DEVELOPMENT OF ELASTOMERIC HYBRID COMPOSITE BASED ON SYNTHESISED NANOSILICA AND SHORT NYLON FIBER

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by
LENY MATHEW

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682022.

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Department of polymer Science
and Rubber Technology
Cochin University of Science and Technology
Kochi-682022

Dr. Sunil K. Narayanankutty
Professor

Certificate

This is to certify that the thesis entitled **"Development of Elastomeric Hybrid Composite Based on Synthesized Nanosilica and Short Nylon Fiber"** is an authentic report of the original work carried out by **Ms. Leny Mathew** under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022. No part of the work reported in this thesis has been presented for any other degree of any other institution.

Kochi
16-02-2009

Dr. Sunil K. Narayanankutty
(Supervising Teacher)

Dedicated to

My husband Geo

and

Children Megha, Varsha and Akash

Declaration

I hereby declare that the thesis entitled **"Development of Elastomeric Hybrid Composite Based on Synthesized Nanosilica and Short Nylon Fiber"** is the original work carried out by me under the guidance of Dr. Sunil K. Narayanankutty, Professor, Department of Polymer Science and Rubber Technology, Cochin University of science and technology, Cochin 682022, and that no part of this thesis has been presented for any other degree of any other institution.

(Leny Mathew)

Cochin
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Preface

Short fiber-rubber composites have achieved significant importance in a variety of engineering as well as consumer goods because of their high strength to weight ratio, manufacturing flexibility and ease of processing. These composites combine the rigidity of the fiber with the elasticity of the rubbers. One of the main advantages of reinforcing elastomers with short fibers is that the fiber can be incorporated as one of the compounding ingredients during the mixing process. Properties of short fiber filled composites primarily depend on good fiber- matrix adhesion. Conventionally a dry bonding system based on hexamethylene tetramine, resorcinol and silica (HRH) is employed to improve the fiber-matrix interfacial adhesion. The role of silica is to improve the wetting of the fiber surface and to control the resin formation. Particle size and surface area play important roles in the activity of silica. Smaller the particle size better will be its efficiency. Added in sufficient quantity, silica can also function as reinforcing filler in a rubber matrix. The hybrid composites resulting from such combination of silica with short fiber and elastomers are expected to possess attractive mechanical properties and cost advantage.

The present study aims at preparation of low particle size (nano-size) silica from a cost effective silica source, sodium silicate, by precipitation method using dilute hydrochloric acid under controlled conditions and utilizing it in the prepartion of hybrid composites based on short Nylon 6 fiber and elastomers. This synthesized silica is also used as a component of the HRH dry bonding system to improve the fiber-matrix interfacial adhesion. Commercial silica is used as a reference material. The matrices used are natural rubber, nitrile rubber, styrene butadiene rubber and chloroprene rubber. The cure, mechanical, thermal and dynamic mechanical properties of nanosilica/Nylon 6 short fiber/ elastomeric hybrid composites are evaluated.

The results of the investigations are presented in nine different chapters, as follows:

Chapter 1 is an introduction and a review of the earlier studies in this field. Scope and objective of the present work are also discussed.

Chapter 2 describes the materials used and the experimental procedures adopted in the present study.

Synthesis of nanosilica using different dispersing agents and characterization are described in chapter 3.

Chapter 4 deals with the performance of nanosilica as a reinforcing filler in natural rubber compound. In this chapter the cure and mechanical properties of the natural rubber compounds containing the nanosilica are evaluated and compared with the properties of the conventional silica composites.

The effect of synthesized nanosilica as a dry bonding component in HRH bonding system is explained in Chapter 5. In this work the effect of nanosilica based tri-component dry bonding system on short Nylon 6 fiber – natural rubber and styrene butadiene rubber composite are reported. This chapter is divided into two sections. Chapter 5A discusses the effect of nanosilica as dry bonding component in short Nylon 6 fiber / natural rubber composites and Chapter 5B discusses its effect in short Nylon 6 fiber / styrene butadiene rubber composites.

Chapter 6 deals with the cure and mechanical properties of the nanosilica / short nylon 6 fiber elastomeric hybrid composites. This chapter is divided into four sections. Chapter 6A discusses the effect of nanosilica as reinforcement in short

Nylon 6 fiber / natural rubber hybrid composites containing HRH dry bonding system. The effect of nanosilica as reinforcement in short Nylon 6 fiber / nitrile rubber hybrid composites containing HRH dry bonding system is described in chapter 6B. Chapter 6C presents the role of silica as reinforcing filler in short Nylon 6 fiber / styrene butadiene rubber hybrid composites. Chapter 6D reports the effect of nanosilica as reinforcement in short Nylon 6 fiber / chloroprene rubber hybrid composites containing HRH dry bonding system.

Thermal characterization of elastomeric hybrid composite based on nanosilica and short Nylon 6 fiber is discussed in the chapter 7.

Chapter 8 deals with the dynamic mechanical behaviour of elastomeric hybrid composites. The dynamic mechanical analysis of short Nylon 6 fiber/nanosilica reinforced natural rubber, nitrile rubber, styrene butadiene rubber and chloroprene rubber based elastomeric hybrid composites has been done with reference to the fiber content, silica content and frequency.

Chapter 9 is a summary of the entire work. All the important points are highlighted here.

Abstract

Nanoscale silica was synthesized by precipitation method using sodium silicate and dilute hydrochloric acid under controlled conditions. The synthesized silica was characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), BET adsorption and X-Ray Diffraction (XRD). The particle size of silica was calculated to be 13 nm from the XRD results and the surface area was found to be 295 m^2/g by BET method. The performance of this synthesized nanosilica as a reinforcing filler in natural rubber (NR) compound was investigated. The commercial silica was used as the reference material. Nanosilica was found to be effective reinforcing filler in natural rubber compound. Filler-matrix interaction was better for nanosilica than the commercial silica. The synthesized nanosilica was used in place of conventional silica in HRH (hexamethylene tetramine, resorcinol and silica) bonding system for natural rubber and styrene butadiene rubber / Nylon 6 short fiber composites. The efficiency of HRH bonding system based on nanosilica was better. Nanosilica was also used as reinforcing filler in rubber / Nylon 6 short fiber hybrid composite. The cure, mechanical, ageing, thermal and dynamic mechanical properties of nanosilica / Nylon 6 short fiber / elastomeric hybrid composites were studied in detail. The matrices used were natural rubber (NR), nitrile rubber (NBR), styrene butadiene rubber (SBR) and chloroprene rubber (CR). Fiber loading was varied from 0 to 30 parts per hundred rubber (phr) and silica loading was varied from 0 to 9 phr. Hexa:Resorcinol:Silica (HRH) ratio was maintained as 2:2:1. HRH loading was adjusted to 16% of the fiber loading. Minimum torque, maximum torque and cure time increased with silica loading. Cure rate increased with fiber loading and decreased with silica content. The hybrid composites showed improved mechanical properties in the presence of nanosilica. Tensile strength showed a dip at 10 phr fiber loading in the case of NR and CR while it continuously increased with fiber loading in the case of NBR and SBR. The nanosilica improved the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness were also better for the nanosilica composites. Resilience and compression set were adversely affected. Hybrid composites showed anisotropy in mechanical properties. Retention in ageing improved with fiber loading and was better for nanosilica-filled hybrid composites. The nanosilica also improved the thermal stability of the hybrid composite better than the commercial silica. All the composites underwent two-step thermal degradation. Kinetic studies showed that the degradation of all the elastomeric composites followed a first-order reaction. Dynamic mechanical analysis revealed that storage modulus (E’) and loss modulus (E”) increased with nanosiica content, fiber loading and frequency for all the composites, independent of the matrix. The highest rate of increase was registered for NBR rubber.

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Chapter 1

Introduction

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1.1 Composites - General Introduction

Composites are one of the most advanced and adaptable engineering materials known to men. Progresses in the field of materials science and technology have given birth to these fascinating and wonderful materials. Composites are heterogeneous in nature, created by the assembly of two or more components with fillers or reinforcing fibers and a compactable matrix [1]. The matrix may be metallic, ceramic or polymeric in origin. It gives the composites their shape, surface appearance, environmental tolerance and overall durability while the fibrous reinforcement carries most of the structural loads thus giving macroscopic stiffness and strength [2]. A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. At present composite materials play a key role in aerospace industry, automobile industry and other engineering applications as they exhibit outstanding strength to weight and modulus to weight ratio. High performance rigid composites made from glass, graphite, kevlar, boron or silicon carbide fibers in polymeric matrices have been studied extensively because of their application in aerospace and space vehicle technology [3-8].

Based on the matrix material which forms the continuous phase, the composites are broadly classified into metal matrix (MMC), ceramic matrix (CMC) and polymer matrix (PMC) composites. Of these, polymer matrix composites are much easier to fabricate than MMC and CMC. This is due to the relatively low processing temperature required for fabricating polymer matrix composite. PMC’s generally consist of synthetic fibers like carbon, nylon, rayon or glass embedded in a polymer matrix, which surrounds and tightly binds the fibers. Typically, the fibers make up about 60 % of a polymer matrix composite by volume. The structure, properties and applications of various composites are being investigated world wide by several researchers [9 -18].

The fibrous reinforcing constituent of composites may consist of thin continuous fibers or relatively short fiber segments. When using short fiber segments, fibers with high aspect ratio (length to diameter ratio) are used. Continuous fiber reinforced composites are generally required for high performance structural applications. The specific strength (strength to density ratio) and specific stiffness (modulus to density ratio) of continuous carbon fiber reinforced composites can be superior to conventional metal alloys. Also depending upon how fibers are oriented within the matrix, composites can be fabricated into products that have structural properties specifically tailored for a particular use. Polymer concretes are increasingly being used in buildings and other structures. They represent a new type of structural material capable of withstanding highly corrosive environments. The high strength to weight ratio and non-corrosive characteristics of these materials like fiber-reinforced plastics can be utilised to build innovative structures, which are, desirable and economical [19].

Although composite materials have certain advantages over conventional materials, they have some disadvantages also. PMC’s and other composite materials tend to be anisotropic; that is, properties like strength, stiffness etc. are different in different directions depending on the orientation of composite constituent materials. These anisotropic properties pose a significant challenge for the designer who uses composite materials in structures that place multi-directional forces on structural members. Also formation of a strong connection between the components of the composite material is difficult. The broader use of advanced composites is inhibited by high manufacturing costs. Development of advanced composite materials having superior mechanical properties opened up new horizons in the engineering field. The advantages such as corrosion resistance, electrical insulation, low thermal expansion, higher stiffness, strength and fatigue resistance make them preferred candidates for many applications [20-25].

1.2 Historical Background

Nature has provided composite materials in living things such as seaweeds, bamboo, wood and human bone. The first reinforced polymeric based materials appear to have been used by the people of Babylonia around 4000-2000 B.C. The materials consisted of reinforced bitumen or pitch. Around 3000 B.C. evidences from various sources indicate that in Egypt and Mesopotamia, types of river-boat were constructed from bundles of papyrus reed embedded in a matrix of bitumen. The art of mummification that flourished in Egypt during 2500 B.C.exemplifies one of the first filament winding process. Suitably treated dead bodies were wrapped in tapes of linen and then impregnated with a natural resin to produce, ultimately a rigid cocoon. The use of lac has been known to India and China for several thousands of years. It is recorded in the Vedas written about 1000 B.C. In India the resin was used as filling for swords hafts and in the manufacture of whetstones by mixing shellac with fine sand. The latter example may be considered as the forerunner of the modern composite grinding wheel. By 500 B.C., the Greeks were building ships with three banks of oars called triremes. They possessed keels that were much longer than could have been accomplished by using a single length of timber. Thus, it can be seen that the origin of composite technology goes back into antiquity.

The relative importance of the structural materials most commonly used, i.e. metals, polymers, composites, and ceramics, to various societies throughout history has fluctuated. Ashby [26] presents a chronological variation of the relative importance of each group from 10,000 B.C. and extrapolates their importance through the year 2020. The information contained in Ashby's article has been partially reproduced in Figure 1.1. The importance of composites has experienced a steady growth since about 1960 and is projected to continue to increase through the next several decades.

The fiber-reinforced polymer market is estimated at almost 1.04 million metric tons (2.3 billion lbs) in 2002, and is expected to increase by 15 % in volume [27]. According to the above report, the market for fiber-reinforced polymers will grow at an average annual growth rate (AAGR) of 3.0 % through the next five years, increasing to 1.2 million tons per year by 2010.

