients are mixed as per the formulation given in Table 3.8.

Table 3.8 Compound formulation

Ingredients	**Gum/Z**	**NC/Z**	**NB3/Z**	**Gum/Pb**	**NC/Pb**	**NB3/Pb**
Neoprene W	100	100	100	100	100	100
Nanoclay	-	5	5	-	5	5
MgO	4	4	4	-	-	-
St. acid	1	1	1	1	1	1
HS	1	1	1	1	1	1
4020	1	1	1	1	1	1
FEF	-	-	15	-	-	15
Pb_3O_4	**-**	**-**	**-**	**6**	**6**	**6**
ZnO	**5**	**5**	**5**	**-**	**-**	**-**
NA 22	0.6	0.6	0.6	0.6	0.6	0.6
MBTS	-	-	-	1.5	1.5	1.5
Total	111.1	128.1	138.1	111.1	128.1	138.1

3.3.3 Results and Discussions

3.3.3.1 Cure Characteristics

The cure characteristics of the different rubber compounds Gum/Z to NB3/Z and Gum/Pb to NB3/Pb were studied at 150 ^{o}C as per respective cure time obtained from rheogram and are given in Table 3. 9.

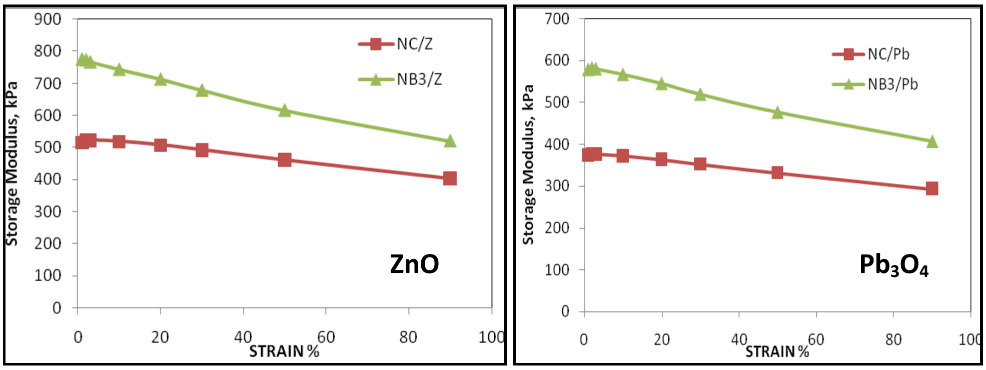
Table 3.9 Cure Characteristics of Rubber Compounds

Sample Designation	**Minimum torque (dN·m)**	**Maximum torque, (dN·m)**	**Scorch time, mts (ts_2)**	**Optimum cure time t_{90} (min)**
Gum/Z	0.48	4.20	5.63	19.22
NC/Z	0.56	4.59	7.03	26.59
NB3/Z	0.73	7.56	4.67	19.87
Gum/Pb	0.53	4.64	5.14	17.71
NC/Pb	0.55	4.93	6.76	16.53
NB3/Pb	0.89	7.71	4.40	15.95

The results show that cure reaction is fast with comparable scorch safety for red lead system compared to zinc oxide. For example nanoclay and dual filler filled rubber compound, the cure time for red lead cured sample is 16 and 15 minutes against 19 and 26 minutes that of zinc oxide.

3.3.3.2 Strain sweep Studies

The strain sweep measurements on vulcanized samples were conducted by RPA 3000 to study the rubber–filler interaction and are shown in Figure 3.3. Strain sweep studies measures variation of storage modulus (G′) with the change in strain amplitude (Payne effect). The testing temperature was selected as 100 °C and the shear strain was varied from 0.5% to 100% keeping the frequency of measurements at 1.0 Hz. Results show that the difference in storage modulus measured at 1% and 100% strain is 88 kPa for NB3/Pb sample against 194 kPa for NB3/Z. The sample NB3/Pb shows minimum value in storage modulus (i.e., lower the Payne effect) due to better polymer filler interaction compared to sample NB3/Z.



(a) **(b)**

Figure 3.3 Strain sweep for composites cured with (a) Zinc oxide and (b) Lead Oxide.

3.3.3.3 Physico-mechanical Properties

A comparative study on the influence of the zinc oxide vs. red lead on the physico-mechanical properties has been carried out and the results are given in Table 3.10. No much difference in the tensile and tear strength properties is observed. Compound with zinc oxide shows marginally higher modulus, tensile strength and comparable electrical resistivity properties.

Table 3.10 Physio-mechanical properties of compounds

S. No.	**Properties**	**Sample Description**					
		Gum/Z	**NC/Z**	**NB3/Z**	**Gum/Pb**	**NC/Pb**	**NB3/Pb**
1.	Hardness, Shore A	38	41	51	37	42	50
2.	Salt water absorption, % at 40°C for 24 hrs (after 1 week)	0.68 (1.81)	0.65 (1.75)	0.60 (1.65)	0.31 (0.66)	0.29 (0.60)	0.26 (0.28)
3.	Tensile strength, (MPa)	8.60	11.35	19.21	8.31	11.19	18.66
4.	M 300% (MPa)	1.58	2.70	4.96	1.52	2.09	4.24
5.	Elongation at Break (%)	1081	1061	849	1085	1061	901
6.	Tear strength (N/cm)	192	263	455	183	254	412
7.	Vol.Resistivity @1000V, Ωcm	4.80×10^{10}	5.08×10^{10}	6.23×10^{10}	6.99×10^{10}	5.16×10^{11}	5.12×10^{11}

Though comparable mechanical and electrical properties are obtained for both curative filled systems, the water absorption of compound with lead oxide curing system is lower than the compound with zinc oxide based cure system. Effect of compound and curing system on tensile strength before and after ageing is studied and the test results are plotted in Figure 3.4.

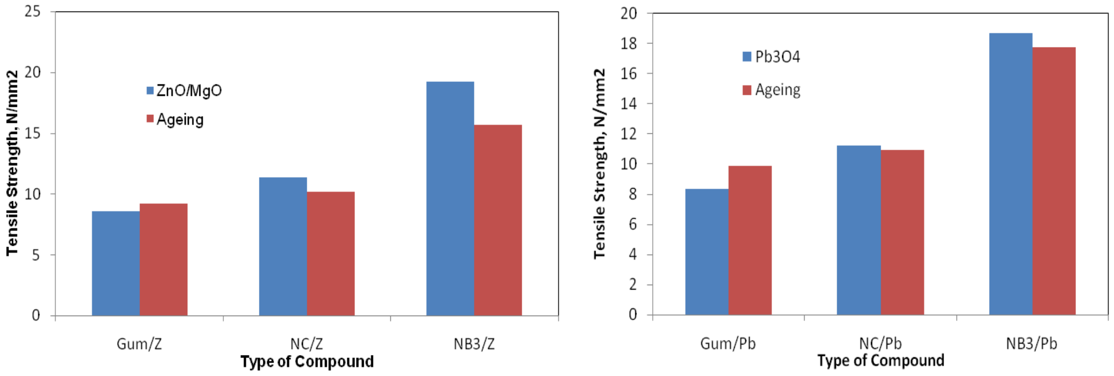


Figure 3.4 Effect of curing agent on tensile strength before and after ageing.

Similar to lower water absorption, retention of tensile strength property after subject to saltwater ageing for 7 days at 40 ^{o}C is higher for compound with lead oxide cure system. The maximum retention is observed for the compound filled with dual filler in lead oxide cure system. The lower absorption and retention of tensile properties on ageing by red lead cured rubber is a result of lower levels of water soluble products formed during vulcanization.

3.3.3.4 Morphology by XRD

The XRD results on organo-clay powder (nanoclay), nanoclay filled CR composites (NC/Z and NC/Pb) and optimised compound containing both nanoclay and carbon black (NB3/Z and NB3/Pb) are shown in Figures 3.5 to 3.7.

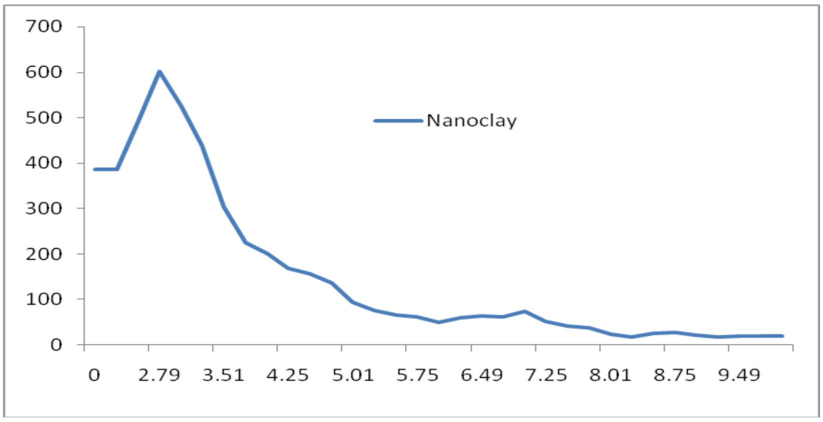


Figure 3.5 XRD Graphs for nanoclay (C15A).

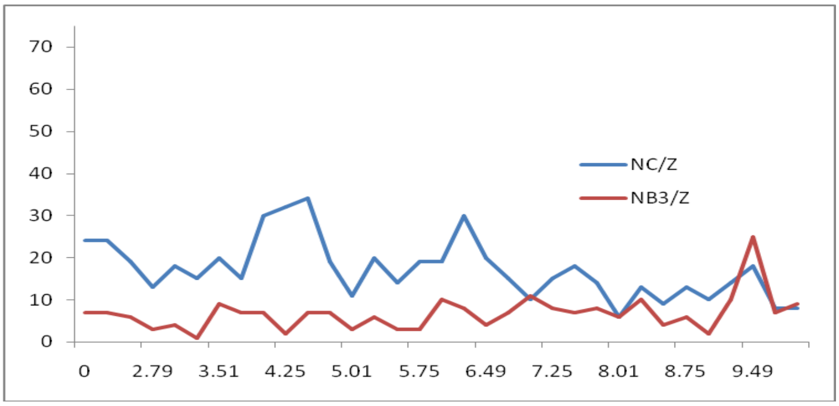


Figure 3.6 XRD Graphs for nanoclay and hybrid filler composites cured by ZnO.

The intensity of the peak reduced for the composites cured by lead oxides compared to composites cured by ZnO system. This can be explained due to faster activity of lead oxide, which facilitates interaction of fillers and increses the gallery gap of nanoclay for improved intercalation.

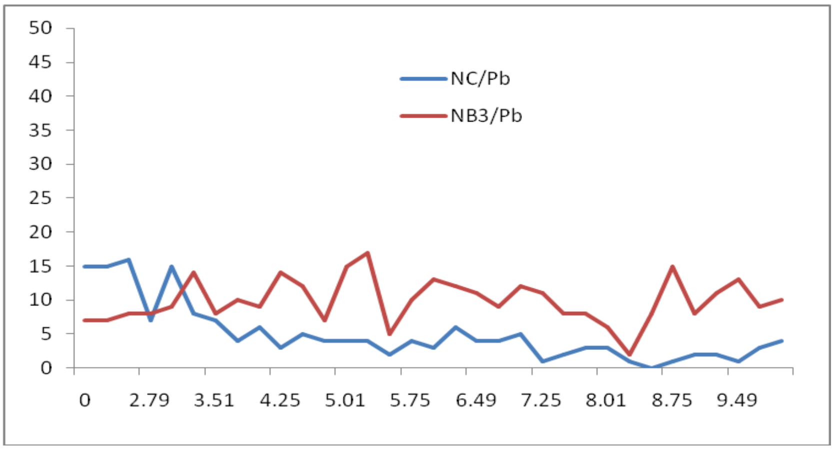


Figure 3.7 XRD Graphs for nanoclay and hybrid filler composites cured by PbO.

3.3.3.5 Dynamic Mechanical characteristics

The dynamic temperature sweep tests were conducted within a temperature range of -60 ^{o}C to + 60 ^{o}C at a heating rate of 5 ^{o}C/ min keeping fixed frequency as 1 Hz and strain at 0.25%. The dynamic elastic modulus E′, loss modulus E″ and damping constant (tan δ) for both cure systems are plotted in Figures 3.8 to 3.13 to compare properties.

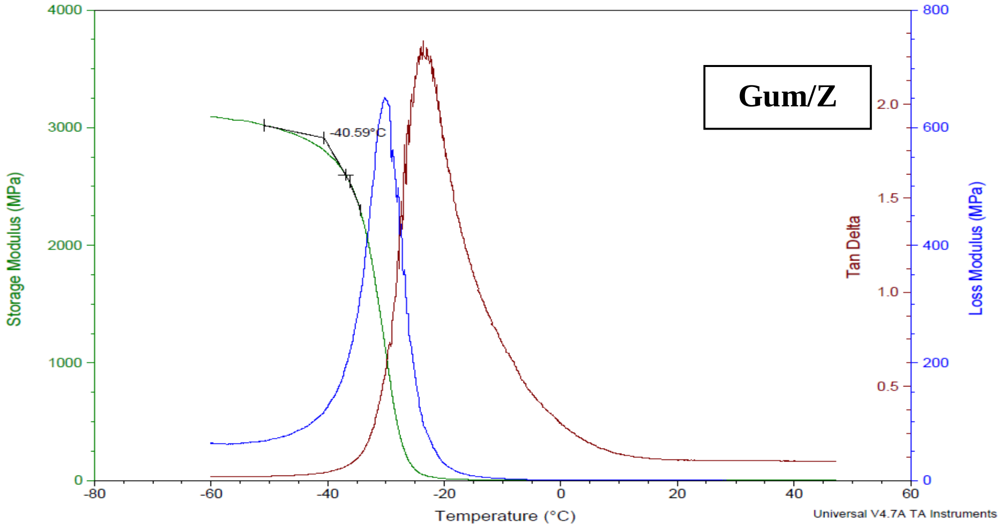


Figure 3.8 Variation of DMA properties with temperature for Gum (ZnO curing).

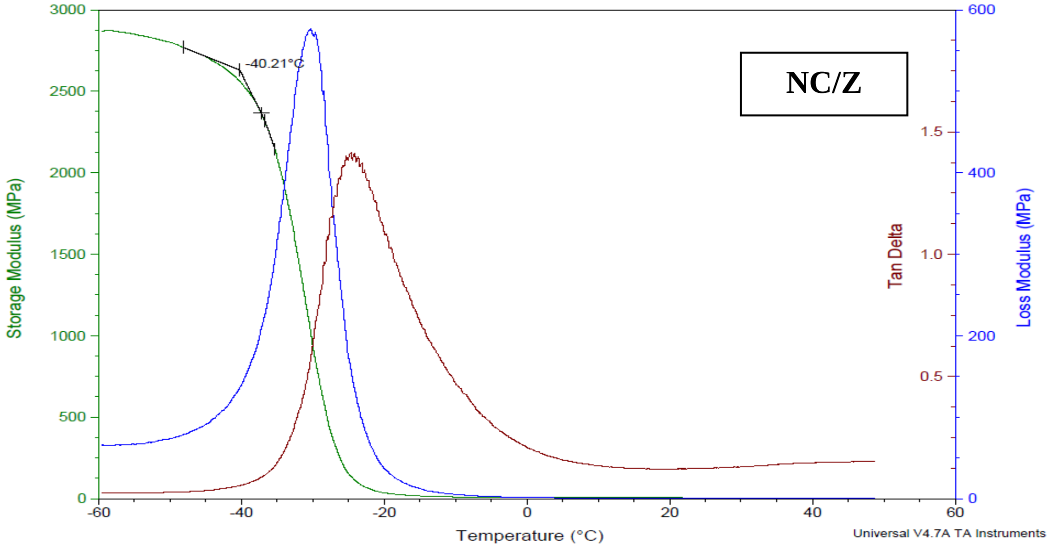


Figure 3.9 Variation of DMA properties with temperature for nanoclay composite (ZnO curing).

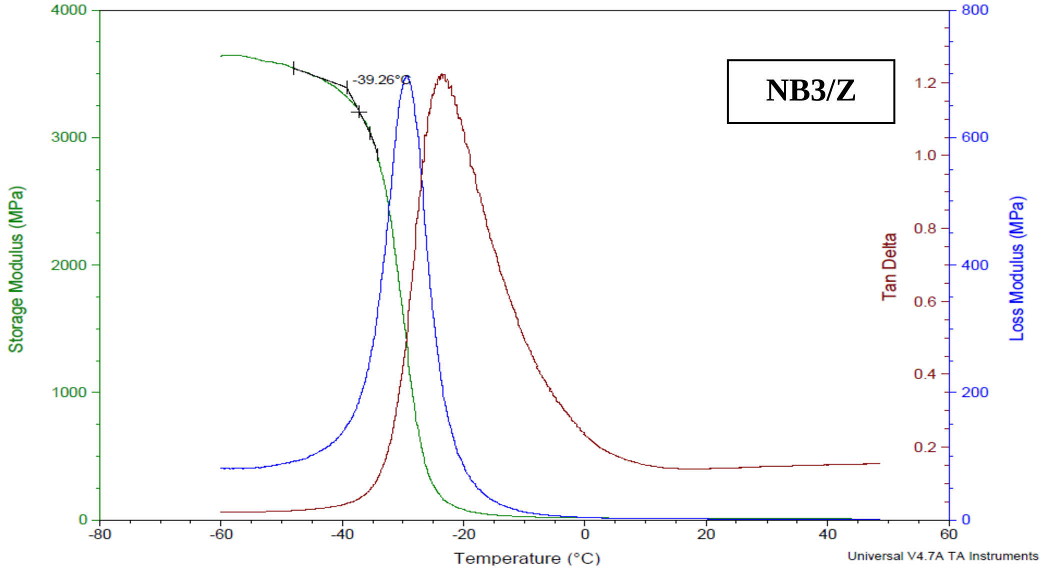


Figure 3.10 Variation of DMA properties with temperature for hybrid filler composite (ZnO curing).

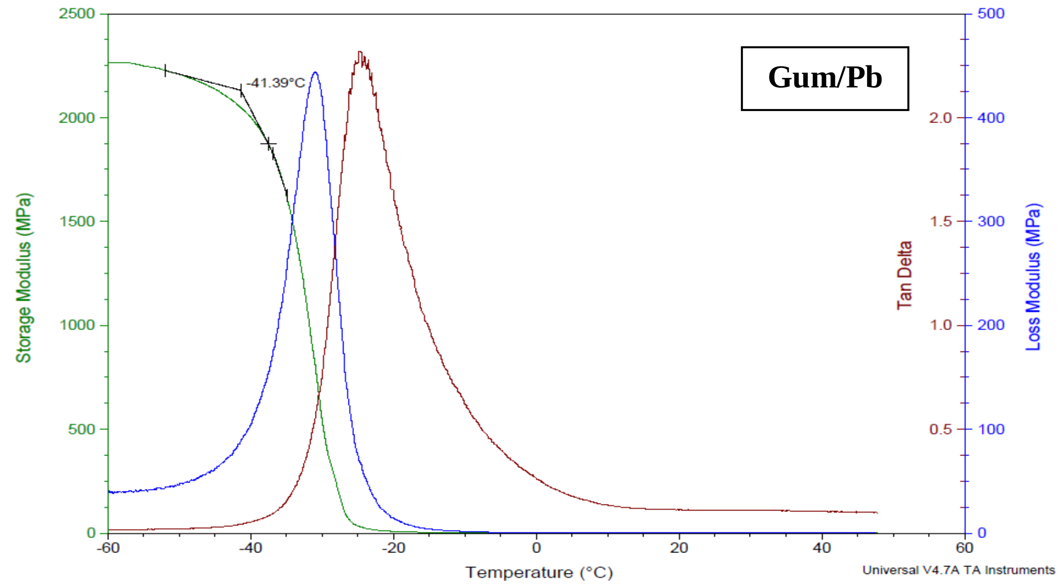


Figure 3.11 Variation of DMA properties with temperature for Gum (PbO curing).

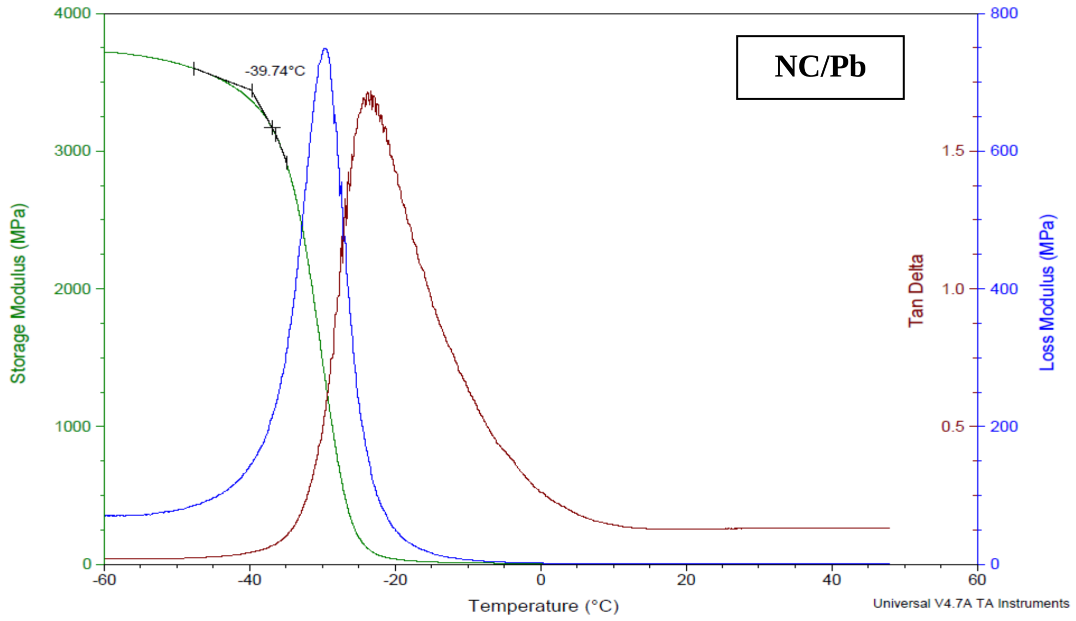


Figure 3.12 Variation of DMA properties with temperature for nanoclay composite (PbO curing).

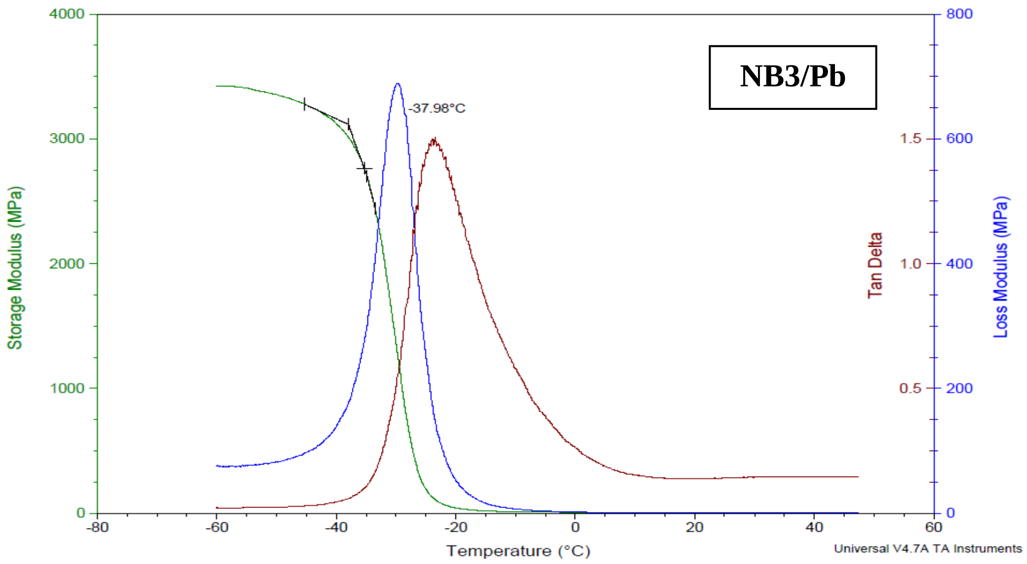


Figure 3.13 Variation of DMA properties with temperature for hybrid filler composite (PbO curing).

