“Study of Kinetics and Properties of PBR/Nano filler Based Composites Prepared via *in- situ* Process Using Ziegler Natta Polymerization Systems”

By

Niravsinh Kosamia

(14MCHE05)

NIRMA UNIVERSITY
INSTITUTE OF TECHNOLOGY
NAAC ACCREDITED ‘A’ GRADE

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481
MAY-2016

“Study of Kinetics and Properties of PBR/Nanofiller Based Composites Prepared via *in- situ* Process Using Ziegler Natta Polymerization Systems”

Project

Submitted in partial fulfilment of the requirements
For the Degree of

Master of Technology
In
Chemical Engineering
(Environmental Process Design)

By
Niravsinh Kosamia
(14MCHE05)

Guided By
Dr. Ganesh C. Basak
&
Prof. Nikita. Choksi

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481
MAY-2016

Declaration

This is to certify that the thesis comprises my original work towards the degree of Master of technology in Environmental Process Design at Chemical Engineering Department, Institute of Technology, Nirma University and not been submitted elsewhere for a degree. Due acknowledgement has been made in the text to all other materials used.

Niravsinh Kosamia
(14MCHE05)

Chapter 1 Undertaking for the Originality of the Work

Niravsinh Kosamia (14MCHE05), gives undertaking that the major project entitled "**Study of Kinetics and Properties of PBR/Nanofiller Based Composites Prepared via *in-situ* Process Using Ziegler Natta Polymerization Systems**" submitted by me, towards the partial fulfilment of the requirements for the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad is the original work Carried out by me and I give assurance that no attempts of plagiarism has been made. I understand, that in the event of my similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

Niravsinh Kosamia

Date:

Place:

Ahmedabad

Endorsed by

Signature of Guide
Dr. Ganesh C. Basak
Senior Manager,
Reliance Technology Group,
Reliance Industries Limited, Vadodara

Certificate

This is to certify that the Project Report entitled "**Study of Kinetics and Properties of PBR/Nanofiller Based Composites Prepared via *in- situ* Process Using Ziegler Natta Polymerization Systems**" submitted by **Mr. Niravsinh Mahendrasinh Kosamia** Student (14MCHE05) towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering Environmental Process Design of Nirma University is the record of work carried out by him under our supervision and guidance. The work submitted has in our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of my/our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

Prof Nikita Choksi
Guide, Assistant Professor
Department of Chemical Engineering
IT, Nirma University

Dr. Ganesh C Basak
Senior manager,
Reliance Technology Group,
reliance Industries Ltd, Vadodara

Dr. S.S. Patel
Head of Department
Department of Chemical Engineering
IT, Nirma University

Dr. P.N.Tekwani
Director
IT, Nirma University

Dr. Jayesh Ruparelia
Professor, P.G. Coordinator
Chemical Engineering Department
IT, Nirma University

Examiners:

Date of Examination:

Abstract

Literature studies envisage that polybutadiene rubber based nano composites are mostly prepared by either using solution method or melt compounding method. But, solution process is economically infeasible and not environmentally benign due to major waste of solvent, while melt intercalation solves the problem associated with solution method, however poor dispersion of nanofillers is observed because of weak interaction between the polymer and nanofillers. This ultimately reduces rubber properties substantially. On the other hand, the advantage of *in situ* approach lies in the better exfoliation achieved compared to melt and solution methods. Therefore, the objective of the present work is to improve dispersion of nanofillers into rubber matrix by *in situ* method during polymerization reaction.

The research interest on multi-wall carbon nanotube (MWCNT) and nano silica (NS) has been increased enormously because of the possible large scale production of these materials. In our earlier study, *ex situ* polybutadiene rubber (PBR) based nano composites were studied and further investigated their physico-mechanical, morphological and thermal properties. Finally the filler concentration in the composites based on their mechanical and thermal properties improvement were optimized. Among the various nanofillers used in *ex situ* process, MWCNT & NS have been chosen for further investigation. In this present work, batch solution polymerizations were performed to study the effect of nanofillers loading on the kinetics of the stereospecific polymerization of 1, 3-butadiene catalysed by Ziegler-Natta catalytic systems and properties of the synthesised *in situ* nano composites. To study the kinetics of polymerization, conversion, yield, viscosity average molecular weight, exothermicity of the reactions were measured. The effect of nano filler concentration showed that adding nanofillers causes no consolidated change in the kinetics curve, whereas there is an optimum dose of MWCNT loading wherein the monomer conversion and yield reached to its maximum level. However, increasing nano silica content results showed no such improvement for Ni based systems, but showed improvement in Co based systems. Moreover the nanofillers did not have any significant effect on microstructure. The best improvement of mechanical and other important properties like hardness; heat build-up etc. was achieved for nano composites containing 0.5 phr MWCNT.

Key words: Polybutadiene rubber, *in situ* polymerization, nanofillers, nanocomposites, physico-mechanical properties

Contents

1 Introduction

2 Composites

3 Experimental

List of figures

List of tables

Chapter 1

Introduction

1.1Rubber

The polymer matrix system is categorised as thermoplastic, thermo set, or elastomeric. A thermoplastic polymer is soft when it should be heated above the glass transition temperature and it should be moulded into desired form by applying cooling. On the other hand thermosetting materials become permanently hard because of cross-linking when heated above Tg. So for this reason thermosetting polymers should not be moulded by softening. Instead, they must be fabricated during the cross-linking process. Rubbers are lesser cross linked polymer systems and have properties that lie between the range of thermosets and thermo plastics. The word rubber signifies a unique group of material which may be identified by their ability under certain condition to undergo a large deformation and recover almost completely and instantaneously on a release of deforming force. The elasticity of rubber is derived by particular kind of molecular structure. The reversible recovery of a deformed rubber to its original state is due to an entropic driving force. The entropy is minimum in the expanded confirmation and maximum in the random coil confirmation. Chemical and physical cross linking is required for desired molecular structure.

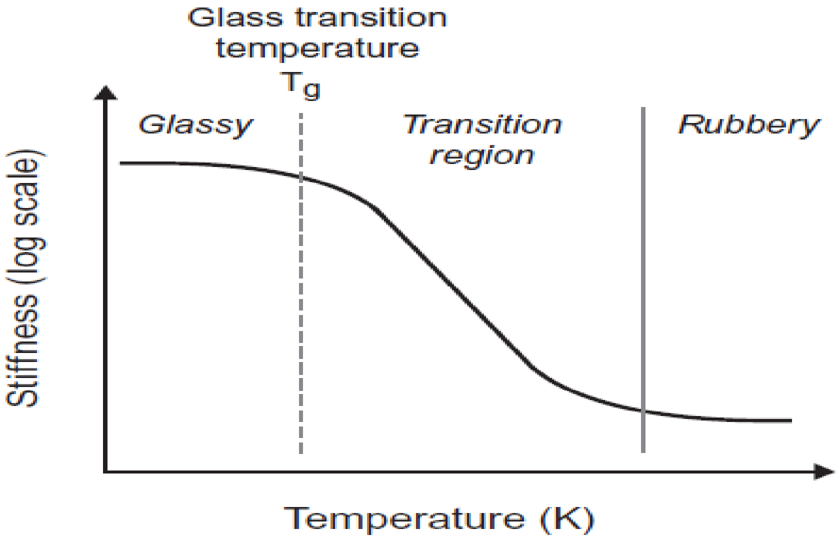


Fig1.1: Various stages of polymers and their dependence on Tg

1.1.1 Natural rubber

The outstanding source of natural rubber is “Hevea Brasiliensis “tree. It was originally derived from the latex obtained in the sap of rubber trees. Although, purified natural rubber can be synthetically prepared. For the softening and improvement of properties and stability of rubber, compounding ingredients can be added. Natural rubber is a polymer of isoprene with chemical formula $(C_5H_8)_n$. The longer polymer chains are break by mastication or passing through the rotating blades. The rubber is compounded with fillers, anti-oxidants, plasticisers, oil and vulcanizing agents. Then the compounded rubber is sheeted and extruded in special shapes and moulded. It is an ideal polymer for various dynamic and engineering applications. Due to its unique elastic property, resilience and toughness, it is the basic constituent of many products used in different field of applications like transportation, industrial, consumer, hygienic, medical sectors and so on.

1.1.2 Synthetic rubber

Despite of several advantages of NR along with modern compounding make it satisfactory for many applications, but due to dependence on natural crop only in tropical countries and relatively poor heat and weather resistance properties, synthetic rubber has come into picture to replace NR in a wide range of applications. The major classes of synthetic rubber are generally made of raw material derived from petroleum, coal, oil, natural gas, and acetylene. The worldwide capacity of all the synthetic rubber is about 13000 kilo tonnes. Rubbers such as butadiene rubber, isoprene rubber, ethylene propylene rubber, styrene butadiene rubber compromise a majority of this volume.

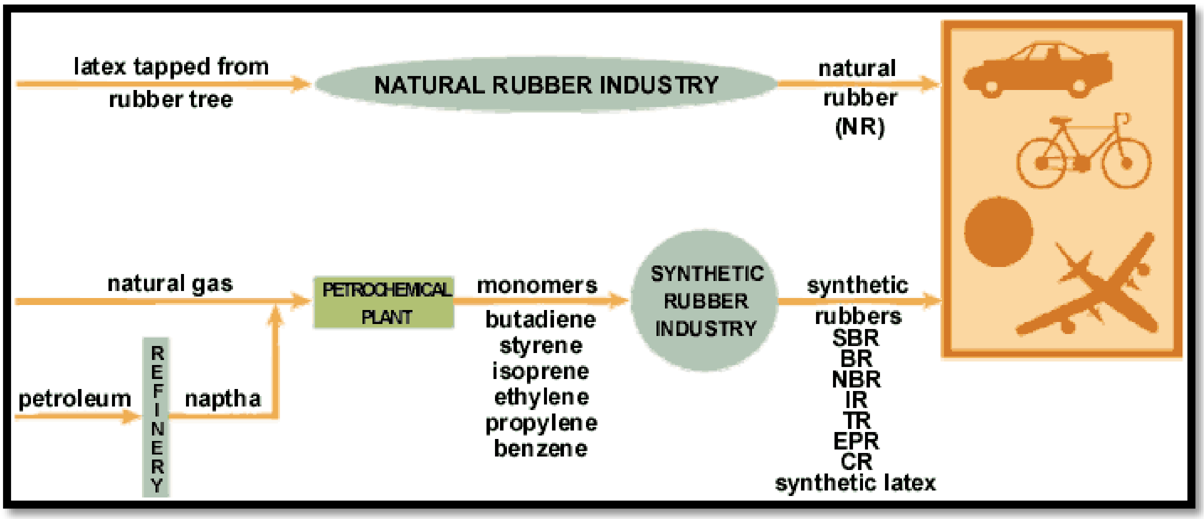


Fig1.2: Different ways of production of synthetic rubber
(https://www.google.co.in/search?q=synthetic+ru)

1.2 Poly butadiene rubber

Poly butadiene Rubber is homo polymer of 1, 3-butadiene monomer containing four carbon atoms, and six hydrogen atoms. The four carbon atoms are in a straight chain containing two double bonds. It is the double bonds that are the key to polymer formation. Consumption of butadiene is 2500000 tones worldwide. The tyre industries consume 60-70% BR to its total production. Four companies account for about 50% of the world capacity for BR. 1, 3 BR is polymerised to produce different isomers but from them only some are elastomers. 1, 4 polymerised BR can exist in cis and trans form depends on orientation of substituent across the double bond.1, 4 BR in both conformation is made by transition metal coordination catalyst closely related to Zeigler-Natta catalyst close to poly olefins. Higher cis content BR is made by anionic catalyst. BR produced by this method contains some presence of ketone, aldehyde, amine, or tin/silica halides. The presence of this functionality leads to strong interaction with filler and leads to lower hysteresis

$CH_2=CH-CH=CH_2$

1, 3 butadiene

Fig 1.3: Chemical structure of 1, 3 Butadiene

1.3Types of Poly-Butadiene rubber

1.3.1 Low cis

The alkyl lithium or “anionic “catalyst system produces a polymer with about 40% cis, 50% Trans and 10% vinyl. This method is very versatile because the growing chain end contains a living anion (negative charge) which can further reacted with coupling agent or other functional group for making of modified poly butadiene. The vinyl content increases the Tg of poly butadiene by creating a stiffer chain structure.

1.3.2 High cis

The transition metal or Ziegler –Natta catalysts produce very “sterioregular” poly butadiene with the polymer chain is on the same side of carbon-carbon double bond. They have usually >95% of cis content, trans content is less than 2% and vinyl content is less than 1%.They have lower value of Tg compare to low cis due to very little amount of vinyl content. Cut growth resistance is very important in tyre industries which are provided by his material.

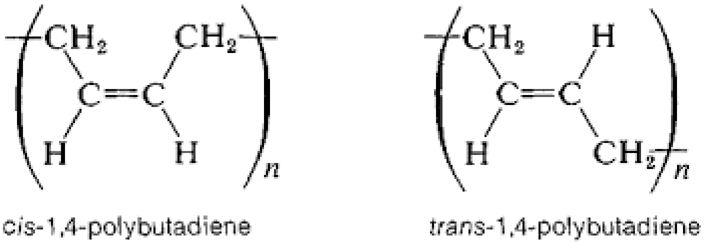


Fig: 1.4 chemical structure of Cis and Trans configuration

1.3.3 Trans poly-butadiene

In the Trans poly butadiene the main polymer chain is opposite site of carbon-carbon double bonds. It is also made from transition metal catalyst.

1.3.4 High vinyl poly-butadiene

High vinyl butadiene have a higher glass transition temperature could be advantageously used in combination with high cis in tyre. The material is produced with alkyl lithium Catalyst.

1.4 Preparation method of polybutadiene rubber

Most BRs are made by a solution process, using either a transition metal (Nd, Ni, or Co) complex or an alkyl metal, like butyl lithium, as catalyst. Since the reaction is very exothermic, and can be explosive, particularly with alkyl lithium catalysts, the reaction is normally carried out in solvents like hexane, cyclo-hexane, benzene or toluene. The solvents are used to reduce the rate of reaction, control the heat generated by the polymerization and to lower the viscosity of the polymer solution in the reactor. A typical BR polymerization would be run at about 20% monomer and 80% solvent. The polymerization can either be a batch process or a continuous process. In batch mode, monomer, solvent and catalyst are charged to the reactor, heated to initiate the process, and then allowed to continue to completion. The polymer solution is then transferred to another vessel or process unit to remove the solvent. In continuous mode, monomer, solvent and catalyst are continuously fed into the bottom of the first of a series of reactors at a temperature suitable for polymerization. The polymerization progresses as the solution flows through the reactors and polymer solution is taken off at the top of the last reactor without stopping the process. The continuous process is the most economical. In both processes, the finished product is usually in the form of bales which weigh from 50 to 75 pounds each.

1.5 1, 3-butadiene polymerization microstructure

1, 3-Butadiene is an organic compound that is a simple conjugated dine hydrocarbons. In terms of connectivity of the polymer chain butadiene can polymerize in cis, trans and vinyl conformation. cis and trans forms arise by connecting the butadiene molecules end to end so called 1, 4 polymerization. In this three connectivity polybutadiene differ in terms of their branching and molecular weight. The Trans double bonds formed during polymerization allow the polymer chain to stay rather straight. The cis double bond cause a bend in the polymer chain from aligning to form crystalline regions which results in larger region of amorphous polymer. It has been found that a substantial percentage of cis double bond configuration in the polymer result in material with flexible elastomer qualities.