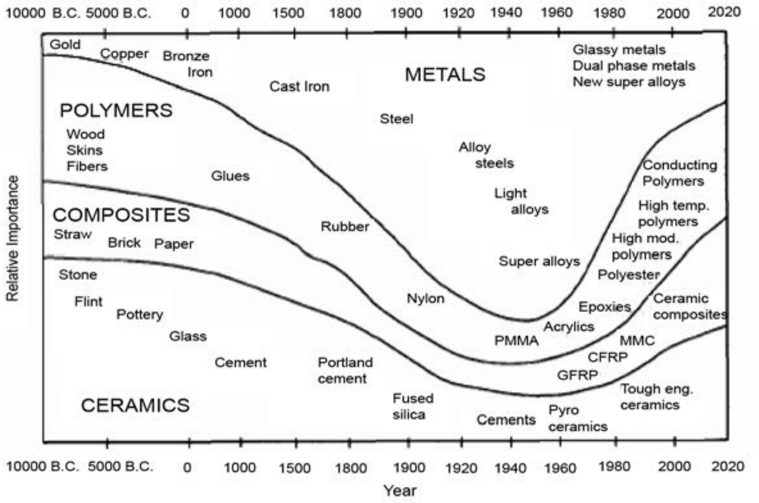
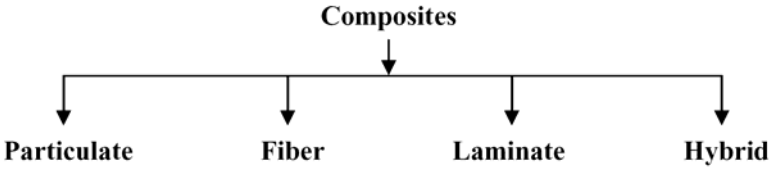


Figure 1.1. Relative importance of material development through history

1.3 Classification of Composites

Based on the types of reinforcement used, the composites are classified as

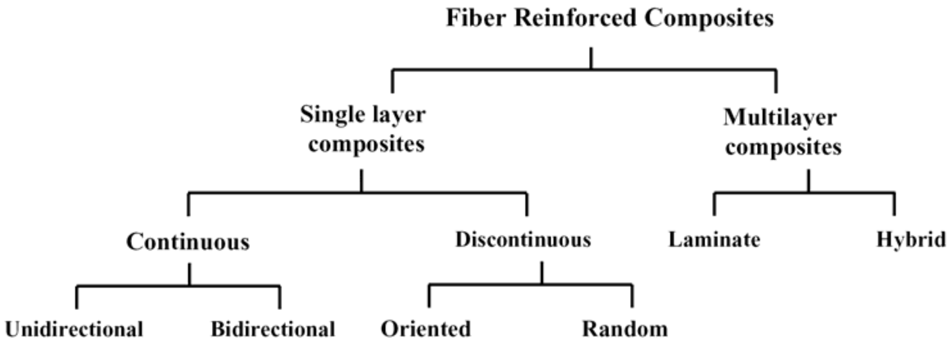


1.3.1 Particulate reinforced composites

A composite whose reinforcement is a particle with all the dimensions roughly equal are called particulate reinforced composites. Particulate fillers are employed to improve high temperature performance, reduce friction, increase wear resistance and to reduce shrinkage [28]. The particles will also share the load with the matrix, but to a lesser extent than a fiber. A particulate reinforcement will therefore improve stiffness but will not generally strengthen.

1.3.2 Fiber reinforced composites

Fiber reinforced composites contain reinforcements having lengths higher than cross sectional dimension. Fibrous reinforcement represents physical rather than a chemical means of changing a material to suit various engineering applications [29]. These can be broadly classified as



Reinforcing fiber in a single layer composite may be short or long based on its overall dimensions. Composites with long fibers are called continuous fiber reinforcement and composite in which short or staple fibers are embedded in the matrix are termed as discontinuous fiber reinforcement (short fiber composites). In continuous fiber composites fibers are oriented in one direction to produce enhanced strength properties. In short fiber composites, the length of short fiber is neither too high to allow individual fibers to entangle with each other nor too small for the fibers to loss their fibrous nature. The reinforcement is uniform in the case of composites containing well dispersed short fibers. There is a clear distinction between the behavior of short and long fiber composites.

1.3.3 Hybrid composites

Composite materials incorporated with two or more different types of fillers especially fibers in a single matrix are commonly known as hybrid composites. Hybridisation is commonly used for improving the properties and for lowering the cost of conventional composites. There are different types of hybrid composites classified according to the way in which the component materials are incorporated. Hybrids are designated as i) sandwich type ii) interply iii) intraply and iv) intimately mixed [30]. In sandwich hybrids, one material is sandwiched between layers of another, whereas in interply, alternate layers of two or more materials are stacked in regular manner. Rows of two or more constituents are arranged in a regular or random manner in intraply hybrids while in intimately mixed type, these constituents are mixed as much as possible so that no concentration of either type is present in the composite material.

1.3.4 Laminates

A laminate is fabricated by stacking a number of laminae in the thickness direction. Generally three layers are arranged alternatively for better bonding between reinforcement and the polymer matrix, for example plywood and paper.

These laminates can have unidirectional or bi-directional orientation of the fiber reinforcement according to the end use of the composite. A hybrid laminate can also be fabricated by the use of different constituent materials or of the same material with different reinforcing pattern. In most of the applications of laminated composite, man made fibers are used due to their good combination of physical, mechanical and thermal behavior.

1.4 Short fiber- Rubber Composites

The term ‘short fiber’ means that the fibers in the composites have a critical length which is neither too high to allow individual fibers to entangle with each other, nor too low for the fibers to lose their fibrous characteristics. A short fiber composite signifies that the two main constituents, i.e., the short fibers and the rubber matrix remain recognizable in the designed material. When used properly, a degree of reinforcement can be generated from short fibers, which is sufficient for many applications.

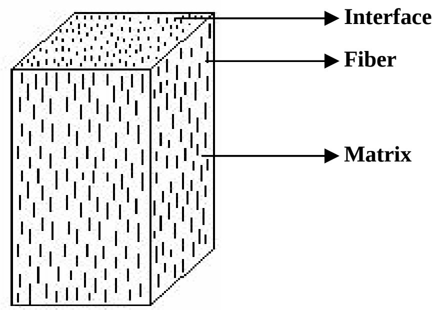


Figure 1.2. Short fiber composite

Short fiber reinforced rubber composites were developed to fill the gap between the long fiber reinforced and particulate filled rubber composites. That is mainly to achieve the high performance of the fiber coupled with easy processability and elasticity of the rubber. Composites in which the short fibers are oriented uniaxially in an elastomer have a good combination of good strength and stiffness from the fibers and elasticity from the rubber. These composites are being used for the fabrication of a wide variety of products such as V-belts, hoses and articles with complex shapes [31-32]. Short fiber reinforced rubber composites possess several advantages over continuous fiber composites [33-36]. Short fibers can be easily incorporated into the rubber compound along with other ingredients. They are amenable to standard rubber processing operations such as extrusion, calendaring, compression molding, injection molding etc. These composites provide high green strength and high dimensional stability during fabrication. Design flexibility is another advantage of these composites. Complex shaped articles which is quite difficult to accomplish with long fiber composites can be fabricated using short fiber composites. Mechanical properties like specific strength and stiffness, reduced shrinkage in molded products, resistance to solvent swelling, abrasion, tear and creep resistance are greatly improved in the case of short fiber composites. Moreover short fibers are cheaper than long fibers. But there are some disadvantages also. Difficulty in achieving uniform dispersion, fiber breakage during processing, difficulties in handling and bonding etc. are some among them.

One of the first reports on short fiber reinforcement of rubber, natural rubber was used by Collier [37] as the rubber matrix, which was reinforced using short cotton fibers. Though NR, the most commonly used elastomeric matrix for short fiber reinforcement, styrene butadiene rubber (SBR), chloroprene rubber (CR), nitrile rubber (NBR) and ethylene propylene rubber (EPDM) also received attention [38- 44].These rubbers were reinforced using short fibers such as cotton, silk, rayon,jute and Nylon [45- 50].

Mingtao Run *et al.* [51] studied crystal morphology and nonisothermal crystallization kinetics of short carbon fiber/ poly(trimethylene terephthalate) composites. Relationship between processing method and microstructural and mechanical properties of poly(ethylene terephthalate) / short glass fiber composites were studied by Mondadori *et.al.* [52]. Das *et al.* [53] reinforced bromobutyl rubber using short Kevlar fiber. Zuev [54] studied the mechanical properties of fiber-filled rubber composites and ways of effective utilization of mechanical properties of fibers in fiber filled rubber composites and compared with those of rubber compound in the absences of fibers. Maya *et al.* [55] presented a review on cellulosic fiber-reinforced green composites. Short Nylon fiber reinforced polypropylene was studied by Thomas *et al.*[56]. Anuar and co workers [57] studied the tensile and impact properties of thermoplastic natural rubber reinforced short glass fiber and empty fruit bunch hybrid composites. In a review, Kun [58] presented the effect of type of fiber, fiber pretreatment, compounding and processing on the product performance properties. Advances in short fiber pretreatment, interfacial adhesion and development of short fiber- rubber composite products were reviewed by Zhou *et al.* [59]. Fiber reinforced plastic and rubber composites for electrical insulators have been manufactured by Kadowaki [60].

Wazzan [61] studied the physico-mechanical properties of EPDM/ Nylon-6 short fiber composites. Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites was studied by Geethamma *et al.* [62]. In the case of soft rubbery composites cellulose fiber has been found to give better reinforcement than glass or carbon fibers [63]. Atomic force microscopy (AFM) studies of short melamine fiber reinforced EPDM rubber was done by Rajeev *et al.*[64]. Short jute fiber reinforced NR composites have been studied by Murty *et al.* [65].Investigations have also been made on short jute fiber reinforced carboxylated nitrile rubber [66]. Cure characteristics and mechanical properties of short Nylon 6 fiber nitrile rubber composites were studied by Rajesh *et al.* [67]. Natural rubber-coir fiber composite was studied by Geethamma et al [68-69]. A novel method for the preparation of short Nylon fiber-natural rubber composites was developed by Bipinbal *et al.* [13], in which short fibers chopped to approximately 6 mm were incorporated in the latex stage and processed into sheet form. By this method, mixing cycle time was reduced without compromising the fiber dispersion. Fiber breakage during mixing was also reduced. Effect of processing parameters on the mechanical properties of short Kevlar aramid fiber- thermoplastic PU composite were reported by Kutty *et al.* [70]. Kutty *et al.* [71] also studied the reinforcement of millable PU with short Kevlar fiber. The mechanical properties of short fiber polymer composites and the influence of surface treatment of short fiber have also been investigated [72-75].The possibility of using natural fibers as reinforcement in polymer based composites has been examined [76-80]. Studies on composites containing short banana fibers and polyester resin have been conducted [81-83]. Effect of short fiber diameter on mechanics of rubber composites was studied by Zhang *et al.* [84]. Rheological properties of short polyester fiber polyurethane elastomer composites with and without bonding agent was reported by Suhara *et al*. [85 - 86]. Suhara *et al*. [87] also studied the thermal degradation of short polyester fiber- polyurethane elastomer composite and found that incorporation of short fiber enhanced the thermal stability of the elastomer.

1.5 Constituents of Short Fiber-Rubber Composites

1.5.1 Rubber matrix

Various elastomers have been used as matrices for short fiber reinforcement. Typically, the matrix has considerably lower density, stiffness and strength than those of the reinforcing fiber material, but the combination of matrix and fiber produces high strength and stiffness, while still possessing a relatively low density. In a composite the matrix is required to fulfill the following functions:

- To bind together the fibers by virtue of its cohesive and adhesive characteristics
- To protect them from environments and handling.

- To disperse the fibers and maintain the desired fiber orientation and spacing.
- To transfer stresses to the fibers by adhesion and / or friction across the fiber-matrix interface when the composite is under load, and thus to avoid any catastrophic propagation of cracks and subsequent failure of the composites.
- To be chemically and thermally compatible with the reinforcing fibers.
- To be compatible with the manufacturing methods which are available to fabricate the desired composite components.

1.5.1.1 *Natural rubber (NR)*

Natural rubber is a high molecular weight polymer of isoprene in which essentially all the isoprenes have the cis 1-4 configuration. The chemical structural formula of natural rubber is shown in figure 1.3.

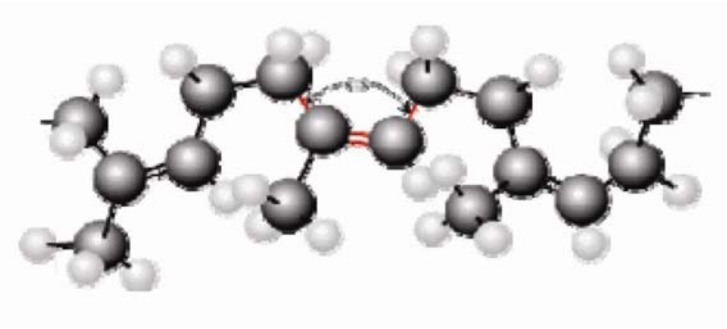


Figure 1.3. Structural formula of Natural Rubber

Among various rubbers, natural rubber is very important since it possess the general features of other rubbers in addition to the following highly specific characteristics. Since it is of biological origin, it is renewable, inexpensive and creates no health hazard problems. It possesses high tensile strength due to strain induced crystallization. It also possesses superior building tack and good crack propagation resistance. Apart from the conventional rubber products, NR finds a few specialized applications. NR is a versatile and adaptable material which has been successfully used for transport and engineering applications such automobile tyres, aero tyres, off-the-road and aerospace industries, civil engineering, railways, vibration engineering etc.