DMA results show that there is a clear improvement in storage modulus and damping constant for dual filler filled CR composite cured with lead oxide system. Material with higher storage modulus and lower damping constant is right candidate for acoustic sensor applications. Though both cured systems show lower damping constant (tan delta) and considered acoustic transparent material, lead oxide cure gives slight lower value requirement of encapsulant materials compared to zinc oxide cure system.

3.3.4 Conclusion

The effect of two types of curing agent on nanoclay and dual fillers filled chloroprene rubber was investigated. The cure reaction is fast with reasonable scorch safety for red lead system. Zinc oxide systems show marginally higher modulus, tensile strength and comparable electrical resistivity characteristics. Vulcanizate with lead oxide showed lower water absorption and maximum retention of properties on ageing. The effect is more pronounced when dual filler is incorporated in lead oxide cure system compared to that with ZnO curing systems. DMA studies proved that lead oxide cure gives slightly better storage modulus and lower damping constant, which is important for encapsulation materials. Nanoclay and carbon black in right proportion and cured by lead oxide cure system gave best balance of properties in CR based compound for development of encapsulant materials for underwater sensor applications.

3.4 Effect of two stage mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/Nanoclay compositions

3.4.1 Introduction

Elastomers are reinforced with fillers to improve their performance by incorporating conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate *etc*. Among all conventional fillers, carbon black is the most important reinforcing filler used in the rubber industry. In the past two decades, research was aimed to develop other reinforcing agents to replace CB in rubber compounds [94]. However, the layered silicates such as nanoclay with very small amount are efficient reinforcement in rubber and other polymers and lead to new and improved properties when compared to conventional micro composites [95–97] that are made using conventional fillers. The unique properties, imparted by nanoclay to rubber composites, have opened up a new prospect in developing CB–NC-hybrid nanocomposites via facilitating the possible partial replacement of CB with NC in rubber products without affecting the critical performance properties [98]. Several studies have described in literature [99, 100] that use of CB–NC hybrid filler in rubber matrix resulted in dramatic improvement of technical properties. In our recent work [101] it is emphasized that the addition of 5 parts of nanoclay to 15 phr carbon black filled CR matrix shows synergistic effect between the fillers and suggests that the reinforcement is due to a more developed filler network formation in hybrid filler system than that in single phase filler.

The present work aims to investigate the effect of two stage mixing and dispersion agent on the morphology and dynamic mechanical characteristics of CR nano-composites. In this study, CR/CB/organoclay (Cloisite 15A) nanocomposites based on five different compositions have been prepared and optimised for encapsulation of underwater acoustic sensors by the addition of dispersion agent and adoption of two stage mixing sequence. Calcium stearate as dispersion agent at constant loading is incorporated in all compositions in place of stearic acid which is a regular activator for sulphur curing and also acts as lubricant during the processing. The morphology of the nanocomposites is examined by high resolution TEM (HRTEM) and XRD analysis and the dynamic mechanical property of the composites has been studied by using a dynamic mechanical analyzer. The present paper discusses a preparation and characterization of CR/CB/nanoclay nanocomposites and optimization in conjunction with the measurement of various other technical properties like mechanical, electrical, and dynamic modulus etc for requirement of encapsulant materials used in underwater acoustic sensor applications.

3.4.2 Preparation of Compound Formulation

3.4.2.1 Effect of dispersion agent on compound formulation

Dispersion agents are mostly fatty acid derivatives and in particular, they improve dispersion of solid compounding materials with their distinct wetting properties. They reduce mixing time and have a positive influence on subsequent processing stages. Dispersion agents are usually added together with the fillers. When fillers are added in two steps the dispersion agents should be added at the beginning. Because of their high effectiveness, low dosage (1-3 phr) is often sufficient depend on filler and polymer matrix. In the present work, calcium stearate is selected to see its effect on filled CR composite. The formulation details are given in Tale 3.11.

Table 3.11 Effect of dispersion agent

Ingredients	**phr (**parts per 100 g of rubber)			
	Control	**CRC-0.5**	**CRC-1.0**	**CRC-2.0**
CR-W	100	100	100	100
Nanoclay	5	5	5	5
ZnO	5	0	0	0
St. acid	1	0	0	0
Cal. Stearate	**0**	**0.5**	**1**	**2**
HS	1	1	1	1
4020	1	1	1	1
FEF	15	15	15	15
Red lead	6	6	6	6
NA22	0.6	0.6	0.6	0.6
MBTS	1.5	1.5	1.5	1.5

3.4.2.2 Effect of two stage mixing on compound performance

All the rubber nanocomposites were prepared using a laboratory 6-inch two-roll mill. The two stage mixing sequence is followed for all five different compositions. The mixing procedure was divided into the two stages. In the first mixing stage, master batch (MB) comprising rubber, partial addition of nanoclay and carbon black, antidegradents and calcium stearate were compounded for 10 minutes and the mixture was ready after maturation time of around 2–3 hrs. MB compound was passed 3–4 times through the rollers having a tight nip gap of <1 mm for better distribution of ingredients. In order to see nanoclay effect alone, composition without addition of CB (Sample No: CR-0) in master batch was also prepared. The details of the formulations and samples identifications are given in Tables 3.12 and 3.13.

Table 3.12 Preparation of master batch (MB) - 1st stage mixing

Components	**Phr (**parts per 100 g of rubber)
Neoprene W	100
Cloisite 15A	3
Calcium stearate	1
TMQ[a]	1
IPPD[b]	1
FEF	10
Total	116

[a] 1,2-Dihydro-2,2,4-trimethyl quinoline, polymerised.

[b] {N-(1,3-dimethylbutyl)-N9-phenyl-p-phenylenediamine.

In the second mixing stage, the remaining nanoclay, carbon black, and cross linking agents like read lead, ethylene thiourea and MBTS were mixed with the first-stage MB mixture.

Table 3.13 Main Formulation - 2nd stage mixing

Components	**Phr (**parts per 100 g of rubber)				
	CR-0	**CR-1**	**CR-2**	**CR-3**	**CR-4**
MB	106 (**w/o FEF**)	116	116	116	116
Cloisite 15A	2	2	2	2	--
FEF[c]	--	---	5	10	10
Red lead (Pb_3O_4)	6	6	6	6	6
ETU (NA22)[d]	0.6	0.6	0.6	0.6	0.6
MBTS[e]	1.5	1.5	1.5	1.5	1.5
Total	116.1	126.1	131.1	136.1	134.1

[c] Fast Extrusion Furnace [d] Ethylene thiourea. [e] Benzothiazyl disulphide.

This rubber compound rubber was then subjected to rheometric study to obtain the optimum cure time by Moving Die Rheometer (MDR 2000 Alpha Technologies, USA) at 150 ^{o}C. The rubber samples were then cured until their optimum curing time (t_{90}) by a hydraulic press at 150°C, cooled to room temperature and kept for 24 h for maturation.

3.4.3 RESULTS AND DISCUSSION

3.4.3.1 *Cure characteristics*

The cure characteristics of the all composition are expressed in terms of scorch time (t_{s2}), optimum cure time (t_{90}) and minimum (M_L) and maximum (M_H) torque values. The compound filled with 1 phr dispersion agent provides optimum cure properties and are given in Table 3.14.

Table 3.14 Cure characteristics for dispersion agent effect

Samples ID	**M_L (N-m)**	**M_H (N-m)**	**t_{S2} (min)**	**t_{90} (min)**
Control	0.78	6.45	5.56	28.04
CRC-0.5	0.58	7.17	4.09	25.62
CRC-1	0.85	6.56	4.88	21.79
CRC-2.0	0.62	5.90	5.01	20.66

The cure characteristics for the effect of two stages mixing on compound formulation are given in Table 3.15. In table 3.15, it can be seen that torque values increased for CB–NC dual phase filler filled CR matrix compared to NC filled sample (CR-0) due to synergism of combination of fillers in a composition.

Table 3.15 Cure characteristics for two stages mixing

Samples ID	**M_L (N-m)**	**M_H (N-m)**	**t_{S2} (min)**	**t_{90} (min)**
CR- 0	0.62	4.29	6.77	19.55
CR-1	0.87	5.84	4.79	16.46
CR-2	0.91	7.41	4.86	19.94
CR-3	1.08	7.89	4.32	19.32
CR-4	1.60	9.90	3.98	24.09

3.4.3.2 Physico-mechanical properties

Tensile and tear strength properties for compound filled with various loading of dispersion agent are given in Table 3.16. The tensile and tear strengths are found to improve for compound (CRC-1) filled with 1 Phr of dispersion agent.

Table 3.16 Physical properties for dispersion agent compositions

Properties	**Sample Description**			
	Control	**CRC-0.5**	**CRC-1.0**	**CRC-2.0**
Tensile Strength (MPa)	17.66	19.39	19.47	16.82
M300% (MPa)	3.54	3.95	4.15	4.61
EB %	903.08	933.83	846.31	689.57
Tear Strength (N/cm)	311.10	330.43	359.53	365.99

Since better mechanical properties are achieved for CRC-1 vulcanizate, further studies are conducted to see two stage mixing effect for all the compound filled with optimum loading of 1 phr dispersion agent. The effect of two stages of mixing on physical properties is given in Table 3.17. The hardness values obtained for the entire compounds are within the range of 53–54 Shore A except for the sample (CR-0) hardness value 48 Shore A. The effect of nanoclay and CB-NC hybrid fillers on mechanical properties of CR was investigated and summarized in table 3.17.

Table 3.17 Physical properties for two stage compositions

Properties	**Sample Description**				
	CR-0	**CR-1**	**CR-2**	**CR-3**	**CR-4**
Tensile Strength (MPa)	14.86	18.26	19.62	16.82	16.35
M300% (MPa)	1.44	2.63	3.45	4.61	5.54
EB %	1085.08	1011.51	867.27	689.57	615.02
Tear Strength (N/cm)	291.09	381.18	481.88	492.34	476.51
Saltwater absorption, % weight gain, 30 ^{o}C for 7 days	0.73	0.68	0.60	0.62	0.67

Sample (CR-0) containing 5 phr nanoclay without CB in CR rubber, the tensile strength, elongation at break, and tear strength 14.86 MPa, 1085 %, and 291 N/cm were shown. Addition of 10 parts fast extrusion carbon black to the 5 phr nanoclay filled CR improves tensile strength from 14.86 to 18.26 MPa and tear strength from 291 to 449 N/cm. The compound (CR-2) has shown further improvement in tensile and tear strength as compared to CR-0 and CR-1 due to synergistic effect of hybrid fillers and the formation of nano-unit structures between CB and NC fillers. With increasing filler loading (CR-3), slight improvement in modulus and tear strength was observed but the tensile strength increases up to 15 phr CB loading, beyond which the properties are not changed considerably. Low water absorption (< 0.69) and volume resistivity in the range of 10^{11} to 10^{12} were obtained for dual filler filled rubber composites compared to water absorption (0.73) and volume resistivity 10^{12} values of CR-0 sample. Hence, it was noted from studies that the best improvement in mechanical strength can be seen in polychloroprene (CR) nanocomposites having 15 Phr carbon black and 5 Phr nanoclay with the addition of dispersion agent and process of using two stage mixing compared to single type of filler or single stage of mixing process used, in general, for preparation of rubber composites elsewhere.

3.4.3.3 XRD Patterns of CR Nanocomposites

Figure 3.14 represents the X-ray diffraction patterns of the CR nanocomposites for all five compositions. To ensure the dispersion of clay into the matrix XRD studies at lower angular range (2–10°) have been carried out. The XRD signatures clearly reveal the signatures of intercalated-to exfoliated structures of nano clay into the CR matrix.

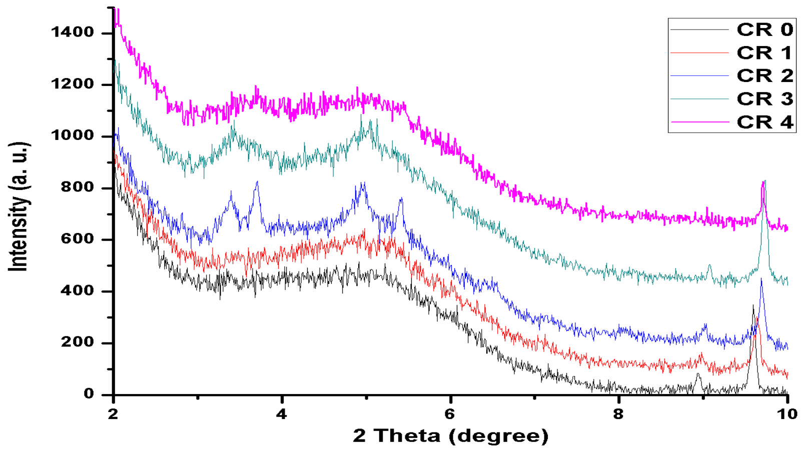


Figure 3.14 XRD patterns of the CR nanocomposites.

The CR4 (containing lowest amount of nanoclay) and CR 0 (without FEF) show distinct signature for near-exfoliated structures. CR 2 and CR 3 show signatures for the formation of nano-unit structures between NC and FEF.

3.4.3.4 Morphology of CR Nanocomposites by TEM

Figure 3.15 shows the result of TEM micrographs of CR nanocomposites. As observed in TEM photomicrographs that the sample CR 0 (without FEF) shows close to exfoliated morphology with signatures of intercalation. In CR1 (10 FEF and 5 clay) does not show any interaction of clay and CB to form the hybrid morphology. CR 2 patterns nano-hybrid morphology. The similar morphology persists in CR 3 with an onset of CB aggregation. CR 4 exhibits complete exfoliation of clay with the usual presence of CB network as shown in before percolation limit.

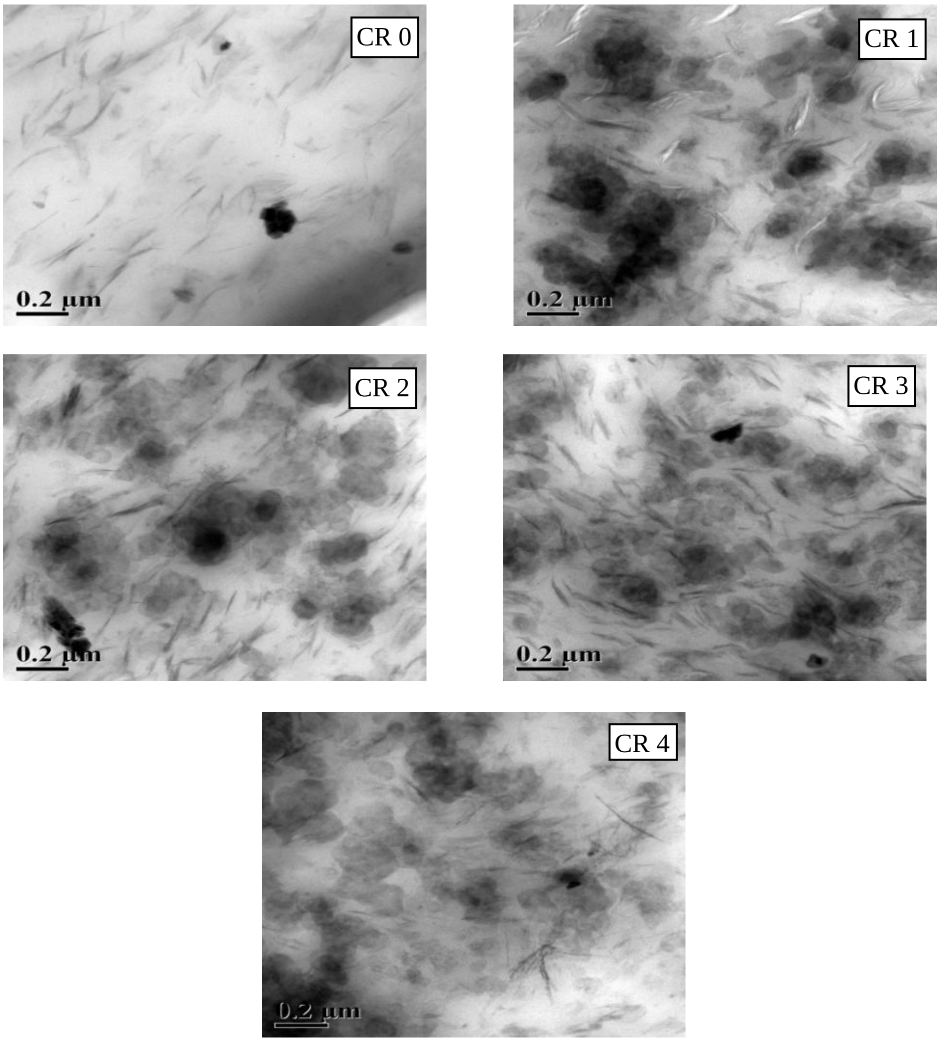


Figure 3.15 TEM photomicrographs of CR based nanocomposites.

3.4.3.5 *Dynamic mechanical properties of CR Nanocomposites*

The dynamic temperature sweep tests were conducted within a temperature range of -60 °C to + 60 °C at a heating rate of 5 °C/min keeping fixed frequency as 1 Hz and strain at 0.25% and the values are given in Table 3.18. The specification requirement of encapsulant is higher storage modulus and lower damping constant. The samples CR-2 and CR-3 shows optimum value of higher modulus and lower tan delta value within a particular temperature range (–20 to 40 °C) indicating better polymer filler interaction. Since onset of CB aggregation is observed for CR3 samples in TEM, CR2 is selected as optimum one and further studied for its properties. The storage modulus with temperature is also plotted in Figure 3.16.

Table 3.18 Temperature sweep (– 60 °C to + 60 °C) at 1 Hz frequency and 0.25% strain.

Sample	**Storage Modulus, E' (MPa)**			**Damping constant, tan δ**		
	–20 °C	0 °C	+40 °C	–20 °C	0 °C	+40 °C
CR0	61.36	11.96	13.84	1.10	0.19	0.10
CR1	98.21	13.49	5.81	1.24	0.25	0.17
CR2	123.00	15.93	9.28	1.25	0.30	0.15
CR3	80.74	13.92	13.13	1.09	0.26	0.10
CR4	77.93	11.53	6.07	1.18	0.30	0.16
CR5	110.00	17.07	5.52	0.98	0.31	0.21

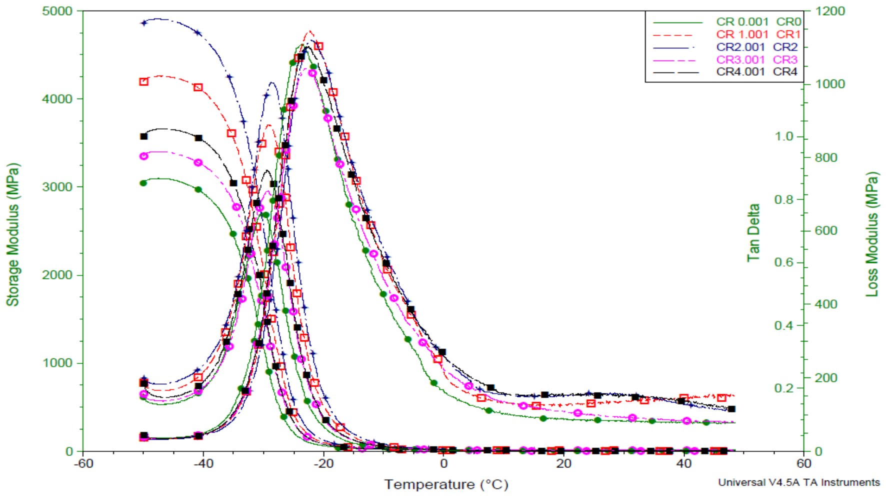


Figure 3.16 DMA plots for CR nanocomposites.

All the samples show a loss peak around –10°C. As filler content increases from CR1 to CR3 tan delta values gets lowered gradually. CR2 sample shows highest modulus among all composition selected which can be attributed due to the presence nano-hybrid morphology observed with the dual phase filler. Time temperature superposition (TTS) was studied for CR2 sample to predict its dynamic mechanical properties at any time and temperature. TTS plot for CR-2 sample results is shown in Figure 3.17.

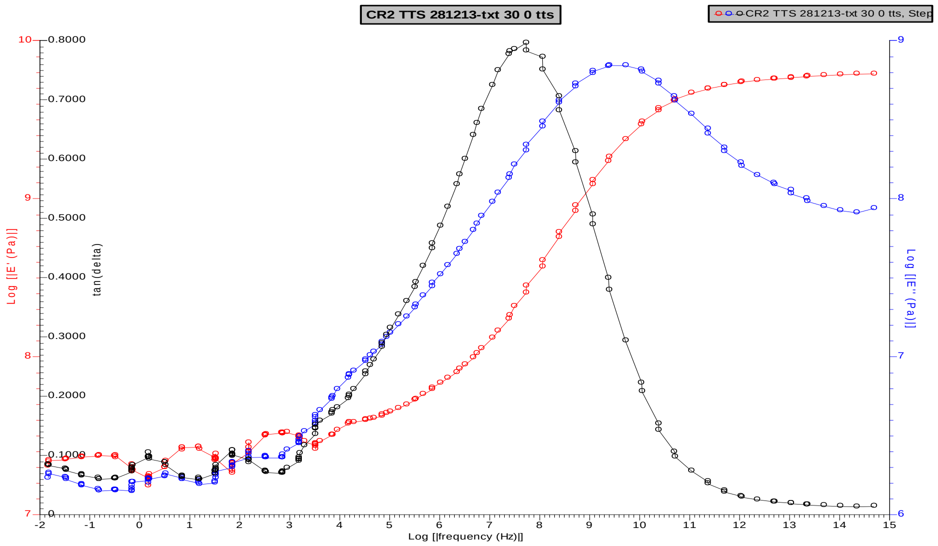


Figure 3.17 TTS plot of sample (CR-2).

It is noted from data analysis that modulus in the range of 2.75 to 3.18 × 10^{-7} MPa and damping constant of approximately 0.15 was obtained in the frequency range of 3–7 kHz, which is operating frequency of underwater sensor of interest. Hence, CR-2 sample is recommended for sensor encapsulation based on low loss tangent and better modulus values as obtained by DMA studies.

3.4.4 Conclusion

In this part of the study, dual filler system comprising of nanoclay and conventional filler carbon black was introduced to prepare nanocomposites based on CR. The effect of addition of dispersion agent and using of two stages mixing technique for carbon black/nanoclay dual-phase filled system in chloroprene rubber was investigated. The compound (CR-2) has shown improvement in tensile and tear strength as compared to CR-0 and CR-1 due to synergistic effect of hybrid fillers and the formation of nano-unit structures between CB and NC fillers. The better dispersion with improved morphology was observed in XRD and TEM analysis that clearly reveals the signatures of intercalated-to exfoliated structures of nano clay. DMA studies proved that CR-2 sample showed optimum value of higher modulus and lower tan δ values for operating frequency requirement for underwater sensors.