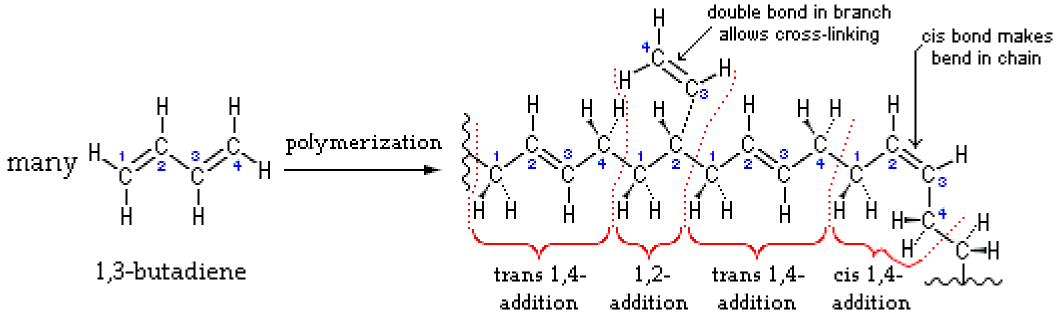


Fig1.5: Mechanism of 1, 3- butadiene polymerization

1.6 Application of polybutadiene rubber

- Poly-butadiene rubber is highly used in various parts of automobile tires. Its uses in the tread portion of giant truck tires help to improve the abrasion.
- In passenger car tires poly-butadiene rubber can be used with SBR in the tread portion.
- It is used in the inner tube of rubber hoses for sandblasting, along with natural rubber. The main idea is to increase resilience. This rubber can also be used in the cover of hoses mainly pneumatic and water hoses.
- This rubber can also be used in railway pads, bridge block, golf ball, foot wear production etc.
- High cis poly-butadiene is used in surface coating, adhesives, thermosetting resin formulations, synthetic drying oils.

1.7 Reliance VMD in polybutadiene business

Quality of polybutadiene rubber under the trade name of “Relflex Cisamer PBR” is benchmarked with global manufacturers linked to the standards of International Institute of Synthetic Rubber Producers (IISRP). Reliance produced 120 KTA PBR per year from Vadodara [PBR-I plant (Co-grades) & PBR-II plant (Ni-grades); 80 KTA] and Hazira manufacturing sites [PBR-III (Ni/Nd swing plant); 40 KTA]. In world scenario, PBR accounts for approximately 25% of the world’s production of synthetic rubber. Seventy percent of total production is used in tire compounds, with another twenty percent being used for production of soles, gaskets, seals, belts, etc. due to its superior elasticity, resilience and abrasion properties. Reliance elastomer supplies poly-butadiene rubber to tyre manufacturer across all segments.

Fig1.6: poly-butadiene rubber bell (synthera reliance year 2014-march)

1.8 Poly butadiene rubber plants

In 1978, IPCL Vadodara, now Reliance Industries Ltd-Vadodara manufacturing division (RIL-VMD), PBR-I manufacturing facility was set with the help of Polysar Canada. The installed capacity of this plant was 20,000 TPA. Later in 1996, another plant was set up with Japan Synthetic Rubber Co Ltd., Japan consisting the capacity of 40,000 TPA. Both the plants use different solvent and catalyst systems.

Sr. No.	Subject	PBR-I	PBR-II
1	Technology	M/S Polysar Canada (1978)	M/S Japan Synthetic Rubber (1996)
2.	Capacity	27 KTPA	43 KTPA
3.	Catalyst	Cobalt Octanoate	Nickel Naphthenate
4.	Co-Catalyst	Diethyl aluminium chloride (Et_2AlCl)	Terithylaluminium (Et_3Al)
5.	Promoter	Water, H20	Boron Trifloride Etherate, BF3ET2.
6.	Solvent system	Benzene/Toluene (70/30)	Toluene Heptane (50/50)
7.	Temperature	24-29°C	65-70 °C
8.	Chain transfer Agent	1,2 Butadiene	-
9.	Short Stop (Terminator)	Methanol	PPA(Phosphate of polyoxyethylene alkyl phenyl ether)
10.	Anti-oxidant	DTBPC (Ditertbutyl-p-cresol)	DTBPC
11.	Reaction time	60-65 min	4 hrs.
12.	No. of Reactors	3	4

13.	Feed Direction	Top-Bottom	Bottom-top (Overflow)
14.	Conversion	60-65%	~90%
15.	Cis	>96%	>96%
16.	Gel Content	<500 ppm	<300 ppm
17.	Molecular Weight distribution	2.5-3.5	3-4

1.9 Fillers

Fillers are the solid substance that can improve the mechanical properties, hardness, tear resistance and processing for the control of thermal conductivity, magnetic properties and thermal expansion. They can be classified as a non-functional or non-reinforcing fillers and functional or rein forcing fillers. Non rein forcing fillers are added to polymer to reduce the cost. They do not have any functional group that can interact with polymers. Reinforcing fillers have a group that can be interact chemically or physically with polymer chain to improve the tensile properties like tensile strength, elongation at break, and modulus. Incorporation of filler in a polymeric material increases density and modulus of composites. Other properties like flow behaviour and thermal barrier properties might also change [2].

Nano fillers

Definition: “Nano fillers are the new class of fillers which have at least one characteristic length scale in the order of nano meter with varying shapes ranging from isotropic to highly anisotropic needle- like or sheet like element.”

1.10 Types of Nano fillers

1.10.1 Carbon Nano tubes

Carbon nano tubes contain a pure carbon atom in cylindrical structure. CNT is divided in to

(1) Single walled carbon nano tubes (SWCNT)

(2) Multi walled carbon nano tubes (MWCNT).

SWCNT having only one layer of graphene sheet and MWCNT had more than one graphene sheet. CNT having diameter in nano sized and length in micro meter range. CNT having a small diameter, higher aspect ratio large conductivity a and very good mechanical property.CNT is the strongest substance having a tensile strength greater than steel but only one sixth weight of steel [3]. CNT had a strong and resilient structures. It can be easily stretched and buckled without failure. Functionalization of CNT improves the dispersion of CNT in to polymer matrix due to the polar group chemically bond on the filler surface. CNT mixed with matrix of styrene butadiene rubber and natural rubber, the reinforcement is achieved by only 3 phr (1.6 vol %) loading of filler and composite shows conductivity of 0.1 scm^{-1}[4].

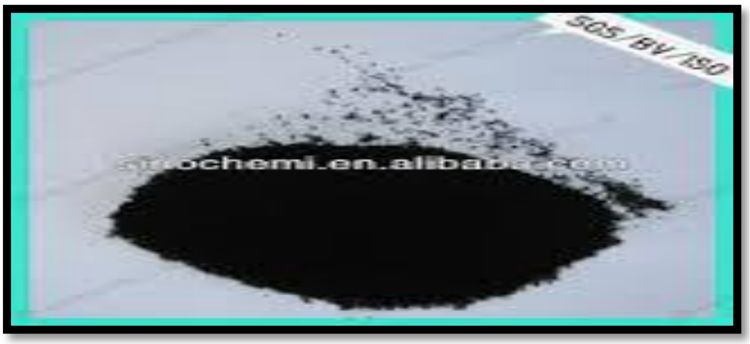


Fig1.7: Carbon nano tubes (Alibaba.com)

CNT based nano composites find its application in chemical sensors, super capacitors, optical materials, automotive and aero special industries, electrostatic dissipation. The Electro chemical modification and surface initiated *in situ* polymerization is the best means for CNT nano fillers.

1.10.2 Nano silica

There is a hydrophilic character of silica surface contributes very extensive interaction with rubber matrices gives excellent change in mechanical property of composites. The dependence of silica filler dimensions on particular rubber matrices cross linking density, catalyst concentration, filler loading is studied by small angle X-ray scattering. At a given value of strain, stress is increased with increasing the silica content.

Fig1.8: Nano silica (Alibaba.com)

The conventional filled silica shows high modulus at low elongation due to formation of larger aggregates of particle and *in situ* silica shows higher modulus at higher elongation. The main drawback of this filler is higher compound viscosity and the incompatibility of silica and rubber the more complex mixing and processing and the longer vulcanization time and the lower cross linking density [5].

1.10.3 Layered silicates

It is the rock forming minerals and main active minerals in soil and clay. These sheet like nano fillers are 1 nm thick and 100s to 1000s of nano meter long, as a result they poses a high aspect ratio. There are two types of micro structure are formed in polymer/layered silicates

- Intercalated: A regular pattern of insertion of polymer in the galleries of silicates.
- Exfoliated: The individual silicates layers are approximately 1nm apart and dispersed in a continuous polymer matrix. This structure exhibits better properties compare to later one because of higher polymer/LS interaction.

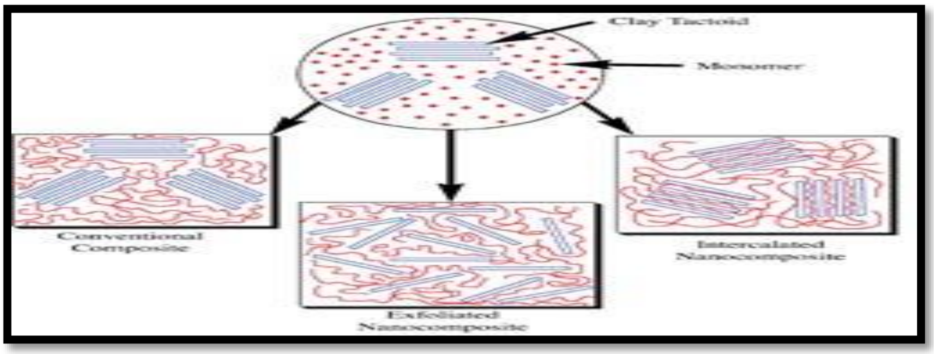


Fig1.9: layered silicate filled Nano composites

(layered+silicate+nanocomposites&rlz=1C1GIGM_en)

1.10.4 Nano clay

The montmorillonite (MMT) clays are naturally occurring substance. The chemical composition of clay affects the final composites properties. This alumina silicates have a sheet like structure and consists a layer of silica, SiO4, tetrahedral bonded to aluminaAlO_6 octahedral in various ways. Smectite clays is the most common MMT clays.

Fig1.10: Nano clay (alibabba)

1.11 Factors affecting the Filler Rubber matrix Dispersion

1.11.1 Particle Size

The filler particle size determines the “inner” or specific surface area which is the potential contact area between filler material and surrounding binder matrix. Since nano materials tend to agglomerate or may already occur in agglomerated states, the resulting surface area is largely affected by the degree of exfoliation and dispersion. Fully exfoliated and perfectly dispersed nano filler will have the greatest effect on the physical properties. The specific surface area is increased 100-fold when going from 10µm to 100nm while keeping the theoretical volume or the filling level constant.

1.11.2 Geometry

The particle geometry will also strongly influence the properties of the nano composite material. Elongated nanostructures such as carbon nano tubes exhibit high aspect ratios. Higher aspect ratios will increase the reinforcing ability on the surrounding matrix material. Therefore nano tubes or other elongated nano fillers excel over spherical particles in terms of reinforcement. Nano tubes can be considered as (quasi-) one-dimensional filler particles in terms of reinforcement. Similar nano materials are nanowhiskers3, nano rods, nano wires and nano fibres which have also been reported as nanoscopic reinforcing filler material for polymers. Natural occurring representatives of a two dimensional filler material are layered silicates or so called nano clays. The most widely used nano clays in material applications are so called montmorillonites as flame retardant in polymers.

Chapter 2

Composites

Principle: “Mixing gives average property”

A composite is a heterogeneous mixture of two or more materials. It consists two phase continuous phase termed as matrix and a dispersed phase termed as filler with recognizable interface boundary. Mainly composites are classified in two types

- Micro composites (conventional)
- Nano composites

The betterment in properties of nano composites compare to micro composites is because of four major effects

- Polymer molecules are wrapping around the stiff additive particles
- Interfacial forces between the two forces
- Distribution of stress/ applied load
- Reinforcing effect

In rubber nano composites one or more phase having a nano scale dimensions are embedded in rubber matrix. The property of nano composites depends on the type of matrix, loading, degree of dispersion, size, shape and orientation of nano particle, interaction between matrix and second phase. Nano composites may be classified as

- Clay- based nano composites
- Silica-based nano composites
- Polyhedral oligomer silsesquioxane-based Nano composites
- Carbon nano tube-based nano composites
- Nano composites based on other nano fillers like metal oxides, hydroxides and carbonates

2.1 History of nanocomposites

Okada et al is provide the first application of polymer nano composites. He invented Nylone-6 by polymerization in the presence of monomer. Right now it is used to make the timing belt cover of Toyota’s car engine and also for the packaging films. In that elastomer act as polymer matrix and different fillers like silica nano particles, layered silica, carbon black, carbon nano tubes, are dispersed on a nano level by different methods. These fillers are one dimensional or two-three dimensional in nature. In 2009, Boeing completed the first successful test flight of the Boeing 787 Dream liner. One of the primary innovations of the Boeing 787 is the extensive use of composites materials. Composites are formed by incorporating multiple phase components in a material in such a way that the property of material is unique. Composite materials comprise half of dream liner weight. For example, the fuselage of the Boeing 787 is made from carbon fibre reinforced plastic (a composite of carbon fibres in an epoxy matrix). The carbon fibres impart strength and stiffness to the material, and the epoxy matrix binds the fibres together [1].

Fig2.1: Boing 787 (Boeing+787&rlz=1C1GIGM_en__606)

2.2 Advantages of nano composites

- Lighter in weight because of low filler loading
- Low cost because, lesser amount of filler used
- Combination of specific properties
- Improved properties compared to conventional filler based composites at a very low loading of filler

2.3 Multi functionality of nano composites

- Transparent , flexible, electrical conducting material
- Good stability against environment circumstances
- Better durability and 100 times more wear resistance to conventional composites
- Toughness and strength altered fracture modes

2.4 Critical issues in nano composites

There is lack of understanding of interfacial bonding between reinforcements and polymer matrix. Following issues are related to nano composites

- Dispersion: uniform dispersion of nano fillers is a major issue because of agglomeration due to van der walls bonding. MWCNT are tangles together like spaghetti.
- Alignment: due to the small size of nano filler it is difficult to align them in matrix. There is a lack of control of orientation of nano filler.
- Volume and rate: for the commercial viability point of view high volume- high rate manufacturing of Nano composites is essential.

2.5 Preparation methods of nano composites

2.5.1 *in- situ* method

This method was first method to synthesize nano composites. It is the conventional method for the synthesis of thermo set nano composites. The monomer is the starting material in this route. The monomer concentration is very little around 20% to 30% in solvent in which it is dissolved. This method widely used when end product is insoluble in solvent. *In- situ* polymerization gives better stress transfer between rubber matrix and filler. In CNT filler system micro molecule chains not allow the filler to form an interconnecting network [10].

2.5.2 Solution method

In this method the polar solvents are used for the nano composites synthesis. The nano fillers are dispersed in polar solvent and then the polymer is dissolved in solvent. Then this mixture is added to solution. In the last this solvent is evaporate under the vacuum. The main advantage of this method is it offers possibilities for the synthesis of nano composites with low or even no polarity. Drawback of this process is it requires large amount of solvents and same quantities of solvent is removed after mixing so it is very long and tedious job.

2.5.3 Melt intercalation

The method is become increasingly popular due to its great application in industries. This method is more flexible than above two methods because of absence of solvents and chemical reaction. In non-polar matrices this method is used by adding a proper component which reduces the interfacial tension between filler and matrix.

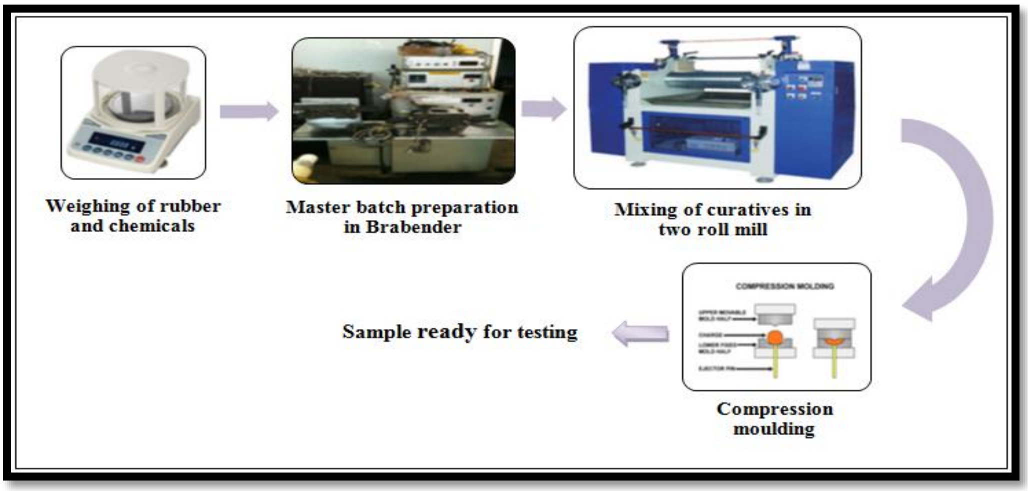


Fig2.2: Ex-situ method for rubber compounding

2.6 Background

The usage of polymer nano composites continues to grow in the automotive sector, due to their exclusive mechanical, chemical, thermal, electrical and barrier properties and contribution to fire retardancy. A market research report, "Nano composites-A Global Strategic Business Report", (Electronics.ca Publications) states that world nano composites market is forecast to reach 1.3 billion pounds (lbs.) by the year 2015, and growth in the nano composites market will be driven by robust demand outlook in the emerging application possibilities in automotive market. By 2011, the automotive sector is expected to become the third-largest market for polymer nano composites applications, with over 15% of the market. Elastomeric nano composites are also gaining momentum in automotive industry especially for tires application due to their low rolling resistance properties, lower weight and superior performance in terms of fuel economy. The key drivers for these materials are growing demand for fuel efficiency, strict automotive standards for safety, enhanced durability and noise reduction. Several methods have been developed to fabricate the polymeric composites with nano fillers including solution compounding, melt compounding, electro spinning, and in situ polymerization.