Reinforcement of NR using particulate fillers and short fibers has been studied at length [88-90]. Cure characteristic and mechanical properties of natural rubber short Nylon fiber composites were studied by Sreeja *et al*. [48]. Atsushi *et al*.[91] studied about the nanostructure in traditional composites of natural rubber and reinforcing silica. Yoshitaka and co workers [92] investigated the friction of short fiber-reinforced rubber on wet surfaces. Sisal and short pineapple fibers have been used for reinforcement of NR [93-97].

1.5.1.2 *Styrene butadiene rubber (SBR)*

Styrene butadiene rubber (SBR) is a non-polar synthetic rubber that is the most commonly used general-purpose synthetic rubber. SBR is a copolymer of styrene and butadiene. Some of the properties of SBR are inferior to that of NR. The green strength, heat build up and tackiness are some examples. It is marketed generally at a lower viscosity than NR and this permits its use in industry without pre-mastication. Abrasion resistance and resistance to degradation under heat are better for SBR than NR. SBR finds applications in tyres, shoe soles, foot wear components, insulation of wires and cables, carpet backing etc… Effect of filler content on the mechanical properties of SBR was studied and results showed that the properties improved with filler loading [98-100]. Thermal degradation of short Nylon fiber reinforced SBR composite was studied by Seema *et al*.[101]. Seema [102] also studied the rheological characteristics of short Nylon 6 fiber reinforced SBR containing epoxy resin as bonding agent. Praveen and co workers [23] studied the effect of filler geometry on viscoelastic damping of graphite/aramid and carbon short fiber-filled SBR composites.

1.5.1.3 *Acrylonitrile butadiene rubber (NBR)*

Acrylonitrile Butadiene Rubber (Nitrile rubber) is a copolymer of acrylonitrile and butadiene and it is a polar specialty rubber. NBR has good resistance to a wide variety of oils and solvents and hence is widely used for products like oil seals, pipe protectors, blow out preventors etc. [103]. Major properties of NBR depend on the acrylonitrile content (ACN) which usually vary from 20-50% by weight. Commercially available nitrile rubbers differ from one another in three respects: acrylonitrile content, polymerization temperature and Mooney viscosity. NBR has high viscosity that can be reduced by mastication. The physical and mechanical properties of NBR reinforced with different fillers have been studied [104-106]. Short fiber reinforced NBR composites were studied by Yoshiki and Sreeja [107-108]. Seema *et al.* studied the effect of an epoxy-based bonding agent on the cure characteristics and mechanical properties of short Nylon fiber reinforced NBR composite [109]. Thermal degradation of melamine fiber reinforced NBR composite was studied by Rajeev *et al*. [110]. Wang *et al.*[111] found that nitrile rubber exhibited the highest interaction with silica probably through the hydrogen bond between the –CN group and silanol groups. Property optimization in nitrile rubber composites via hybrid filler systems was studied by Nugay [112].

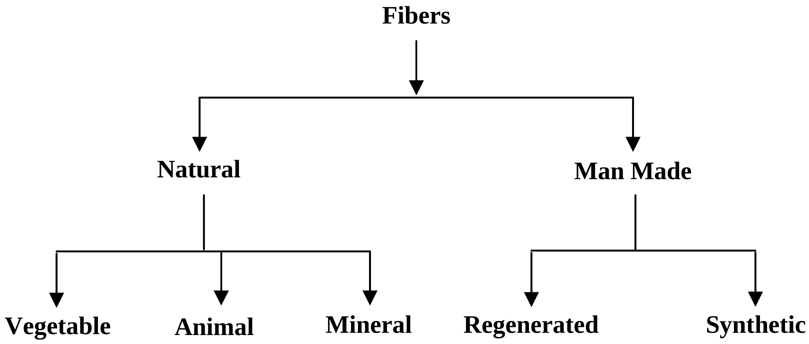
1.5.1.4 *Chloroprene rubber (CR)*

Chloroprene rubber (Neoprene) also comes under the category of specialty rubbers. This rubber is used in specific applications which require solvent resistance, fire resistance and thermal resistance. Neoprene does not require sulphur for vulcanization. Its general physical properties are enhanced by compounding it with metallic oxides such as ZnO and MgO. Polychloroprene’s heat and flex resistance make it an excellent choice for application such as industrial and automotive hoses, V- belts, transmission belts, conveyor belts, escalator hand rails, motor mountings, wire and cables and adhesives. Neoprene also received much attention of many researches [113-115]. Effects of fiber loading and matrix strength on physical properties of the short aramid fiber reinforced chloroprene rubber composite was investigated by Park and co workers [116].

Butadiene rubber (BR), ethylene propylene rubber (EPR), Butyl rubber (IIR), polyacrylic rubbers, fluorocarbon rubbers, silicone rubbers and polyurethane rubbers were also used as matrix materials for short fiber reinforcement [61,117-124]. Many researchers used rubber-rubber and rubber-plastic blends as matrix materials for short fiber composites. Boustany *et al.*[125] used NR-SBR blends as the matrix in the short fiber reinforcement using cellulose fiber. A 50/50 blend of ethylene vinyl acetate and EPDM reinforced using short carbon fibers was studied by Das *et al.* [126]. Zhang *et al.* [127] prepared short sisal fiber reinforced epoxidized natural rubber/ polyvinyl chloride blend. Zebarjad *et al.* [128] observed that the modification of PP with a combination of EPDM rubber and glass fiber could be used for improving the mechanical properties of the plastics. Arroyo and Bell [129] studied the effect of short aramid fibers on the mechanical behavior of isotactic PP and EPDM rubber and their blends. Sreeja and Kutty [130-131] prepared natural rubber-whole tire reclaim-short Nylon fiber composites and studied the effect of urethane based bonding agent on the cure characteristics and mechanical properties.

1.5.2 Fiber reinforcement

‘Fiber’ is defined as any single unit of matter characterized by flexibility, fineness and high aspect ratio [132]. It is a slender filament that is longer than 100 μm or the aspect ratio greater than 10. Fibers have a fine hair like structure and they are of animal, vegetable, mineral or synthetic origin [133]. Fibers are broadly classified into types as natural and man made or synthetic.



Fiber reinforced rubber compounds play a crucial role in high pressure hoses, transmission belts, conveyor belts and tires. Until about 1890, only natural fibers were available. Just before the end of the 19 th century the first synthetic fiber based on cellulose, rayon was developed. These cellulose yarns are considered to be half synthetic, because the raw material is still a natural polymer, cellulose. DuPont developed the first fully synthetic fiber Nylon 66, it was commercially introduced in 1936 (Carothers). A few years latter, Nylon 6 (Schlack, 1941) and polyester (Whinfield & Dickson, 1942) were introduced. The development of “advanced fibers” took place around 1970. Most of these fibers were produced from fully aromatic polymers with high temperature stability. Eventually this led to the discovery of the liquid crystalline PPTA (paraphenylene terephthalamide), the first super strong fiber (DuPont and Akzo Nobel). The second super strong fiber was gel spun poly ethylene, Dyneema of DSM, introduced in 1979.

1.5.2.1 *Natural fibers*

Extensive research has been done on the reinforcement of elastomers using natural fibers. The reinforcement of elastomers using cellulose fiber was studied by different authors [134-139]. Jute and silk fibers were also added to different rubber matrices for the preparation of short fiber rubber composites [65, 140-143]. Sisal, coir, coconut and pineapple leaf fibers were also used to reinforce various elastomeric matrices [69, 94, 96, 124,127,144-145].

1.5.2.2 *Synthetic fibers*

(a) Glass fiber

Glass fiber is the best known reinforcement in high performance composite applications due to its appealing combination of good properties and low cost. The major ingredient of glass fiber is silica which is mixed with varying amounts of other oxides. The different types of glass fibers commercially available are E and S glass. The letter ‘E’ stands for ‘electrical’ as the composition has a high electrical resistance and ‘S’ stands for strength. Glass fibers are used successfully for reinforcing the plastics and therefore, the suitability of this fiber as a reinforcing material for rubbers has been studied. High initial aspect ratio can be obtained with glass fibers, but brittleness causes breakage of fibers during processing. Czarnecki and White [146] reported the mechanism of glass fiber breakage and severity of breakage with time of mixing. Rubber latex also reinforced using glass fibers [147-148]. Gregg [149] reported that the tensile strength of glass fiber-rubber composite decreased with increased atmospheric humidity during glass fiber storage. Marzocchi [150] developed glass fiber-elastomer composites with improved strength and wear resistance to be used in auto tires, V-belts and conveyor belts. Murty and co-workers [136, 151-152] studied the extent of fiber-matrix adhesion and physical properties of short glass fiber reinforced NR and SBR composites. Oh and Joo [153] reported the effect of glass fiber dimension on the mechanical properties of glass fiber reinforced PP/EPDM blends.

(b) Carbon fibers

Carbon fiber is the one of the important high performance fiber used in short fiber-polymer composite. They are commercially manufactured from three different precursors rayon, polyacrylonitrile (PAN) and petroleum pitch. They are mainly used in aerospace industry due to its outstanding mechanical properties combined with low weight. Though carbon fibers are extensively used in polymer composites, its application in rubber matrices is limited to specific end use, mainly in electrically conductive composites. Yagi and co-workers [154] were granted a European Patent for the invention of highly conductive carbon fibers for rubber and plastics composites. They dispersed fibers in the matrix by kneading. Jana and co-workers [155 -156] studied the electrical conductivity of randomly oriented carbon fiber-polymer composites. Das *et al.* [126,157-158] reported the various aspects of electrical conductivity of short carbon fiber reinforced EVA, EPDM and their blends. Pramanik *et al.* [159-160] studied the resistivity of short carbon fiber reinforced nitrile rubber composites. The effect of incorporation of short carbon fiber in the thermoplastic elastomers was studied by Correa *et al.* [161], Roy and co-workers [162-164] Shonaike and Matsuo [165] and Ibarra *et al.* [166-167]. The effect of short carbon fibers on the anisotropic, swelling, mechanical and electrical properties of radiation cured SBR rubber composites were studied by Abdel-Aziz *et al.* [168]. Older and Kumar [169] developed an ablative materials for solid propellant rocket motor using carbon fiber and rubber matrix. A tire tread compound composed of silica, carbon black and carbon fiber was developed by Verthe *et al.* [170].

(c) Aramid fibers

'Aramid' is a generic term for aromatic polyamide fibers. The first commercial p- aramid fiber (Kevlar) was introduced in 1971 [171]. Several aspects of aramid fiber reinforcement of elastomeric matrices and thermoplastic elastomers were discussed by various authors [172-176]. Sunan *et al.* [177] compared the reinforcing effect of as received and hydrolysed Kevlar fiber reinforced thermoplastic elastomer (Santoprene) composites.

(d) Nylon fibers

Nylons are aliphatic polyamides, which was the first synthetic fiber to be commercialized (1939). Nylons are derived from a diamine and a dicarboxylic acid. Because a variety of diamines and dicarboxylic acid can be produced, there are very large number of polyamide materials available to prepare Nylon fibers. The most common versions are Nylon 66 and Nylon 6. Nylon 66 which is widely used as fiber is made from adipic acid and hexamethylene diamine. The commercial production of Nylon 6 begins with carprolactum. Nylon fiber has outstanding durability and excellent physical properties. The main features are exceptional strength, high elastic recovery, abrasion resistance, lusture, washability, resistance to damage from oil and many chemicals, high resilience, colourability, smooth, soft and long lasting fibers from filament yarn, light weight and warm fabrics from spun yarn. Like polyester fiber, Nylon has high melting point which conveys good high temperature performance. Table1.1 gives the typical physical properties of Nylon fibers.

The reinforcement of rubbers using Nylon fibers was reported by various authors [13,101-102]. Cure characteristic and mechanical properties of short Nylon fiber reinforced NBR and CR composite containing Epoxy based bonding agent was investigated by Seema *et al.* [109,113]. Physico-mechanical properties of EPDM/ Nylon 6 short fiber composite was studied by Wazzan [61]. Senapati *et al.* [178] studied the effect of short Nylon fiber on the mechanical properties of NR vulcanizates. Sreeja *et al.* [48, 108, 179] studied short Nylon 6 fiber reinforced NR, NBR, SBR composite and found that short Nylon 6 fiber enhanced the mechanical properties of those rubbers. Dynamic viscoelastic properties of Nylon short fiber reinforced elastomeric composites were studied by Chen *et al.* [180].