CHAPTER 4

NITRILE RUBBER NANOCOMPOSITES

4.1 INTRODUCTION

Rubber is an excellent material usable for underwater applications because of its easy fabrication. Conventional rubber compounds based on chloroprene and nitrile rubbers with high loading of fillers are currently employed as acoustic transparent window for encapsulation of transducers [102, 103]. Nitrile Rubber (NBR) is used as encapsulant and O-ring in underwater application where both acoustic and oil resistant properties are important. Nitrile rubber (NBR) is preferred over chloroprene rubber (CR), where oil resistance is important particularly in towed array sensors. The conventional rubber composites prepared with large particle size fillers absorb substantial amount of water and alter properties leading to product failures during their service life. Though many studies conducted on conventional rubber composites, not much research has been done for rubber nanocomposites for underwater acoustic application. The technical property improvement of nanocomposite leads the researchers to switch over to dual filler based rubber nano-composites for the production of potentially valuable materials [104, 105]. Herrmann et al. [106] reported superior mechanical properties in hydrogenated acrylonitrile butadiene rubber (HNBR) nanocomposites having CB (N339) and NC as compared to nanocomposites containing single type of filler. Feller et al. pointed out the occurrence of the adsorption of montmorilonite platelet on CB aggregates that can be reflected in percolation threshold, storage and loss moduli [107]. Konishi and Cakmak established the formation of 'nano-unit' comprising of primary particles of carbon black and nano-clay platelets that contributes substantially in electrical properties of the composites [108]. Praveen et al. also explained 'nano-unit' like microstructure formation in case of a clay loading of 10 phr along with 20 phr of CB in SBR nano-composite, resulting in dramatic improvement of technical properties [109]. Etika et al. put forward a theory based on 'haloing effect' that involves stabilization of the NC platelets by surrounding CB particles [110]. This unique microstructures development ultimately influences the electrical and mechanical properties of rubber nanocomposites having both carbon black and nano-clay as a filler system.

Elastomer nanocomposites based on NBR, Carbon black (CB) and Cloisite 15A Nanoclay (NC) are prepared via melt compounding using two roll mixing mill. Combination of CB along with variation in NC dosage has been carried out in order to evaluate the best possible composition for under water acoustic encapsulant. Calcium stearate was incorporated in place of stearic acid to aid in dispersion of NC in polymer matrix [111]. After preliminary investigation a modified formulation was also derived. The developed nanocomposite is well characterized by physico-mechanical and electrical properties. The morphology of the nanocomposites was examined by HRTEM and XRD analysis and it was correlated with dynamic mechanical study (DMA). The application window of the developed nanocomposites was also envisaged from DMA analysis. Acoustic measurements confirm the suitability of the prepared nano-composites to be used as an encapsulant for under water application.

4.2 Preparation of nitrile nanocomposites

All the NBR based nano-composites containing CB (reduces surface electromagnetic induced disturbances without affecting the volume resistivity) and NC were prepared at room temperature in an open two roll mill (Schwabenthon, Berlin, Germany) of 300 mm length and 170 mm diameter with a friction ratio of 1:1.2 for 20 mins.

Table 4.1 Compounding formulation of NBR based encapsulant

Ingredients	**Phr (parts per hundred rubber)**					
	A	**B**	**C**	**D**	**E**	**F**
Nitrile rubber	100.0	100.0	100.0	100.0	100.0	100.0
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5
Accinox TMQ[a]	1.2	1.2	1.2	1.2	1.2	1.2
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Calcium stearate	1.0	1.0	1.0	1.0	1.0	1.0
Nanoclay	−	3.0	5.0	10.0	5.0	5.0
FEF N550	20.0	20.0	20.0	20.0	30.0	40.0
GPF-N660	10.0	10.0	10.0	10.0	10.0	10.0
Aromatic oil	2.0	3.0	3.0	3.0	4.0	5.0
ZDEC[b]	1.0	1.0	1.0	1.0	1.0	1.0
TMTD[c]	1.0	1.0	1.0	1.0	1.0	1.0
MBT[d]	0.5	0.5	0.5	0.5	0.5	0.5

[a]TMQ - 2, 2, 4-Trimethyl-1,2-dihydroquinoline [b]ZDEC – Zinc diethyldithiocarbamate
[c]TMTD – Tetramethyl thiouram disulphide [d]MBT – Mercaptobenzothiazol

The rheometer operated at 150 °C for half an hour maintaining a ±3° arc oscillation throughout the experiment. After mixing, the rubber compounds were allowed to settle for 24 h at room temperature (25 °C). Finally, these compounds were molded in the form of 1.5-2 mm thick sheets in an electrically heated hydraulic press at 150 °C. For each sample, molding time was maintained according to the respective OCT. The formulations of unmodified and modified NBR nano-composites are furnished in Tables 4.1 and 4.2.

Table 4.2 Optimized modified NBR formulation

Ingredients	**Phr (parts per hundred rubber)**			
	$B_{(mod,C,ZDEC(nil))}$ **[B1]**	**$B_{(mod,\ C\ interchanged)}$** **[B2]**	**$D_{(mod)}$** **[Dmod]**	**$B_{(mod\ cure\ package)}$** **[B3]**
Nitrile rubber	100.0	100.0	100.0	100.0
Sulphur	0.5	0.5	0.5	0.5
Accinox TMQ[a]	1.2	1.2	1.2	1.2
Zinc oxide	5.0	5.0	5.0	5.0
Calcium stearate	1.0	1.0	1.0	1.0
Nanoclay	3.0	3.0	10.0	3.0
FEF N550	20.0	–	20.0	20.0
GPF-N660	–	20.0	–	10.0
Aromatic oil	2.0	2.0	2.0	3.0
TMTD	1.0	1.0	1.0	1.0
MBT	1.0	1.0	1.0	1.0

4.3 Results and Discussion

4.3.1 Cure characteristics

Cure studies of NBR formulations were done in a Monsanto Rheometer 100S for 30 min at 150 °C and ±3° arc and the results are given in Table 4.3. Here it is important to mention that though a maximum torque for each of the samples has been mentioned, yet actually all reflected a marching behavior leveling out to a quasi plateau. This reflected the cure safety of all the samples.

Table 4.3 Cure characteristics of NBR based nanocomposites

Sample Designation	**Initial torque (dN·m)**	**Minimum torque (dN·m)**	**Maximum torque (dN·m)**	**Delta torque**	**Scorch time t_{s2} (min)**	**Optimum cure time t_{90} (min)**
A	43	20	72	52	1:30	10:00
B	45	24	79	55	0:45	10:00
C	45	25	78	53	0:45	10:00
D	44	24	78	54	0:45	10:00
E	45	27	83	56	0:50	10:00
F	52	29	89	60	0:50	10:00
[B1]	38	22	69	47	0:45	7:00
[B2]	38	21	68	47	1:00	5:50
[Dmod]	38	22	67	45	0:45	7:50
[B3]	36	22	71	49	0:45	6:50

It can be seen from the Table 4.3 that in modified formulation initial torque value decreases due to lower amount of reinforcing filler thus resulting in lower green strength. Lower amount of delta torque can also be explained from the same reason. Among the modified formulation [Dmod] having higher dosage of nano-clay results in highest optimum cure time.

4.3.2 Density and Hardness

The densities and hardness values of the nano-composites are summarised in Table 4.4. Both the values confer well to the requirements and vary according to the filler loading.

Table 4.4 Density and hardness of NBR nanocomposites

Sample designation	**Density (g/cc)**	**Hardness (shore A)**
A	1.152	68
B	1.155	70
C	1.152	70
D	1.155	70
E	1.163	75
F	1.175	80
[B1]	1.063	50
[B2]	1.089	49
[Dmod]	1.092	51
[B3]	1.104	51

Densities of the sample were targeted to be kept minimum to minimise the loss. With lowering amount of black, densities of the samples also decreases. Hardness of the samples were also checked and found to be as per requirement and follows the same trend as found in densities. Sample F having highest loading shows highest density and hardness value.

4.3.3 Mechanical properties

The details of mechanical testing data are furnished in Table 4.5. From the data, the synergistic effect on blacks and nanoclay in improving the mechanical properties of composites can be understood.

Table 4.5 Mechanical properties of NBR based nano-composites

Sample designation	**Tensile strength (MPa)**	**Modulus at elongation**			**%EB**
		100%	**200%**	**300%**	
A	11.6	1.39	2.56	3.9	690
B	11.9	1.73	2.90	4.9	614
C	11.1	1.85	3.47	5.3	562
D	11.1	2.12	3.89	5.9	515
E	12.8	2.12	4.13	6.4	553
F	13.9	2.78	5.7	8.9	455
[B1]	7.6	1.46	---	---	586
[B2]	6.5	1.25	2.08	3.07	590
[Dmod]	14.5	1.68	2.79	4.02	820
[B3]	14.3	1.37	2.25	3.31	771

The composites containing 5 phr of clay in conjunction with 20 phr of FEF filler (Dmod) and a combination of 3 phr clay with 20 phr FEF and 10 phr GPF (B3), respectively, resulted in best combination of mechanical properties. It is interesting to note that both the composites have displayed significantly high elongation at break.

4.3.4 X-ray diffraction studies

The XRD data of NBR based nano-composites were obtained from the diffractrogram and are presented in Table 4.6.

Table 4.6 XRD data for NBR based nano-composites

Param-eters	**Sample designation**										
	Pristine Clay	A	B	C	D	E	F	[B1]	[B2]	Dmod	[B3]
θ Value	1.49	---	1.17	1.15	1.15	1.13	1.09	1.065	1.105	1.115	exfoliation
$d_{(001)}$ space (nm)	2.96	---	3.771	3.853	3.836	3.904	4.047	4.16	4.05	3.95	
FEF/GPF/NC(15A)	N.A	20/10/0	20/10/3	20/10/5	20/10/10	30/10/5	40/10/5	20/0/3	0/20/3	20/0/10	20/10/3

The diffractograms were obtained by plotting scattering angle and intensity. Figure 4.1 shows diffraction curves for the unmodified NBR based nanocomposites. The result indicates that these nanocomposites show an intercalated type of morphology. The XRD diffractogram of modified NBR formulation shown in Figure 4.2 also indicates intercalated morphology except sample B3 where no diffraction peak is visible indicating an exfoliated morphology. Higher dosage of nano-clay leads to the formation of highly aggregated structure thereby reducing the possibility of exfoliation.

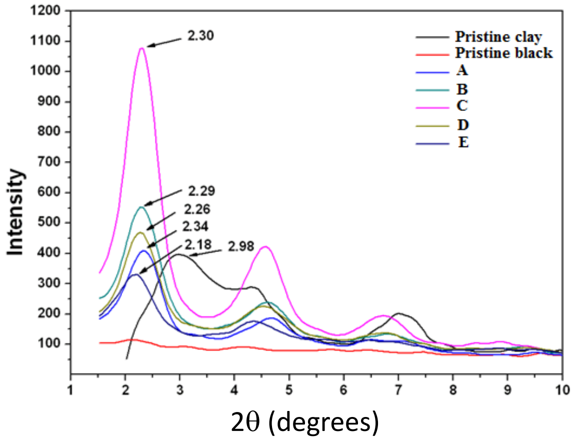


Figure 4.1 X-ray diffraction of un-modified NBR based nanocomposites.

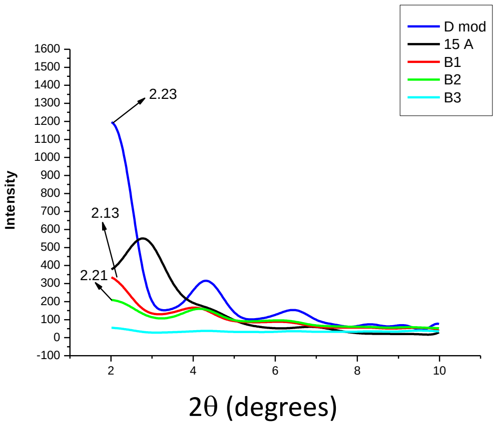


Figure 4.2 X-ray diffraction of modified NBR based nanocomposites.

4.3.5. Transmission Electron Micrograph studies

Transmission Electron Microscope allows a qualitative understanding of the internal structure and can directly provide information in real space, in a localized area on morphology and defect structures. Since the silicate layers are composed of heavier elements (Al, Si and O) than the interlayer and surrounding matrix (C, H and N), they appear darker in bright-field images. Therefore, when nanocomposites are formed, the intersections of the silicate sheets are seen as dark lines which are the cross sections of the silicate layers. Black tube like structures represents ZnO particles. The black spot represents carbon black particles. The two types of black that were used in this case differ only in particle size viz. FEF: 40 nm and GPF 50 nm. TEM micrograms of all the NBR nanocomposite samples (unmodified and modified) were recorded after cryo-microtomy and are presented in Figures 4.3 to 4.10.

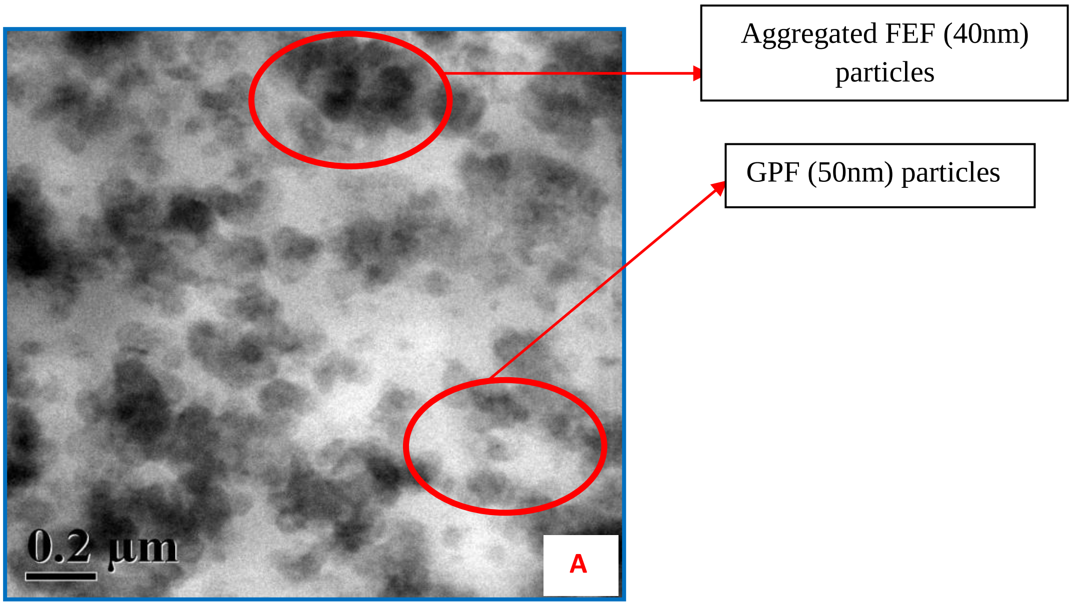


Figure 4.3 HRTEM image of NBR A.

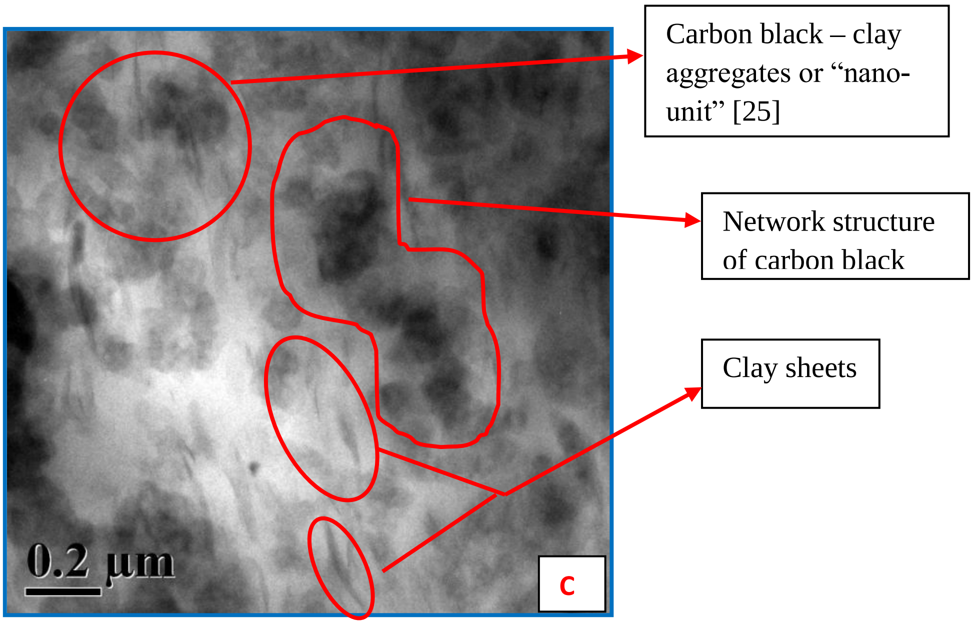


Figure 4.4 HRTEM image of NBR C.

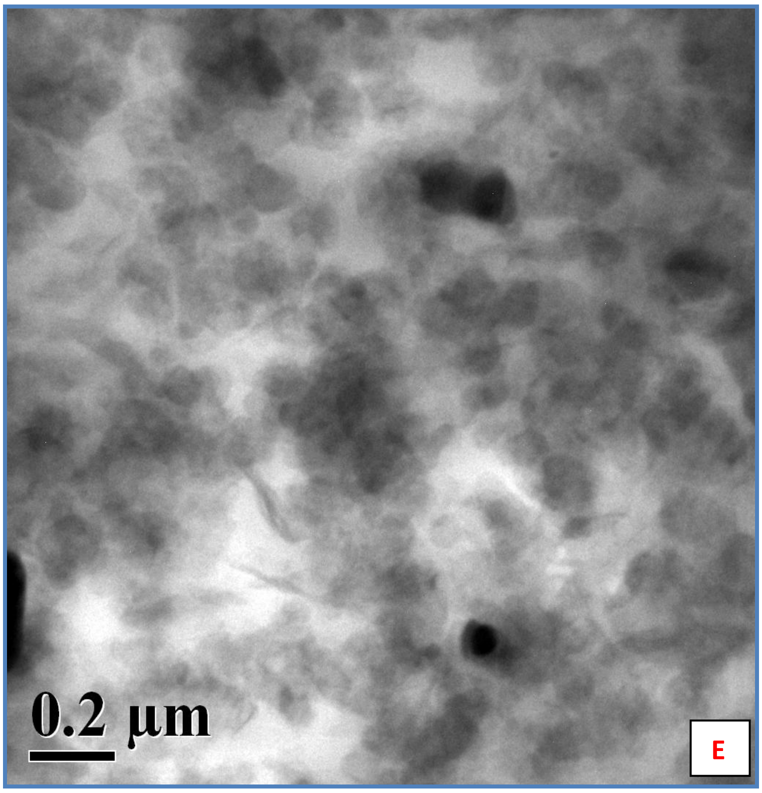


Figure 4.5 HRTEM image of NBR E.

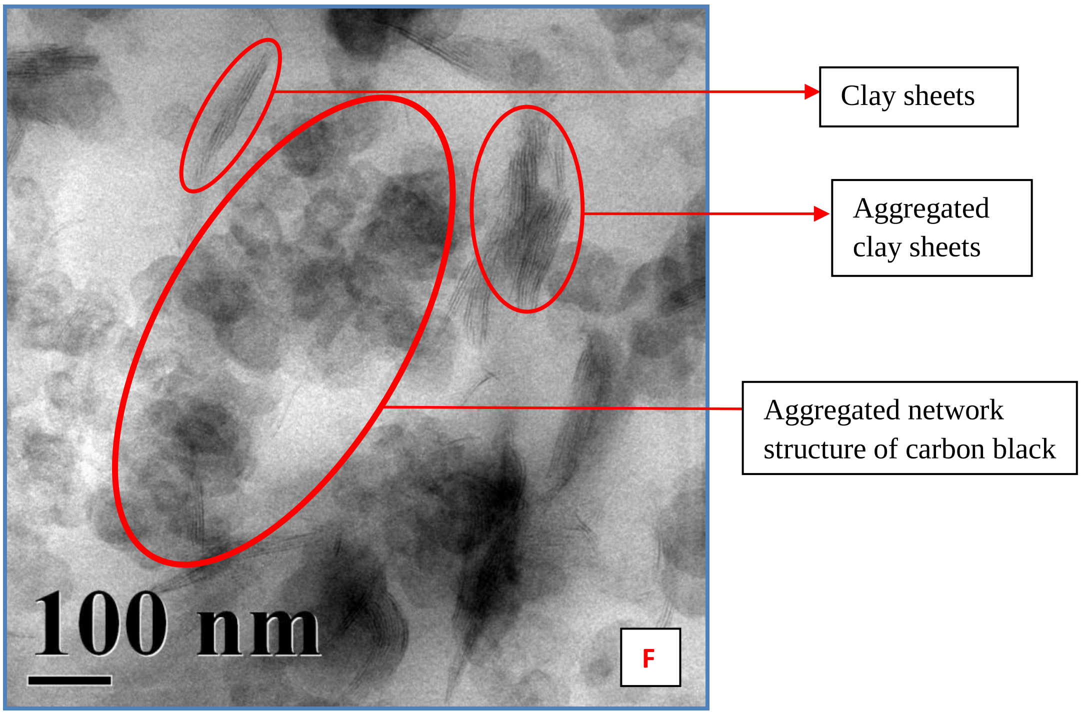


Figure 4.6 HRTEM image of NBR F.

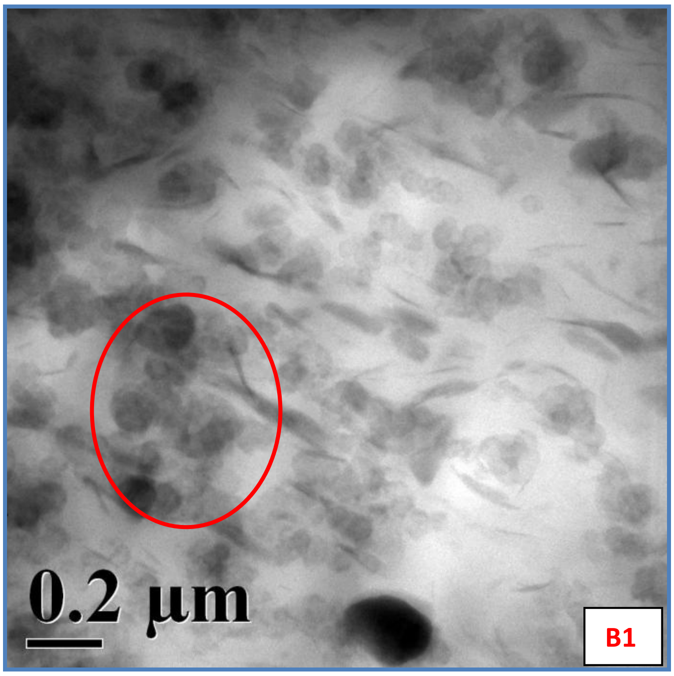


Figure 4.7 HRTEM image of B1.

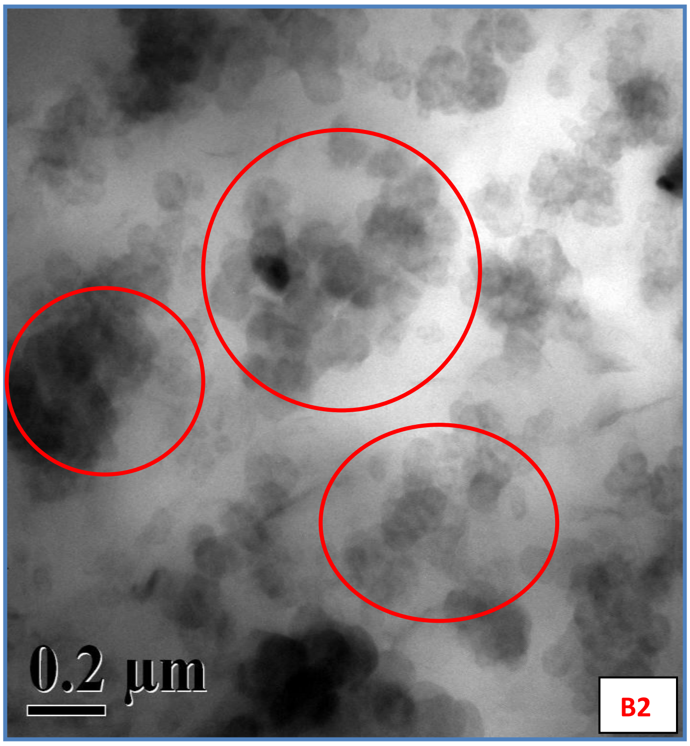


Figure 4.8 HRTEM image of B2.