The global automotive tire industry is expected to reach an estimated value of $249.9 billion by 2019. To effectively and economically take advantage of any use of MWCNTs or nano silica in the tire formulations, manufacturers need the freedom of diluting a preformed MWCNT/nano silica-rubber master batch and the ability to blend the master batch with different rubbers to produce tires for different climatic conditions. For example, PBR is a major component in tire industry. This requires a good understanding of the MWCNT/nano silica dispersion and mechanical properties of the diluted compositions in comparison with the original master batch in order to design high performance products.

Rubber nano composites have attracted considerable interest in the last few decades because of their outstanding mechanical, thermal and barrier properties as compared to the conventional micro-composites, usually at very low filler content. Literature studies envisage that polybutadiene rubber based nano composites are generally prepared by either using solution method or melt compounding method. But, solution process is economically infeasible and not environmentally benign due to major waste of solvent, while melt intercalation solves the problem associated with solution method, however poor dispersion of nano fillers is observed because of weak interaction between the polymer and nano fillers. This ultimately reduces rubber properties substantially. On the other hand, the advantage of *in situ* approach lies in the better exfoliation achieved compared to melt and solution methods. Therefore, the objective of the present work is to improve dispersion of nano fillers into rubber matrix by in-situ method during polymerization reaction. Recently, the research interest on carbon nanotubes (CNTs) and nano silica (NS) has been increased enormously because of the possible large scale production of these materials. Moreover, MWCNT and NS have several benefits over other fillers in the perspective of industrial applications due to its less complex nature and cost effectiveness due to the requirement of the low loading to achieve comparable composite properties.

Reliance having a world class manufacturing facilities (cobalt and nickel grades) at Vadodara manufacturing division having a combined capacity of 70,000 Metric tonnes per year. A state of the art Nickel/Neodymium based swing plant with capacity of 40,000 metric tonnes per year has been commissioned at RIL, HMD, thus making Relflex a unique brand offering Cobalt, Nickel and Neodymium based synthetic grades. Major application for PBR is in tire industry due to its superior elasticity, resilience and abrasion properties.

In our earlier research work, the study of physico-mechanical, morphological and thermal properties were investigated based on polybutadiene rubber nano composites via *ex situ* method. Finally, the optimization as well as choice of fillers for further study based on their mechanical and thermal properties improvement was also explored. Among the various nano fillers used in *ex situ* process, MWCNT and NS have been chosen for further investigation.

Literature search shows that rubber nano composites are mostly prepared using solution or melt intercalation method. Very few literatures are available which emphasize on *in situ* rubber nano composites. As per our information, there has been no study on the MWCNT or nano silica filled PBR nano composites by *in situ* method. Additionally, the major challenges are still exist how to replace carbon black and silica which is mostly used in bulk amount in rubber matrix with nano fillers and also how to improve the efficacy of proper dispersion and distribution of nano fillers into rubber matrix. The *in situ* preparation method for rubber nano composites are still in stage of infancy as per their process and application are concerned.

2.7 Literature study

Incorporation of only 3 wt. % MWCNTs in ABS leads to significant enhancement in the tensile strength (up to 69.4 MPa) which was equivalent to 29% increase over pure ABS. The effect of MWCNTs on the structural behaviour of ABS under tensile loading showed a ductile to brittle transition with increase concentration of MWCNTs. The results of enhanced mechanical properties were well supported by micro Raman spectroscopic and scanning electron microscopic studies. In addition to the mechanical properties, electrical conductivity of these composites increased [8].

Styrene–butadiene styrene tri-block copolymer (SBS) was reinforced with multi-walled carbon nanotubes (MWCNTs) by the interaction through melt mixing. The tensile strength of SBS/MWCNT composites increased with increasing MWCNT content [9].

Mechanical tests demonstrate that the NBR/nano-silica based polymer nano composites possess greatly increased the elastic modulus and tensile strength, and desirably strong interfaces [10].

Functionalization of CNT yet leads to additional enhancement in modulus. Due to the interaction of CNT hydroxyl and polymer carboxyl groups [11].

A significant progress in the area of the preparation and utilization of nanotube/ polymer composite materials in recent years with particular attention to their mechanical and electrical properties can be observed in a number of articles. However, the effect of unmodified CNTs on the reinforcement and dynamic mechanical performance as well as electrical properties of rubber composites is not remarkable and much lower [12].

Zhang et al carried *in situ* modification of MMT with latex compounding method and prepare SBR/MMT nano composite, the tensile strength is 4 times higher than non-modified SBR/MMT nano composite [13].

Jeo net al synthesis modified Na-MMT using ethylene glycol as modifier to improve dispersion in rubber matrix [14].

Bokobza investigate that for polydimethylsiloxane based nano composites *in situ* filling process is most efficient [15].

Ikeda and Poompradub evaluate that conventional filled silica shows high modulus at low elongation due to formation of larger aggregates of particle and *in situ* silica shows higher modulus at higher elongation [16].

Ikeda et al find nano silica particles up to 80 Phr synthesised by sol-gel reaction gives more dispersion than commercially dispersed conventional method [16].

Cui et al synthesised PET/LDH by *in situ* polymerization by ester in charge reaction and poly condensation reaction and achieve partially exfoliated structure [18].

Dash et al synthesis poly anthrenicacid/MWCNT composites by in situ chemical oxidative polymerization [18].

Four different technologies with Ziegler–Natta catalysts can be used in the commercial production of BR with high 1,4-cis repeating unit levels; titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd) are the most commonly used metals in these catalyst systems [19].

W. M. Saltman and L. J. Kuzma in their report for the comparison between nickel and cobalt based catalyst systems, predicted that when nickel was used in recipes which gave solid polybutadienes of high molecular weight. With cobalt, only very low molecular weight liquid polybutadienes were obtained. When water activated cobalt catalyst is added to analogous nickel systems, only slight more viscous liquid polymers result [20].

Gaylord et al. presented that Kinetic studies for polymerization of butadiene with aluminium trisso butyl titanium tetrachloride catalyst system in presence of heptane and they showed that the rate of disappearance of butadiene is dependent upon the molar ratio of the two catalyst components and the total concentration of the catalyst system [21].

The kinetics of polymerization of butadiene with catalyst prepared from some aluminium hydride derivatives,AlI_3, $TiCl_4$ was investigated by Mazzei et al. and it was found that the reaction rate were 1st order with respect to monomer and catalyst concentration [22].

J. A. J. Honig, R. P. Burford and R. P. Chaplin had studied the complex kinetics of cobalt based catalyst system in toluene as solvent by varying monomer and catalyst concentration. They established molecular weight relationship as a function of conversion, indicates that changes in molecular weight development occur at high conversions [23].

Marechal et al. reported the use of bis (π-allyl)nickel trifluoroacetate for the polymerization of 1,3-butadiene benzene which they found to be 1st-order reaction on monomer and catalyst [24].

The catalytic behaviour of the nickel stearate-diethyl aluminium chloride (DEAC) system in the polymerization of butadiene in toluene was discussed by Lee and Hsu.It was found that the overall rate of polymerization decreases with time but approaches a constant rate after about 10-30 min of reaction time depending on the relative amounts of the catalyst components. The propagation reaction was found to be first order with respect to monomer concentration. No appreciable termination reaction was observed [25].

Dilip Chandra et al. reported the kinetics of Ziegler Natta polymerization of 1, 3-butadiene with a CoX_2-MAO catalytic system and it was found to be 1st order with respect to monomer concentration. The overall kinetic scheme for this process was [26]

$dm/dt=k_p [M][C^*]$

Where $[C^*]$ is the concentration of active complexes.

$[M]$ = Molar concentration of monomer.

A kinetic modelling study was conducted for the Ziegler-Natta polymerization of BD with cobalt octanoate/DEAC/water catalyst by Lee et al. The model equations for the single and dual site models were analytically solved and the closed form expressions for conversions of both number and weight average molecular weight were obtained [27].

Yoshimoto et al. investigated the effects of polymerization time, catalyst concentration, and monomer concentration and polymerization temperature on the rate of polymerization and the molecular weight and the microstructure of the polymer.

The rate equation used is

$-dm/dt = Kp [C]. [M]$

It was found that the rate of polymerization depends on the first order of the monomer concentration and catalyst concentration [28].

A numbers of organic compounds are reported in the literature as the CTA. Examples are water, hydrogen, ethylene, propylene, alpha-olefins, allene, cyclooctadienes, cyclohexadienes, imides, ketones, alcohols, esters, nitriles, alkyl and alkenyl halides, thiophene, triethylamine and anisole [29].

The preferred solvents for 1, 3-butadiene polymerization are benzene or toluene. There are other solvents like heptane and cyclohexane which are also reported in literature. Advantage of using aromatic solvent is that they keep the polymer and catalyst in soluble form [30].

The nature of solvents employed in polymerization plays a definitive role in determining the polymerization rate, polymer molecular weight and its microstructure. Most of the laboratory polymerization studies of 1, 3-butadiene are done with single solvent whereas industrial plant polymerization are performed in mixed solvents. Typically, a mixture of benzene and low boiling olefins are employed for this purpose [31].

Natta and Porri have reported that the rate of polymerization depends on aromatic solvent used and decreases in order: Benzene >Toluene >Xylene >Mesitylene. [32].

Dielectric constant of the solvent has no effect on polymer cis content. However, conversion decreases with increasing solvent dielectric constant [33].

Chandran et al. reported that cobalt salicyclaldimine complexes with ethyl aluminium sesquichloride (EAS) forms highly active 1,3-BD polymerization catalysts, and these complexes yield highly Cis-1,4-polybutadiene(>94%) with negligible amounts of 1,4-trans.They also showed that the cis-content and MW decreases as polymerization temperature increases and also the yield & cis-content depends on BD concentration [34].

Jang et al. investigated the activation of a metal alkyl free Ni based catalyst with $B (C_6F_5)_3$ in the polymerization of 1,3-BD and it was found to have high catalytic activity & 1,4-cis stereo regularity. Variations in the molar ratio of $B(C_6F_5)_3$ to Ni affected catalytic activity,1,4-cis stereo regularity and the MW of polybutadiene and the rate of polymerization were found to be 1st order with respect to monomer concentration [35].

M.c.thoratan reported that the polymerization results obtained when the triethyl aluminium was replaced with other alkyl aluminium and BF3.Et_2O with other BF3 complexes or HF.Et_2O both the polymerization rate and the polymer viscosity decreased significantly as the length of the alkyl group in the alkyl aluminium increased from C_1 to C_6 [36].

Quirk et al. showed that higher and lower amounts of water, decreased conversion, broadened the molecular weight distribution and increased the molecular weight in BD polymerization using neodymium versant based catalyst [37].

BR-Nd have superior mechanical properties and the dynamic properties such as abrasion resistance, resistance to bending, fatigue, resilience and heat build-up. It is the potentially the best high-cis BR for applications that require high performance [38].

The polymerization of BD by neodymium, diisobutylaluminium hydride and tert-butyl chloride was studied by mello et al. and it was found that the cyclohexane has marked effect on the polybutadiene molecular weight properties. The increasing cyclohexane content decreases the molecular weight and increases the molecular weight distribution [39].

The ternary catalyst system Nd(carboxylate)$_3$/tertbutyl/diisobutyl alumiunium hydride for the polymerization of 1,3-BD was studied with respect to halide/Nd ratio and halide type. And it was found that the lowering of the halide/Nd ratio result in lower conversion to polymer & a change in polymer molecular .weight distribution [40].

Leo et al. presented a general scheme to explain in a qualitative and quantitative manner various features of Ziegler-type polymerization such as the dependence of polymerization rate on monomer concentration, the dependence of rate on aluminium alkyl, dependence of rate on catalyst ratio, the factors upon which molecular weight dependent, the effect of temperature on molecular weight, the effect of temperature on polymerization rate, the stereospecific polymerization aspects [41].

Chapter: 3

3.1 Materials

Monomer

1, 3Butadiene was obtained from 1 litre S.S.Bomb from PBR-2 plant, RIL-VMD, Vadodara.

Table 3.1: Properties of monomer

Chemical name	1, 3 Butadiene
Formula	C_4H_6
Physical state	liquid under pressure
Colour	Colourless
Molecular weight	54.09
Boiling point	10.85 ˚C
Vapour pressure	1.45 Bar at 20 ˚C

Solvents

Heptane – Toluene mixed solvent was obtained from PBR-2 plant, RIL –VMD, Vadodara. Before distillation the % moisture in the solvent is 250 to 280 ppm. After distillation the moisture content is reduce up to 15 ppm. Toluene rich solvent is used for catalyst because the catalyst used in this process is not so much soluble in paraffinic hydrocarbon such as heptane.

Catalysts

Nickel naphthenate (NIC), Triethyl aluminium (TEAL), and Boron triflouride etherate (BRF) is obtained from PBR-2 plant, RIL-VMD, Vadodara.

Multiwall carbon nanotubes

Purchased from intelligent materials Ltd. Sample purity is 80-99 volume % determined by Raman spectrophotometer and SEM analysis. Specifications are indicated in below table

Table 3.2: Characteristics of carbon nanotube in general

Colour	Black
Form	Powder
Diameter	6-9 nm
Length	5 micro meter
Specific surface area	90-350 m^2/gm.
Boiling point	2640 ℃
Bulk density	0.05-0.17gm/cm^3

Short stop

Methanol is obtained from PBR-1 plant, RIL-VMD, Vadodara. Phosphate of polyoxyethylenealkyle phenyl ether (PPA) was obtained from PBR-2 plant, RIL-VMD, Vadodara.

Anti-oxidant

Di- tertiary butyl p-cresol (DTBPC) was obtained from PBR-2 plant, RIL-VMD, Vadodara. DTBPC used as an antioxidant in methanol. 0.5% (w/v) of DTBPC solution in methanol was used to terminate the reaction.

3.2 Feed preparation

The monomer is dissolved in dry solvent (Toluene + Heptane). The schematic diagram of feed preparation set up is shown in below figure. The monomer from S.S bomb bubbled through the traps containing 8% solution of TEAL and activated molecular sieves and then in to flask containing a dry solvent. The feed concentration is measured gravimetrically.