Table 1.1. Typical physical properties of Nylon fibers

Property	Continuous filament	Staple
Tenacity at break N / tex, 65 % RH, 21 °C	0.40 - 0.71	0.35 - 0.44
Extension at break, %, 65 % RH, 21 °C	15 - 30	30 - 45
Elastic modulus N / tex, 65 % RH, 21 °C	3.5	3.5
Moisture regain (%) 65 % RH, 21 °C	4.0 - 4.5	4.0 - 4.5
Specific Gravity	1.14	1.14
Approx.volumetric swelling in water,%	2 - 10	2 - 10

Short Nylon fiber reinforced SBR composites for V-belt applications were reported by King *et al.* [181]. Ye *et al.* [182] incorporated short Nylon fiber into SBR and BR matrices and reported that the vulcanization time increased with fiber content. Seema *et al.* [101,104] also reported the thermal degradation of short Nylon 6 fiber reinforced NBR and SBR composites. Short Nylon fiber and vinylon fiber reinforced nitrile rubber and SBR were studied by Zhou *et al.* [183]. They also studied the effect of fiber pretreatment on properties of short Nylon fiber-rubber composites [184-185]. They introduced an effective interfacial thickness concept based on Halpin –Tsai equation to characterize the fiber-rubber interfaces. The reinforcement and orientation behavior of short Nylon fibers in NR, SBR and CR were studied with emphasis on the determination of ideal aspect ratio for fibers by Bhattacharya [186]. Mechanical properties of short Nylon fiber reinforced SBR/NR composites were studied in detail by Ma *et al.*[187]. Zhang *et al.* [188] studied the influence of loading level of Nylon fiber in NR and polyester fiber in CR and proposed a model to calculate the structure of interfacial layer. Rajesh *et al.* [67]

studied the cure and mechanical properties of short Nylon fiber NBR composites. The influences of fiber length, loading and rubber crosslinking systems on the properties of the composites were analysed. Processing parameters of short Nylon 6 fiber reinforced SBR composites with respect to the effect of shear rate, fiber concentration and temperature on shear viscosity and die swell was studied by Seema and Kutty [189].

1.6 Reinforcing Mechanism of Short Fibers

The reinforcing mechanism of fiber in a unidirectional composite can be explained as follows. The composite satisfies the equation 1.1 when a tensile or compressive load is applied parallel to the fiber direction. This equation is applicable under perfect conditions of adhesion between fiber and matrix [190].

$$\varepsilon_c = \varepsilon_f = \varepsilon_m \qquad \text{..} (1.1)$$

where ε_c , ε_f and ε_m are the strain in composite, fiber and matrix respectively. If it is assumed that both fibers and matrix behave elastically, then the following equations can be applied.

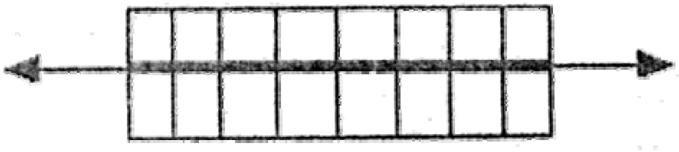
$$\sigma_f = E_f\, \varepsilon_f \qquad \text{..} (1.2)$$

$$\sigma_m = E_m\, \varepsilon_m \qquad \text{..} (1.3)$$

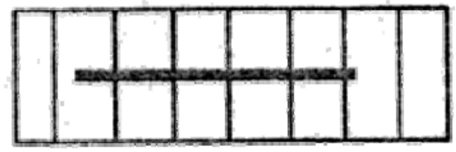
Hence

$$\sigma_c / E_c = \sigma_m / E_m = \sigma_f / E_f \qquad \text{..} (1.4)$$

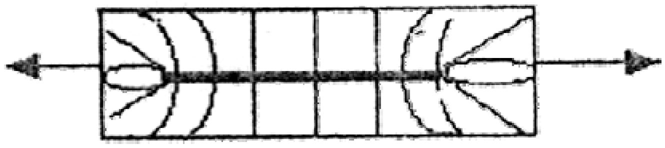
where σ_c, σ_f and σ_m are stress developed in composites, fiber and matrix respectively. Similarly, E_c, E_f and E_m are the modulus of composites, fiber and matrix, respectively. Generally E_f is greater than E_m and so the stress in the fiber is greater than that in the matrix. Thus the fiber can bear a major part of the applied load. In the analysis of long fiber- reinforced composites, any effect associated with fiber ends are neglected. But in the case of short fiber reinforced composites, the end effects become progressively significant due to the decrease in aspect ratio of the fiber. This result in the reduction of fiber efficiency in reinforcing the matrix and also causes an early fracture of the composite.



(a). Continuous fiber composite deformed



(b). Short fiber composite un-deformed



(c). Short fiber composite deformed

Figure 1.4. Effect of stretching force on the strain around long and short fiber in a low modulus matrix

Consider an oriented fiber composite in which fibers are aligned parallel to the direction of application of force. A single fiber is embedded in a matrix of lower modulus. Imagine perpendicular lines running through the fiber - matrix interface in a continuous manner in the unstressed state as shown in the figure 1.4(b). The matrix and the fiber will experience different tensile strains because of their different moduli. When the composite is loaded axially, the longitudinal strain in the matrix will be higher than that in the adjacent fiber due to lower modulus of the former. When force is applied, the imaginary vertical lines in the continuous fiber composite will not be distorted (Fig.1.4(a)). But these lines in short fiber composite will be distorted as in figure 1.4(c) because at the region of fiber ends, the matrix will be deformed more than that in the region along the fiber. This difference in the longitudinal strains creates a shear stress distribution around the fibers in the direction of the fiber axis and so the fiber is stressed in tension. The applied load is transferred from matrix to fiber across the interface because of this shear stress distribution.

When mechanical force is applied to the polymeric matrix, it spreads smoothly through the matrix until it reaches the matrix- fiber interface. If the interface is well bonded, the stress is transferred across it into the fiber and then spread throughout the fiber. This process occurs at all the fiber- matrix interfaces in the composite. Thus it is obvious that load will be transferred to the fiber only if the interface is strong and a perfect bond exists between the two constituents. Hence strong interface is a must for high reinforcing efficiency.

1.7 Factors affecting the properties of Short fiber- Rubber Composites

1.7.1 Type and fiber breakage

The importance of fiber length and its influence on the properties of the composites were studied by several researchers [191-194]. In a composite material fiber length is a critical factor which should not be too long so that they entangle with each other causing problems of dispersion. But a very small length of fiber does not offer sufficient stress transfer from the matrix to the fiber. The severity of fiber breakage mainly depends on the type of fiber and its initial aspect ratio. Fibers like glass and carbon are brittle and they posses a low bending strength than Nylon fiber which are more flexible and resistant to bending. For each type of fiber there exists a certain aspect ratio below which no further breakage can occur depending on its resistance to bending. If the mix viscosity is high, more shear will be generated during mixing and thus exceeding the critical bending stress of the fiber which eventually results in severe breakage. O'Connar [195] has reported the fiber breakage during mixing. Murthy and De [151] suggested that the breakage of the fiber is due to the buckling effect. De *et al.* [142-143,196] have studied the breakage of jute and silk fibers in NR and NBR and found that the breakage of silk fibers is less than that of jute fibers. Considerable fiber breakage occurred during mixing of fibers with high aspects ratio (as high as 500) resulting in reduction in aspects ratio [197]. Noguchi *et al.* [198] reported that short PET fibers did not break up during the milling process and they are well dispersed, but carbon fibers did break up during milling, the fiber length being reduced to about 150 μm. Significant breakage of short Kevlar fibers during mixing in Brabender plasticorder in TPU matrix was reported by Kutty *et al.* [70,199].

1.7.2 Critical fiber length and aspect ratio of fiber

The fiber ends in the short fiber reinforced composites play a major role in the determination of ultimate properties of the composite. The concept of critical fiber length over which the stress transfer allows the fiber to be stressed to its maximum, or at which efficient fiber reinforcement can be achieved has been used to predict the strength of the composites. Broutmann and Agarwal [191] have done a theoretical analysis on the mechanism of stress transfer between matrix and fiber of uniform length and radius and have given the following expression for the critical fiber length (l_c).

$$l_c/d = \sigma f_u/2\tau_y \qquad \text{.........} (1.5)$$

where d is the diameter of the fibre, σf_u is the ultimate fiber strength, and τ_y is the matrix yield stress in shear. The aspect ratio (the length to diameter ratio) (l/d) of fibers is a major parameter that controls the fiber dispersion and fiber matrix adhesion that gives the optimum performance of short fiber polymer composites. If the aspect ratio of the fiber is lower than the critical aspect ratio, insufficient stress will be transferred and the reinforcement will be inefficient. Several researchers [142,200-202] have suggested that an aspect ratio in the range of 100-200 is essential for high performance fiber- rubber composites for good mechanical properties. However Chakraborthy [143] has observed that an aspect ratio of 40 gives optimum reinforcement in the case of carboxylated nitrile rubber composite reinforced with jute fiber. Murthy and De [65,203] have reported that an aspect ratio of 15 and 32 are sufficient for reinforcement of jute fiber in NR and SBR respectively. It was reported that for synthetic fiber like polyester and Nylon aspect ratios of 220 and 170, respectively give good reinforcement in natural rubber vulcanizates [204-205]. Hong Gun Kim [206] investigated the effects of fiber aspect ratio in short fiber reinforced composites.

1.7.3 Fibre orientation

Fiber orientation has a significant influence on the physico mechanical properties of short fiber reinforced rubber composites [207-208]. The preferential orientation of fibers in the matrix results in the development of anisotropy in the matrix. With respect to orientation two limits are explained as longitudinal (along machine direction) and transverse (across machine direction), as given in figure 1.5. It was observed that during mixing procedure lower the nip gap, higher the anisotropy in tensile properties of the composites implying greater orientation of fibers. This is represented as anisotropy index, which reduces gradually with increasing nip gap. Akthar *et al.* [209] found a small nip gap and single pass in the mill to be the best. During processing and subsequent fabrication of short fiber polymer composites, the fibers orient preferentially in a direction depending upon the nature of flow i.e., convergent and divergent as explained by Goettler [210]. If the flow is convergent the fibers align themselves in the longitudinal direction and if it is divergent they orient in the transverse direction.

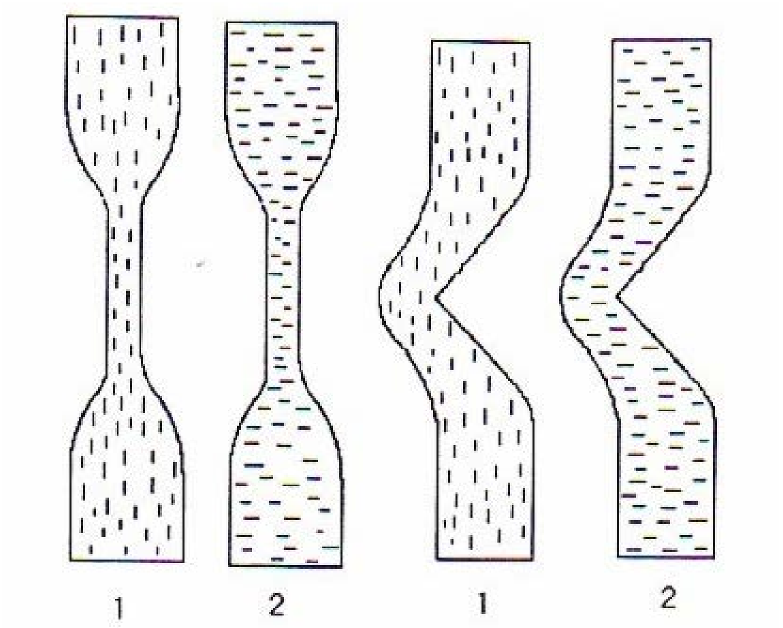


Figure 1.5. Schematic representation of the (1) longitudinal (2) transverse orientation of the fibers in the rubber matrix

In longitudinally oriented composites the effective stress transfer from the matrix to the fiber occurs in the direction of fiber alignment and greater strength and reinforcement will be experienced by the composite. In transversely oriented composites the stress transfer takes place in a direction perpendicular to the fiber alignment and hence fracture of the sample occurs at a lower tensile stress which may be equal or lower than the strength of the matrix. Recently Thomas and co workers [68] have evaluated the percentage (%) extent of orientation from green strength measurements, by using the following equation

$$\text{Orientation \%} = \frac{S_L/S_{G,L}}{S_L/S_G + S_T/S_G} \qquad \text{..(1.6)}$$

where S represents green strength of the composite and subscript L, T denotes longitudinal and transverse orientation, respectively and G represents the gum compound. Many researchers have used SEM to study the fractured surface to determine the fiber orientation [211-212]. Senapati *et al.* [213] reported that two passes through tight nip gave optimum mechanical properties for short PET/NR composites. The effect of mill opening and the friction ratio of the mill and temperature of the rolls on the orientation of short Kevlar fibers in TPU matrix has been described by Kutty *et al.* [70].