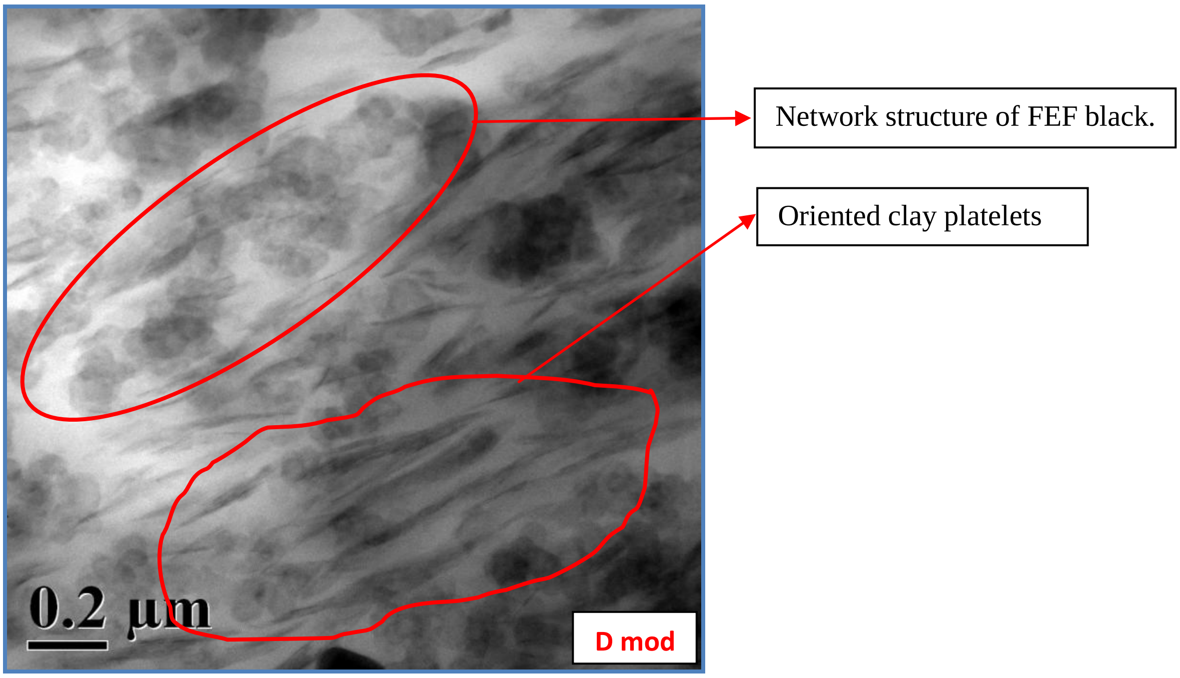


Figure 4.9 HRTEM image of Dmod.

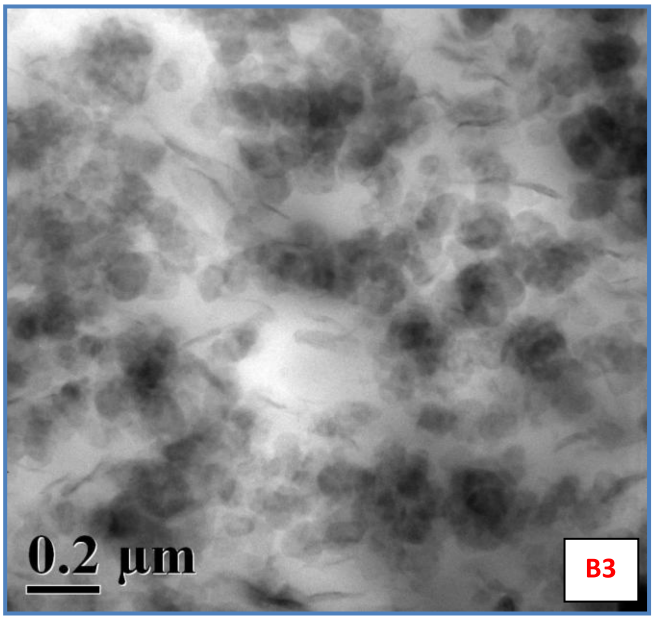


Figure 4.10 HRTEM image of B3.

For sample A (Figure. 4.3), no nanoclay is observed. Two types of carbon black is well characterised by their agglomeration tendency and extent of agglomeration. For sample C (Figure 4.4), presence of carbon black – clay 'nano-unit' was observed along with the formation of network structure of carbon black. Due to higher dosage of filler: (40 FEF) + (10 GPF), sample E (Figure 4.5) shows here filler aggregation, which is quite higher than other formulations, with occasional presence of nano-clay. Due to higher dosage of carbon black with respect to nano-clay in both E and F (Figure 4.6) carbon black structure dominates over nano-clay structure. For sample B1 (Figure 4.7), only one type of carbon black (FEF) is observed here with occasional clustering. The clay platelets are well separated but not uniformly dispersed. For sample B2 (Figure 4.8), agglomeration of GPF black was observed with poor dispersion of nano-clay which is reflected in its poor mechanical properties (lowest amongst the modified formulation). For sample [Dmod], (Figure 4.9) the dispersion has a particular direction with formation of network structure of FEF black particles which is reflected in its tensile strength. This morphological structure is distinctively distinct than all other formulation especially from B3 (Figure 4.10), where due to the presence of both types of black particles, filler-filler agglomeration tendency is found to be higher.

4.3.6 Crosslink density and water absorption

Schematic presentation of the crosslink density is presented in Figure 4.11. With increase in filler dosage as from A to F, physical crosslink density shows a gradual increasing trend. Combination of filler system shows better results in this respect, which is evident in case of modified NBR formulations.

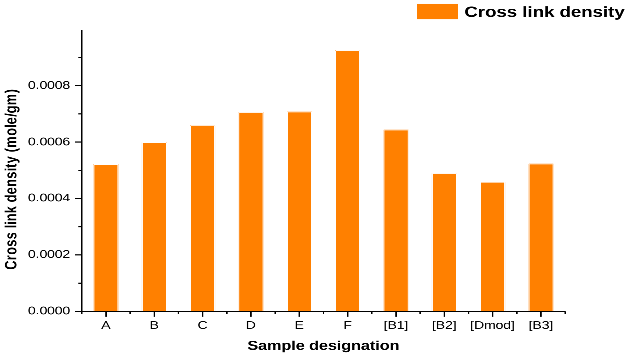


Figure 4.11 Crosslink density by equilibrium solvent swelling method.

From the plot of water absorption study (Figure 4.12), it can be seen that with increasing amount of nano-clay and combination of filler, resistance to water ingress increases. In case of sample F, higher amount of FEF filler leads to great extent of self aggregation rather than uniform distribution to prevent water absorption. In case of modified NBR formulations, B1 and B2 shows somewhat higher water absorption probably due to lower amount of nanoclay and usage of single filler system.

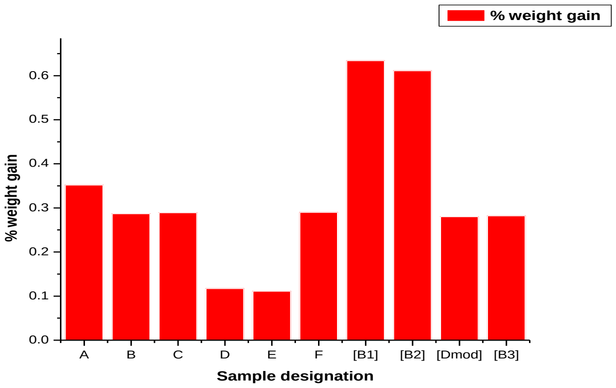


Figure 4.12 Water absorption study of NBR nano-composites.

For Dmod and B3, higher amount of nano-clay and a combination of filler system accounts for their low water uptake respectively. Thus, it can be concluded that except B1 and B2, all the samples offered water absorption values within the tolerance level (0.5%).

4.3.7 Electrical properties

4.3.7.1 Volume Resistivity

The DC volume resistivity of samples were measured and tabulated in Table 4.7. The DC volume resistivity data indicates that all the nano-composites falls under insulating category. With increasing filler dosage volume resistivity decreases almost linearly.

Table 4.7 DC Volume resistivity values

Sample designation	**DC volume resistivity (Ω Cm)**	**Thickness (mm)**
A	7.2970 E10	0.226
B	4.1406 E10	0.249
C	4.1036 E10	0.246
D	4.0759 E10	0.242
E	4.2214 E10	0.231
F	1.7270 E10	0.229
[B1]	7.6988 E10	2.38
[B2]	7.1364 E10	2.25
[Dmod]	7.7915 E10	2.45
[B3]	6.0822 E10	2.35

4.3.7.2 Dielectric Properties

Dielectric properties of the unmodified NBR composites and modified NBR composites where shown in Figures 4.13 and 4.14, respectively. Dielectric constant and dielectric loss were studied in the frequency range of 10 Hz – 1 MHz. Generally, the dielectric constant of a polymer arises due to the various polarization phenomena (electronic, dipole, ionic and interfacial) that come into play when the polymer is subjected to an oscillating electric field. With higher amount of filler as in sample F, interfacial polarization dominates as more interconnected network structure is formed, which is reflected in its higher dielectric constant value.

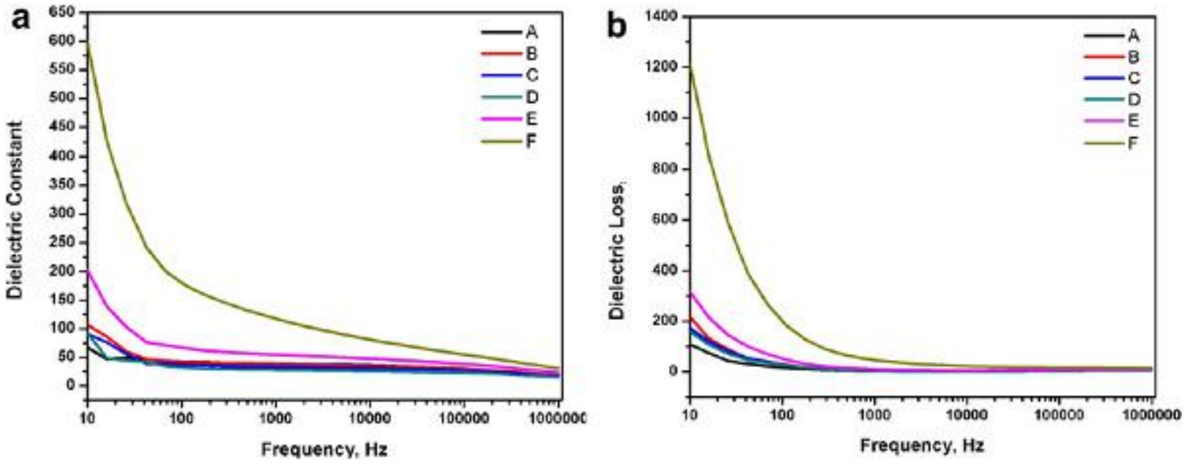


Figure 4.13 Dielectric constant and dielectric loss plot of unmodified NBR nano-composites.

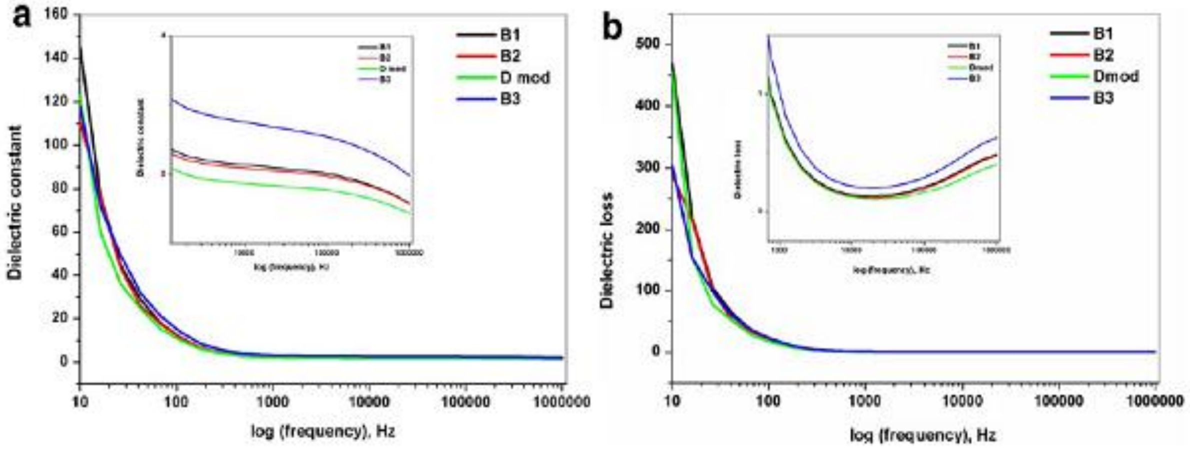


Figure 4.14 Dielectric constant and dielectric loss plot of modified NBR nano-composites.

D.C and dielectric loss values in the frequency range of 2–10 kHz for modified NBR formulations are given in Table 4.8. In the modified formulation B1, having 20 phr of high structure FEF black, shows higher DC at low frequency than Dmod as in the latter case presence of 10 phr nanoclay disrupts the structure of FEF. At higher frequency, B3 offers higher DC than Dmod. It is observed that for both the cases, the dielectric constant decreases with increasing concentration of nanoclay while it increases with increasing amount of carbon black filler.

Table 4.8 D.C and dielectric loss values in the frequency range of 2–10 kHz for modified NBR formulations

Frequency (Hz)	Dielectric constant				Dielectric loss			
	[B1]	**[B2]**	**[Dmod]**	**[B3]**	**[B1]**	**[B2]**	**[Dmod]**	**[B3]**
749.8	2.62	2.54	2.34	3.42	1.02	0.98	0.98	1.33
1211.5	2.38	2.32	2.11	3.11	0.61	0.59	0.58	0.81
1957.3	2.27	2.22	1.99	2.96	0.39	0.38	0.37	0.54
3162.2	2.21	2.16	1.94	2.87	0.27	0.26	0.25	0.37
5108.9	2.18	2.13	1.90	2.82	0.19	0.18	0.18	0.28
8254.0	2.15	2.10	1.88	2.78	0.16	0.14	0.14	0.23
13335.0	2.13	2.08	1.86	2.74	0.14	0.13	0.12	0.21

4.3.8 Dynamic Mechanical Analysis

4.3.8.1 Strain and Temperature sweep studies

The *Payne effect (Fletcher – Gent effect, 1953)* is directly related to the dynamic property of the vulcanised rubber. The reason for this kind of effect is filler-filler interaction, which decreases at higher strains. Above approximately 0.1% strain, the storage modulus decreases rapidly with increasing amplitude. At large strain amplitude ~20% the storage modulus approaches a lower bound. The Payne effect depends on the filler content of the material and vanishes for unfilled elastomers. The change in storage modulus for modified NBR formulation is shown in Figure 4.15. From Figure 4.15, it can be seen that sample F, having highest dosage of filler initially shows highest storage modulus and at the same time shows highest extent of structure breakdown (fall in storage modulus: Payne effect). In case of sample D formation of a nano-unit like structure is envisaged which is reflected in its higher storage modulus value and at the same time shows highest extent of structure breakdown (fall in storage modulus: Payne effect). In case of sample D formation of a nano-unit like structure is envisaged which is reflected in its higher storage modulus value at lower strain rate, while sample E showed a lower storage modulus value.

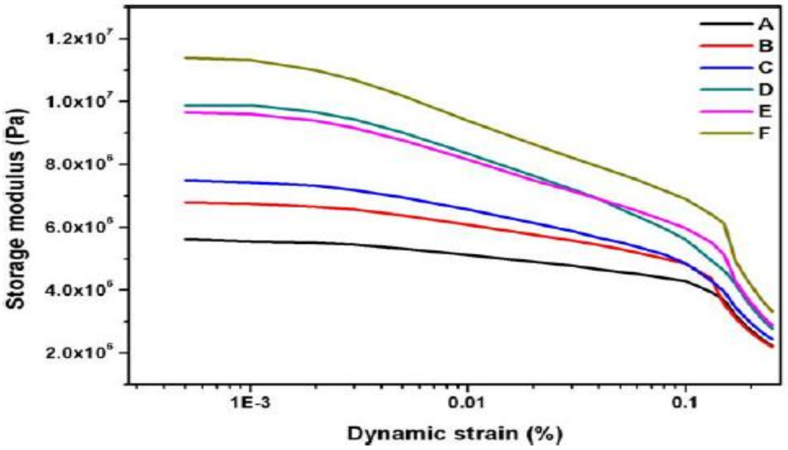


Figure 4.15 Change in storage modulus for modified NBR formulation.

With increasing in strain a distinct crossover is observed probably due to the breakdown of nano-unit structure at higher strain rate. Sample E can sustain higher strain rate and its fall in modulus is also shallow. Change in storage modulus in case of samples C, B, A is related to their filler loading. In case of modified formulation shown in Figure 4.16, Dmod shows maximum structure breakdown and also highest storage modulus, once again indicating probable formation of a nano-unit like structure with 2:1 ratio of black and nano-clay. In case of B2 presence of low structure GPF leads to much lower amount of filler interaction.

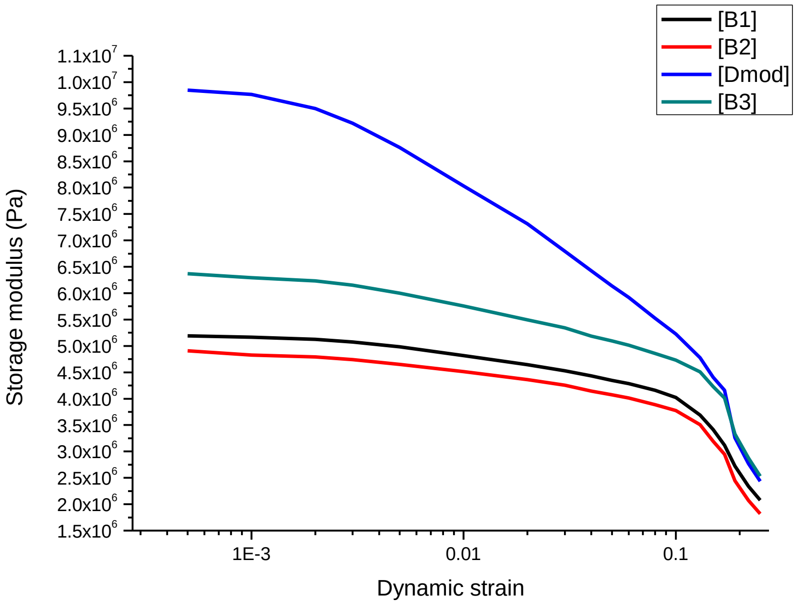


Figure 4.16 Change in storage modulus for modified NBR formulation.

The plot of storage modulus with temperature also showed a similar trend as found in strain sweep. All the samples show a loss peak ~0 °C. Tan δ overlap for NBR composites are shown in Figure 4.17. As filler content increases from A to E, tanδ values is lowered gradually. For sample E an additional relaxation is observed after glass transition probably due to the formation of more random structure.

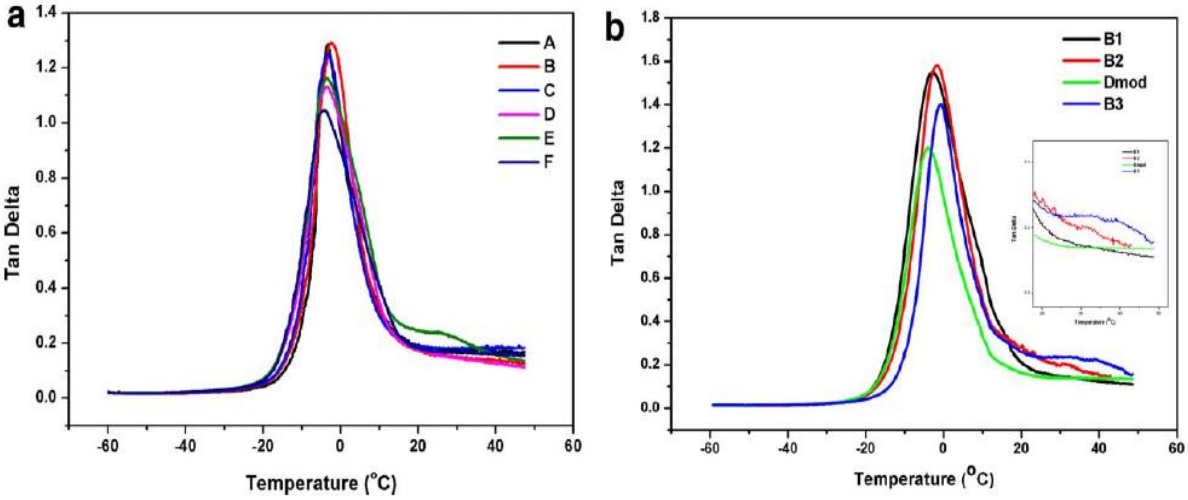


Figure 4.17 Tan delta overlap for NBR based nanocomposites.

Also modified formulation, a crossover of B3 is observed over B1, which can be attributed due to the presence of both FEF and GPF black in the former case. From the plateau region it can be seen that residual modulus for Dmod is highest, thereby supporting the formation of nano-unit like structure with 2:1 ratio of FEF black and nano-clay. Plot of tan δ indicates lowest loss in case of Dmod and an additional relaxation in case of B3 due to more random association of fillers.

4.3.8.2 Time Temperature Superposition

Modulus of a polymer is a function of time as well as temperature. In principle, the complete modulus versus time behavior of any polymer at any temperature can be measured. Time temperature superposition was done only for the two samples Dmod and B3 at 30 °C and it is represented in Figure 4.18. For sample Dmod, the loss tangent shows a lower value up to about 100 Hz.

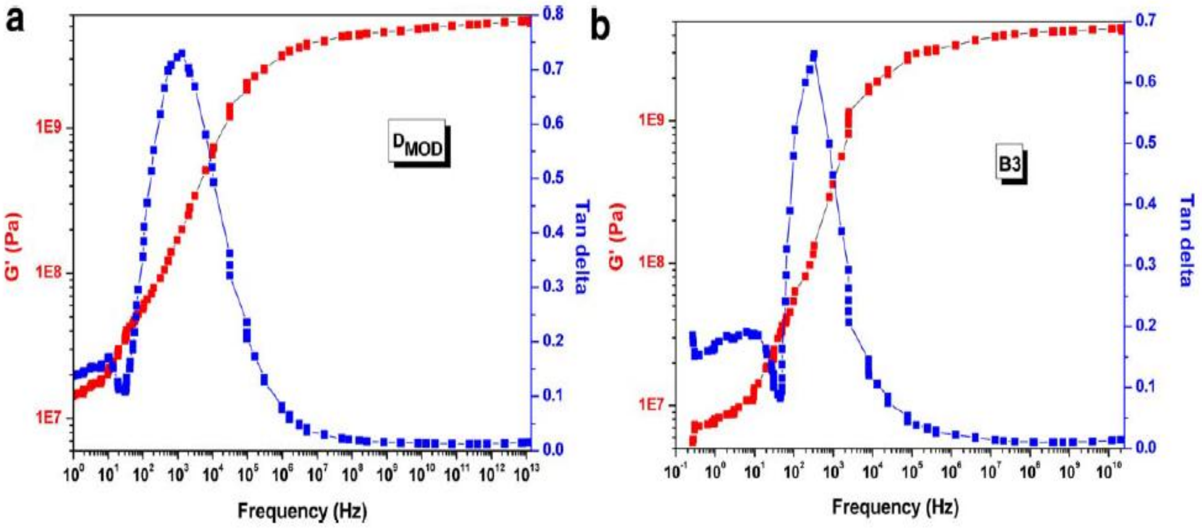


Figure 4.18 TTS plot of Dmod and B3.

An additional inflection point can be seen which corresponds to the breakdown of 'nano-unit' structure. Peak value of tan δ is observed at about 1.3 kHz. Thus in the frequency range of interest the sample shows low loss modulus and low loss tangent. For sample B3, storage modulus increases to 4320 MPa and then levels out. Loss modulus peaks to 251 MPa at about 2.5 kHz. Peak value of tan δ is observed at about 980 Hz.