% Feed concentration= Weight of Butadiene monomer / [Weight of Butadiene +Weight of solvent]*100

Normally monomer concentration is kept 20-22% in solvent

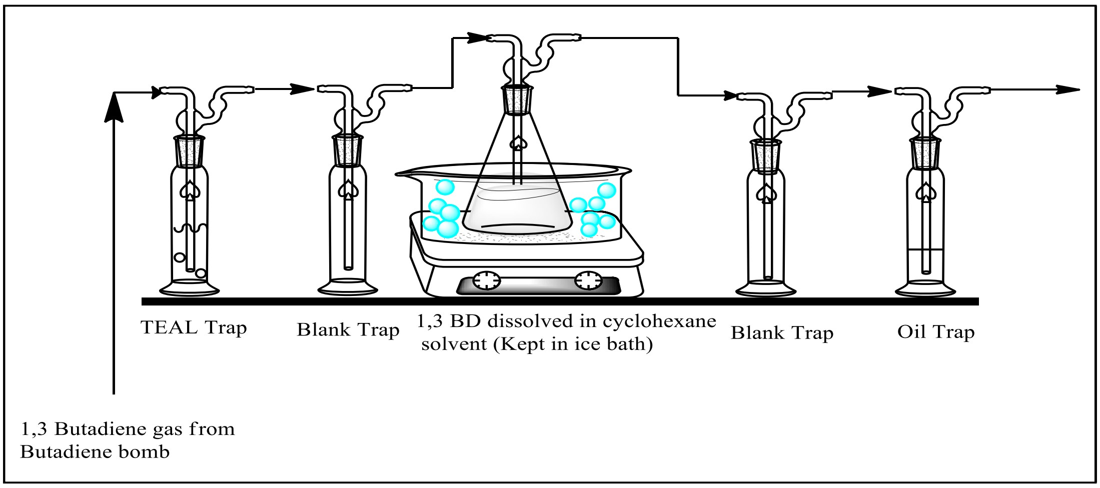


Fig3.1: schematic diagram of feed preparation set up

3.3 Polymerization Reaction

3.3.1 Ageing

Catalyst ageing plays a major role in polymerization. Mooney viscosity is improved after ageing. The optimum ageing temperature is 20℃ and ageing time is 60 minutes above or below of this temperature the conversion is decrease.

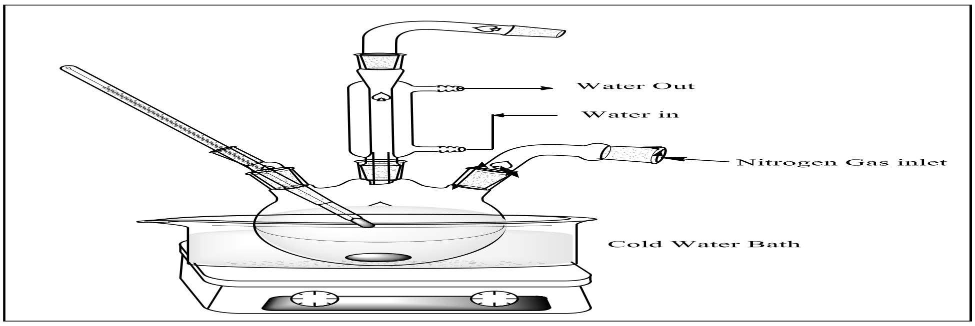


Fig3.2: schematic diagram of Ageing set up

3.3.2 Polymerization reaction

The reaction is very moisture sensitive. For making the reactor moisture free, hot air is supplied through heat gun for 20-30 minutes. Then nitrogen gas is passed through the reactor fussing is done for 10 minutes. Then 350 ml of feed containing the monomer is add in to reactor and Nano fillers (MWCNT or Nano silica) is mixed with feed for 5-7 minutes at 250 rpm of anchor speed. The catalysts are added in the reactor and maintain the reactor temperature 60℃ for 3 hours. The reaction is very exothermic. The reactor temperature is maintained by the means of indirect heat transfer equipment.

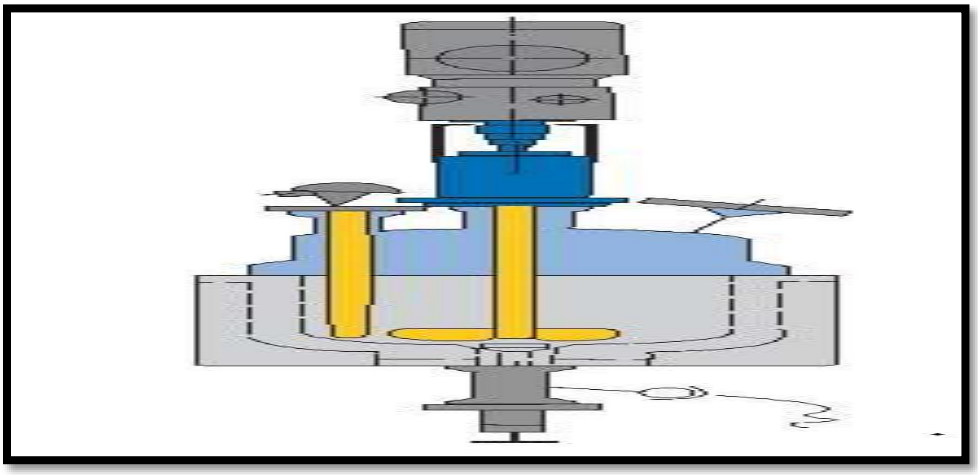


Fig 3.3: polymerization autoclave reactor (technical data sheet of reactor)

3.3.3 Polymer recovery

As the reaction is occurred the reaction mass becomes viscous and this shows the polymer formation. At the end of three hour polymerization is terminated by adding PPA dissolved in little amount of dry solvent. Then the by lowering the temperature of reactor at room temperature Methanol containing 0.5% of DTBPC is added in reaction mass. The rubber is formed and it is separated from methanol by using decantation.

3.3.4 Sample drying

The rubber obtained from polymerization is kept in Petri dish in fuming hood at room temperature for one day. Rubber is cuts in small pieces and washes in water. The wash product is kept at room temperature for one day and it is dried in vacuum own operated at 60℃ under the vacuum for 6hours.

3.4 Yield and conversion

Conversion is calculated by taking a ratio of 1, 3 Butadiene rubber to 1, 3 Butadiene monomer.

% conversion= [Weight of rubber produced /Monomer feed] *100

3.5 Safety precautions

All the chemicals is very hazardous so they are operated under fume hood and the inert atmosphere is maintained by nitrogen purging. The entire reaction is done with all safety equipment like safety glasses, lab coat, mask and hand gloves.

3.6 Mooney viscosity

It signifies the viscosity of a rubber or compound, is measured in Mooney shearing disk viscometer. It is indicated by the torque required to rotate the disk embedded in a rubber/compound specimen and enclosed in the die cavity under specified conditions. Viscosity of rubber or compound plays vital role in deciding its processing behaviour.

Fig3.4: Mooney viscometer (Mooney viscosity technical data sheet)

3.7 Master and final batch preparation

Once the rubber is formed in desired Mooney range then anti-oxidants, ASTM oil, zinc oxide and stearic acid are mixed with that rubber in a two roll mill at 60 to 80˚C. At 100 to 180˚C curing agent is added to master batch. And then the sample is sending for testing.

3.8 Test methods

3.8.1 Rheological Study

Rheological study of the prepared polymer sample is done in Oscillating Disc Rheometer (ODR) in which isothermal curing characteristics of the rubber compound can be measured along with torque, scorch time, cure rate, and curing trend as per ASTM D2048, ISO 3417, and DIN53529-3.

3.8.2 Tensile and Tear Properties

The stress-strain test in tension, including ultimate tensile and elongation, is probably still the most widely used test in the rubber industry. Among the purposes for such tests are: to ensure that all compounding ingredients have been added in the proper proportions, to determine rate of cure and optimum cure for experimental polymers and compounds, for special purposes, and to obtain an over-all check on the compound.

Tensile properties are determined on a universal testing machine (model Instron-3366, UK). Testing is performed at room temperature. Tensile strength (TS), Modulus (MOD) at 100% and 300% elongation and % elongation at break (%EB) are determined at a deformation speed at 500 mm/min. The mean value of three measurements is reported here. The tensile properties are reported as per ASTM D412-00.

3.8.3 Hardness

Hardness, as applied to rubber, may be defined as the resistance to indication under conditions which do not puncture the rubber. The compression-moulded specimens (6 mm thickness) are tested to determine the hardness data with an International Rubber Hardness Dura meter (Wallace Test Equipment, England) as per ASTM D2240-05.

3.8.4 Abrasion

Abrasion test done using DIN abrader to determine of elastomers in regard with the frictional in rubber products such as conveyor belts, tiers, hoses, floor covering etc. since wear is always a result of abrasion. It is done under ASTM D5963, DIN 5316.

3.8.5 Heat Build-up

The heat build-up of the prepared composites was determined on Goodrich Flexometer according to ASTM D 623. Specimen dimension was 17.8 mm (dia) * 5 mm (height). Test piece was cycled at 1800cycles/in with stroke of 4.45 mm was at 100°C temperature rise (T) was measured after 25 min and reported as heat build-up.

3.8.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used to determine the microstructure of solid rubber and rubber process oil. It is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. It works on ASTM D3677 and ISO 4650 standards. Cis, Trans and vinyl contents are determined by PERKIN ELMER 1600 Series FTIR spectrophotometer using frequencies at 740, 965 and 910-915 cm^{-1} respectively.

Method:

1. 0.075 gm. of the polymer was dissolved in 10 ml of carbon disulphide by keeping it overnight.
2. The IR spectrum of the film was recorded in the range of 650-1100 cm^{-1} on PERKIN ELMER IR spectrophotometer.
3. Cis, Trans and vinyl peaks were noted at 740, 965 and 910-915 cm^{-1}.
4. The base line was drawn by extending the vinyl peak at 995 cm^{-1} and estimating at the level at 965 cm^{-1} for Tran's peak. The values of base line absorbance obtained on multiplying with factors 1, 0.118 and 0.164 gave the respective contents for cis, Trans and vinyl in the sample.

3.8.7 Thermal analysis (TGA-DTG)

TGA is done using Thermo gravimetric analyser from TA Instruments (SDT Q600 V20.9) at heating rate of 10°C per min in N2 atmosphere. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time composition of materials and to predict their thermal stability at temperature up to 800°C. TGA can characterize materials that exhibit weight loss or gain due to decomposition, oxidation or dehydration.

3.8.8 ICP elemental analysis

Weight approximately1gmof sample in cruisible. Then add 3ml concentrated sulphuric acid and allow the sample to evaporate at 400°C. Then cool it again and add 2ml of sulphuric acid and allow the sample to evaporate at 400°C. Again add 2ml of sulphuric acid do same as done before. Put the cruisible in furnace overnight at 550°C. And then add 5 drop of concentrated HCL and then add 5ml of mili Q water 5ml and filter the solution and make up 25ml with mili Q water.

3.8.9 Intrinsic Viscosity:

0.2 % (W/V) of rubber solution is prepared using toluene. The solution is shaken well and kept overnight. Then it is filtered and 15 ml of sample is taken in Ubbelhode Viscometer. Viscometer bath temp is kept at 30 ˚C. The flow time (t_1) of solution is measured. Then the solution is diluted by adding 5 ml toluene. At least four consecutive dilutions are done. At every concentration, flow time is measured. Flow time (t_0) of pure toluene is also measured.

The relative viscosity is measured as t_1 / t_0.

Specific Viscosity, $\eta_{sp} = (t_1 / t_0) - 1$

Reduced Viscosity, $\eta_{red} = \eta sp / C$ (cm^3/gm)

Reduced viscosity is plotted against concentration. Using intrinsic viscosity and Mark Houwink equation, molecular weight can be determined.

$$\boldsymbol{\eta_{int} = K M^a}$$

Where M = Viscosity average molecular weight & K and are Mark-Houwink constants.

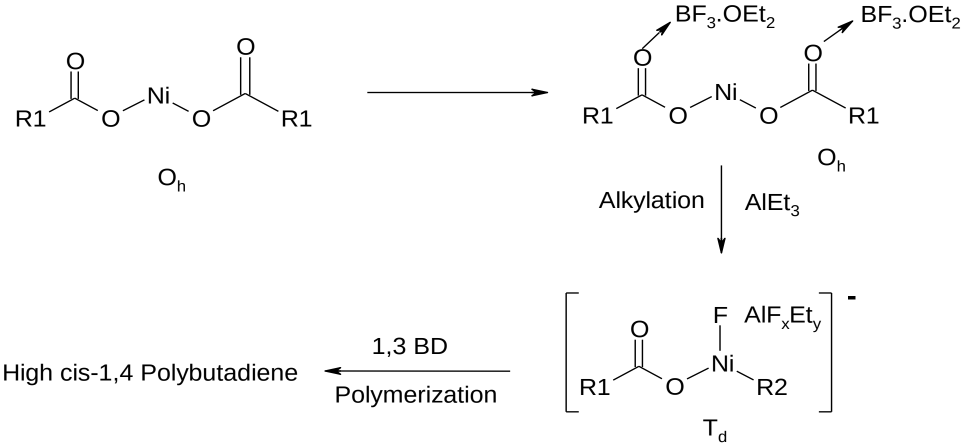
K = 0.000305 & a = 0.725 for solvent toluene and polybutadiene rubber at 30 ˚C.

Chapter: 4

Results and Discussion

4.1 Polymerization of 1, 3 butadiene using Nickel catalyst

In the present thesis the polymerization of butadiene with nickel based catalyst system is examined in details. Nickel based catalyst system is comprised of Nickel Naphthenate (NIC),Boron Trifluoride Etherate (BRF), Triethylaluminium (TEAL).The mechanism of butadiene polymerization with this catalyst system is shown in Scheme1. In presence of BRF, TEAL acts as alkylating agent. TEAL alkylates the nickel naphthenate (NIC) and changes its coordination geometry from Oh to Td and generates a vacant site where monomer can attach and thus facilitating the polymerization. In absence of BRF, TEAL reduces the NIC to Ni (0) and polymerization cannot take place. Thus, BRF/TEAL ratio plays a vital role in this polymerization. In the established technology, these catalyst components are aged before transferring to the polymerization reactor. In our earlier study, we have observed that catalyst ageing plays a major role on polymerization. The conversion was maximum at the ageing temperature of 20°C. Hence, afterwards, catalysts were aged at 20°C.



Where, R1-COO = naphthenate, R2 =Et

Scheme 1: Mechanism of Ni-based polybutadiene rubber

4.1.1 Mooney viscosity and catalyst optimum dosage

We have targeted the tire grade polybutadiene rubber production at a lab scale. Our desired Mooney range was 40-45. Literature studies reflect that the BRF/NIC ratio has a maximum effect on Mooney control. So we have varied this ratio by keeping TEAL/NIC and BD/NIC constant. The reaction temperature, reaction time and ageing time are also kept constant and concentration was chosen based on plant recipe. The effect of BRF/NIC ratio on Mooney viscosity value of rubber is depicted in Table 4.1. From the Table 4.1, it can be seen that viscosity value decreases with increasing ratio of BRF/NIC which is further reflected in Fig. 4.1. The desired Mooney value was obtained at BRF=12 mmphgm and NIC=0.38 mmphgm and we have to kept this dosage for throughout the project.

Table4.1**:** Effect of BRF/ Nic ratio on Mooney viscosity

Boron triflouride BRF (mmphgm)	Nickel nephthenate (Nic) (mmphgm)	BRF/Nic ratio	Mooney viscosity
8	0.32	25	62
12	0.38	31.57	41.7
17.6	0.32	55	22
34.2	0.32	106.87	12.2

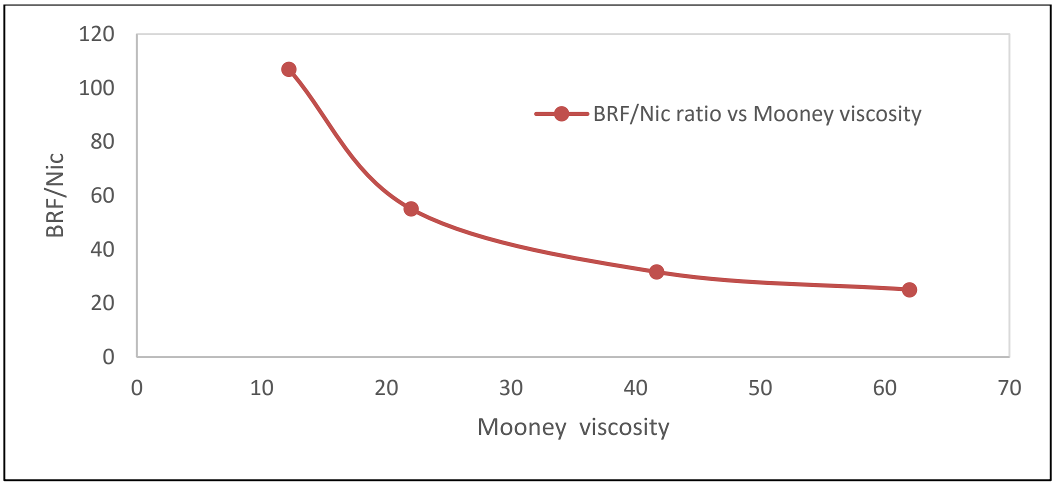


Fig 4.1: Effect of BRF/Nic ratio on Mooney viscosity

4.1.2 Blank reaction without Nanofiller

In order to understand the exothermic nature of the reaction, a blank experimental run without using any nano filler has been carried out, as shown in Table 4.2 and Fig.4.2. From the reaction exotherm, it can be easily visualised that the maximum exotherm generated at the initial stage of the reaction and it didn't change much afterwards.