1.7.4 Fiber dispersion

Good dispersion of short fibers in the rubber compounds is an essential requisite for high performance composites. The naturally occurring cellulosic fibers tend to agglomerate during mixing due to hydrogen bonding. A pretreatment of fibers at times is necessary to reduce fiber-fiber interactions. Natural fibers treated either with carbon black or compositions containing latex were found to be dispersing well in the rubber matrix [214]. Fiber length has also a role in facilitating better dispersion. Derringer [215-216] has used commercially available fibers such as Nylon, rayon, polyester and acrylic flock cut into smaller lengths of 4mm to study dispersion.

1.7.5 Fiber concentration

Concentration of fibers in the matrix plays a crucial role in determining the mechanical properties of the fiber reinforced polymer composites. A lower concentration of fibers gives lower mechanical strength. This has been observed not only in rubbers [217] but also in thermoplastic elastomeric matrices [162,199,213,218]. This behavior has been attributed basically to two factors, (a) dilution of the matrix which has a significant effect at low fiber loadings and (b) reinforcement of the matrix by the fibers which becomes increasingly important as fiber volume fraction increases. At low fiber content, the matrix is not restrained by enough fibers and highly localized strains occur in the matrix at low strain levels causing the bond between fibers and the matrix to break, leaving the matrix diluted by non reinforcing debonded fibers. At high fiber concentrations, the matrix is sufficiently restrained and stress is more evenly distributed thus the reinforcement effect outweighs the dilution effect [219]. As the concentration of fibers is increased to a higher level the tensile properties gradually improve to give strength higher than that of the matrix. The concentration of fibers beyond which the properties of the composite improve above the original matrix strength is known as optimum fiber concentration. In order to achieve improvement in mechanical properties with short fibers, the matrix is loaded beyond this volume fraction of fiber. In rubbers this optimum fiber concentration is quite often found to lie between 25 and 35 phr. This has been observed by several researchers [96,134-135, 220-221] for various natural and synthetic fibers in rubbers. Quite often at concentration beyond 35 to 40 phr the strength again decreases, because there is insufficient matrix material to adhere the fibers together.

1.7.6 Fiber- matrix adhesion

Proper reinforcement of rubber matrix using fibers can be achieved only if there exist adequate adhesion between the fiber and the rubber. The fiber- matrix adhesion is important in determining the mechanical, dynamic mechanical and rheological characteristics of the composites since the stress transfer occurs at the interface from matrix to fiber. In short fiber-rubber composites, after the selection of suitable fiber and rubber matrix, the next most important parameter is the achievement of adequate adhesion between the fiber and the matrix.

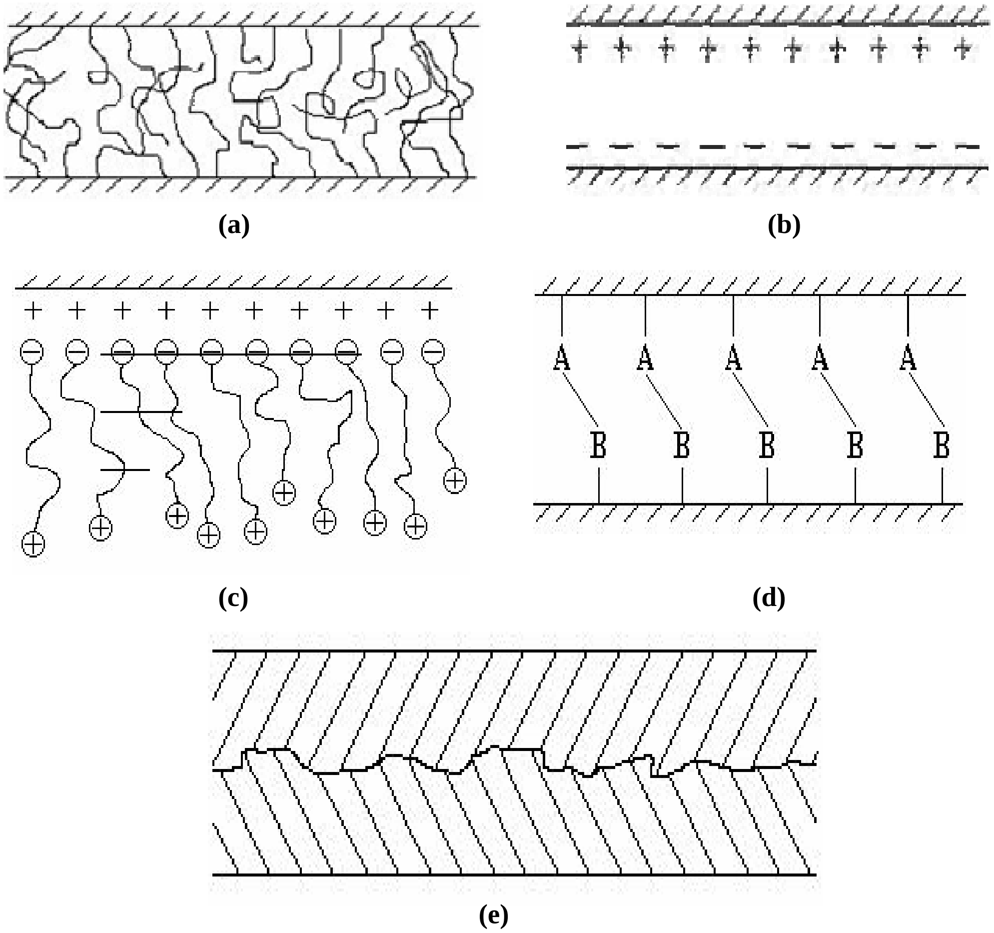
The fiber- matrix interface adhesion can be explained by five main mechanisms.

(i) Adsorption and wetting

This is due to the physical attraction between the surfaces, which is better understood by considering the wetting of solid surfaces by liquids. Between two solids, the surface roughness prevents the wetting except at isolated points. When the fiber surface is contaminated, the effective surface energy decreases. This hinders a strong physical bond between fiber and matrix interface.

(ii) Interdiffusion

Polymer molecules can be diffused into the molecular network of the fiber surface as shown in figure 1.6 a. The bond strength will depend on the amount of molecular conformation, constituents involved and the ease of molecular motion.



(a) (b)

(c) (d)

(e)

Figure 1.6. Schematic representations of various fiber matrix adhesions.

(iii) Electrostatic attraction

This type of linkage is possible when there is a charge difference at the interface. The electrostatic interaction at the interface is shown in figure 1.6 (b) & (c). The anionic and cationic species present at the fiber and matrix phases will have an important role in the bonding of the fiber matrix composites via electrostatic attraction. Introduction of coupling agents at the interface can enhance bonding through the attraction of cationic functional groups by anionic surface and vice versa.

(iv) Chemical bonding

Chemical bonds can be formed between chemical groups on the fiber surface and a compatible chemical group in the matrix as shown in figure 1.6 (d). The type of bond determines the strength. Interfacial chemical bonding can increase the adhesive bond strength by preventing molecular slippage at a sharp interface during fracture and by increasing the fracture energy by increasing the interfacial attraction.

(v) Mechanical adhesion

Mechanical interlocking at the fiber-matrix interface is possible as given in figure 1.6 (e). The degree of roughness of the fiber surface is very significant in determining the mechanical and chemical bonding at the interface. This is due to the larger surface area available on a rough fiber. Surface roughness can increase the adhesive bond strength by promoting wetting or providing mechanical anchoring sites.

Naturally occurring fibers such as cotton, cellulose, etc., have short whiskers protruding from the surface, which help to give a physical bond when mixed in rubber. Glass, Nylon, polyester and rayon have smooth surfaces and adhesion of these fibers to the rubber matrix is comparatively poor. In addition, these synthetic fibers have chemically unreactive surfaces, which must be treated to enable a bond to form with the rubber. In general, the fibers are dipped in adhesives in the latex form and this technology is the most common one used for continuous fibers.

Fiber adhesion to rubber compound is always a field of extensive research [222-226]. The adhesion between elastomers and fibers was discussed by Kubo [227]. Hisaki *et al.* [228] and Kubo [229] proposed a three-layer model composed of fibers, adhesive agents and elastomers to explain the adhesion between elastomers and fibers. Effect of adhesive-coated glass fiber in natural rubber (NR), acrylonitrile butadiene rubber (NBR), and ethylene-propylene-diene rubber (EPDM) formulations, with respect to the cyclic loading, abrasion, and accelerated aging was studied by Rathinasamy and coworkers [230]. Sreeja *et al.* reported the use of a urethane- based bonding agent for improving fiber-matrix bonding in short Nylon 6 reinforced NBR and SBR composites [231-232]. Effect of ureathane based bonding agent on the cure and mechanical properties of short fiber-polyurethane elastomer composites have been reported by Suhara *et al.* [233-234]. Effect of Epoxy based bonding agent on the cure, mechanical, thermal and rheological properties of short Nylon-6 fiber reinforced NBR, SBR and CR composites have been studied by Seema *et al.*[101-102,104,109,123,189].

1.7.6.1 *HRH dry bonding system*

The dry bonding system commonly used in rubbers is the HRH system consisting of hydrated silica, resorcinol and hexamethylene tetramine to create adhesion between fiber and rubber matrix. Compared to adhesive dipping, the use of a tricomponent dry bonding system is easy. This is because, the constituents of the dry bonding system can be added to the rubber matrix like any other compounding ingredients and extra processes like dipping and drying can be avoided. Figure1.7 shows the schematic representation of the enhanced adhesion between Nylon 6 fiber and natural rubber due to the presence of HRH bonding system [235].

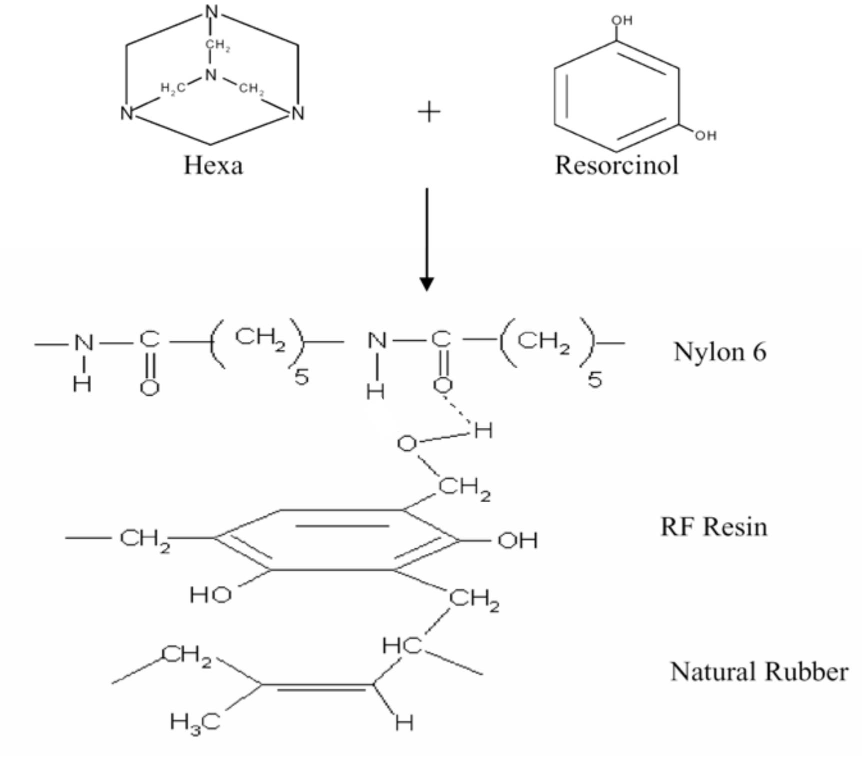


Figure 1.7. Mechanism of the HRH bonding in Natural Rubber –Nylon 6 fiber composites.

The history of dry bonding system dates back to 1967, when Dunnom [236] observed a marked difference in the adhesion level by adding silica to a compound containing resorcinol and hexa. Derringer [216], Goettler and Shen [237], Murty and De [63] and O'Connor [195] described the various aspects of short fiber adhesion to rubber in the presence of the dry bonding system. The use of HRH dry bonding system in various short fiber-rubber composites was described by several other authors [13, 84, 141-143, 203]. Setua and De [196] found that in short silk fiber reinforced nitrile rubber composites, the adhesion between fiber and matrix was complete only when all the three components of the dry bonding system were present together. They also reported that a properly bonded fiber-filled matrix showed good ageing resistance.

Ramayya *et al.* [238] replaced silica by carbon black in the tricomponent dry bonding system to study the adhesion between the rayon fiber and natural rubber and reported that the highest degree of bonding was achieved when silica was replaced with carbon black. Murty and De [65] made similar observations. However, Murty *et al.* [151] observed that the presence of carbon black did not increase the level of adhesion between short jute fiber and natural rubber. Akthar *et al.* [209] reported that although the properties of short silk fiber reinforced thermoplastic elastomers showed improvement on the addition of the dry bonding system, the comparatively long cure time required for the full development of adhesion between the fiber and matrix was the major disadvantage associated with the incorporation of the bonding system. Suhara *et al.* [239] reported that in presence of HRH bonding system, the water liberated during resin formation caused hydrolysis of urethane linkages and hence HRH system could not be used as interfacial bonding agent for polyurethane-short polyester fiber composites. Rajeev *et al.* [106] studied the effect of dry bonding system in improving the adhesion between the fiber and matrix of short melamine fiber-nitrile rubber composite. Rajeev et al [64] also investigated the atomic force microscopy of short melamine fiber reinforced EPDM rubber composites containing HRH dry bonding system.