4.3.9 Acoustic Test

Insertion loss was measured for both optimised compounds (D_{MOD} and B3) in the frequency range of 500 Hz to 4 kHz at room temperature. Figure 4.19 show the effect of frequency on insertion loss of the materials. Insertion loss values for D_{MOD} and B3 material was less than 0.2 dB and 0.4 dB respectively. It is observed from acoustic measurement that both materials values are close to 0 dB throughout the frequency range, which is suitable for acoustic transparent materials for transducer encapsulation application.

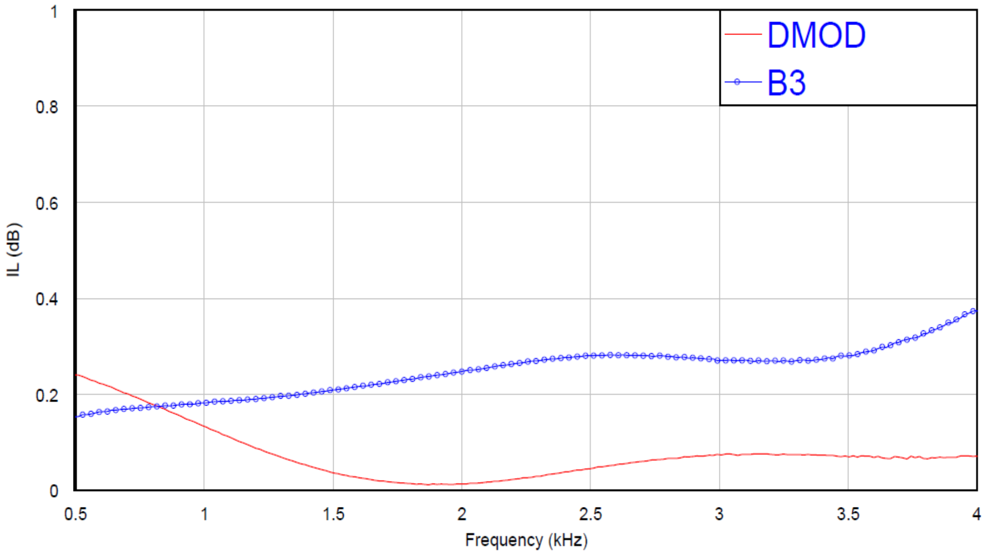


Figure 4.19 Insertion loss of materials with frequency

4.3.10 Conclusions

A NBR rubber based nano-composite formulation, to be used as an underwater encapsulant material is successfully developed satisfying all the requirements. The nanocomposite was first tuned to get low water absorption, better mechanical (static and dynamic), and electrical properties by intercalation or exfoliation. The morphology of the nano-composites is well explained using XRD and TEM analysis. Formulation Dmod and B3 are found to be suitable for the particular application. From the DMA analysis it is envisaged that Dmod can be used in low frequency region, whereas the latter one is suitable for high frequency region. The encapsulation material while meeting the primary function of protecting sensor material from sea water must also possess the requisite acoustical properties for transmitting the maximum acoustic power from transducer to water medium.The unique hybrid filler nanostructure is responsible for indulging such a judicious combination of properties.

CHAPTER 5

STUDIES ON RUBBER ADHESIVE BASED ON CHLOROPRENE RESOLE BLEND

5.1 INTRODUCTION

Acoustic transducers such as projectors and hydrophones used for the underwater applications are encapsulated in polymeric materials. Specialty adhesive with improved salt water resistant coupled with high electrical insulation resistance is employed for bonding various substrates during fabrication and moulding of transducers and other products for underwater application like cable splicing, moulding of rubber junction boxes, transducer encapsulation etc. Chemlok grade specialty adhesive of foreign origin was used for intended application at present. However, faced with a situation of the supplier often changing the grades and it has become unviable to dependent on them, it is hereby attempted to develop a substitute for underwater applications as a part of this thesis work.

An adhesive is a substance capable of holding material together by surface attachment. The term adhesive includes cement, glue, paste, mucilage etc. The materials being joined are called adherends [112]. Rubber based adhesives are used both as latex adhesives and as solvent cements. Most rubber for adhesives is utilized in solvent-cement form. The rubber is dissolved in the solvent by high-speed mixers; other ingredients may include tackifying resins, fillers, softeners, antioxidants, and vulcanizing agents [113]. Neoprene or polychloroprene is the basis for one of the largest and most important groups of rubber adhesives [114]. The rapid development of bond strength of films from solution, combined with tack or auto adhesion as well as resistance of the cured glue line to heat have led to widespread use of neoprene adhesives in the shoe, furniture, automotive and construction industries. Neoprene adhesive are conventionally applied by spraying, curtain coating, roller coating and brushing. Neoprene is similar in physical properties to natural rubber, but is stronger and has better ageing and high temperature properties. Cured neoprene films are more rigid than thermoplastic adhesives, but not as rigid as epoxy or phenolic adhesives.

Neoprenes have good resistance to water, salt spray, commonly encountered chemicals and biodeterioration. For structural and dynamic applications, neoprene elastomers are blended, in general, with fillers like carbon black [115], synthetic resin like phenolic resins [116, 117] and adhesion promoter like organofunctional silanes [118, 119], to improve mechanical strength, heat stability and to bond dissimilar substrates.

Solvent based rubber adhesives play an important role in construction of acoustic transducers used in underwater applications. Since most of the transducer component involve different substrate's interface bonding, selection and correct use of adhesives are vital. In this paper, adhesive compositions based on neoprene rubber/resin blend have been attempted for bonding vulcanized rubber-to-rubber and vulcanized rubber to primed metal substrates for underwater applications. The adhesive is flexible, heat reactive non-black type that suits well for producing bonded transducer components with good insulation properties. Evaluation of the hot bond strength and short and long-time saltwater aging indicate retention of maximum strength properties and higher thermal stability of bond formed. Consistency and repeatability for the different batches of resin and adhesive was ascertained from the test results obtained. The particular adhesive composition has been found to be improved adhesive strength and stronger bonding affinity for bonding Neoprene (CR), Nitrile (NBR) and Styrene Butadiene (SBR) rubber substrates and Neoprene rubber (CR) to primed metal substrates such as Titanium (Ti), Stainless steel (SS) and Aluminium (Al). This adhesive find also useful for cable splicing and Post Vulcanisation (PV) bonding of transducer components for electrical applications due to its better insulation properties and durability in underwater marine environments.

5.2 MATERIALS AND INSTRUMENT TECHNIQUES

The elastomer used was chloroprene rubber (Neoprene AD-20 grade of Dupont Dow Elastomers, USA) purchased from their Indian distributor M/s. Pollmann India Limited, Mumbai. Zinc oxide (Specific gravity - 5.5, Zinc oxide content- 98%) was supplied by M/s Meta Zinc Ltd., Mumbai. Active Magnesium oxide (AR grade of specific gravity 3.2) was supplied by S D Fine Chemicals, Mumbai. Phenolic resin (GRADE HR 6411) having specific gravity (1.085 - 1.105) and methylol content (14-18%) was supplied by M/s. Bakelite Hylam Limited, Mumbai. All other compounding ingredients such as Vulcanox HS (polymerized 2,2,4 trimethyl 1,2-dihydroquinoline), ethylene thiourea (NA-22) and solvents like toluene, acetone, trichloroethylene etc were obtained from local rubber chemical suppliers and used as such. The cure characteristics of the different rubber compositions for preparation of substrates and rubber compound mix for preparation of adhesives have been determined by using moving die rheometer (MDR 2000), Alpha technologies, USA. Adhesives are evaluated for peel strength and the tests are 180 degree stripping test carried out by a Universal Testing Machine (Zwick 1476) as per ASTM D 903 [120]. This method is commonly used when one adherend is flexible enough to permit a 180^o turn near the point of loading. Peel values are recorded in Newton per millimeter (N/mm) of width of the bonded specimen.

5.3 SUBSTRATES AND THEIR SURFACE PREPARATION

The compound recipes used for preparation of rubber substrates are selected from neoprene, nitrile and Styrene-butadiene rubbers for the evaluation of adhesive composition. The compounding for the preparation of rubber substrates was done on a laboratory size two roll mill. The compounding ingredients were added as per ASTM D3186 [121] in the following order: activators, fillers, processing aids, accelerators and curing agents.

Table 5.1 Rubber substrate's compounding recipe

CR		**SBR**		**NBR**	
Ingredients	**Phr**	**Ingredients**	**Phr**	**Ingredients**	**Phr**
CR (W)	100	SBR	100	NBR	100
Stearic acid	1	Stearic acid	1	Sulphur	0.75
Vulcanox HS	1	Vulcanox HS	2	Stearic acid	1.0
4020	1	4020	2	ZnO	3.0
FEF (N550)	30	ZnO	5	Vulcanox HS	1.5
HAF(N330)	10	FEF	50	MT (N990)	50
Naphthenic Oil	12	Talc	100	Naphthenic Oil	5
Red Lead (Pb_3O_4)	13	DibutylPthalate	10	MBT[4]	0.5
Ehylenethiourea	0.6	TMTD[2]	0.5	ZDC[3]	1.5
MBTS[1]	1.5	Sulphur	0.75	TMTD	1
MC wax	1.0				

[1] Benzothiasoledisulphide, [2]Teteramethyl thiuram disulphide
[3]Zinc diethyl dithiocarbamate, [4]Mercaptobenzothiazole

After mixing, these compounds are subsequently moulded in an electrically heated hydraulic press at 150 °C to form strips of 100 mm × 25 mm × 2 mm size. The time of cure was selected for preparation of rubber substrates in accordance with the results of cure studies initially performed on a MDR 2000. The formulations used for the compounding of substrates are given in Table 5.1. Proper preparation of the surfaces of the materials to be bonded is one of the most important factors influencing adhesion in any bonding process [122]. Metal strips (100 mm × 25 mm) are machined from 1 mm thick sheets to study bonding between rubber and metal substrates. Mechanical cleaning (surface roughening) is followed on both metal and rubber substrates with a No. 100 emery paper followed by solvent degreasing on metals by trichloroethylene and on rubber substrates by rubbing with acetone wetted soft cloth.

5.4 PREPARATION OF ADHESIVES AND BOND FORMATION

The different ingredients of the adhesive formulation and their proportions investigated in the study are tabulated in Table 5.2. Preparation of adhesive is done by a 2-stage process.

Table 5.2 Preparation of compound mix (CM)

Ingredients	**Phr**
Neoprene AD	100
MgO	4.0
ZnO	5.0
HS	1
Na22	0.6
Total	110.6

In the first stage, weigh required quantity of rubber and ingredients and get mixed in two roll mill to prepare compound mix (CM) as per the order given in Table 5.2. The required quantity of compound mix is weighed in a balance and placed in a beaker filled with the solvents (Part A). For better dissolution, cut small pieces from CM and put it into solvents keeping it overnight for uniformity. The second stage is preparation of resin mixture in the solvent as per details given in Part B. There are four types of resin mixes prepared as per the details of ingredients given in Part B. The method of preparation of formulation for different adhesive compositions is given in Table 5.3.

Table 5.3 Formulation of different adhesive composition

PART A				
Ingredients/Sample ID	**Gum**	**A**	**B**	**C**
Compound Mix (CM)	110.6	110.6	110.6	110.6
PART B				
Resol resin+MgO Pyrogallol	0 0	25+0 0	25+2.5 0	12.5+0 12.5
Toluene and Xylene (3:1)	To adjust to get 20 % solid content			

GUM - Adhesive (Gum), without any resin
A - Adhesive (*A*), with resole resin
B - Adhesive (*B*) with resole resin and MgO complex
C - Adhesive(C*)* with resole resin and trihydroxy phenol complex

These two solutions (Table 5.3, Part A and Part B) are finally mixed to get adhesives. These four different types of adhesives (GUM, A, B and C) is made ready for bonding applications. In all adhesives, solvents are adjusted to get 20% solid content to apply over substrates by brush coating. All substrate surfaces must be clean, dry and dust free before applying adhesives for bonding. For bonding rubber to rubber, thin adhesive layer is applied over both rubber substrates surfaces. Primer (Chemlok 205) is applied over metal substrate's surface followed by adhesive cover coating for bonding metal to rubber substrates. Parts should be mated or placed in a mould as soon as possible after solvent dried up in adhesive applications. Cross-link formations in rubber (vulcanization) and bond formation to metal are done simultaneously. Adhesive coated metal component should be placed in the mould cavity kept at a temperature of 150 ^{o}C. A gauge pressure of about 70–105 kg/cm^2 is maintained for apprx. 25–30 minutes. At the end of the permitted curing period, the moulded items are ejected.

5.5 RESULTS AND DISCUSSION

Neoprene adhesives are prepared from available rubber chemicals and incorporation of resins by different methods. The performances of adhesives are evaluated by studying the effect of adhesives types and ageing on peel strength properties and the results are discussed in this paper.

5.5.1 Solubility

The choice of solvent to be used in the preparation of a neoprene adhesive will have profound effect on its final properties. The selection of solvent is very important for synthesis of adhesives and also it affects solution viscosity, application of properties in the formation of film thickness and to some extent ultimate bond strength. The solvent combination of toluene/xylene is selected to dissolve resin and other ingredients for preparation of adhesive.

5.5.2 Evaluation for adhesion strength

Neoprene based adhesive are prepared using formulations of adhesive without resin (gum), adhesive (A) where resin is added with CM and adhesive (B) where resin and extra MgO reacted complex is added with CM and adhesive (C) where 50% of resole resin is replaced by trihydroxy phenol and mixed with CM. Test samples are prepared using these four types of adhesives and evaluated for peel strength for bonded cured CR to CR substrate. The test results are shown in Figure 5.1. It was found that the adhesive strength for adhesive (A) shows good improvement of about 40% increase in peel strength compared to adhesive (gum). But for adhesive (B), an increase in 70% of peel strength was observed compared to the adhesive test sample prepared without incorporating the resin. Adhesive (C) showed an increase of 35% in peel strength compared to the adhesive (gum) test sample.

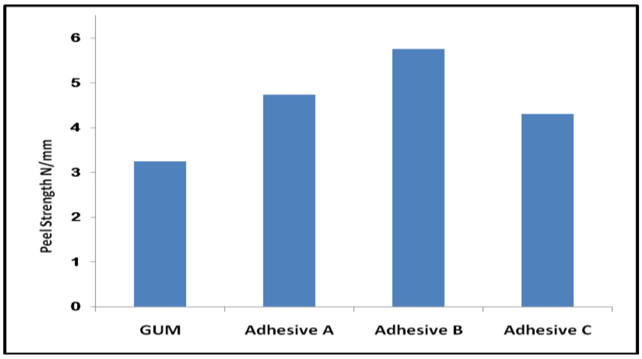


Figure 5.1 Peel strength for different adhesives (CR substrates).

5.5.3. Adhesion strength for different substrates

The adhesive (B), which shows high peel strength value, is selected for further study. The peel strength was determined using different substrates and the results are shown in

Figure 5.2. It is observed that adhesive (B) is very good for bonding neoprene-to-neoprene, neoprene to stainless steel, aluminium and Titanium etc.

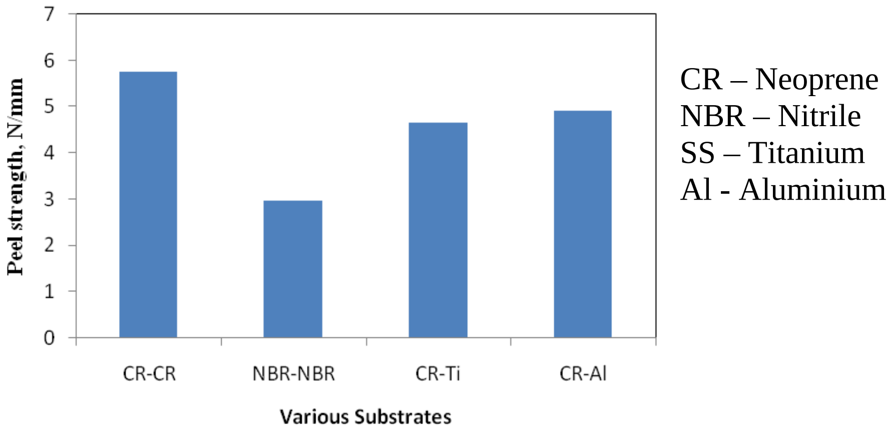


Figure 5.2 Peel strength for different substrates.

5.5.4. Adhesion strength on ageing

Saltwater Ageing: Test samples also prepared in sufficient numbers and placed in salt water (3.5% NaCl) keeping temperatures at 70 ^{o}C, 50 ^{o}C and 40 ^{o}C in an air oven and taken out at different duration and evaluated for 180^{o} peel strength for CR–CR substrate. Time required for 10% reductions in peel strength at different temperatures are measured and the values are given in Table 5.4.

Table 5.4 Retention of adhesion strength on saltwater ageing

Samples in Salt water (days)	Retention of Peel strength		
	70 ^{o}C	**50 ^{o}C**	**40 ^{o}C**
10 days	90%	-	-
109 days	-	90 %	-
500 days	-	-	>98 %

It is observed from test results that the samples kept at 70 ^{o}C showed retention of 90% of the property after 10 days of aging. Sample kept at 50 ^{o}C took 109 days to reduce its initial value by 10%. The sample kept at 40 ^{o}C retained its maximum properties even after 500 days of aging in salt water.

5.5.5. Adhesion strength for nanocomposites substrates

The optimized adhesive (Adh B) has been completely evaluated for peel strength and ageing properties. Since CR and NBR based nanocomposite are to be bonded with different substrates for encapsulation of transducers and to work in underwater environment, adhesion properties are need to be evaluated. The developed adhesive has got excellent bondability with CR based nanocomposite substrate (CR2) but bonding with nitrile based nanocomposite substrate (B3) is poor. In order to enhance bondability of nitrile based nanocomposite, commercial adhesives (Chemlok 6260) are tried and compared with developed adhesives for bonding both CR and nitrile nanocomposite substrates. However, both adhesive have shown good bonding with CR substrates, Chemlok grade adhesive, CH 6260 bonds well with NBR substrates as shown in Figure 5.3.

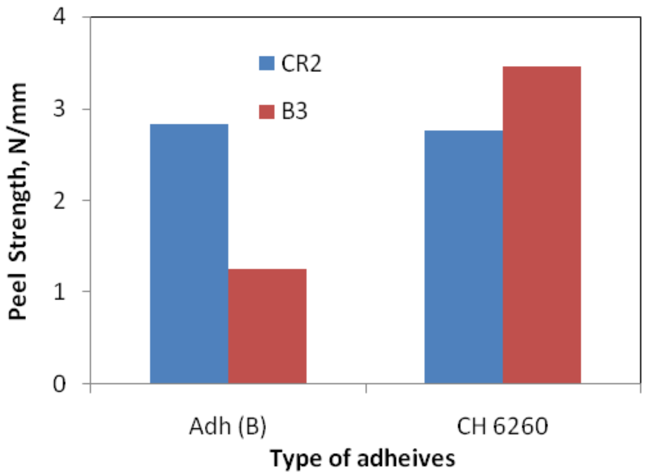


Figure 5.3 Effect of adhesive for Nanocomposite substrates

5.6. CONCLUSION

Chloroprene rubber and resole type phenolic resin are effectively used for the preparation of rubber based solvent adhesive for underwater transducer applications. The adhesive resin composition**,** Adhesive (B)**,** of the present study found to be of improved adhesive strength, superior in heat resistance and long-term stability and showed very good bondability to neoprene-neoprene and neoprene-metal substrates. Results showed that particular adhesive is quite good for bonding other rubbers and rubber to metal. It is found that the adhesive developed using modified reactive resin complex showed a 77% increase in strength than the composition without any resin. Evaluation of the hot bond strength and short and long-time saltwater aging indicate retention of maximum strength properties and higher thermal stability of bond formed. This particular adhesive found useful in producing bonded transducer components where insulation resistance is prime importance such as hydrophone encapsulation, junction box and cable splicing, etc.

CHAPTER 6

COMPARISON OF OPTIMIZED CR AND NBR NANOCOMPOSITE PROPERTIES WITH STANDARD REFERENCE COMPOUND

6.1 INTRODUCTION

The most important applications of passive materials in underwater sensor are window materials for encapsulation of transducers. The primary function of encapsulation material is to serve as the protective covering material for transducer elements. Chloroprene rubber compound filled with high loading of fillers like carbon block, talc and calcium carbonate etc are used at present for encapsulation of underwater sensors. This conventional rubber compound considered as reference compound (RC) during their service absorb substantial amount of water significantly and alter properties leading often to product failures or de-rated performance. Having considered technical difficulties of present compound, a study have been conducted to develop CR and NBR based nanocomposite with functional improvement. The use of nanofiller in rubber compound result partial replacement of carbon black and other mineral fillers and modify functional property of encapsulation materials. For development of improved rubber compound, the existing compound was studied for physical properties and generated data for comparison with nanocomposites. The present work discusses a preparation and characterisation of reference compound and comparison of properties with nanocomposites for encapsulation applications.

6.2 PREPARATION OF RUBBER COMPOSITES

The compound formulations for reference compound and nanocomposites are prepared in a laboratory mixing mill. Mixing of compound for reference is followed as per the order in single stage mixing (RC) but for nanocomposites two-stage mixing is practiced to get better dispersion of nanofiller. The mixing step followed for nanocomposite is preparation of master batch containing CR and nanoclay and then other ingredients are mixed (CR2 and B3) as per the formulation given in Table 6.1.

Table 6.1 Compounding formula of rubber vulcanizates

Ingredients	**Parts/100 Rubber (phr)**		
	Reference Compound (RC)	**Nanocomposites (CR2)**	**Nanocomposites (B3)**
Neoprene (CR-W)	100.00	100	-
Nitrile (35% ACN)	-	-	100
Nanoclay	-	5.0	3.0
Stearic Acid	1.0	-	-
Sulphur	-	-	0.5
ZnO	-	-	5.0
Calcium stearate	-	1.0	1.0
Vulcanox HS	1.0	1.0	1.0
Vulcanox 4020	1.0	1.0	-
FEF, N550	30.0	15.0	20.0
GPF, N660	-	-	10.0
Talc	70.0	-	-
Ppted. $CaCO_3$	20.0	-	-
Naphthenic oil	12.0	-	-
Aromatic oil	-	-	3.0
Red lead (Pb_3O_4)	13.0	6.0	-
Ethylenethiourea (NA22)	0.6	0.6	-
Dibenzothiazyldisulphide (MBTS)	1.5	1.5	-
Microcrystalline wax	1.0	-	-
TMTD	-	-	1.0
MBT	-	-	1.0
Batch Weight	**350.1**	**131.0**	**141.5**

6.3 RESULTS AND DISCUSSION

6.3.1 Rheometric Properties

The cure characteristic of all compounds was studied. The rheological properties of both reference compound and nanocomposites were studied using a rubber process analyzer (RPA, Monsanto, Germany) at 150 ^{o}C as per respective cure time obtained from rheogram and are shown in Table 6.2.

Table 6.2 Cure Characteristics of Rubber Compounds

S. No.	Properties	Test Standard	RC	CR2	B3
1	Minimum Torque (M_L),(**N**-m)	ASTM D 2084	1.02	0.91	0.80
2	Maximum Torque (M_H) (**N**-m)	,,	10.10	7.41	9.01
3	Scorch Time (t_{s2}), Minute	,,	4.50	4.86	2.18
4	Cure Time (t_{c90}), Minute	,,	30.0	19.94	17.51

6.3.2 Strain–sweep studies

The strain sweep measurements on vulcanizates were conducted by RPA 3000 to study the rubber–filler interaction. RPA can do strain sweep tests in which the variation of storage modulus (G′) with the change in strain amplitude (Payne effect) are measured. The testing temperature was selected as 100 ^{o}C and the shear strain was varied from 0.5% to 120% keeping the frequency of measurements at 1.0 Hz. Storage modulus of two different strains is given in Table 6.3 and Figure 6.1 shows strain sweep for three different composites. It is clearly understood that minimum variation in storage modulus (i.e., lower the Payne effect) is observed for nanocomposite due to better filler and rubber interaction compared to reference compound.