Table 4.2: Temperature profile for Blank reaction

Time(Minutes)	Bath temperature (Tb)	Reactor temperature (Tr)	Set temperature (Ts)	Temp difference (Tr-Tb)
0	21.7	22	60	0.3
36	59.9	61	55	1.1
38	57.28	63	50	5.72
40	56.85	63	57	6.15
79	58.99	62	59	3.37
114	60.1	62	61	1.9
128	60.99	63	61	2.01
150	61.99	64	61	2.01
163	61.99	64	62	2.01
189	63.01	65	63	1.99
197	61.94	64	62	2.06
210	61.97	64	62	2.03

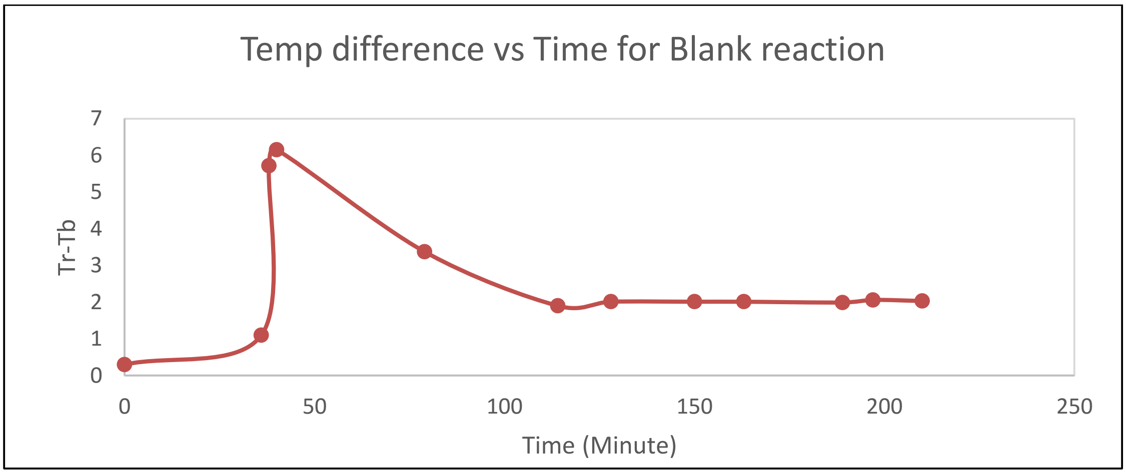


Fig4.2: Exothermic nature of Blank reaction

4.1.3 Influence of CNT filler on butadiene polymerization

Since exothermic nature of the reaction is already been identified in blank reaction, there for the effect of nano fillers on the same has been further carried out. The temperature profile along with time is shown in the Table 4.3. From the Table 4.3, it can be seen that the temperature rise was maximum in the initial stage of the reaction and afterwards temperature did not change much. The starting reaction was 26oC at the reactor and the temperature increased almost double of initial temperature around 10 minutes. This corresponds to exothermic nature of the reaction. The reaction exotherm against time of the reaction is plotted is shown in Fig.4.3.

Table: 4.3 Temperature profile of CNT filled reaction

Time(Minutes)	Bath temperature (Tb)	Reactor temperature (Tr)	Set temperature (Ts)	Temp difference (Tr-Tb)
0	25.83	25	60	-0.83
10	49.91	49	50	-0.91
21	33.91	59	70	25.09
41	58.8	59	75	0.02
92	63.1	67	20	3.9
109	59.11	65	20	5.89
128	53.81	61	70	7.19
139	54.2	65	20	10.8
178	52.24	61	75	8.76

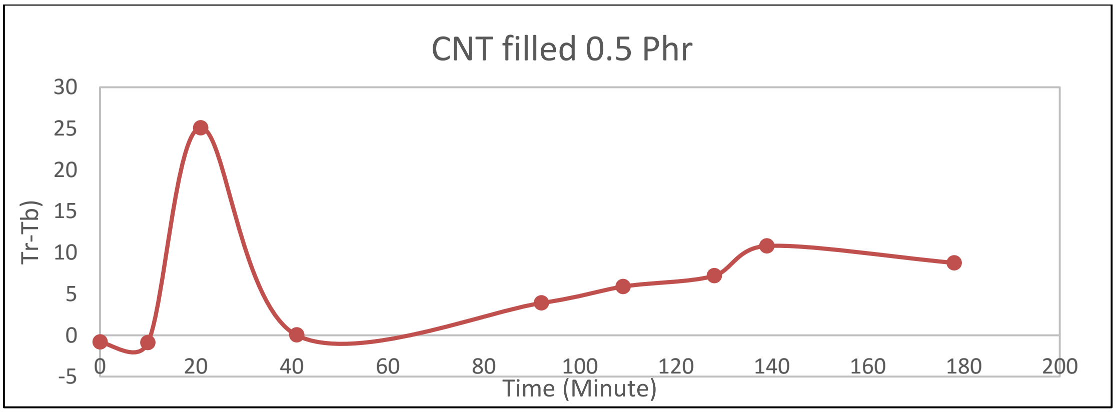


Fig 4.3: Exothermic nature of CNT filled polymerization reaction

4.1.4 Influence of Nanosilica filler on butadiene polymerization

As discussed earlier for the carbon nanotube system, we have further extended our study with the help of nano silica filler and examined the effect of reaction exotherm in the presence of fixed doses of nano silica. Table 4.4 includes the temperature profile of nano silica embedded system against time of the reaction. The comparison to carbon nanotube, the initial exotherm is little bit higher for nano silica system. Initial temperature reactor temperature was 23˚C and increased to 60˚C. The nature of isotherm may depend on the surface chemistry of two different types of nano fillers (from the determination of particle size and the Brunauer Emmett Teller (BET) surface area (m^2/g); MWCNT: O.D. -25-30 nm, surface area: 450-500; NS: 5-10 nm, surface area: 490-500). The above discussion of temperature profile against reaction time has been further reflected in Table.4.4.

Table 4.4: Temperature profile for Nano silica filled reaction

Time(Minutes)	Bath temperature (Tb)	Reactor temperature (Tr)	Set temperature	Temp difference (Tr-Tb)
0	23.44	23	60	-0.44
23	59.96	60	60	0.04
34	55.94	63	56	7.06
56	59.96	62	60	2.04
66	59.97	61	60	1.03
74	59.98	61	60	1.02
105	60	61	60	1
117	59.99	61	60	1.01
149	61	62	62	1
189	61.99	63	62	1.01
204	61.99	63	62	1.01
209	61.99	63	62	1.01

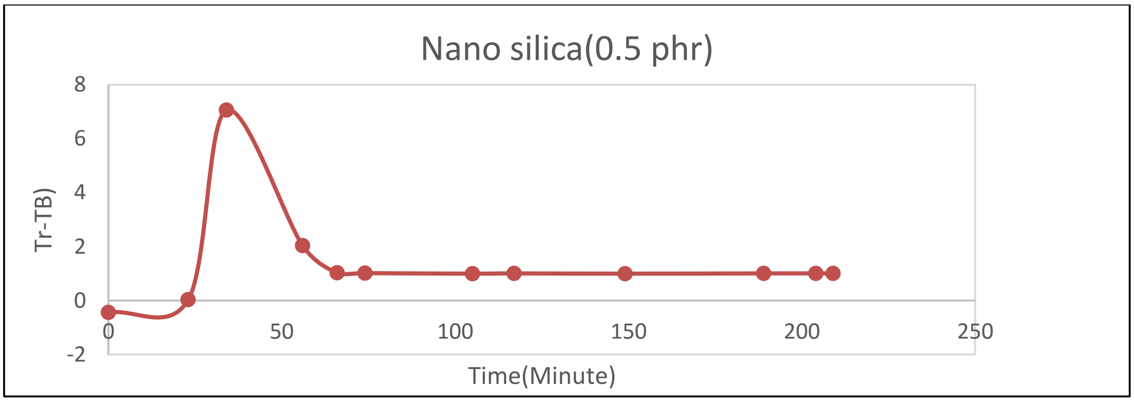


Fig 4.4: Exothermic nature of Nano silica filled polymerization reaction

4.1.5 The effect of nano fillers on conversion (%) and yield of butadiene polymerization

Interestingly the exothermic nature of butadiene polymerization didn't much affected in presence of nano filler. Since there is a no influence of exotherm in presence of nano fillers, the conversion and yield of butadiene polymerization were examined in Table 4.5. It can be seen that the conversion and the yield marginally enhanced in presence of CNT but not for nano silica. The higher the surface area of nano filler may help the catalyst particle to properly dispersed and initiate the polymerization reaction at faster rate. The marginal enhancement may be further improved with an optimum condition.

Table 4.5: Effect of nano filler on yield and conversion

Sample	**Avg. conversion (%)**	**Avg. Yield (gm.)**
Blank reaction	89	45
0.5 phr CNT filled PBR	91	51
0.5 phr nano silica filled PBR	86	43

4.2 Kinetic Studies

The recipe for the kinetic studies for Nickel based catalyst system was decided as per the above optimized doses.

Monomer: 2.32mol/l

NIC = 3.8mmphgm

TEAL = 39mmphgm

BRF/TEAL= 1.07

Catalyst ageing temperature was 20°C, catalyst ageing time was 60min, and reaction temperature was 60°C [unless otherwise mentioned].A typical plot of time vs. conversion is shown in Fig. 4.5 Initially polymerization proceeds rapidly after that it slows down. The curve does not pass through the origin due to slight formation of polymer during the heating period prior to the normal polymerization.

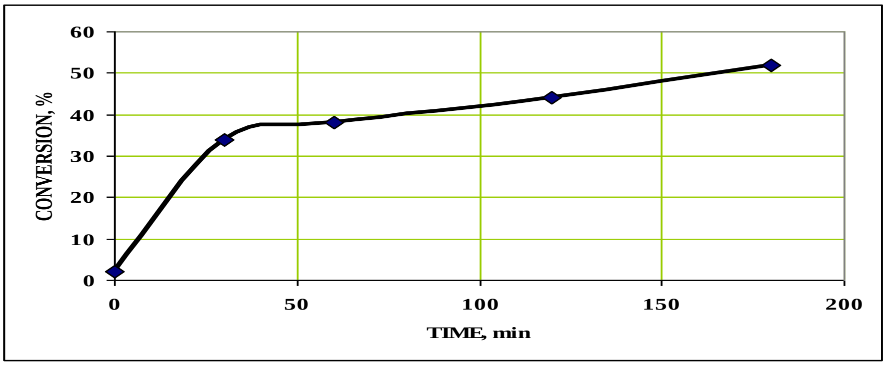


Fig. 4.5: Course of the conversion as a function of time

The following equation is considered for the kinetics of the stereo specific polymerization of butadiene in solution.

$$\frac{-dC_M}{dt} = k[C_M]^a [C_C]^b \text{ .... [1]}$$

Where, $\frac{-dC_M}{dt}$ = Rate of disappearance of monomer or rate of polymerization.

k = Rate constant

C_M = Monomer concentration, moles/l

a = Reaction order with respect to monomer concentration.

C_C = Catalyst concentration.

b = Reaction order with respect to catalyst concentration

t = Reaction time

The order of the reaction with respect to monomer and to catalyst was determined and the activation energy was calculated. In our previous work on nickel polymerization, it was observed that the polymerization is 1st order with respect to monomer concentration as well as catalyst concentration. Since, CNT acts as reinforcing filler, it does not take part in the reaction but in presence of CNT, the reaction kinetics and mechanism may be changes which have been explored in this research work. Moreover, in presence of CNT, the marginal improvement of conversion and yield obtained which in turn indicates that CNT must have play a major role during polymerization and therefore activation energy , microstructure and viscosity molecular weight, thermal and elemental analysis of the CNT containing polymerization system have been studied.

In our previous investigation for simple Ni-polymerization system, it was observed that the activation energy of the polymerization based on this catalyst system was found to be 14.5kcal mol^{-1}.

4.3 Determination of activation energy of Ni-based polymer in presence of CNT

The activation energy is determined according to the Arrhenius equation

$$k = f(T) = Ae^{-E/RT} \quad \text{...} [2]$$

Where T is absolute temperature

For this purpose, polymerization reactions were taken at 55, 60 and 65°C at constant concentration of catalyst and monomer

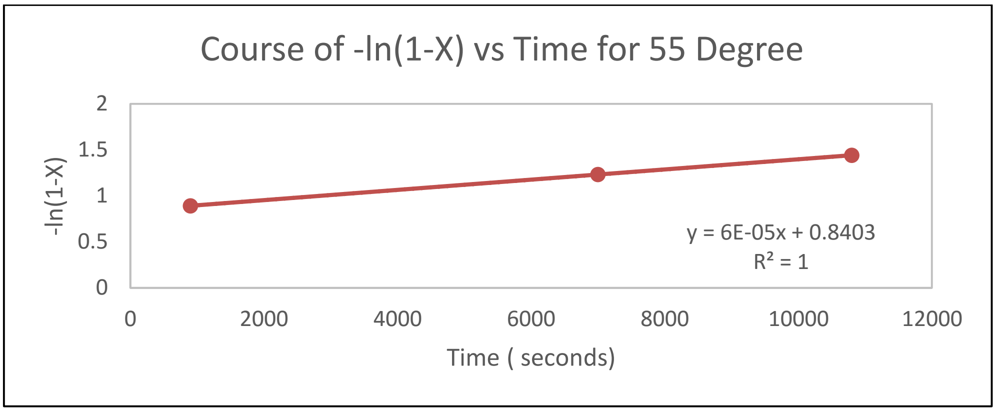


Fig4.6: course of –ln (1-X) vs. Time for 55 °C

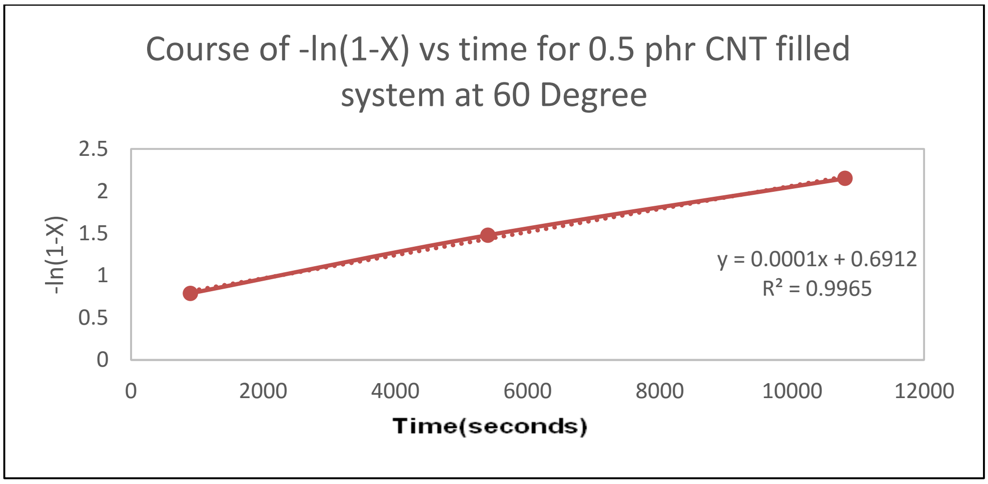


Fig: 4.7: Course of –ln (1-X) vs. Time for 60 °C

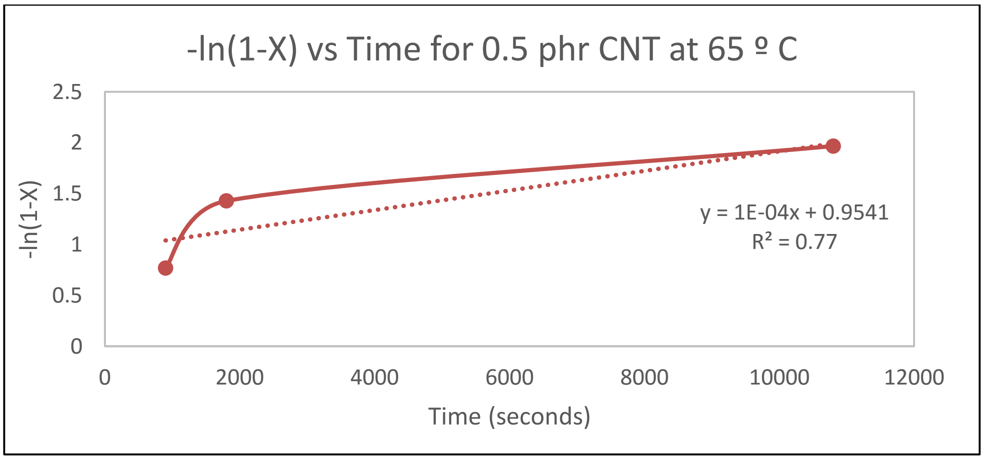


Fig: 4.8: Course of –ln (1-X) vs. Time for 65 °C

In Fig 4.6, 4.7, and 4.8 $-\ln(1-x)$ as a function of time at various temperatures is plotted. Rate constants at different temperatures are calculated from the slope of the lines plotted in Fig.4.9 the values of rate constants are calculated from the slope of the line.