To improve the adhesion between fibers and matrix various oxidative and non - oxidative chemical treatments are available for natural and synthetic fibers [240-241]. Anthome *et al.* [242] and Coran *et al.* [243] have reviewed the reinforcement of elastomers with various treated short cellulosic fibers and their mechanism of reinforcement. Several researchers have investigated the use of treated short natural fibers like jute, coir, sisal, oil palm, bamboo etc. as reinforcing elements for rubber composites [134-136,203,244-245]. Improvement of interfacial adhesion of poly (m-phenylene isophthalamide) short fiber-thermoplastic elastomer composites was achieved with N-alkylation on fiber surface [246]. The interlaminar shear strength of rare earth treated aramid fiber reinforced epoxy composites was studied by *Wu et al.* [247]. Debasish and co workers [87] investigated the effect of bonding agent on cure and mechanical properties of alkali treated glass fiber filled natural rubber composites. A good extent of adhesion is required for high performance short fiber composites. The main problem with adhesion in short fiber- rubber composites is that it cannot be measured quantitatively. The adhesion level can be qualitatively assessed from the shapes of the stress- strain curves and the study of fracture surfaces using scanning electron microscope techniques. Restricted equilibrium swelling technique can also be used to evaluate adhesion [248]. But this measurement is inaccurate since the restriction may be due to the presence of fibers and the adhesion cannot be separated out. In the case of viscoelastic properties, with the increase of adhesion level a high shear will be experienced at the interface thereby the mechanical loss associated with it also increases [249]. At elevated temperature the interface deteriorates and the value decreases.

1.8 Multicomponent System

The development of composite materials based on two or more different types of fillers in a single matrix leads to multicomponent system composites with a great diversity of material properties. The multicomponent system also known as hybrid composites. The reinforcement may be fibers, particulate fillers or both. Research has revealed that the behavior of hybrid composites appears to be the weighted sum of the individual components in which there is a more favorable balance between the advantages and disadvantages inherent in any composite material [250]. It is generally accepted that properties of hybrid composites are controlled by factors such as nature of matrix, nature, length and relative composition of the reinforcements, fiber matrix interface and hybrid design [251-252]. Sisal and glass fibers are good examples of hybrid composites possessing very good combined properties [253]. Due to the superior properties of glass fibers, the mechanical properties of the hybrid composites increase with increase in the volume fraction of glass fibers. Thomas *et al.* [252] have studied the properties of sisal / saw dust hybrid fiber composites with phenol formaldehyde resin as a function of sisal fiber loading. It was found that mechanical properties like tensile and flexural strength increased with sisal fiber content. This is due to the fact that the sisal fiber possesses moderately higher strength and modulus than saw dust. Mishra *et al.* [254] studied the mechanical properties of sisal and pineapple /glass fiber reinforced polyester composites. They found that the addition of small amount of glass fibers to the pineapple leaf fiber and sisal fiber reinforced polyester matrix enhanced the mechanical properties of the resulting hybrid composites. Rozman *et al.* [255] studied the tensile and flexural properties of polypropylene / oil palm / glass fiber hybrid composites and found that incorporation of both fibers into the polypropylene matrix improved the tensile and flexural strength by the increasing level of overall fiber loading. Junior *et al.* [256] used plain weaved hybrid ramie-cotton fibers as reinforcement for polyester matrix. The tensile behavior was dominated by the volume fraction of the ramie fibers aligned in the test direction. Cotton fiber had a minor reinforcement effect. This was due to the weak cotton polyester interface as well as poor cotton alignment. Hybrid composites containing glass fiber mat and coir fiber mat in polyester matrix was prepared by Rout *et al.* [257]. Hybrid composites containing surface modified coir fibers showed significant improvement in flexural strength and reduced water absorption. Sreekala *et al.* [258] prepared high performance phenol formaldehyde composite reinforced with oil palm and glass fibers. It has been found that there exists a positive hybrid effect for the flexural modulus and unnotched impact strength. Natural rubber composite reinforced with sisal/oil palm, sisal/coir hybrid fibers were prepared by Maya *et al.* [259] and Haseena *et al.* [260] found that the hybridization had a significant effect in improving the mechanical properties of the natural rubber composite when compared with the composite containing individual fibers.

The hybrid composites based on particulate fillers and fibers has also been studied [261-263]. Synthesis, fabrication, mechanical, electrical, and moisture absorption study of epoxy polyurethane-jute and epoxy polyurethane-jute-rice/wheat husk hybrid composites was reported by Mavan et al [264]. Jamal and co-workers [265] studied the tensile properties of wood flour / kenaf fiber polypropylene hybrid composites. Study on morphological, rheological, and mechanical properties of PP/SEBS-MA/SGF hybrid composites was done by Mohseni *et al.* [266]. Property optimization in nitrile rubber composites via hybrid filler systems was reported by Nugay [112]. Rheological behavior of hybrid rubber nanocomposite was studied by Bandyopadhyay and co workers [267].

1.9 Nanocomposites

Nanocomposites are a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range [268-270]. Nanometer is an atomic dimension and hence the properties of nanoclusters or parcticles are reflective of atoms rather than bulk materials. An example for nanocomposite in nature is the natural bone consisting of approximately 30 % matrix material and 70 % nanosized mineral. Here the matrix material is collagen fibers (polymer) and the mineral is hydroxyapatite crystals of 50 nm x 25 nm x 3nm size (ceramic). The outstanding reinforcement of nanocomposite is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase. The nanolayers have much higher aspect ratio than typical microscopic aggregates [268,271-272]. The three major advantages that nanocomposites have over conventional composites are as follows.

- Lighter weight due to low filler loading
- Low cost due to fewer amount of filler use

- Improved properties such as mechanical, thermal, optical, electrical, barrier etc., compared with conventional composites at very low loading of filler.

Three types of nanocomposites can be distinguished depending upon the number of dimensions of the dispersed particles in the nanometer range [268] as follows

- Nanocomposites that can be reinforced by isodimentional nanofillers which have three dimensions in the nanometer range. Eg:-Spherical silica nanoparticles obtained by *in-situ* sol-gel methods [273-274] or by polymerization promoted directly from their surface [275].
- Nanocomposites which can be reinforced by fillers which have only two dimensions in the nanometer scale. Eg:- Carbon nanotube [276-277] or cellulose whiskers [278-279]
- The reinforcing phase, in the shape of platelets, has only one dimension on a nano level. Eg: - Clays and layered silicates.

Polymer based organic / inorganic nanocomposites have gained increasing attention in the field of materials science [280-282]. Effect of acrylic polymer and nanocomposite with nano-SiO_2 on thermal degradation and fire resistance of ammonium polyphosphate–dipentaerythritol–melamine (APP–DPER–MEL) coating was studied by Zhenyu and co workers [283]. Effect of microstructure of acrylic copolymer / terpolymer on the properties of silica based nanocomposites prepared by sol–gel technique was studied by Patel *et al.* [284]. Bandyopadhyay *et al.* [285] studied the reaction parameters on the structure and properties of acrylic rubber / silica hybrid nanocomposites prepared by sol-gel technique.

1.10 Silica

Silica, or silicon dioxide, SiO_2, in its pure form is colorless to white. Silica is widely and abundantly distributed throughout the earth, both in the pure state and in silicates, (e.g., in quartz, agate, amethyst, chalcedony, flint, jasper, onyx and rock crystal), opal, sand, sandstone, clay, granite and many other rocks. Silica occurs in several forms and is insoluble in water, slightly soluble in alkalies and soluble in dilute hydrofluoric acid. It exists in two varieties, amorphous and crystalline. In crystalline forms, the structures are characterized by tetrahedral configuration of atoms within the crystals, whereas in the amorphous forms, the SiO_4 (silicate) subunits show no regular lattice pattern in the structures. In silicon dioxide, silicon atom uses d orbitals for bonding and hence SiO_2 exists as infinite three-dimensional structures and it is a high melting solid [286]. Silica which is amorphous contains about 4% water and can be represented as $SiO_2.nH_2O$. It consists of silicon and oxygen arranged in a tetrahedral structure. Surface silanol concentration (silanol groups – Si-O-H) influence the degree of hydration. Water content can affect processing and vulcanization [287]. Absorbed water can decrease cure time, tensile strength and also abrasion resistance [288]. The hydroxyl groups on the surface of the silica control surface acidity. This intrinsic acidity can influence vulcanization. These sites affect the rubber filler interaction. A general silica structure is depicted in Figure l. 8.

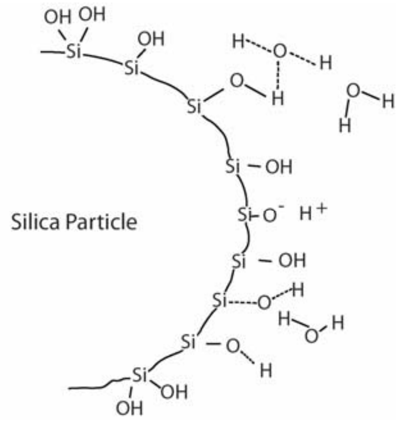


Figure l. 8. Adsorptive nature of silica filler

1.10.1 Silica versus carbon black

Compared to carbon black, silica is characterized by weaker filler-polymer interactions and stronger filler-filler interactions. This results in a higher compound viscosity, higher modulus at low strain amplitudes, lower modulus at high strain amplitudes and lower bound rubber content [289]. However, the silica in combination with a coupling agent has a higher reinforcing effect and different dynamic mechanical properties compared to carbon black [290]. When replacing carbon black by silica combined with a coupling agent the following properties are influenced predominantly.

- Tear, abrasion and heat resistance
- Flex stability
- Hardness, stiffness and modulus
- Tack
- Heat build up
- Resilience

The stronger reinforcing effect of silica compared to carbon black allows the reduction of the filler content without any negative influence on the property profile, but with an additional positive effect on elasticity due to the higher ratio of elastic component to damping filler. This results in an additional reduction of the rolling resistance. The stability of the covalent silica - polymer network results in a lower rate of breaking and reformation of the silica - polymer bonds compared to the carbon black - polymer network during a deformation cycle, resulting in a decrease of the loss modulus. A low value of the loss modulus together with a high value of the storage modulus results in a low value of the phase angle. As both, loss modulus and storage modulus, depend on deformation, the phase angle is also influenced by the applied strain, it increases with increasing deformation [288].

1.10.2 Production and characterization of silica

Acidification of alkali silicate solutions under controlled conditions produces precipitated silica [291].

$$\mathbf{Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2O + SiO_2} \quad \text{.......................................} (1.7)$$

Colloidal pyrogenic silica is produced by reaction of silicon tetrachloride at high temperatures with water.

$$\mathbf{SiC1_4 + 2\ H_2O \rightarrow SiO_2 + 4HCl} \quad \text{.......................................} (1.8)$$

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silica is too active and expensive [292]. Precipitated silica is silicon dioxide containing about 10 - 14% water. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness. It is being used in the manufacture of translucent and coloured products, shoe soling, tyres and other mechanical rubber goods. Fumed or pyrogenic silica is silicon dioxide containing less than 2% combined water. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicone rubbers [293]. Characterization of silica filler is also based on particle size and specific surface area. Surface area measurement is usually done by nitrogen adsorption (BET) method. Also pH, chemical composition and oil absorption are specified. The smallest physically observable primary particle for precipitated silica is about 15-20 μm and for fumed silica it is about 15 μm in size. The surface forces of the small primary particles are so high that many particles agglomerate to form the so-called secondary particles. Usually the shear forces generated during rubber mixing is not sufficient enough to disperse primary filler particles in the rubber [292]. The secondary particles of silica fillers form further agglomerates. They form chain-like structures, the so-called tertiary structures. Though the tertiary structures are also relatively stable, they get more or less shattered by the shear forces during mixing [292]. The higher the shear force, the better the dispersion.

1.10.3 Nanosilica

Nanosilica consists of spherical particles having a diameter less than 100 nm. Chemically speaking, they are made of silicon and oxygen atoms (Fig.1.9).

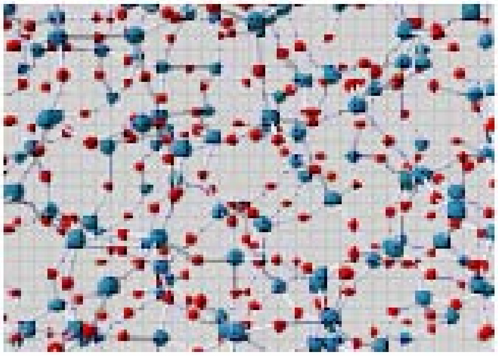


Figure 1.9. Chemical structure of nanosilica [🟦 : Si, 🟥 : O].