Table 6.3 Storage modulus at two different strains

Storage Modulus (G′), kPa	RC	CR2	B3
at 0.7 % Strain	1245	652	729
at 100 % Strain	481	433	318
ΔG′ **G′ (0.7 – 100)**	764	219	411

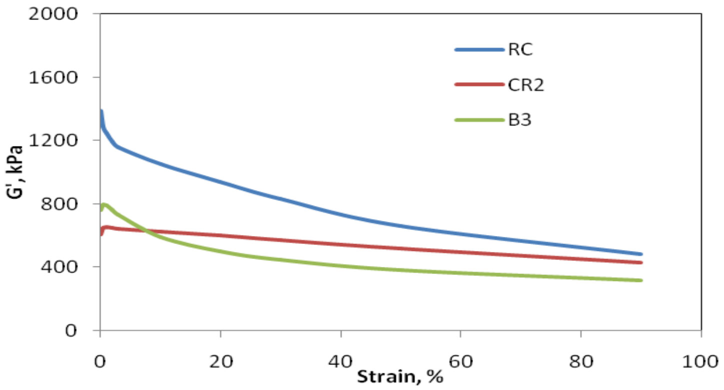


Figure 6.1 Strain sweep for three different composites.

6.3.3 Physico-Mechanical properties

The compression moulded sheets were used for evaluation of vulcanisate properties using universal testing machine as per the ASTM standards and the values are given in Table 6.4. Tensile strength of nanocomposite based on CR found to increase enormously due to effective reinforcement of nanoclay in CR matrix compared to nitrile nanocomposite and microcomposite. However, tear strength and elongation at break (EB) are enhanced for both nanocomposites. The increase in tear strength is due to the fact that the layered structure of clay diverts the tear path, which in turn imparts high tear strength to nanocomposites. In addition, increased value of elongation at break observed for nanocomposite because of the layer of silicate structure restricts the tearing of polymer molecules under stretching during tensile test. The other properties volume resistivity and water absorption matches with reference compound.

Table 6.4 Physico-Mechanical properties

Properties	**Test Standard**	**RC**	**CR2**	**B3**
Hardness (Shore A)	ASTM D 2240	67	54	57
Water absorption % weight gain, 40 °C 24 hrs, 3.5 % NaCl solution	ASTM D 471	0.5	0.6	
Tensile strength (MPa)	ASTM D 412	9	16	9
Elongation at Break %	,,	400	867	606
Tear strength (N/cm)	ASTM D 624	273	622	347
Volume resistivity @ 1000 V(Ωcm)	ASTM D 257	10^{11}	10^{10}	10^{10}

6.3.4 Dynamic mechanical properties

The dynamic temperature sweep tests were conducted within a temperature range of -60 ^{o}C to + 60 ^{o}C at a heating rate of 5 ^{o}C/min keeping fixed frequency as 1 Hz and strain at 0.25%. The dynamic elastic modulus E′, loss modulus E′ and damping constant (tanδ) for reference compound and nanocomposites are plotted in Figures 6.2–6.4. The specification requirement of encapsulant is higher storage modulus, lower loss modulus and lower damping constant. Reference compound shows both higher storage and loss modulus due to higher loading of fillers and onset of CB aggregation.

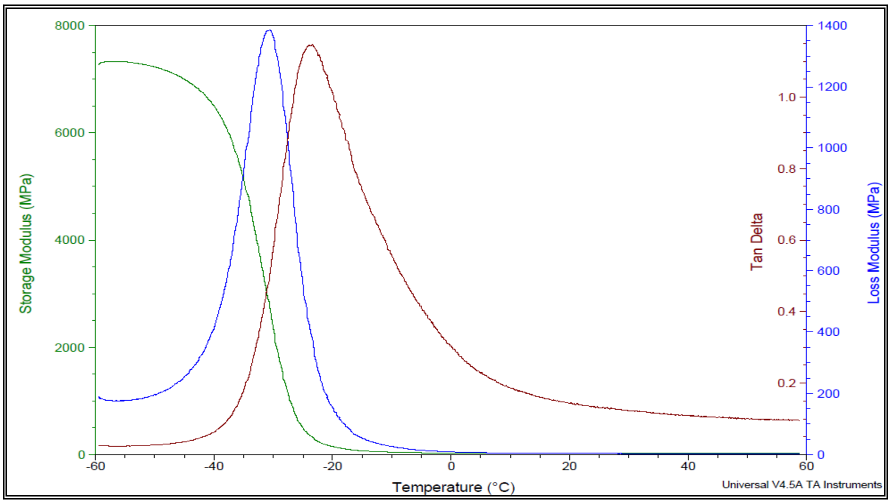


Figure 6.2 DMA plots for CR Compound (RC).

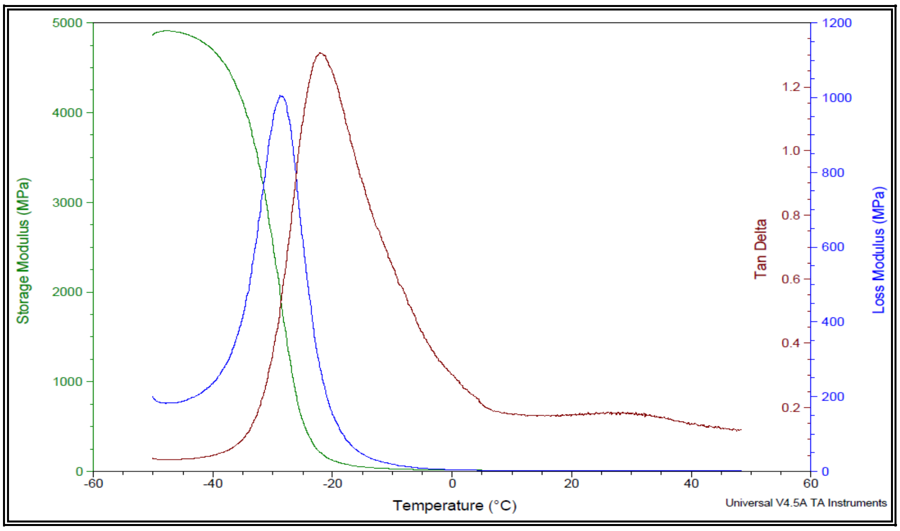


Figure 6.3 DMA plots for CR nanocomposites (CR2).

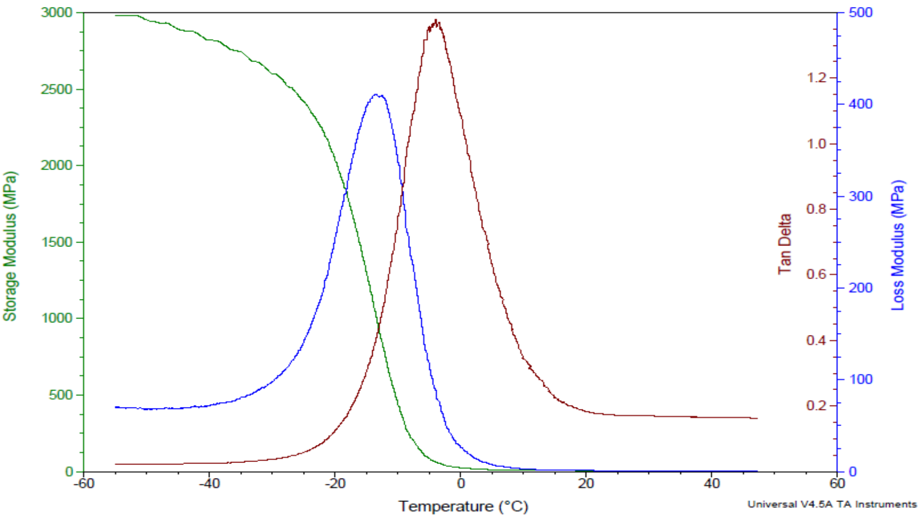


Figure 6.4 DMA plots for NBR nanocomposites (B3).

However, CR and NBR nanocomposites showed clear enhancement in storage modulus and equivalent damping constant due to strong effect of nanoclay and lower loading of fillers on the dynamic properties of nanocomposites. Since both nanocomposites show moderate storage modulus and lower damping constant (tan δ), it is considered to be acoustically transparent materials for underwater transducer.

6.3.5 Time Temperature Superposition (TTS graph)

Time temperature superposition (TTS) was studied for reference compound and nanocomposites samples to predict their dynamic mechanical properties at any time and temperature. Viscoelastic parameters measured at constant temperature for varying frequencies are given in Table 6.5.

Table 6.5 DMA viscoelastic parameters vs. frequency at 30 ^{o}C

Frequency (Hz)	RC			CR2			B3		
	E′, (MPa)	E″, (MPa)	*tan* δ	E′, (MPa)	E″, (MPa)	*tan* δ	E′, (MPa)	E″, (MPa)	*tan* δ
0.1	14.4	2.91	0.20	20.9	1.71	0.08	5.25	1.02	0.14
1	17.3	3.50	0.20	23.4	1.80	0.07	8.08	2.26	0.27
10	20.5	4.15	0.20	28.7	2.01	0.06	9.44	7.08	0.75
100	25.4	5.10	0.20	26.5	5.30	0.19	45.9	49.2	1.07
1000	30.5	6.32	0.21	54.8	25.0	0.45	267	229	0.85
3000	34.5	7.61	0.22	76.8	42.9	0.55	524	347	0.66
5000	36.1	8.21	0.22	86.5	52.1	0.60	647	386	0.92
7000	37.2	8.65	0.23	97.7	62.6	0.64	747	418	0.55
10000	38.0	9.00	0.23	113	77.4	0.68	853	426	0.49

Test results show that storage modulus and loss modulus increases with increase in frequency for all three samples. Higher storage modulus, lower loss modulus and low damping constant values are obtained for CR2 sample compared to RC and B3 samples. TTS plot of master curve for samples RC, CR-2 and B3 at reference temperature are plotted in Figures 6.5 to 6.7.

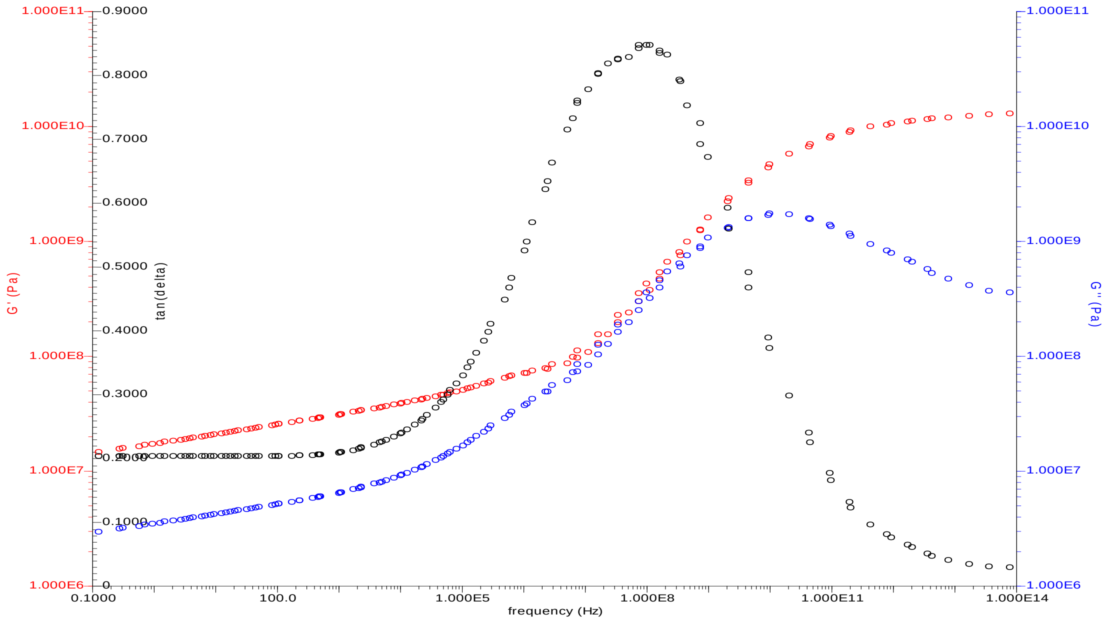


Figure 6.5 TTS plot of sample RC.

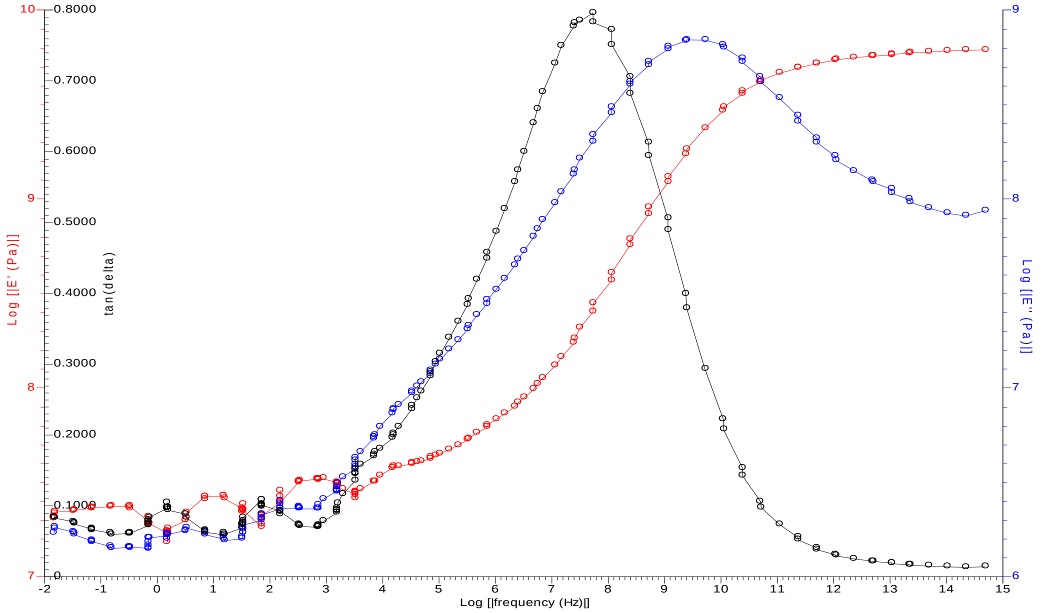


Figure 6.6 TTS plot of sample CR2.

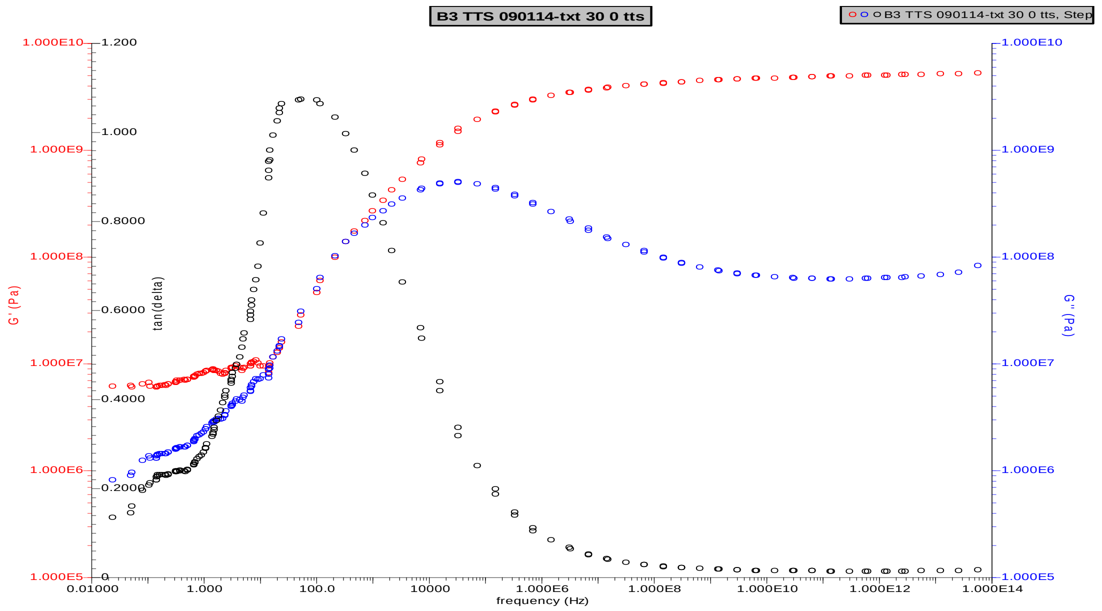


Figure 6.7 TTS plot of sample B3.

6.3.6 Evaluation of adhesive for bonding of substrates

Two types of adhesives have been studied for bonding three different compounds and the results are plotted in Figure 6.8. The developed adhesive, Adh(B) has provided excellent bonding strength for both CR based reference compound (RC) and CR based nanocomposite (CR2).

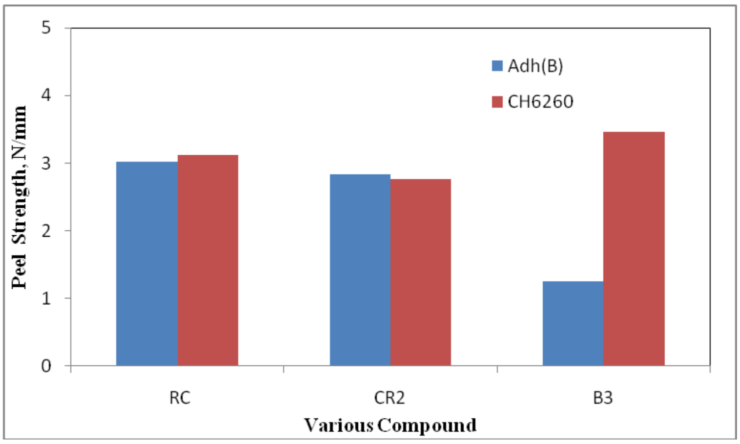


Figure 6.8 Effect of Adheives for various compounds**.**

However, for improved bonding strength of nitrile based nanocomposite substrate (B3), Chemlok grade adhesive, CH 6260 is selected. The bonded substrates prepared from three different compounds are placed in saltwater at 40 °C and the peel strength values are monitored after a week and a month. Figure 6.9 is plotted for rubber to rubber substrates and Figure 6.10 is plotted for rubber to metal substrates. It is observed from the test results that adhesive bonding strength is retained for nanocmposites compared to reference compound substrates.

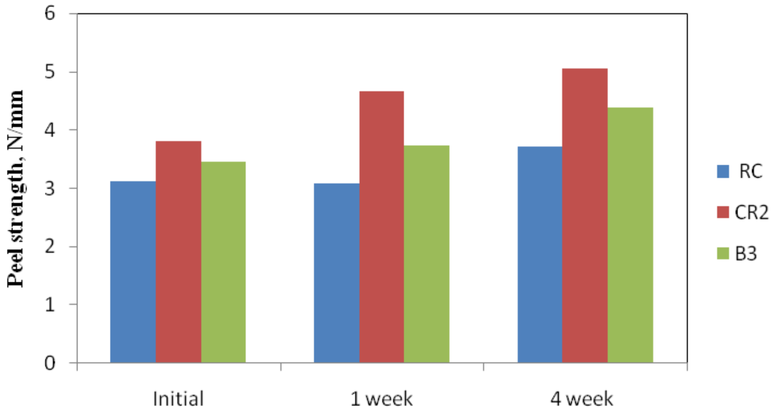


Figure 6.9 Peel Strength on ageing in salt water at 40 °C (Rubber – Rubber substrates)

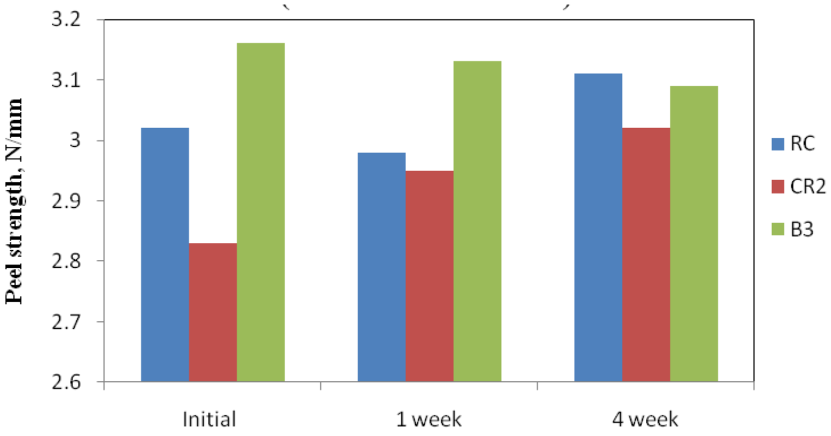


Figure 6.10 Peel Strength on ageing in salt water at 40 °C (Rubber – Metal substrates)

6.3.7 Ageing properties

Polymers are widely used in marine environments due to their excellent properties and good weathering resistance. The assessment of the durability of elastomeric products subjected to marine environment is a major issue for several industrial areas (offshore oil and gas industries, harbour and naval applications, renewable marine energy etc) and for better evaluation of maintenance periods and total lifetime. Even if marine ageing of polymeric materials has been widely investigated [123], very few papers investigate the ageing mechanisms of marine environment on elastomers [124–126]. The influence of the marine environment is complex, and depends clearly on the compound used. Ageing causes hydrolysis, additive extraction and oxidation on polymers with time [127, 128]. Short term ageing test is planned to perform on nano and micro fillers filled CR and NBR composite. The evolutions of electrical and dynamic mechanical properties are investigated to assess the ageing effect and their consequences in saltwater environment. An investigation was carried out on the influence of water absorption on mechanical, volume resistivity and dynamic mechanical properties of chloroprene and nitrile rubber composites in this chapter.

6.3.7.1 Ageing for Water absorption on CR nanocomposites

The test was done according to ASTM 471. Water absorption behavior of all composites has been studied on rubber samples cut from moulded sheet of dimension (25 mm × 25 mm × 2 mm). The samples were put in 3.5% NaCl solution for 24 hrs and 7 days and the weight change observed are given in Table 6.6. Water absorption is calculated using the equation

$$\text{Water absorption} = (W_2 – W_1) \text{ x } 100/W_1,$$

where W_1 and W_2 are the initial and final weights of the samples.

Table 6.6 Water absorption

Properties	**Sample Description**				
	CR-0	**CR-1**	**CR-2**	**CR-3**	**CR-4**
Saltwater absorption, % weight gain, 30 ^{o}C for 7 days	0.73	0.68	0.60	0.62	0.67

6.3.7.2. Tensile properties on ageing

Materials resistance to seawater was ascertained after subjecting the samples for a change of time at constant temperature. Dumbbell specimens cut from the vulcanizates are subjected to salt-water immersion and change in tensile properties is measured with increase of time. Test samples were immersed in seawater and kept in a hot air oven at reference temperature. After different time intervals on ageing, samples were removed from oven and its change in properties like tensile strength, elongation at break and modulus were measured and the values are given in Table 6.7. Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing. Figure 6.11 shows retention or tensile strength on ageing and better ageing resistance is observed for nanocomposites.