Table 4.6: Rate constants at different temperature

Temperature, (°C)	**k, (Sec^{-1})**	**1/T**	**Log K**
55	6.00E-05	0.003049	-4.2
60	0.0001	0.003003	-4
65	1.00E-04	0.002959	-3.9

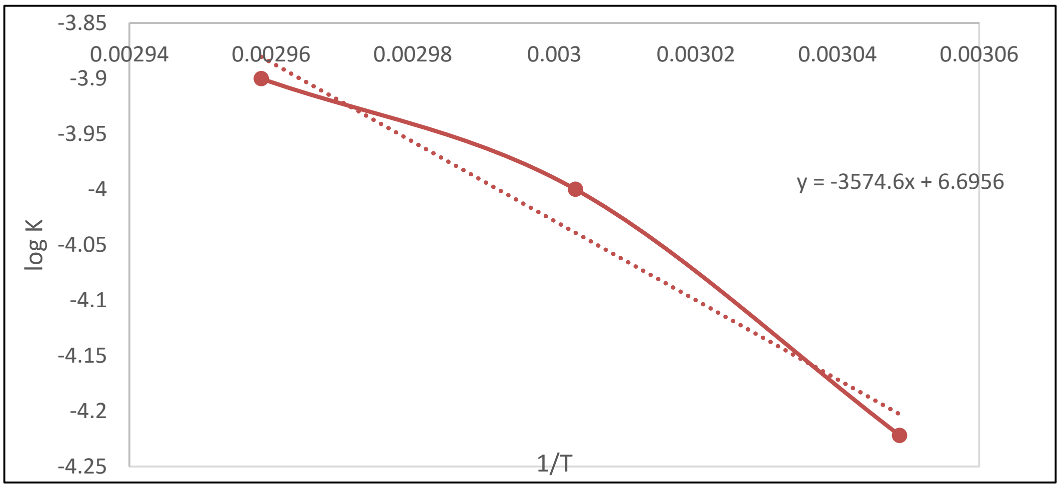


Fig 4.9: log K vs. 1/T plot for activation energy calculation

The slope of the line = $\frac{-E}{2.3R}$ = -3574.6.. [3]

R =1.98 Cal K^{-1} mol^{-1}So, activation energy, E = 16278.72 Cal mol^{-1}= 16.27kcal mol^{-1}

Although, we have observed that in presence of CNT Nano filler, the conversion has marginally improved but from activation energy calculation, it was found that CNT delayed the polymerization reaction. The activation energy of CNT filled Ni-polymerization is higher (16.27kcal mol^{-1}) as compared to Ni-polymerization devoid of CNT (14.5 kcal mol^{-1}). Therefore, first the microstructure of polymer was studied with time for both nano filler and devoid of nano filler system to see whether there is any effect of CNT.

4.4 Effect of CNT nano filler on polybutadiene rubber Microstructure

Table 4.7: Microstructure of PBR for Blank reaction at 60 °C

Reaction time(minute)	**15**	**30**	**60**	**90**	**180**
Cis (%)	94.43	94.18	95.58	94.82	94.166
Trans (%)	2.40	2.49	1.84	2.24	2.70
Vinyl (%)	3.15	3.32	2.57	2.93	3.31

Table 4.8: Microstructure of PBR for CNT filled system at reaction at 60 °C

Reaction time(minutes)	**15**	**30**	**60**	**90**	**180**
Cis (%)	91.95	93.6	94.26	94.04	93.53
Trans (%)	2.91	2.03	1.64	1.79	2.52
Vinyl (%)	5.12	4.37	4.09	4.17	3.93

From Table 4.7 and 4.8, it can be seen that the microstructure of the polymer initially changed in presence of CNT; cis content was reduced from 94 to 91 % whereas vinyl content was increased from 3 to 5. But at the end of the reaction (which is a standard polymerization time) the microstructure does not change much. This indicates that CNT does not take part in the reaction of Z-N polymerization. Furthermore, the viscosity average molecular weight of the polymer was determined. From Table 4.9 it can be seen that the molecular weight of the CNT polymer is significantly decreased (~23 %) in comparison to blank polymerization system.

Table 4.9: Intrinsic viscosity and viscosity average molecular weight

Sample Name	**Intrinsic Viscosity**	**$M_{avg} * 10^5$**
Blank	2.6	2.73
0.5 phr CNT	2.3	2.22

This implies that CNT may act as a chain transfer agent which ultimately reduces the molecular weight of the polymer. In order to understand in detail mechanistic study, the elemental analysis (ICP-OES) as well as thermo gravimetric was carried out. From the elemental analysis study depicted in Table4.10, it is clearly seen that the catalyst (Nickel Naphthenate), co-catalyst (Triethylaluminium) and promoter (Boron Trifluoride Etherate) does not properly participated in the reaction. The concentration of Al, Ni and B has been drastically increased in presence of CNT. This might be the fact that CNT hindered the monomer site for polymerization reaction and therefore the larger quantity of metal components is remained as a residue in the system. It is also to be mentioned here that CNT does not content this much large quantity of element in its composition and this definitely comes from the reaction. The results are in line with residue calculated from Thermo gravimetric analysis (shown in Table 4.11).

Table 4.10: Elemental analysis of PBR

Elements	Unit	Blank rubber	0.2 phr	0.5 phr	1phr
Al	µg/g	526	2616	2258	2002
Ni	µg/g	33	139	121	104
B	µg/g	2	5	6	7

Table 4.11: Residue calculation from thermo gravimetric analysis

Sample Name	**Residue (%)**
Blank	1.95
0.2 phr	2.42
0.5 phr	2.30
1 phr	2.22

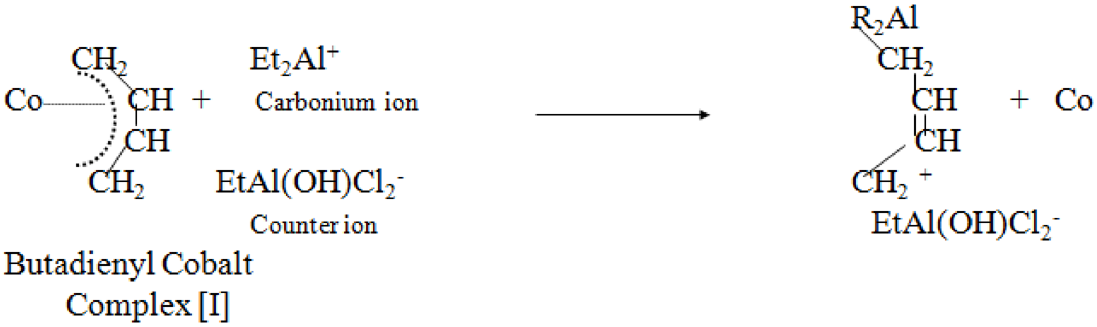
Part 2: Polymerization of 1, 3 butadiene using cobalt catalyst

The literature studies revealed that cobalt catalyst system works excellent in aromatic solvents. Moreover, the carcinogenic solvent benzene is used for the same purpose in RIL-VMD as per licensor technology. In our R &D laboratory, extensive study has been carried out in order to replace benzene with non-carcinogenic solvent like cyclohexane. Also, the kinetic study was also carried out to understand the reaction order, activation energy along with influence of catalyst dosing, monomer concentration and temperature too. But in presence of nanofiller the kinetic study is still not available. Therefore, in this part of the dissertation, butadiene polymerization and its kinetics were studied in the non-carcinogenic solvent, cyclohexane in presence of nanofillers. Furthermore, it has been also noticed that in presence of 0.5 phr either of MWCNT or NS in Co-based polybutadiene rubber, the conversion of the polymer increases. The percent improvement is higher for MWCNT system (~ 75 %) as compared to NS system (~34 %). Additionally, the microstructure of the polymer does not change in presence of either NS or MWCNT.

The mechanism of cobalt catalysed butadiene polymerization is shown in Scheme 2.

$$Et_2AlCl + H_2O \rightarrow EtAl(OH)Cl + C_2H_6$$

$$Et_2AlCl + EtAl(OH)Cl \rightarrow Et_2Al^+ + EtAl(OH)Cl_2^-$$



Scheme 2: Mechanism of cobalt catalysed polymerization

4.5 Kinetic Studies

Here the recipe for this study was optimised as below

10.0 mmphgm of DEAC = 5.85 ml

1.03 mmphgm of cobalt octanoate = 0.12 ml

W/Al = 0.28

Feed moisture = 15ppm

Feed density =0.073

Monomer in feed = 51.1

Total volume of feed = 350ml

A typical plot of conversion vs. Time for cobalt based system is shown as below in Figure 4.10. Initially the polymerization was rapid but after some time it increased slowly. The average conversion of blank systems was 30 %. From Figure 4.10, it is seen that the reaction is followed a first order kinetics. It has been already established in our earlier investigation that the reaction is first order with respect to monomer and catalyst concentration. So, it is obvious that the reaction should follow the first order kinetics in presence of minute quantity of nanofillers which eventually does not take part in the reaction.

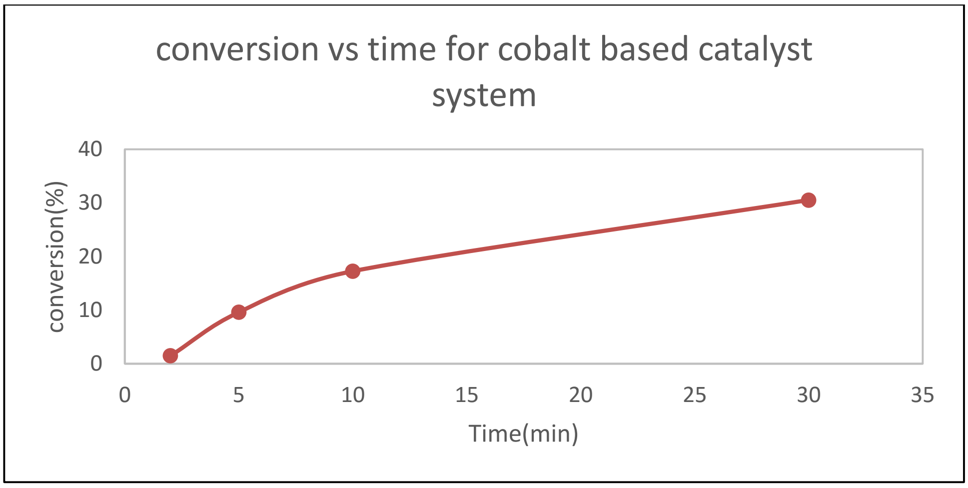


Fig4.10: course of conversion vs. time for cobalt based system

4.6 Activation energy calculation for cobalt based Ziegler-Natta catalyst polymerization system

The polymerization reaction is first order with respect to monomer and catalyst concentration so the activation energy is calculated by the means of Arrhenius equation which is stated that

$$k = f(T) = Ae^{-E/RT}$$

Where T is the absolute temperature

For this purpose we take the reaction at 20° C, 24° C, and 30 ° C and finds the value of rate constant at this temperature.

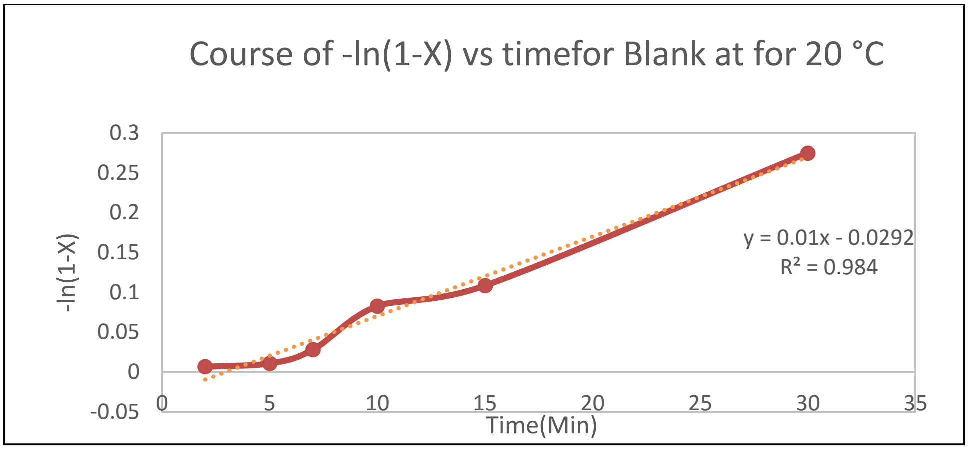


Fig 4.11: Course of –ln (1-X) vs. time for 20 º C

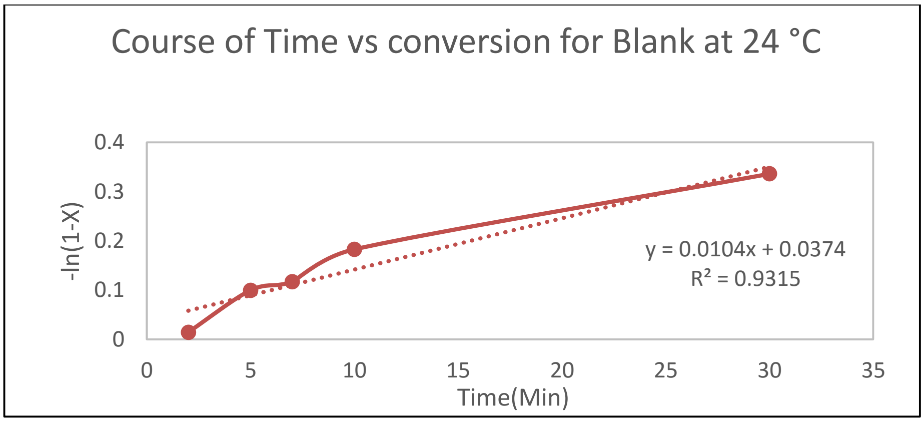


Fig 4.12: course of –ln (1-X) vs. time for 24 º C

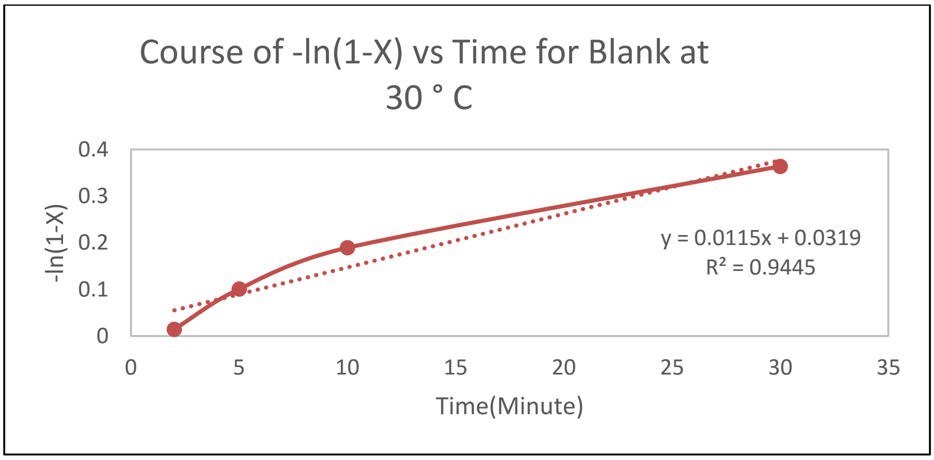


Fig 4.13: course of –ln (1-X) vs. time for 30 º C

From the above graph rate constant values are as shown in below (Table 4.12). Log k vs. 1 /T is plotted in Fig 4.14.