Although silica was up to now widely used in polymer formulation as additives to master the system rheology and enhance mechanical properties of the polymers, nanosilica throws the door wide open for new applications. Silica synthesis evolved during last decades from thermal hydrolysis of silane resulting in not easily dispersible aggregated, nanoparticles to sol-gel process resulting in well-defined nanoparticles highly compatible with the targeted matrix. Processes enabling chemically tuned and well integrated particles together with the nanoscale effect are a highway to high performance nanocomposite materials having enhanced mechanical properties and excellent surface properties.

1.10.3.1 *Synthesis of nanosilica*

Several methods are used to produce nanosilica from various sources [294-299]. A cheap and environment friendly route towards the synthesis of Poly(vinyl alcohol) / nanosilica hybrid composites has been presented by Tapasi *et al.* [300]. This is a sol-gel method in which the acid plays a catalytic role in enhancing sol-gel condensation of silicon alkoxides within poly (vinyl alcohol). First colloidally stable silica was prepared by the acid neutralization with an objective to increase the gelation time and decrease rate of self-condensation of silica. At lower PVA concentration the silica has a tendency to undergo self-condensation and at higher PVA concentration, co-condensation occurs.

Nanosilica can be synthesized by precipitation method using sodium silicate and hydrochloric acid in presence of a polymeric dispersing agent. Poly (vinyl alcohol), starch and carboxy (methyl cellulose) were found to be good dispersing agent because they are macromolecules and contain a large number of hydroxyl groups per molecule.

Dispersing agents used in the synthesis of nanosilica

(a) Carboxy (methyl cellulose) (CMC)

Carboxy (methyl cellulose) (CMC) is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid. Sodium carboxy methyl cellulose is an anionic water soluble polymer. The CMC structure is based on the β-(1⟶4)-D-glucopyranose polymer of cellulose. Different preparations may have different degrees of substitution, but it is generally in the range 0.6 - 0.95 derivatives per monomer unit. CMC molecules are somewhat shorter, on average, than native cellulose with uneven derivatization giving areas of high and low substitution.

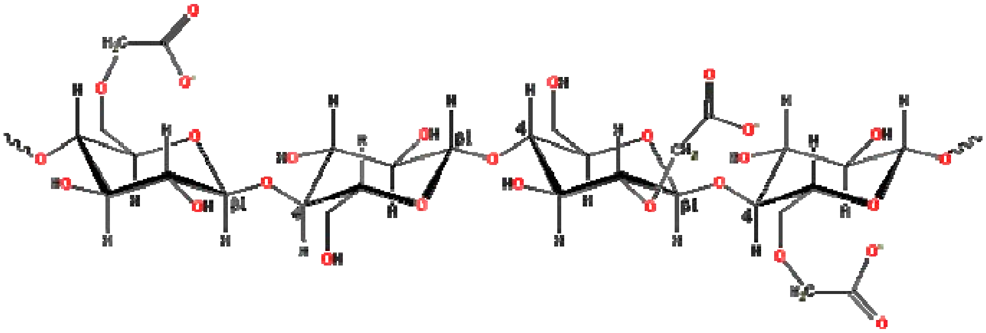


Figure 1.10. Structural unit of Carboxy methyl cellulose

This substitution is mostly 2-O- and 6-O-linked, followed in order of importance by 2, 6-di-O- then 3-O-, 3, 6-di-O-, 2, 3-di-O- lastly 2, 3, 6-tri-O-.linked. It appears that the substitution reaction is a slightly cooperative (within residues) rather than random process giving slightly higher than expected unsubstituted and trisubstituted areas. CMC molecules are most extended (rod-like) at low concentrations but at higher concentrations the molecules overlap and coil up and then, at high concentrations, entangle to become a thermoreversible gel. Increasing ionic strength and reducing pH both decrease the viscosity as they cause the polymer to become more coiled.

(b) Starch

Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of polymers of α-D-glucose units in the $^4C_1$ conformation. In amylose these are linked - (1⟶4)-, with the ring oxygen atoms all on the same side, whereas in amylopectin about one residue in every twenty or so is also linked - (1⟶6) - forming branch-points. The relative proportions of amylose to amylopectin and - (1⟶6) - branch-points both depend on the source of the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none (~3%)

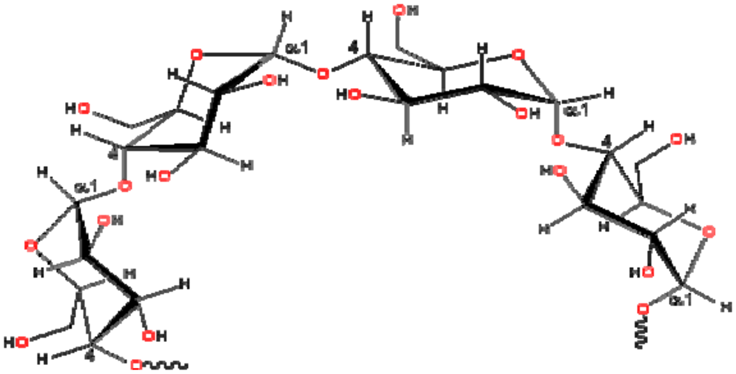


Figure 1.11. Structure of amylose

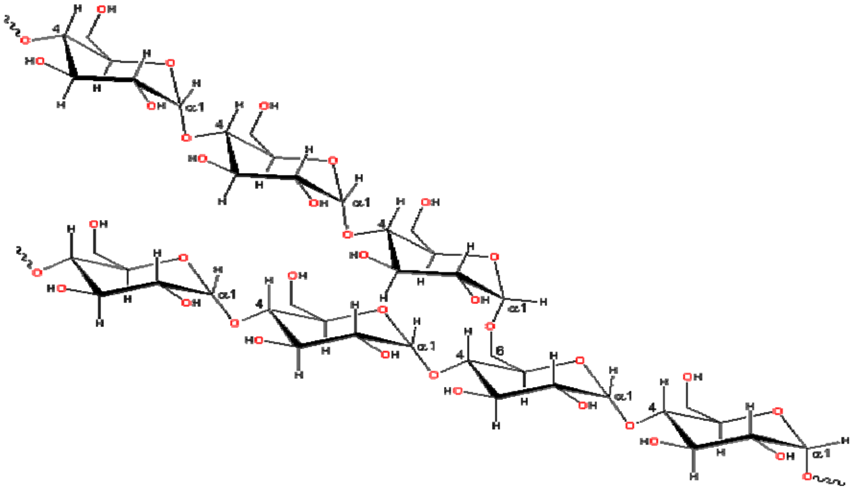
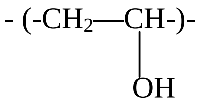


Figure 1.12. Structure of amylopectin

(c) Poly (vinyl alcohol)

Poly (vinyl alcohol) is a water-soluble polymer having the following structure:



$$-(-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-)-$$

It dissolves slowly in cold water, but more rapidly at elevated temperature and can usually be dissolved completely above 90°C. The aqueous solutions are not particularly stable especially if traces of acid or base are present. The solutions can undergo a complex series of reversible and irreversible gelation reactions. For example, cross-linking can occur at ether linkages, resulting in increased viscosity through the formation of insoluble products.

1.10.3.2 *Applications of nanosilica*

- Nanosilica can be compounded with rubber and can be used for making shoe outsoles and rubber foot wear components due to high abrasion resistance, good grip and non dusting qualities of nanosilica.

- Due to their optimal property, nanosilica is used in battery separators.
- Nanosilica enhances polymer property like flame retardency, barrier properties / transparency and scratch resistance
- Nanosilica is also used as micro cellular products, like shoes, mat, etc.. due to their foaming control
- In opto-electronics nanosilica is used in protective coatings and encapsulation of electro-optically active materials.
- It is used in drug encapsulation; as catalytical vehicles and supports, preparations, particular calibration standards, chromatography, other separations and catalysis.
- It has been found that silica aero gels coated on surface of granular activated carbon has four times more ability to remove uranium, chromium and arsenic from water supplies.
- Nano- sized silica abrasives are being researched for use in chemical-mechanical polishing of copper, to minimized mechanical stress during polishing and reduce defects such as surface scratches, copper peeling, dishing and erosion.
- Nanosilica filled room temperature vulcanized silicone rubber has higher erosion resistance, lower hydrophilicity and lesser surface roughness and which is used as insulators in coastal areas
- The film of nanosilica known as Xerocoat, when applied to glass / mirror cuts unwanted reflections from glass, letting more light through, hence reduces fogging and improves vision.

1.11 Application of Nanosilica / Short fiber / Elastomeric hybrid Composites

The main application areas for short fiber hybrid composites are hose, belting, solid tyres and pneumatic tyre components. When continuous cord in rubber hose is replaced with short fibers, it makes easy processing, economy and higher production rate. These find applications in the automotive industry as well as for general purpose utility hoses. Hybrid composite can be utilized as the sole reinforcement for a moderate performance hose or as auxiliary reinforcement with cord constructions. They can provide stiffening to soft inner tubes for the application of metal braids and can extend hose life by bridging the stresses across weaker filaments. Power transmission belts, more precisely V-belts are the earliest practical application of rubber fiber composites. A V-belt running over pulleys is subjected to very severe stresses when bent and flexed at a frequency of thousands of cycles per minute. Tensile stresses resulting from static tensioning and load transmission are supported by the reinforcing cord. The compressive side wall pressures are supported mainly by the base rubber. The ideal material for this part of the V-belt must exhibit high modulus in the transverse direction and low modulus coupled with high flexibility in the axial direction. Such complex properties can best be achieved in an anisotropic rubber / short fiber hybrid composite. Short fibers have the potential for reinforcing low performance tyres. In automotive and truck tyres they find application in better abrasion resistance for the chafer strip and in improved cut resistance to treads especially for trucks and OTR vehicles. In tyre chafing resistance can be improved by adding short fibers to the surface of the fabric. The apex of radial tyre has been successfully reinforced with short fibers to give it more stiffness. A small amount of short fibers in the tread of a truck tyre can reduce the rolling resistance considerably. Sheet roofing can benefit greatly by the use of short fiber hybrid composites. As short fibers have higher green strength and cut, tear and puncture resistance, they can be used for sheeting. Seals and gaskets are potentially large markets for short fiber reinforcement. Short fiber reinforcement offers excellent creep resistance to seals and gaskets at elevated temperatures. Chopped Nylon fibers are used to improve the wear of shoe soles. Other applications are hard roll covers, oil well packing, bearings, diaphragms, dock and ship fenders etc. Short fibers can reinforce and stiffen rubber in fenders and other impact applications.

1.12 Scope and Objectives of the Present Work

The concept of nanostructured material design is gaining widespread importance among the scientific community. The strong reinforcement at low volume fractions generated tremendous interest in the industry and research circles. Recent attention has been focused on the suitability of such composites in high performance application. The concept of short fiber based hybrid nanocomposites for load bearing applications is fairly new. Property enhancements are expected due to higher Young's modulus of the short fibers and fine distribution of reinforcing nanofillers such as nanosilica, carbon nanotube etc. The studies so far reported proved that utilization of short fibers as reinforcement in polymer composites offer economical, environmental and qualitative advantages. By incorporating particulate nano filler along with short fibers, high performance hybrid composite can be prepared. They may find application in automotives, belts, hoses and building industry. However, elastomeric hybrid composites based on short fiber and nanofiller have not been subjected to a systematic evaluation.

With the growing demand of nanosilica, economic competition and ecological pressure, there is an increasing need to synthesis nanosilica from a cost effective source and by a cheap method. The addition of nanofillers to rubbers can bring about dramatic changes in the properties of rubbers. The concept of condensation of silica particle into a dispersed polymeric matrix by the catalytic action of an acid was adopted from the work of Kotoky and Dolui [300]. Since the desired product was silica and not the polymer / silica nanocomposite the polymer concentration was kept low. It was expected that the precipitated silica would be collected in the polymer matrix and hence its agglomeration would be prevented. The addition of the dispersing agent would produce a matrix into which synthesized silica would be incorporated, thus producing silica in the nanoscale. The interaction between the hydroxyl groups of dispersing agent and the hydroxyl groups of silica would result in co-condensation. The synthesized silica after complete drying is to be calcined to remove the dispersing matrix and to obtain pure silica. The presence of organic molecule eliminate the need for the usage of coupling agent during nanocomposite preparation

The use of short fibers as reinforcing agents in elastomers opens up a new avenue for the utilization of waste fibers, available in plenty from fiber and textile industries. Recently, short fibers have found a variety of applications in rubbers due to the ease of mixing and consequent processing advantages in fabricating products of complicated design coupled with greater reinforcement. The properties of short- fiber containing composites depend critically on fiber content, orientation and fiber - matrix interface bond strength. A detailed study of the effect of these parameters on the composite properties will be highly informative. A strong interfacial bond can effectively transfer load from the matrix to the fiber and hence can improve the overall performance of the composite. The interfacial bond is usually strengthened by using bonding agents. HRH based bonding agent is widely used. The role of silica in HRH bonding system is to increase the wettability of fibers. Lower the particle size higher the surface area. Hence nanosilica can be more effective in improving the wettability of fibers. The use of nanosilica in HRH bonding system can improve adhesion between the fiber and the matrix. SEM studies provide idea about the interface.