Table 6.7 Tensile property on ageing

Properties	**CR2**		
	Initial	Ageing after 7 days at 40 °C	Ageing after 45 days at 40 °C
Tensile Strength, MPa	16.43	17.61	16.73
M300%, MPa	3.38	3.14	3.78
EB%	871	886	757
	B3		
Tensile Strength, MPa	9.98	9.87	10.19
M300%, MPa	3.22	3.37	4.62
EB%	605	664	568
	RC		
Tensile Strength, MPa	9.54	9.39	8.89
M300%, MPa	5.58	5.62	5.78
EB%	495	492	475

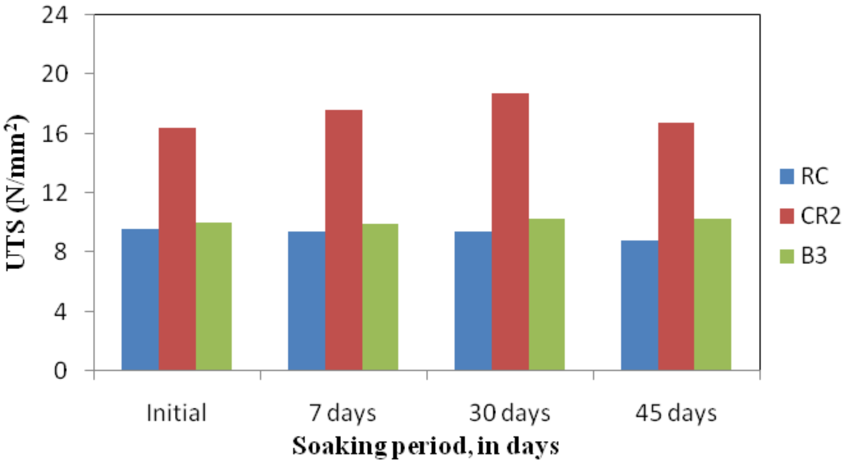


Figure 6.11 Tensile strength on ageing in salt water at 40 °C.

The same dumbbell specimens were used to see change in elongation at break (EB). Measurement of EB is helpful to study ageing effect within short period. Ultimate elongation versus soaking period is plotted graphically in Figure 6.12.

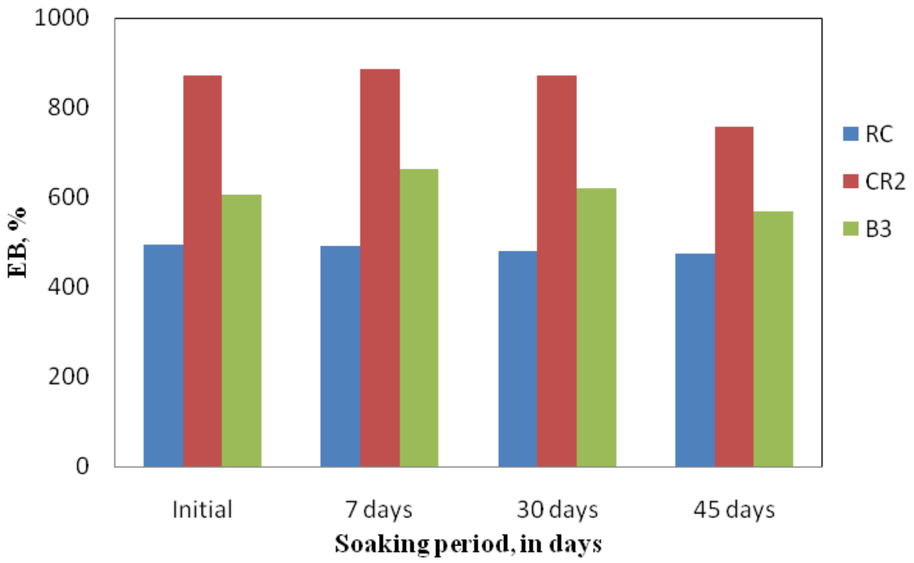


Figure 6.12 EB on ageing in saltwater at 40 °C.

Test results show that EB value and retention of property on ageing is higher for nanocomposites compared to reference compound. The reason is due to layer of nanoclay structure restricts the tearing of polymer molecules under stretching during tensile test.

6.3.7.3 Volume resistivity on ageing

Ageing study has been conducted to see the influence of salt water on volume resistivity of rubber vulcansizates as per ASTM D 257 standard. Figure 6.13 shows change in electrical resistivity after soaking the test samples in salt water for 145 days at 40 °C. It is observed that volume resistivity of reference compound (RC) reduced one order of magnitude on ageing but nanocomposite samples (CR2 and B3) do not show variation in resistivity value for continuous soaking period of 145 days.

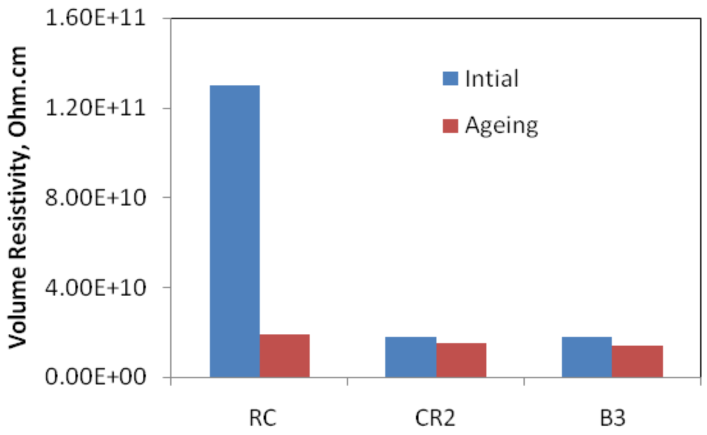


Figure 6.13 Volume resistivity for three composites.

6.3.7.4 Dynamic property on ageing

Dynamic mechanical properties were studied after the samples are subjected to saltwater ageing at 70 °C. Rectangular samples are cut from respective vulcanized sheet and properties measured after ageing in saltwater in the interval of 1 week and 2 months. Storage modulus against temperature range from –60 to –50 °C is measured and plotted graph with values obtained on initial and after ageing for a week and 2 months. Though all composites follow the same pattern, the reference compound exhibits higher storage modulus as shown Figure 6.14 initially due to higher loading of carbon black.

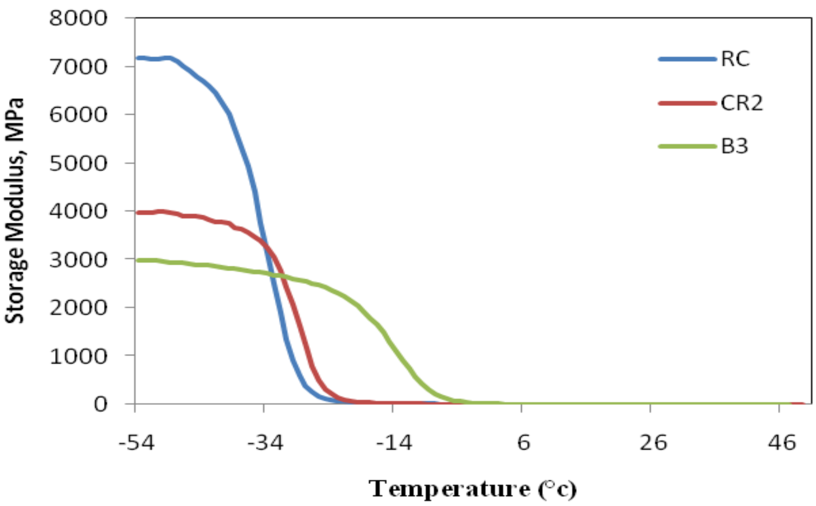


Figure 6.14 Storage Modulus vs. Temperature (Initial).

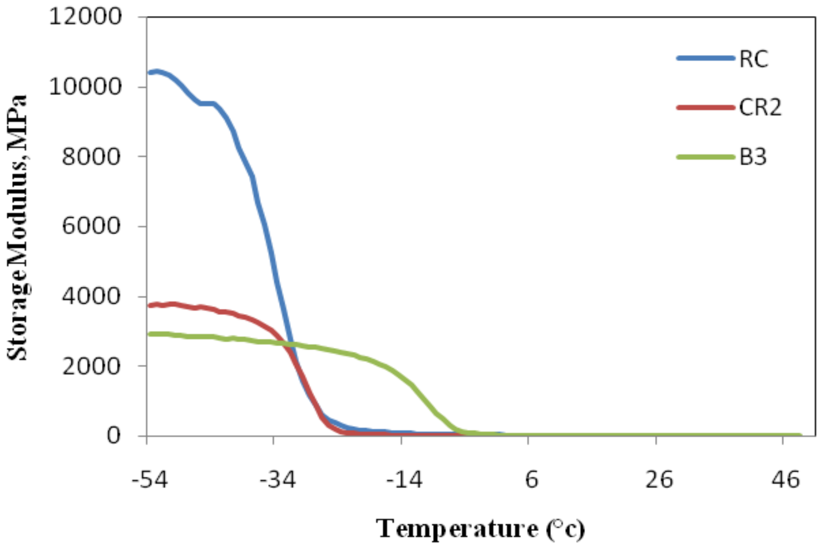


Figure 6.15 Storage Modulus vs. Temperature (After 1 week).

Storage modulus increased under the influence of ageing due to further cross-linking observed with reference compound compared to nanocomposites. However, Nanocomposite does not show variation in dynamic mechanical properties even after ageing for 2 month at 70 °C. It is understood that retention of dynamic properties are higher for nanocomposite samples as observed from Figures 6.15 and 6.16).

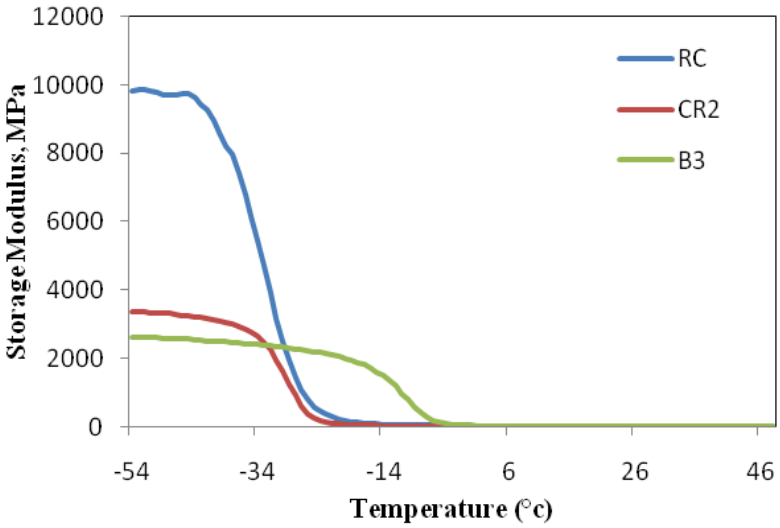


Figure 6.16 Storage Modulus vs. Temperature (After 2 months).

Damping constant against temperature range from –60 to –50 °C is also measured and plotted graphically with values obtained on initial and after ageing for a week and 2 months as shown in Figures 6.17–6.19. Measurement of damping constant gives idea of selecting low damping materials for better acoustic properties.

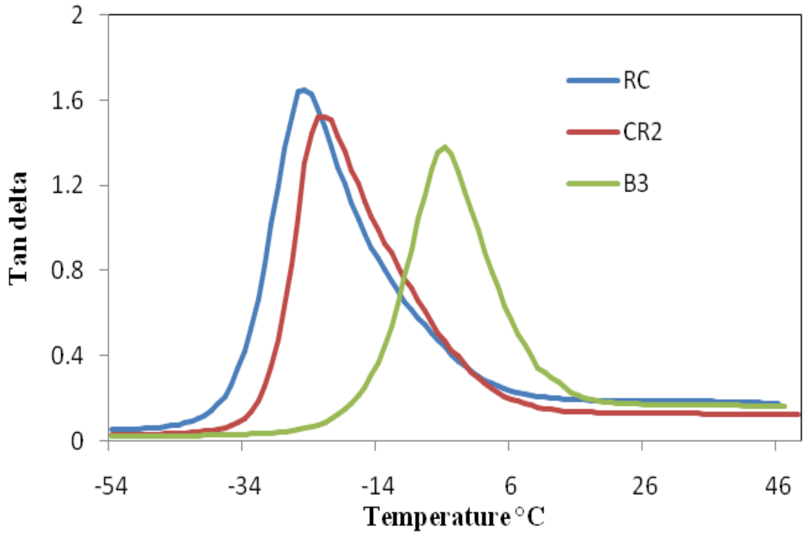


Figure 6.17 Damping Constant vs. Temperature (initial).

The results from Figure 6.17 show that the initial value of tan δ decreases for nanocomposites compared to reference compound. This is because the improved polymer filler interaction of nanocomposites limits the mobility of the rubber chains and hence reduces the damping of the composites.

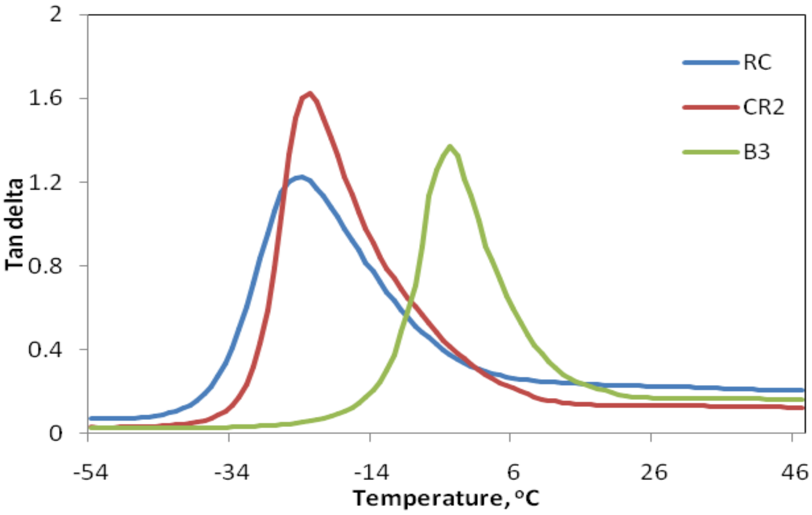


Figure 6.18 Damping Constant vs. Temperature (after 1 week).

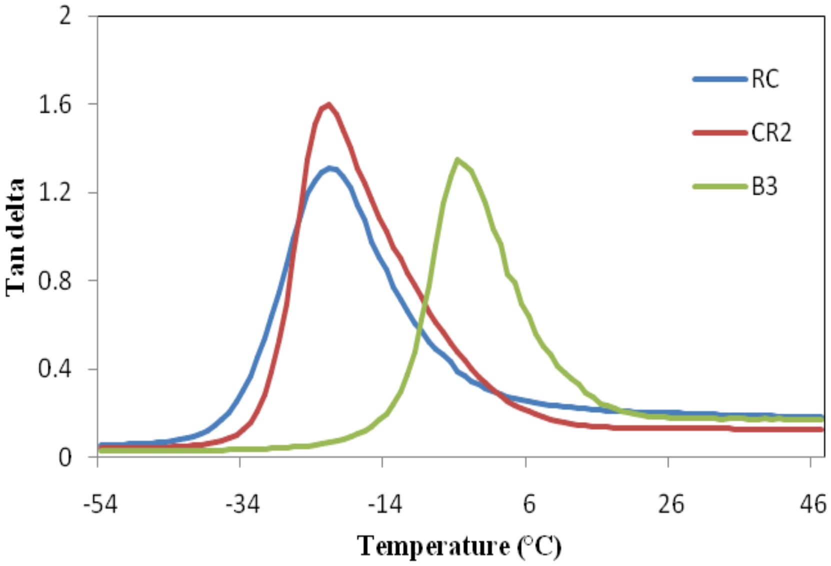


Figure 6.19 Damping Constant vs. Temperature (after 2 months).

From the above tan delta graphs, tan δ reduced for reference compound from initial value of 1.6 to 1.2. This is due to further cross linking reaction and plasticizing effect of water on ageing in water. There is no fall in tan δ for nanocomposites samples due to retention of elastic property and water resistant characteristics in salt water environment.

6.4 DIFFUSION AND PERMEABILITY OF WATER IN RUBBER COMPOSITES

Elastomers are used to isolate undersea electronic devices, such as sonar transducers and hydrophones, which must maintain their integrity for a long period, perhaps as much as 15 years. The ability of rubber to isolate a system from water is, of course, the key property. Water diffusion and permeation through exposed rubber surfaces is a major determinant of reliability in underwater devices such as underwater cables and transducers, etc and affects physical, mechanical and electrical properties of rubbers. The molecular diffusion of water through elastomers is an important consideration in undersea application [129]. Diffusivity could be determined by simple ways from water absorption experiments [130, 131]. Numerous studies have been done in the development of innumerable experimental techniques to measure the diffusivity of liquids through rubbers [132] and the basic mechanism of water absorption in rubber vulcansizates containing hydrophilic impurities is known [133]. VanAmerongen [134] reviewed diffusion of matter in rubbers. The rate of water absorption and desorption in polymer is diffusion-controlled and strongly temperature dependent. Estimation of water intake by rubber through diffusion is crucial for their service life of transducers. Samples of rubber (25 mm × 25 mm × 2 mm) are cut out from sheets made with different composition and immersed in (3.5% NaCl) saltwater solution contained in glass bottles. Samples are dried to constant weight and readings are noted with time to calculate diffusion coefficient from weight gain of samples. The values for three composites are given in Table 6.8.

Table 6.8 Diffusivity of composites

Samples	**Diffusion coefficient. D $\times 10^{-6}$ cm^2/hr**
RC	5.26
CR2	4.65
B3	3.92

Results show that diffusivity for reference compound is slightly higher compared to nanocomposite due to higher loading of carbon black and other mineral fillers. NBR nanocomposite shows lower diffusivity compared CR based nanocomposite.

Permeability is a fundamental property of an elastomer. It is often desired to measure the rate of transmission of a vapor or liquid through the elastomer. The compounds were molded to prepare 2 mm thick sheets. Permeation rates were measured using the gravimetric cup method (ASTM D1653-72) with an area of exposure 25 cm^2. These cups were then placed in a desiccator over silica gel, and the whole assembly was kept in an oven maintained at the desired constant temperature (40 °C). The weight loss (in mg) was noted until equilibrium was reached and results of the measurement are used for calculation of permeation rate. The permeability values are given in Table 6.9.

Table 6.9 Permeability of composites

Samples	**Permeability gm/cm/cm^2/hour**
RC	1.17×10^{-7}
CR2	1.23×10^{-8}
B3	3.92×10^{-8}

Results show that permeation rate measured at constant temperature of 40 ^{o}C decreased for nanocomposites compared to reference compound. The improvement of permeability in nanocomposites is due to decrease of diffusive passage in polymer sheets by addition of layered silicate of nanoclay in addition to carbon black filler.

6.5 ACOUSTIC PROPERTIES

Polymers are widely used for functional encapsulation in the electro-acoustic sensors. The encapsulation material while meeting the primary function of protecting sensor material from sea water must also posses the requisite acoustical properties for transmitting the maximum acoustic power from transducer to water medium [135]. The rubber used for acoustical purpose can be classified into three categories namely, acoustically transparent, reflective or an absorber [136, 137]. Acoustics absorbers are important for sonar transducers, acoustic baffles, acoustic calibration facilities and also for reduction of sound radiation and echoes from ships and submarines. Acoustic reflectors are used as decouplers as well as in sonar dome wedges. Acoustic window materials act as the coupling medium between the transduction material and water. Since rubbers can function as acoustic absorber, reflector and window material, it is very essential to evaluate the acoustic performance of encapsulant materials. The acoustic behavior is experimentally measured by impulse method in water filled impedance tube and the details of test experiment are explained in experimental methods. The specimen is a cylindrical bush of height 25 mm and 50 mm diameter usually prepared by compression molding technique without any air occlusion. It is pasted to SS disc of 50 mm diameter and thickness 10 to 15 mm. The acoustical transparency of rubber material was studied by measuring the percentage of sound transmitted through and reflected from the sample of material immersed in water. The echo reduction and insertion loss of the samples unit are decibel and plotted against frequency. The acoustic properties of the optimized CR and NBR nanocomposites are compared with that of conventional microcomposite.

The composite used for encapsulation application should be acoustically transparent. For acoustic transparency measurement, echo reduction and insertion loss are to be determined. The values of these two parameters should be very small or close to zero in order to behave material acoustically transparent [138]. Echo reduction (ER) or reduction in sound reflection was measured for all the three materials in the frequency range of 3 kHz to 15 kHz at room temperature. For echo reduction test, the sample is inserted into the tube from the top. It measures of how much incident sound pressure is reduced after reflection. Figure 6.19 show the effect of frequency on echo reduction of the materials. Echo reduction values are more close to zero for reference compound compared slightly higher values for nanocomposites.

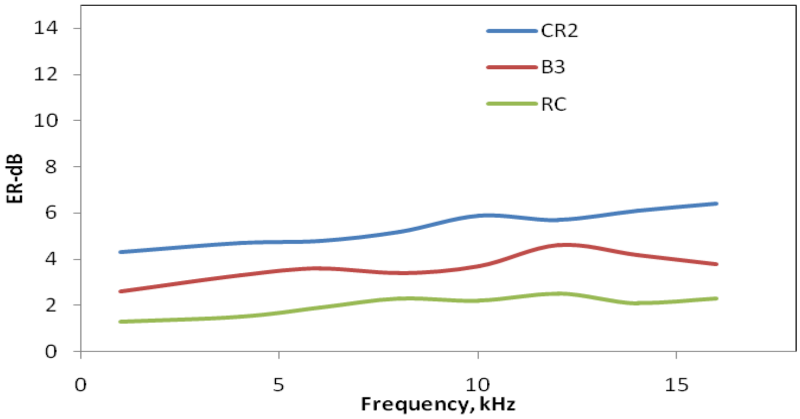


Figure 6.20 Echo reduction of materials with frequency.

For insertion loss measurement, the sample is positioned inside the tube at a depth of two meters from the top. The sample is suspended through a single stranded nylon string. A probe hydrophone is positioned just behind the sample to receive the transmitted signal. Insertion loss was measured for all the three materials in the frequency range of 1 kHz to 4 kHz at room temperature. Figure 6.21 shows the effect of frequency on insertion loss of the materials.

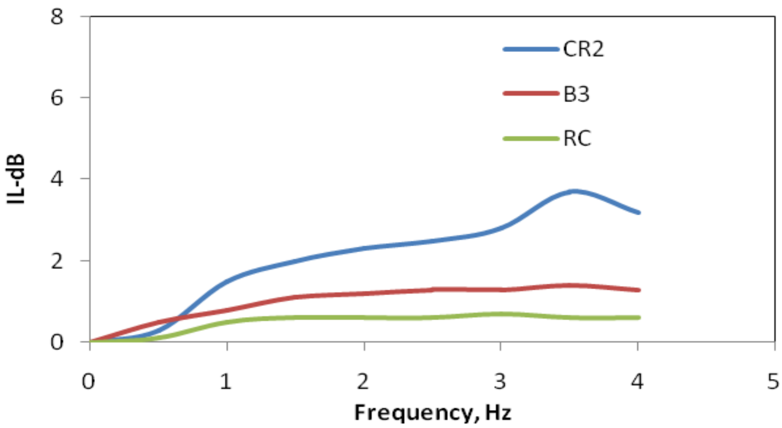


Figure 6.21 Insertion loss of materials with frequency.

Insertion loss values for RC and B3 samples were less than 2 dB in comparison with CR2 sample. However all three samples show acoustic transparency characteristics due to lower values of echo reduction and insertion loss.

6.6 CONCLUSIONS

The properties of microcomposites and nanocomposite are investigated for comparison in terms of mechanical, electrical, dynamic mechanical properties and ageing characteristics. Nanocomposite improves the physic-mechanical properties particularly tensile and tears strength retaining comparable water absorption and electrical resistivity over microcomposite. Better polymer and filler interaction was observed for nanocomposite due to lower Payne effect. DMA studies proved that both micro and nanocomposite show lower damping constant, which is important for encapsulation materials. Bondability of substrates is evaluated and the right adhesives are recommended for improved adhesion strength. Short term ageing study revealed that both nanocomposites retained their maximum properties and shown lower values of diffusivity and permeability requirement of encapsulation materials. Though acoustic evaluation of nanocomposites samples shows lesser value, all three composites are found to be acoustically transparent. It is concluded that nanocomposites containing a mixture of organoclay and CB in right proportion can be a substitute for microcomposite in terms of mechanical, electrical and water resistant properties and can be useful as encapsulant for underwater transducer applications.