Table 4.12: rate constant value at Different temperature

Temperature (°C)	**K(sec^{-1})**	**Log K**	**1/T**
293	0.01	-2	0.003413
297	0.0104	-1.9829667	0.003367
303	0.0115	-1.9393022	0.0033

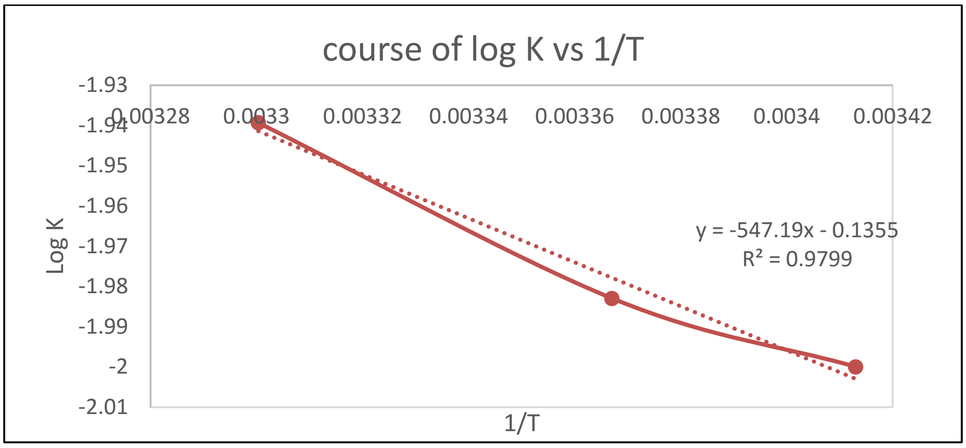


Fig 4.14: course of log K vs. 1/T

The slope/2.303R = -547.19 ……………………………………………………….. [4]

Where R =1.98 Cal K^{-1} mol^{-1}

So, Activation energy, E = 2495.1535 Cal mol^{-1}= 2.491kcal mol^{-1}

In order to understand the influence of MWCNT nano filler on the activation energy of co based butadiene polymerization system, the kinetic study using MWCNT for Co based polybutadiene rubber system has been carried out. For that purpose we take the reaction at 23 ºC, 25 ºC, 30 ºC the profiles of –ln (1-X) vs. time are as shown in below (Fig. 4.15, 4.16 & 4.17).

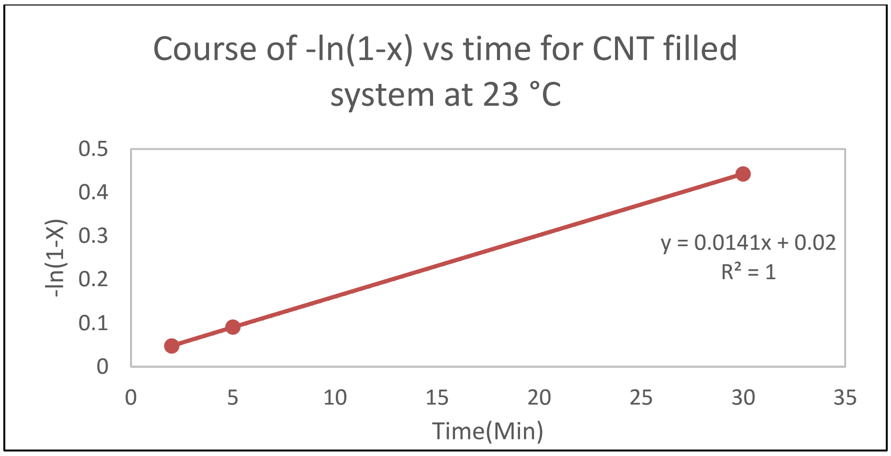


Fig 4.15: course of –ln (1-X) vs. time for 23 ° C

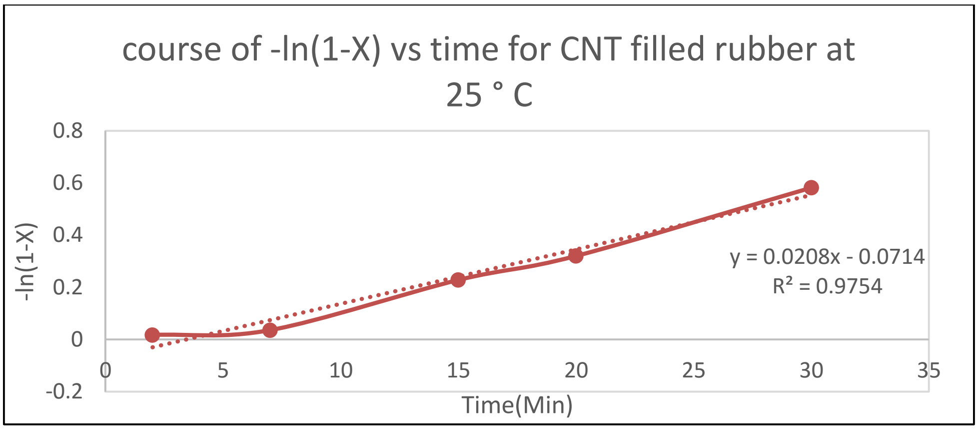


Fig 4.16: course of –ln (1-X) vs. time for 25 ° C

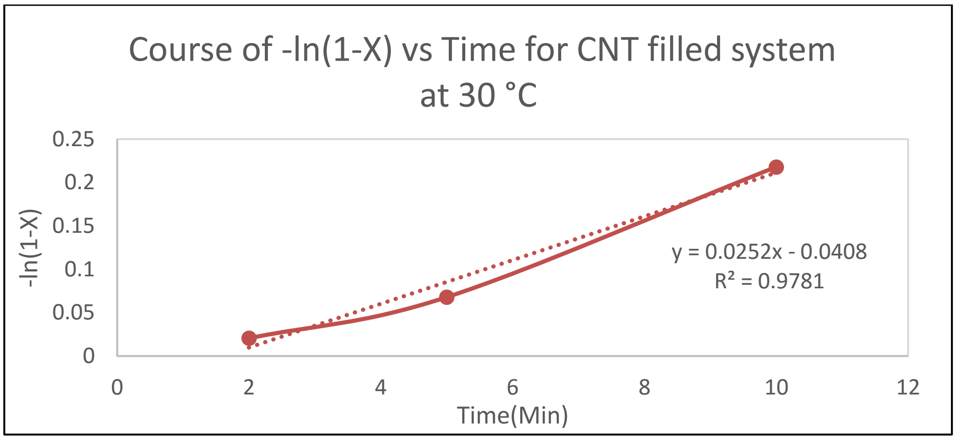


Fig 4.17: course of –ln (1-X) vs. time for 30 ° C

From the above graphs we found the values of rate constants which is shown in below (Table 4.13). Log k vs. 1 /T is plotted in Fig 4.18.

4.13: Rate constant value at Different temperature for CNT filled reaction

Temperature	K	1/T	LOG K
296	0.0141	0.003378378	-1.85078
298	0.0208	0.003355705	-1.68194
303	0.0252	0.00330033	-1.5986

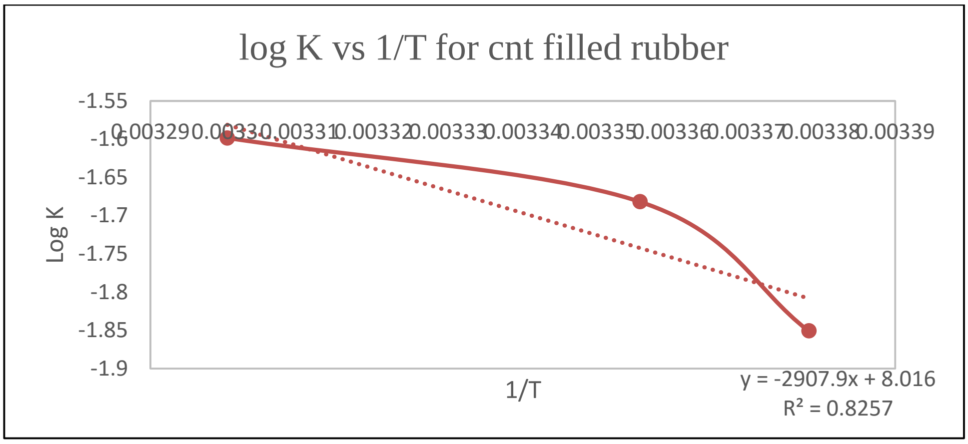


Fig 4.18: course of log K vs. 1/T for CNT filled system

The slope/2.303R = -2907.9 ……………………………………………………….. [5]

R =1.98 Cal K^{-1} mol^{-1}

So, Activation energy, E = 13259.84 Cal mol^{-1}= 13.259 kcal mol^{-1}

So here we can see that the activation energy of CNT filled system is higher than blank system. This implies that polymerization reaction get delayed due to the presence of CNT.

4.7 Evaluation of MWCNT based butadiene nano composites

Any rubber is evaluated as per ASTM standard. MWCNT- BR is compared with butadiene rubber in below tables.

4.7.1 ASTM formulations

Table 4.14 ASTM formulation

	Plant rubber	0.5 phr CNT	Plant rubber	0.5 phr CNT
Weight of samples(gm.)	100	100	100	100
IRB-8 (gm.)	60	60	40	40
ZNO (gm.)	3	3	3	3
Stearic acid (gm.)	2	2	2	2
Naphthenic acid (gm.)	15	15	15	15
TBBS (gm.)	0.9	0.9	0.9	0.9
SOL. S (gm.)	1.5	1.5	1.5	1.5
Total Phr	182.4	182.4	162.4	162.4

4.7.2 Mixing parameters

Table 4.15 Mixing parameter for rubber compounding

Mixing time(minute)	9	9	9	9
Batch weight(gm)	70	70	70	70
RPM	60	60	60	60
TCU	60	60	60	60
Remarks	10 pass on mill	10 pass on mill	10 pass on mill	10 pass on mill

4.8 Rheo study

The Rheometric study of the ASTM formulated compound and 0.5 phr nano filler loaded compound has been carried out in order to understand the curing as well as processing characteristics of the rubber. The lowest torque value recorded on the graph, measured in dN*m, is called ML (Moment Lowest). It is a measure of stiffness of uncured rubber compound at a given temperature. TS2 provides information about scorch time or at which point the curing actually starts. The highest torque recorded on the graph, measured in dn*m, is called MH (Moment Highest). The difference between highest and lowest torque (Delta Tq) gives an indirect measurement of physical cross linked formed in the rubber compound. The higher the Delta Tq, the higher will be the physical strength of rubber. TC 90 provides the information that how long the rubber piece has to be kept in the moulding press for complete curing. Cure rate implies the nature of the curing. Reversion implies the property deterioration of particular rubber compound after complete curing.

The influence of both nano fillers on curing study of rubber compound has been studied and provided in Table 5.5. Rheomteric study of PBR based rubber composites and nano fillers embed PBR nano composites. The study indicates that the material is less scorch safety in presence of nano fillers but the physical property depending upon physical crosslink has been enhanced. However, materials require more time for curing in presence of nano fillers as compared to compound devoid of nano clay. On the other hand, reversion value indicates that the nano filler embedded rubber compound shows more stable in physical properties.

Table4.16: Rheometric study of rubber composites

	Plant rubber	0.5 Phr CNT	Plant rubber	0.5 Phr CNT
ML(dN-M)	9.62	11.9	6.34	7.41
MH(dN-M)	38.61	42.23	32.06	35.21
Ts2(min)	4.11	3.62	6.03	5.33
TC90(Min)	10.86	11.35	12.87	12.47
Final Tq (dN-M)	38.39	42.18	31.96	35.16
Cure rate	4.29	3.92	3.76	3.89
Reversion %	0.76	0.16	0.39	0.18
Delta Tq (dN-M)	28.99	30.33	25.72	27.8

4.9 Mechanical and other important properties

The mechanical as well as important properties in terms of end use application have been further carried out and are shown in Table 5. From rheomteric study, it can be inferred that the nano fillers embedded rubber compound should show good mechanical properties. The similar kind of results has been reflected in tensile strength data. The tensile strength of 0.5 phr loaded MWCNT shows 21 % improvement as compared to compound containing plant rubber. On the other hand, silica shows marginal improvement of tensile strength. Moreover, the modulus and elongation both increase with incorporation of nano filler. The interaction between nano fillers and rubber matrix has been further reflected from their hardness value as in both the cases, the hardness increase in presence of nano filler irrespective of their different nature. However, the abrasion loss property does not change much; it remains almost constant in both the nano fillers. Interestingly, it is also noticed that the heat build-up of the system decrease with incorporation of nano filler which is essentially required in rubber product application. With decreasing heat build-up of rubber compound, the rolling resistance of rubber significantly reduce which ultimately improve the fuel economy. This has positive impact in tire industry.

Table 4.17: Study of mechanical and other important properties

	Plant rubber	0.5 Phr MWCNT	Plant rubber	0.5 Phr MWCNT
Tensile strength (MPa)	14	17	11	12
Elongation at Break (%)	475	534	492	542
Mod at 300% Elongation(MPa)	7.5	8.1	5.1	4.8
Hardness	55.6	59.1	47.3	50.1
Specific gravity	1.103	1.114	1.048	1.065
HBU (°C)	39.0	34.0	22.0	20.0
Abrasion loss(gm.)	0.045	0.042	0.042	0.042
Abrasion loss (mm^3)	40.8	37.5	40.5	39.7

4.10 Thermal properties

The glass transition temperature (T_g) of a polymer was determined form DSC study. The DSC results shown in Fig. 4.19a-b indicates that T_g of the polymer did not change significantly after incorporation 0.5 phr MWCNT into the rubber matrix. The glass transition temperature of *in situ* prepared 0.5 phr MWCNT based polymer was obtained around -106 °C while the T_g of the blank polybutadiene rubber was -107 °C (Fig. 4.19a).

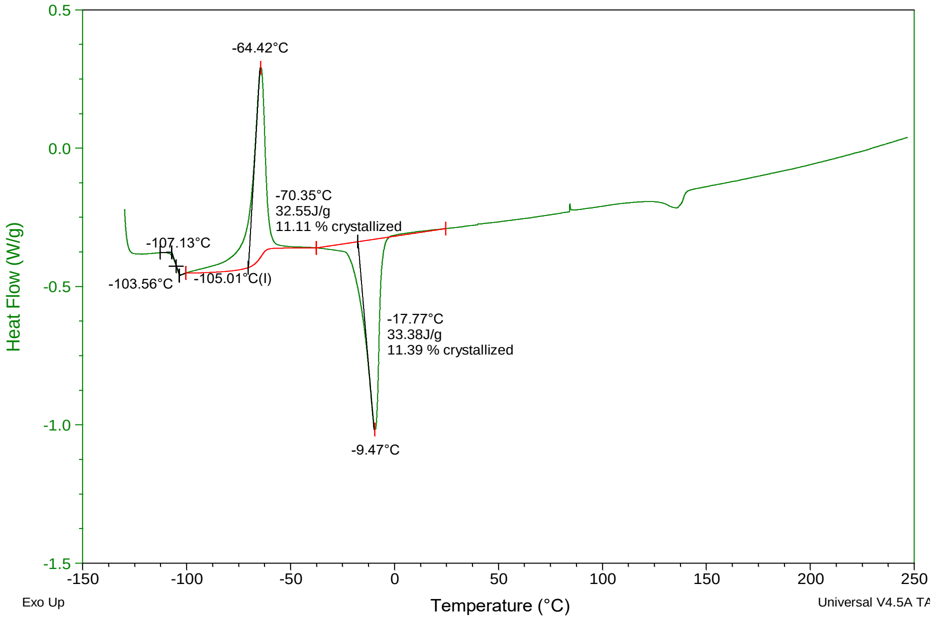


Fig. 4.19a: DSC results of Ni-based polybutadiene rubber

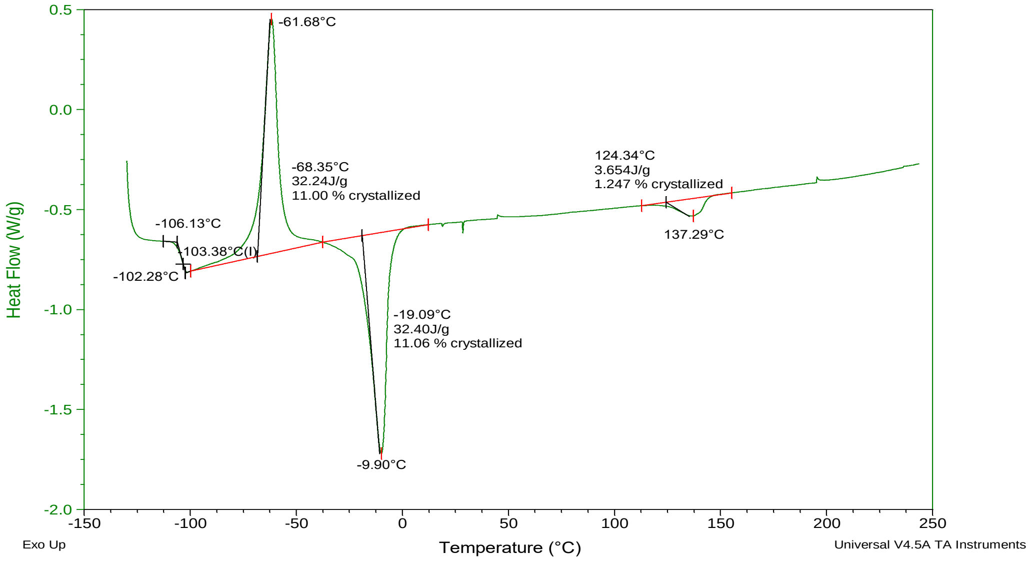


Fig. 4.19a: DSC results of Ni-based polybutadiene rubber

The marginal improvement of T_g may be considered the restriction of polymer mobility in presence of MWCNT. This implies the interaction of MWCNT with rubber matrix. This has been further clarified in thermo gravimetric analysis results shown in Fig. 4.20 a-b. It was observed that T_{max} of the polymer was marginally enhanced in presence of MWCNT.

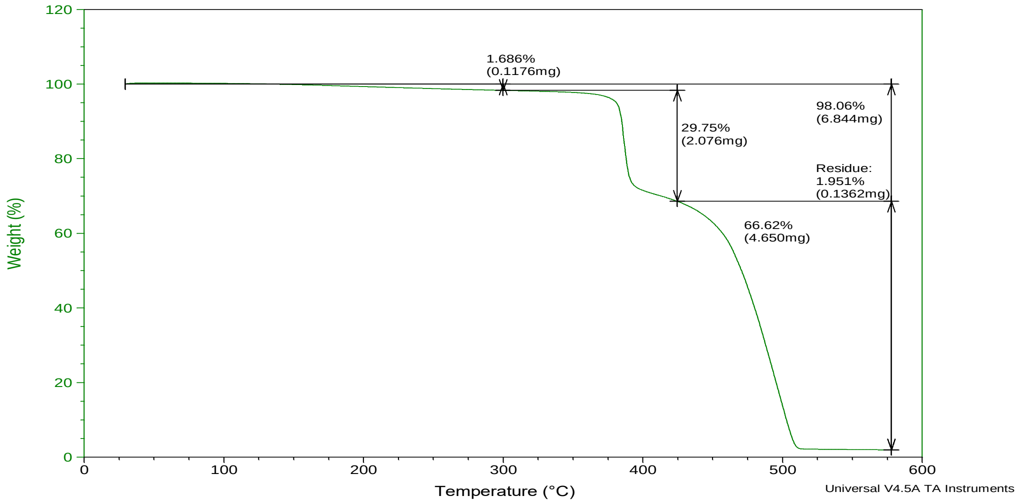


Fig. 4.20a Thermo gravimetric curves of blank Ni-based BR

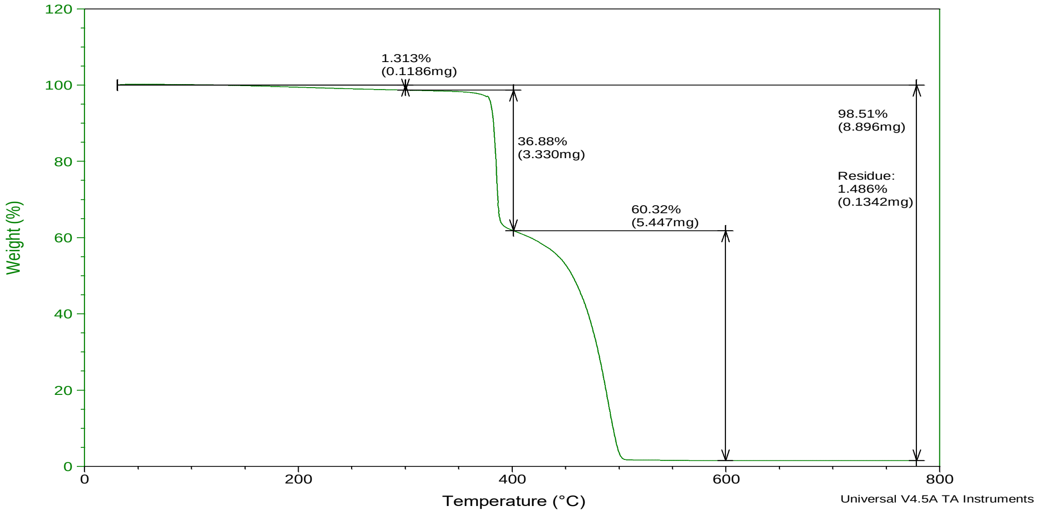


Fig. 4.20b Thermo gravimetric curves of Ni-based polybutadiene rubber nano composites containing 0.5 phr MWCNT

This is further in line with the results obtained from stress-strain analysis results given in Table 4.13. The structure property relation of BR matrix and nanofillers were also established with X-Ray Diffraction (XRD), which is used to study the expansion of the nano fillers interlayer distance (Table 4.14). XRD patterns of BR/MWCNT hybrids and its raw sample are provided in Table 4.14. The diffraction peaks of composites are shifted towards low-angle direction, which indicates effective expansion of the interlayer distance of MWCNT within the BR composites.

Table 4.18: XRD results of Blank PBR and MWCNT embedded PBR

Sample Name	**2ϴ (Å)**	**d-spacing (nm)**
Blank	4.2	20.8
In BR/MWCNT-0.5	2.3	38.0

Chapter 5

Summary and Conclusions

In research area, one of the biggest challenges is to obtain a homogeneous dispersion of MWCNT and NS in a rubber matrix. This is due to presence of strong van der Waals interactions between individual tubes of MWCNT and hydrogen bonding of the silanol groups present onto silica surface. This eventually leads to significant aggregation and agglomeration that makes poor dispersion. This eventually reduces the expected property improvements. The surface characterises of the particles (e.g. reactive/functional groups, wettability and surface energy) and the chemical nature of the rubber matrix epitomizes the main key parameters for these interactions.

A homogeneous distribution and a good dispersion are essential for mechanical reinforcement of rubbers. Therefore, best filler (multi-wall carbon nanotube, MWCNT, nano silica, NS) obtained from *ex situ*, was subjected to dispersion in butadiene rubber matrix through *in situ* polymerization process. Such exercise is expected to improve its dispersion in polybutadiene rubber matrix. However, the BR based nanocomposites are successfully prepared by *in situ* methods. Effect of nanofiller loading on the properties of prepared nano composites is investigated. Moreover, the reaction behaviour in terms of exothermicity and conversion has also been studied. In addition, the microstructure analysis and thermal properties have been examined. The intricate analysis and subsequent discussion on the experimental finding leads to the following conclusions:

1. Nanofillers have positive impact on the kinetics of the butadiene polymerization irrespective of change in microstructure of rubber.
2. The effect of nanofiller concentration exhibited that adding of nanofillers causes no consolidated change in the kinetics curve, whereas there is an optimum dose of MWCNT loading wherein the monomer conversion and yield reached to its maximum level. However, increasing nanosilica content results showed no such improvement for Ni based systems, but showed improvement in Co based systems.
3. The activation energy of the polymerization based on Ni- catalyst system in presence of 0.5 phr MWCNT was found to be 16.3kcal mol^{-1} as compared to

blank polymerization (14.5 kcal mol^{-1}). This implies that MWCNT delayed polymerization reaction.

4. The activation energy of the Co- based polymerization based system was found to be 2.5 kcal mol^{-1}. On the other hand, in presence of 0.5 phr MWCNT, it was found to be 13.2 kcal mol^{-1}.
5. The best improvement of mechanical, thermal and other important properties likes hardness; heat build-up etc. was achieved for nano composites containing 0.5 phr MWCNT.
6. MWCNT imparts considerable enhancement in physico-mechanical properties of BR nano composites. Nano composites show better properties at lower filler loading as compared to conventional nano composite prepared via *ex situ* process. Henceforth, much lighter rubber product can be produced by *in situ* nano composite route.
7. The thermal properties are also improved in the nanocomposites compared to gum BR vulcanizate and the results corroborated well with physico-mechanical properties. Moreover, X-ray diffraction of nanocomposites showed intercalated structure at low filler loading.

Chapter 6

Scope for future work

A compressive kinetic study of *in- situ* prepared nanocomposites can be carried out in near future in order to explore the following points;

1. Influence of different types of Nanofiller and optimization of filler dose on kinetic study of Ni/Co-based polymerization system.
2. Characterization and insights of polymerization chemistry in presence of nanofillers.
3. Physico-mechanical, thermal rheological and morphological studies of *in situ* nano composites for diverse end-use applications.

Bibliography

[1] Okada. A.Fukoshima, Y. Inagaki, S. Et al (1998) composite material and process for manufacturing. US patent 4.739.007

[2] Ajayan P, Zhou O, Dresselhaus M, Dresselhaus G, Avouris P. Applications of Carbon Nanotubes in Carbon nanotubes. Springer Berlin / Heidelberg 2001, p. 391-425.

[3] Dujardin e,ebbesonT.W M.J phy.rev , B 58,14,013

[4] Breiner, J.M., Mark,J.E.Beucage, sci. Polym. Phys.37, 1421-14279(1977)

[5] P.B.Messersmith and E.P.Giannelis, chem., matter, 6, 1791, 1994 Current topics in elastomers research, edited by Anil K. Bhowmick, CRC Press

[6] Manufacturing techniques of rubber nano composites by Jun Ma, Li-qunzhang, and Li-Geng

[7] Dash, M.P., Tripathy, M., sasmal, (2010) poly/MWCNT nanotubes composites Sci., 45 (14), 38735-3865

[8] Hofmann, w. (1994) Rubber technology hand book

[9] Nano composites state of the art, Ranimol Stephen and sabu Thomas, department of polymer science and rubber technology, Cochin University of science and technplogy, coachin, kerala.

[10] Manufacturing techniques of rubber nano composites, jun ma , li-qun zhang, li geng, being university of chemical technology.

[11] Synthesis of polymer nano composites: review of various techniques by joel fawaz and vikas mittal

[12] Rubber technology and manufacturer hand book, second addition

[13] Manufacturing techniques of rubber nano composites by Jun Ma, Li-qunzhang, and Li-Geng

[14] Puffr, R, Spatova , J.L., and Brozek,J.(2013) clay minera/polyamide nano composites obtained bu *in situ*polymerization or melt intercal;ation. Appl. Clay Sci., 83-84, 294-299.

[15] Bokobza,L.:Elastomeric composites . I.Silicone composites .J.Appl.polym.sci.93,2095-2104(2004)

[16] Ikeda, Y., poompradub, S., Morita, Y., et al.: preparation of high performance nano composite elastomer:effect of reaction conditions on *in situ* silica generation of high content in natural rubber.J.Sol-gel Sci.Technol.45, 299-306(2008)

[17] Ikeda Y., Kameda, and Y.: Preparation of green composites by sol-gel process: *in situ*silica filled natural rubber. J.Sol-gel sci. Technol 31, 137 -142 (2004)

[18] Cui W., Jiao, Q., Zhao, Y., Li, H., Zhou,M. (2012) preparation of of poly layered double hydroxide nano composites by *in situ* polymerization polym.Lett.,6(6), 485-493

[19] N.pires, A.Ferreira, C.Lira, P.Coutinho, L.Nicolini, B.Soares, F.Countinho; J App. Polymer science;Vol-99,88-99, (2006).

[20] Saltman W. M., Kuzma L. J, , Preparation and Properties of Polydienes Rubber Chem. Tech., 46, 1055. (1973)

[21] N.G Gaylord, T.K Kwei and H.F Mark;J. Polymer science;Vol-42, 417,(1960).

[22] A.Mazzei,M.Araldo,W.Marconi and M.deMalde;J polymer science, part A;Vol-3, 753(1965)

[23] Honig J. A. J., Burford R. P., Chaplin R. P., J. Polym. Sci.: Part-A, 21, 2559. (1983).

[24] J.C Marechal, F.Dawans, and P.H.Teyssie; J polymer science part A-1; Vol-8, 1993(1970)

[25] Dong-Ho Lee and C. C. Hsu; J. App. Polymer Science, Vol. 26, 653-666 (1981).

[26] D.C DebNath ,C M.Fellows and Takeshi Shiono;Macromolecular Research;Vol-14,No.3, 338-342. (2006).

[27] Tai-Yong lee,Singgih nitrahardjo and Sunggyu Lee;J. app. polymer science,Vol-53, 1605-1613,(1994).

[28]T.Yoshimoto,K.Komatsu,R.Sakata,K.Yamamoto,Y.Takauchi,A.Onishi,K.Ueda;Die Makromolekulare Chemie, Vol-139, 1970, 61.(1970)

[29] Hsu C. C., Ng L., AIChE Journal, 22, 66. (1976).

[30] Natta G., Porri L., “Polymer Chemistry of Synthetic Elastomers”, Part-2, edited by J P Kennedy and E Tornqvirst, John Wiley and Sons, Inc., New York, 597. (1967)

[31] Upadhyay V. K., Sivaram S., Indian Journal of Technology, 25, 669. (1987),

[32] Natta G., Porri L., “Polymer Chemistry of Synthetic Elastomers”, Part-2, edited by J P Kennedy and E Tornqvirst, John Wiley and Sons, Inc., New York, (1967), . 597.

[33] Upadhyay V. K., Sivaram S., Indian Journal of Technology, 29, 579. (1991).

[34] Chandran,Kwrak, Sik ha;Catalysis today Vol-131,505-512, (2008)

[35] Youngchan Jang,Dai seung Choi,Shin Han; J.polymer science part A,Vol-42, 1164-1173,(2004).

[36]M. C. Throkmorton ; J.Applied Polymer Science, Vol. 42, , 3019-3024 ,(1991)

[37] R.P.Quirk, A.M. Kells, K.Yunlu, J.P Cuif; Polymer; Vol-41, 5903-5908,(2000)

[38] N.pires, A.Ferreira, C.Lira, P.Coutinho, L.Nicolini, B.Soares, F.Countinho; J App. Polymer science; Vol-99, 88-99, (2006).

[39] I. L.Mello, F. M.B. Countinho , D. S.S Nunes, B. G. Soares, M .A.S Costa, L. C . Maria; European Polymer Journal ; Vol-40, 635-640. (2004).

[40] D. Wilson, J. Jenkins, K. Derek; Polymer Bulletin (Berlin); Vol-34, 257-264. (1995)

[41] L.Reich, S.S Stivala; J. Polymer Science: Part A; Vol-1, 203-216, (1963)