CHAPTER 7

SUMMARY AND CONCLUSION

7.1 SUMMARY

Rubber components play a vital role in underwater acoustic application. The most important use of rubber is encapsulation of sensor elements. Transducers and their passive components are generally encapsulated with polymeric materials to provide hydrolytic stability while allowing the passage of acoustical energy. The primary function of an encapsulation material is to protect the acoustic sensors from heat, oil, weather, sea water and mechanical breakage and also works as an electrical insulator. The critical parameters for selection of encapsulants include acoustic transparency, low mechanical loss tangent, high insulation resistance, sea water compatibility and no major polymeric transition in/near the frequency and temperature ranges of interest. Rubbers employed for encapsulating acoustic sensors must have both electrical and acoustic properties as desired. The conventional microcomposite based on high loading of fillers filled neoprene (CR) and nitrile (NBR) rubber compound during their service absorb substantial amount of water significantly and alter the performance characteristics leading often to product failures or de-rated performance. These reasons inspired to study synergistic effect of nano and micro hybrid filler on polymer composites. The objectives of the present research investigation is to study the effect of carbon black and nanoclay fillers on properties like physico-mechanical, electrical, dynamic mechanical and water absorption properties of chloroprene and nitrile rubber vulcansizates for underwater transducer encapsulation application.

The performance of sonar transducers are critically dependent on selection of right materials and process used for preparation of encapsulation. The functional property requirement of encapsulant used in underwater transducer is not only depend on the polymers but also largely depend on the fillers and curing agent systems. Rubber compounding and process methods are important issues in optimization of formulation for encapsulant materials. In the present work, synergistic effect and optimum loading of carbon black and nanoclay are studied. Process of single and double stage mixing with dispersion agent effects is then investigated to generate viable formulation with improved performance requirement of encapsulation. The present study resulted to replace some parts of carbon black and other mineral fillers in a transducer encapsulant formulation by few parts of layered silicate and achieve improved mechanical, water resistant and dynamic mechanical characteristics without sacrificing other properties. Different rubbers are used in transducers manufacturing to meet specific requirements. Polychloroprene and Nitrile rubbers are found maximum use in underwater transducer encapsulation application due to easy processablity and tunability. Nitrile rubber (NBR) is preferred over chloroprene rubber (CR), where oil resistance is important particularly in towed array sensors. There is also requirement of development of NBR based nanocomposite for encapsulation of transducers, which are housed in lubricating oil filled long length towed array made of polyurethane tube. Morphology and viscoelastic properties are important in controlling damping and acoustic properties of the composites. Influence of fillers and curing agent on dynamic mechanical and dielectric properties of NBR based nanocomposite to optimize the process and formulation to work in encapsulation application have been investigated.

Almost all acoustic transducers used for the underwater applications are encapsulated using rubber or rubber like materials. In transducer fabrication, there is a requirement of adhesive for joining the different parts of the transducer such as the rubber to rubber, rubber-to-metal parts or polymer-to-PZT elements of the sensor and cable splicing, etc. Adhesives play an important role in electro acoustic transducers used in underwater applications. Since commercial adhesives are difficult to get and not consistent for providing electrical and adhesion property requirement of underwater transducers, the present study resulted in development of adhesive for bonding different transducer components. Key properties of adhesive critical to encapsulation of transducers such as bondability with dissimilar substrates, electrical resistivity and retention of properties on ageing have also been studied.

Finally, systematic investigation based on chloroprene rubber and nitrile rubber formulations were carried out to develop suitable nanocomposites based encapsulation materials for underwater transducer applications. A detailed study has been conducted on the presently used reference rubber compound and generated data for comparison of nanocomposites properties to select improved materials composition for encapsulation applications. The composite used for encapsulation application should be acoustically transparent. The encapsulation material while meeting the primary function of protecting sensor material from seawater must also posses the requisite acoustical properties for transmitting the maximum acoustic power from transducer to water medium. The acoustic properties such as echo reduction and insertion loss have been evaluated. The transducers are encapsulated with acoustically transparent rubber composites for water tightness. The ability of rubber to isolate a sensor from water is, of course, the key property. Since these materials undergo ageing and their properties change significantly during the service life of sensors, study has also been carried out to see influence of water absorption on mechanical, volume resistivity and dynamic mechanical properties of chloroprene and nitrile rubber composites. The thesis has been divided into seven chapters and the contents of each chapter results are briefly summarized below.

Chapter 1 deals with the general introduction to underwater electro acoustic transducers, active materials, rubbers as passive acoustic materials, current status of encapsulation of transducers and review of literatures pertains to reinforcement of rubber using organoclay, synergistic effect of hybrid fillers and preparation of rubber nanocomposite. The scope of the present investigation, background and motivation of the investigation and objectives of this study are also dealt in this chapter.

Chapter 2 describes the details of selection and specification of rubbers, nanoclay, carbon black, dispersion agent and other compounding ingredients etc. The different testing equipments such as MDR, RPA, UTM, DMA, XRD, TEM, and pulse tube test setup are explained with manufacturer's specifications, experimental procedures and techniques adopted in the present research work.

Chapter 3 deals with the preparation, optimization and characterization of carbon black and nanoclay filled polychloroprene. The chapter is dealt in four sections; **Section 3.1** describes study on the effect of addition of nanoclay on physico-mechanical, electrical and water absorption properties in chloroprene rubber. CR composites have been compounded with four different loading of nanoclay viz., 2.5, 5.0, 7.5 and 10.0 wt% and have been characterized by cure characteristics, physico–mechanical, and water absorption behaviours. The present study helped to optimize nanoclay loading in chloroprene rubber and enhances overall improvement in tensile, tear and water resistant properties without compromise in electrical resistivity. **Section 3.2** deals synergistic effect of carbon black and nanoclay in CR, which contained constant loading of nanoclay (5 Phr) and carbon black at different concentrations.

Influence of carbon black on the cure behaviour, mechanical and electrical properties and morphology changes in polychloroprene clay nanocomposites have been examined. Structural analysis and morphology characteristic of nanoclay and hybrid filler s filled CR have been studied by using XRD and TEM. The ability of the synergistic fillers in reinforcing rubber composite would contribute to the increase in overall properties of CR composites. **Section 3.3** details the specific study conducted on comparative performance of curing agents on physico-mechanical and dynamic mechanical properties of CR compositions. Interaction or effect of two types of curing agents on nanoclay and nanoclay/carbon black reinforced chloroprene rubber compounds are examined to see the efficiency of curing agent and to evaluate the best possible composition with improved water resistant property for under water acoustic encapsulant. **Section 3.4** deals detailed study on effect of two stages mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/Nanoclay compositions. The study covers adoption of mixing technique and use of dispersion agent to get better dispersion of fillers and low damping rubber composite, which in turn decide to select right composition and process for preparation of better encapsulation of transducers

Chapter 4 deals with the preparation, optimization and characterization of carbon black and nanoclay filled nitrile rubber. Synergistic effect of carbon black and nanoclay on physico-mechanical, electrical, morphology and dynamic mechanical characteristics is investigated in NBR samples**.** Dynamic mechanical and dielectric properties have also been presented. The specific studies include type and loading of carbon black and curing agent on performance of nitrile compound for encapsulation application. The all composites were performed for physico-mechanical properties such as water uptake, density, hardness, tensile strength and crosslink density. The dielectric properties and Payne effects of the composites have been studied by using DEA and DMA. Two best composites are optimized based specification requirement of encapsulation and recommended for frequency requirement of acoustic transducers used in underwater applications.

Chapter 5 deals about the details of development and testing of adhesive required for rubber encapsulation of transducers. Studies on adhesive include formulation of specialty adhesive, evaluation for bonding different substrates such as rubber to rubber and rubber to metal substrates and its ageing characteristics. Comparison of adhesive performance with commercial one was established. Explored bondability of adhesive with conventional and nanocomposite substrate’s surfaces to work in salt water environment.

Chapter 6 covers extensive evaluation of nanocomposite properties in comparison with presently used conventional rubber compound. This chapter covers consolidation of experimental study in terms of mechanical, electrical, dynamic mechanical properties and ageing characteristics. Polymer filler interaction and damping properties of the composites have been studied using RPA and DMA. Short term ageing effect on mechanical, electrical and dynamic mechanical properties and retention of properties after subjected to salt water immersion was evaluated to see the permanence of composites. The study also discussed acceptance of optimized composite selected for encapsulation of transducer as a means of assessing the composite is acoustically transparent. The echo reduction and insertion loss of the samples are determined by plotting the acoustic parameters against frequency. This chapter covered complete analysis of overall properties requirement and presented in details to qualify improved performance of nanocomposite over microcomposite for encapsulation application.

Finally, summary and conclusion of these research investigations are highlighted in **Chapter 7**. Furthermore, the scope for further research and references are cited at the end of the chapter.

7.2 CONCLUSIONS

The conclusions of the research work reported in this thesis in reference to its scope and objectives are briefly summarized below.

A systematic investigation on development and characterisation of chloroprene (CR) and nitrile (NBR) rubber nanocomposites based encapsulants for underwater transducers application were carried out. The effect of carbon black and nanoclay fillers on properties like physico-mechanical, electrical, dynamic mechanical and water absorption properties of CR and NBR rubber vulcansizates have been thoroughly investigated.

The preliminary study mainly focused on the preparation and characterisation of chloroprene rubber nanocomposites. Chloroprene rubber nanocomposites with four different loading of nanoclay were prepared. The cure time is reduced by almost six minutes for compounds containing 5 phr of nanoclay as compared with the unfilled CR. This effect is attributed to the accelerating effect of the ammonium groups of the organic cations present on nanoclay. It is seen that addition of 5 phr nanoclay in chloroprene rubber enhance overall tensile, tear and water resistant properties without compromise in electrical resistivity. Though mechanical properties are enhanced by addition of nanoclay, required hardness was not achieved for intended application and hence further research focused on understanding the synergistic effect of nanoclay and carbon black for improvement in functional property.

The effect of carbon black on CR-clay nanocomposites was further investigated to improve functional property requirement of encapsulants. A considerable decrease in cure time was observed with the addition of NC and CB on gum compound but increases with CB loading. This may be attributed to the presence of functional group on NC and basic nature of CB, which facilitate the curing reaction of CR. CR nanocomposites with a combination of nanoclay and carbon black show synergism effect and improve overall properties especially mechanical properties in large extent. Incorporation of a small amount of nanoclay about 5 phr along with 15 phr carbon black in chloroprene rubber enhanced tensile strength by 90% and tear strength by more than 100% in comparison with compound containing either carbon black or nanoclay alone. Furthermore, the improvement in properties due to synergistic effect of filers was well understood and confirmed by XRD and TEM image analysis.

Influence of curing agents on nanoclay and nanoclay/carbon black reinforced chloroprene rubber compounds are examined to see the efficiency and interaction of curing agents. Rubber and filler interaction were studied by RPA and DMA. RPA and DMA results that lead oxide cure gives better rubber filler interaction and improved storage modulus and lower damping constant, which is important for encapsulation materials. Compound with lead oxide showed lower water absorption and maximum retention of strength properties on ageing. The effect is more pronounced when dual filler is incorporated in lead oxide cure system than compounds with ZnO curing systems.

Process method and preparation of nanocomposite are given prime importance apart from filler and curing agent effect. A detailed study on effect of two-stage mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/nanoclay compositions has been carried out. Better dispersion with improved morphology in XRD and TEM clearly reveals the signatures of intercalated-to exfoliated structures of nano clay into the CR matrix. DMA studies proved that CR-2 sample shows optimum value of higher modulus and lower tan delta values for operating frequency requirement of underwater sensors.

Having understood the process and materials effect on preparation of CR based nanocomposite, development of nanocomposite technology has also been extended to nitrile (NBR) rubber. This presumes importance from application perspective of transducer encapsulations. Nitrile rubber is preferred over chloroprene rubber (CR), where oil resistance is important particularly in towed array sensors. Synergistic effect of carbon black and nanoclay on physio-mechanical, electrical, morphology and dynamic mechanical characteristics of NBR is extensively investigated and the results are concluded in this study**.** Rubber nanocomposites based on NBR, Carbon black (CB) and Nanoclay (NC) are prepared via melt compounding using two roll mixing mill. Calcium stearate was incorporated in place of stearic acid to aid in dispersion of NC in polymer matrix. The developed nanocomposite was well characterized by physico-mechanical and electrical properties. The morphology of the nanocomposites was examined by HRTEM and XRD analysis and correlated with dynamic mechanical study (DMA).

Cure characteristics of NBR composites reflected a marching behaviour levelling out of a quasiplateau, which indicates the cure safety of all the samples. Initial torque and delta torque values are lower for modified formulation due to lower amount of reinforcing filler and replacement of dithiocarbamate accelerator due to its delaying action in cure rate. The mechanical property of the composites containing 5 phr of clay in conjunction with 20 phr of FEF filler (Dmod) and a combination of 3 phr clay with 20 phr FEF and 10 phr GPF (B3), respectively, resulted in best combination of mechanical properties particularly high elongation at break. Morphology improvement and formation of hybrid nanostructures observed for Dmod and B3 samples were confirmed by XRD and TEM images. Dielectric property of the composites shown that the dielectric constant decreases with increasing concentration of nanoclay while it increases with increasing amount of carbon black filler. At higher frequency B3 offered higher resistivity than Dmod.

The dynamic mechanical properties of the nanocomposites have been studied and observed lower Payne effect for B3 compared to Dmod. Time temperature superposition (TTS) was done for the two samples Dmod and B3 at 30 ^{o}C. Peak values of tan δ are observed for Dmod at about 1.3 kHz and 980 Hz for B3 samples respectively. TTS in dynamic mechanical analysis test of the composites indicated lower mechanical loss in the frequency range of interest. Finally acoustic properties of two composites have been analysed and compared with control compound to assess acoustic transparency characteristics. Insertion loss values for nanocomposites are comparable with control compound and show less than 1 dB throughout the frequency range of 0.5–4 kHz. The study on NBR nanocomposite concluded that Dmod can be used in the low frequency region, whereas B3 is suitable for the high frequency region for application. The unique hybrid filler nanostructure is responsible for indulging such a judicious combination of properties. The advantages accruing due to overall property enhancement, including lower water absorption, and better electrical and excellent acoustic properties of NBR composites make it suitable as underwater acoustic transparent materials for transducer encapsulation application.

In the construction of transducer engineering, adhesive is considered an important material next to rubber as it is required to bond dissimilar components during encapsulation process. Speciality adhesives based on neoprene rubber/resin blend have been formulated and detailed study carried out for bonding vulcanized rubber-to-rubber and vulcanized rubber to metal substrates to work in a marine environment. The adhesive has been optimized based on special compounding, mixing technique, ease of application method etc and achieved 70% increase in peel strength value compared to unfilled gum. The bondability of nanocomposite substrates has also been evaluated using optimized adhesive and compared with commercial Chemlok electrical grade adhesive. Evaluated bond strength on aging under heat and saltwater environment and retained maximum strength properties. This particular adhesive found useful in producing bonded transducer components where insulation resistance is prime importance such as hydrophone encapsulation, junction box and cable splicing, etc.

An extensive experimental study has been conducted to evaluate nanocomposite properties in comparison with presently used conventional rubber compound and consolidated results in terms of mechanical, electrical, dynamic mechanical properties, acoustic and ageing characteristics. Single stage mixing followed for preparation of microcomposite where as for nanocomposites two-stage mixing was practiced to get better dispersion of nanofiller. A reduction in cure time was obtained for nanocomposites due to the presence of nanoclay. The dynamic viscoelastic properties of nanocomposites versus microcomposites have been analysed using strain sweep measurement by RPA. Minimum variation in storage modulus (i.e., lower the Payne effect) was observed for nanocomposites due to stronger and more developed filler and rubber network compared to reference compound. Tensile and tear strength of nanocomposites found to increase enormously due to effective reinforcement of nanoclay in rubber matrix. In addition, elongation at break unusually increases for nanocomposite because of the layer of silicate structure restricts the tearing of polymer molecules under stretching during tensile test. The other properties like volume resistivity and water absorption matches with reference compound. It is found that the nanocomposites with the hybrid fillers shows the better mechanical properties compared to microcomposite.

DMA studies indicated that increased value of storage and loss modulus was observed for microcomposite due to higher loading of fillers and onset of CB aggregation. TTS plot of master curve shown that storage modulus and loss modulus increases with increase in frequency for all three samples. Lower loss modulus and low damping constant values are obtained from master curve for CR2 sample compared to RC and B3 samples. However, both micro and nanocomposite show lower damping constant, which is important for encapsulation materials.

Adhesion strength properties evaluated for all three substrates using developed and Chemlok grade adhesives and observed that adhesion was good for both CR based reference compound (RC) and CR based nanocomposite (CR2) bonded using adhesive, Adh(B). However, improved bonding is achieved for nitrile substrates using Chemlok adhesive as developed adhesive give lower strength for the same substrate. In addition, high retention of bond strength was obtained for nanocomposites compared to reference compound substrates surface.

A short-term evaluation of functional property changes in mechanical, volume resistivity and dynamic mechanical properties of chloroprene and nitrile rubber composites have been investigated. Short term ageing was conducted in salt water environment and retention of properties such as mechanical strength, electrical properties and dynamic mechanical parameters are measured. Test results show that retention of tensile strength and EB% property on ageing is higher for nanocomposites compared to reference compound. The same pattern was followed for volume resistivity and dynamic mechanical properties, as nanocomposites do not show much variation on ageing. The ageing study results that both nanocomposites retained their maximum properties and shown lower values of diffusivity and permeability requirement of encapsulation materials. The last but most important acoustic properties are evaluated for all three composites. Echo reduction and insertion loss were studied for optimized nanocomposites and proved the developed composites are considered to be acoustically transparent materials. Results show that though nanocomposites acoustic transparency characteristics are slightly less as measured from the values of echo reduction and insertion loss compared to reference compound, all three compound are considered to be acoustically transparent materials for underwater transducer applications.

The present investigation revealed that nanocomposites containing a mixture of organoclay and carbon black in right proportion can be a substitute for micro composite in terms of mechanical, electrical and water resistant properties and can be useful as encapsulant for underwater transducer applications. CR based nanocomposite can be selected for application which require transducer operation in low frequency region and directly in contact with water environment where improved salt water resistant and bondability is prime requirements. Nitrile rubber (NBR) is preferred over chloroprene rubber (CR) for application, which requires transducer operation in high frequency region or application, where oil resistance is important particularly in towed array sensors. The significant enhancement of material's unique properties and easy processability of nanocomposite could be a promising candidate over micro composite for encapsulant use in underwater sensor applications.

7.3 SCOPE FOR FURTHER WORK

The present objective of the work was met with development of encapsulant materials with improved functional properties by nanotechnology route. Though there were improvements in technical properties of the composites with the addition of both nanoclay and carbon black, there is ample scope for carrying out further extensive investigations as follows. The present composites were prepared using two roll mixing mill. Different process or mixing techniques such as Brebender plsticorder and Banbury mixer can be tried to improve the dispersion of nano fillers and hence the improvement in performance of end products. Preparation of pre-pregs loaded with nanoclay of different size and blending with other ingredients in rubber compounding is an area of research that can be investigated.

Though it has been found that nanoclay reinforce effectively in CR and NBR matrix and shows synergism with carbon black, much light could not be shed on the synergistic effect of these nanoclays with other carbon black types and silica. Study should also be explored to see effect of various dispersion agents effects other than calcium stearate. Addition of different fillers and disperser results various complex phenomena at the interface of the polymer-filler and filler-filler interfaces need to be understood properly. Based on the results obtained in this study, further investigation is necessary for understanding the curing kinetics of the compounds and long term ageing effect on the performance of vulcanizates.

Underwater transducers are generally designed to operate in the region of a few hundred Hz to say 80 kHz. Dynamic mechanical properties are directly related to acoustic properties and hence any change in the dynamic properties is bound to reflect in the acoustic behavior as well. A more detailed study is quite essential in order to understand relationship between viscoelastic behaviour and acoustic performance of passive acoustic materials. Further studies are recommended to undertake a work on establishing the correlation between the viscoelastic parameters and acoustic behaviour and thus establish a mathematical model on their relationship. This would contribute immensely to the development of advanced materials for future underwater sensors applications. Finally, improved products can be fabricated and evaluated for actual encapsulation applications.

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APPENDIX-I

LIST OF PUBLICATIONS

I Papers Published in International Journal

1. **P. Annadurai**, T. Mukundan and Rani Joseph, "Influence of carbon black in polychloroprene organoclay nanocomposite with improved mechanical, electrical and morphology characteristics", Intl. Journal of Plastics, Rubber and Composites: Macromolecular Engineering, Vol. 42, No. 9, 2013, pp. 379–384.

2. **P. Annadurai**, S. Kumar, T. Mukundan, Rani Joseph, P. Sarkar and S. Chattopadhyay, "Effect of Nanostructures of Modified Clay–Carbon Black on Physico-Mechanical, Electrical and Acoustic Properties of Elastomer-Based Composites", Intl. J. Polymer Composite, DOI 10.1002/pc.23351, 2014.

3. **P. Annadurai**, P. Jayesh, T. Mukundan, Rani Joseph and T. Santhanakrishnan, "Studies on effect of curing agents on properties of carbon black–nanoclay reinforced CR based nanocomposites", Polymer Bulletin **(Communicated)**.

4. **P. Annadurai**, P. Jayesh, T. Mukundan, Rani Joseph and T. Santhanakrishnan, "Influence of dispersing agent and method of mixing on performance of carbon black-nanoclay reinforced CR compound for encapsulation of underwater acoustic sensors", Bulletin of Materials Science **(Communicated)**.

5. **P. Annadurai**, P. Jayesh, R. Rajeswari and T. Santhanakrishnan, "A study on composition and ageing effect on adhesion properties of CR based adhesive for acoustic sensor applications", The Journal of Adhesion **(Communicated)**.

II Papers Published in In-house DRDO Journal

1. **P. Annadurai** and T. Mukundan, "Polymer Clay Nanocomposites for Functional Application", Sea Tech Journal, Vol. 8, 2011, pp. 85–91.

III Papers Presented in International Conferences

1. **P. Annadurai**, P.N. Mohandas, P. Jayesh and T. Mukundan, "Polychloroprene–Clay Nanocomposites: Influence of compounding Techniques", Intl. Rubber Conference (IRC), held at Mumbai, India, 17–19 November 2010.

2. **P. Annadurai**, C.G. Padmakumar and P. Jayesh, "Development of rubber adhesive based on chloroprene resole blend for underwater transducer application", Intl. Seminar on Acoustics organized by NPL, CSIR, New Delhi, India, 10–15 November 2013.

3. **P. Annadurai**, T. Mukundan, Rani Joseph and S. Chattopadhyay, "Effect of two stage mixing and dispersion agent on morphology and dynamic mechanical properties of CR/CB/Nanoclay compositions for underwater acoustic application", Intl. Conference on Polymers and Allied Materials (CLAM), IIT, Patna, India, 30–31 May 2014.

4. **P. Annadurai**, T. Mukundan and Rani Joseph, "Comparative evaluation of Polychloroprene based micro and nanocomposites as encapsulants for underwater transducers", Intl. Conference on Advancements in Polymeric Materials (APM), IISc, Bangalore, India 20–22 February 2015.

IV Papers Presented in National Conferences

1. **P. Annadurai**, T. Mukundan and S. Chattopadhyay, "Studies on morphology and mechanical properties of Clay-reinforced NBR Nanocomposites as encapsulant for use in underwater sensors", National Conference on Microscopy in Material Science and Biomimetic Technology at DMSRDE, DRDO, Kanpur, India, 26–28 February 2015.

2. **P. Annadurai**, T. Mukundan and Rani Joseph, "Comparative study on curing agents on nanoclay reinforced chloroprene rubber for acoustic sensor application", Paper presented at National Conference on Acoustics, NIO, Goa, India, 07–09 October, 2015.