Hybridization is commonly used for improving the properties and for lowering the cost of conventional composites. It is generally accepted that properties of hybrid composites are controlled by factors such as nature of matrix, nature, length and relative composition of the reinforcements, fiber matrix interface and hybrid design. The hybrid composites based on nanofillers and fibers need to be studied in detail. The service requirements of the elatomers in different areas of application are so wide that NR alone can not meet all of them. Of the many synthetic rubbers being used currently, SBR, NBR and CR find major applications. The performances of these hybrid composites can be evaluated by studying their physical and mechanical properties.

Knowledge of the degradation characteristics of the composites is important in many applications. The thermal stability of the hybrid composite may be influenced by the presence of short fibers and nanosilica. Thermogravimetry can be used to study the thermal degradation behavior of the composites.

Fiber matrix interaction in composites can be studied in detail based on the response of the material to dynamic strains. The nature of the modulus curves is likely to be a good indication of the fiber- matrix interaction and the nature of the interface.

The main objectives of the present work are summarized as follows:-

- To synthesize nanosilica from cheap source such as sodium silicate and make the process less expensive.
- To improve the interfacial adhesion between short Nylon fiber and different rubber matrices
- To compare the performance of nanosilica and commercial silica in NR compounds.
- To evaluate the effect of nanosilica as reinforcing filler in Nylon 6 short fiber hybrid composites based on NR, SBR, NBR and CR .
- To study the viscoelastic properties of the hybrid composites.
- To study the thermal degradation behavior of the hybrid composites.

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Chapter 2

Materials and Experimental Techniques used

Contents

This chapter gives a brief description of the materials and experimental procedures adopted for the present investigation.

2.1 Materials

2.1.1 Elastomers

2.1.1.1 *Natural rubber (NR)*

Natural rubber used for the study was ISNR 5 obtained from Rubber Research Institute of India, Kottayam, Kerala. The molecular weight, molecular weight distribution and non rubber constituents of natural rubber are affected by clonal variation, season and methods of preparation [1]. Hence rubber obtained from same lot has been used in this study. Its specifications are given in table 2.1

Table 2.1. Specifications of the natural rubber

Dirt content, % by mass	0.05
Volatile matter, % by mass	0.5
Nitrogen, % by mass	0.3
Ash, % by mass	0.4
Initial plasticity number,P_0	30
Plasticity retention index, PRI	60

2.1.1.2 *Acrylonitrile butadiene rubber (NBR)*

Acrylonitrile butadiene rubber (NBR) used was Aparene N553 grade with 33% acrylonitrile content, supplied by M/S Apar Polymers Ltd., India. Its Mooney viscosity [ML (1+4) at 100^0 C] was 45

2.1.1.3 *Styrene butadiene rubber (SBR)*

Styrene butadiene rubber (SBR) used was Techlen SBR 1502 grade with 23.5 % bound styrene content supplied by M/S Hyundai Techlen USA. Its Mooney viscosity [ML (1+4) at 100^0 C] was 52

2.1.1.4 *Chloroprene rubber (CR)*

Chloroprene rubber (CR) used in this study was Skyprene with a Mooney viscosity [ML (1+4) at 100^0 C] of 47 supplied by M/S Toyo Soda Mfg. Co. Ltd., Tokyo.

2.1.2 Short Nylon 6 fiber

Nylon 6 fiber obtained from M/S SRF Ltd., Chennai, India, was chopped to approximately 6mm. Specifications of Nylon 6 fiber are given in the table 2.2

Table 2.2. Specifications of Nylon 6 fiber

Breaking strength	28.3 kgf - 31.5 kgf
Elongation at break	27.5 % - 36.5 %
Twist	S 392 - 374
Denier	3656 - 3886

2.1.3 Hexamethylene tetramine (Hexa)

Hexamethylene tetramine used was laboratory grade supplied by M/S E-Merck Mumbai., India.

2.1.4 Resorcinol

Resorcinol was supplied by M/S E- Merck Mumbai., India.

2.1.5 Commercial silica

Commercial grade silica supplied by M/S Minar Chemicals, Kochi. was used.

2.1.6 Sodium silicate

60 % solution of sodium silicate obtained from M/S Minar Chemicals, Kochi was used.

2.1.7 Hydrochloric acid (HCl)

AR HCl manufactured by M/S Loba chemicals Mumbai with an acidimetric assay of 35-38% was used.

2.1.8 Carboxy methyl cellulose (CMC)

Carboxy methyl cellulose manufactured by M/S Polex Laboratories Mumbai was used

2.1.9 Soluble starch

Soluble starch manufactured by M/S Polex Laboratories Mumbai was used.

2.1.10 Poly (vinyl alcohol) (PVA)

Poly (vinyl alcohol) used was manufactured by M/S Polex Laboratories Mumbai. Its molecular weight is 14,000.

2.1.11 Other chemicals

Compounding ingredients used for the work were zinc oxide, supplied by M/S Meta Zinc Ltd. Mumbai; Stearic acid, supplied by M/S Godrej Soap (P) Ltd. Mumbai; N-Cyclohexyl-2-Benzothiazole Sulphenamide (CBS), supplied by M/S Polyolefins Industries Ltd. Mumbai, Tetramethyl-thiuramdisulphide (TMTD) procured from M/S NOCIL, Mumbai, N (1,3-dimethylbutyl) N-phenyl-*p*- phenylene diamine (6PPD), supplied by M/S Bayer India Ltd. Mumbai., Magnesium oxide, supplied by M/S Merck India Ltd., Mumbai, Ethylene thiourea (NA 22), obtained from M/S Akrochem Corporation, USA and Sulfur, supplied by M/S Standard Chemicals Company, Pvt. Ltd., Chennai.

2.2 Experimental methods

2.2.1 Synthesis and characterization of nanosilica

2.2.1.1 *Synthesis of nanosilica*

(a) Experimental set up.

The experimental set up consists of: -

Reactor

Since the experiments were carried out in small scale, a 3000ml Borosil beaker was used as the reactor.

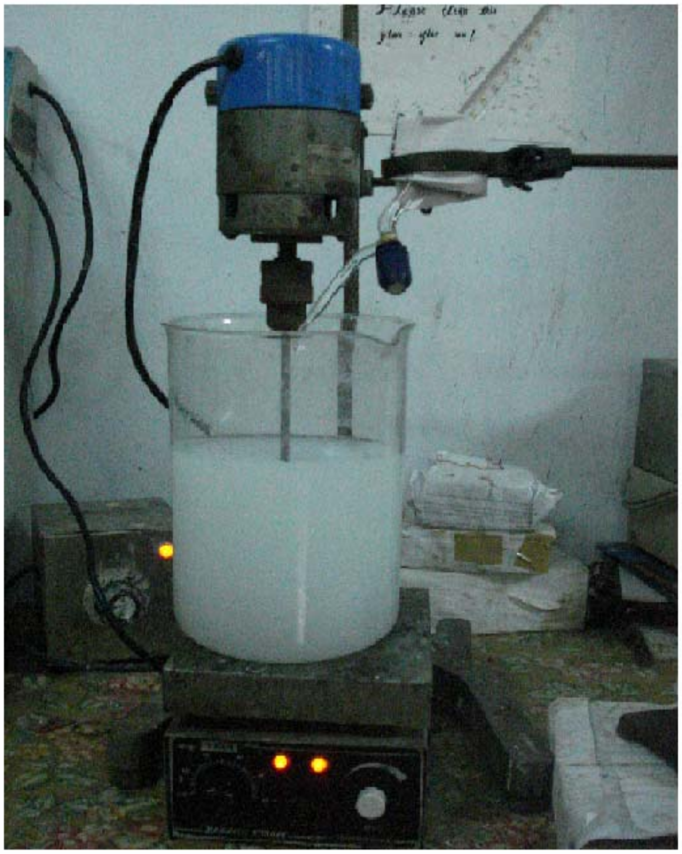

Figure 2.1. Reactor with stirring cum heating arrangement

Stirring cum heating arrangement

Mechanical stirrer was used for stirring. The speed of the stirrer was varied from 40 rpm to 100 rpm based on the concentration of the slurry and the optimum was found to be 60 rpm. Heating was done using a hot plate which was set constant at 60 ^{o}C.

Filtration assembly.

Vacuum filtration was done using a Buchner funnel, suction flask, tubing and a vacuum pump.

Drying assembly

Hot air oven with a temperature setting adjustable to 300 ^{o}C was used.

(b). Procedure

15 % sodium silicate solution was prepared with the dispersing medium solution taken in the reacting vessel. Then 1 N HCl, was added to it slowly with stirring at a temperature of 60 ^{o}C. The pH of the mixture was maintained between 1and 2. During the addition of HCl, instantaneous gelation occurred sometimes and stirring became difficult. So distilled water was added to keep the reaction mixture in a 25 % slurry form. The reaction mixture was stirred continuously for a period of 2 hours and the temperature was maintained at 60 ^{o}C. This reaction conditions enabled the uniform distribution of the dispersive agents such as poly (vinyl alcohol), starch or carboxy methyl cellulose in the reaction solution, so that it could act as a matrix to collect the formed particles. In the absence of heating the dispersing agents agglomerated in the reaction medium. It also enabled the conversion of silicic acid, formed by the reaction between HCl and sodium silicate, into silica.

The reaction between sodium silicate and dilute HCl is given below:

$$\mathbf{Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl} \quad \text{..(2.1)}$$

$$\mathbf{H_2SiO_3 \rightarrow SiO_2 + H_2O} \quad \text{..(2.2)}$$

The acid plays a catalytic role in enhancing the co-condensation of silicon oxides within the dispersing agent’s matrix. It is expected that the addition of the above dispersing agent would produce a matrix into which synthesized silica would be incorporated, thus producing silica in the nanoscale. The interaction between the hydroxyl groups of dispersing medium and the hydroxyl groups of silica would results in co-condensation. Hydrogen bonding between the polymer and the developing polysilicate network leads to system homogeneity.

After completion of reaction, the resultant slurry was kept at room temperature for 24 hours. It was then filtered by vacuum filtration. A suction flask with Buchner funnel and tubing to vacuum were used. Two filter papers cut exactly to the inner diameter of Buchner funnel was placed in the funnel. First water was poured into the funnel and then vacuum pump was started and when water started collecting in the flask, slurry was slowly poured into the funnel, always maintaining a slurry level of not more than 50% of the funnel height. After completely emptying out the slurry into the funnel, the washing was started by adding distilled water into funnel. The washings continued until all the sodium chloride was removed. After filtration cum washing, the cake collected on the filter paper in the Buchner funnel was scraped out using a scrapper and spread evenly on a glass plate of dimension 20 cm × 20 cm. This was then placed in a hot air oven at a temperature of 60 ^{o}C for 24 hrs. The cake thus obtained was then ground to obtain fine powder of silica. The synthesized silica after complete drying was calcined in muffle furnace at 600 ^{o}C for six hrs to remove the dispersing agent’s matrix. The purer silica particles obtained were then characterized by using various technique such as TEM, SEM, FTIR, BET, TGA etc..

2.2.2 Characterization of nanosilica

The characterization of synthesized silica particles were done using various techniques which are described below.

2.2.2.1 *Bulk density*

Determination of the bulk density of the material was done as per ASTM D 1895-96 test method A. Two important terms used are apparent density and bulk density.

Apparent density is the weight per unit volume of a material including voids inherent in the material. Bulk density is defined as the weight per unit volume of a material. It is primarily used for pellets. The test can provide a gross measure of particle size and dispersion, which can affect material flow consistency and reflect packaging quantity.

(a) Apparent density

Measuring unit is a cylindrical cup of 100±0.5 ml capacity having a diameter equal to half of the height. For e.g. 39.9 mm inside diameter by 79.8 mm inside height. Funnel having 9.5 mm diameter opening at the bottom and mounted at a height of 38 mm above the measuring cup. Bulk density was determined as per the above ASTM standard. Bulk density value is recorded as g/cm ^{3}.

2.2.2.2 *BET adsorption*

Surface area of the silica was determined by the BET method using nitrogen isotherm on a Micromeritics Tristar 3000, surface area and porosity analyzer. Surface area was determined using the equation

$$S_{BET} = 4.353\ Vm \qquad \text{...} (2.3)$$

where S_{BET} is the surface area in m ^{2} / g and Vm is the molar volume of adsorbate gas (N_2) at STP.

2.2.2.3 *X-Ray diffraction (XRD)*

The XRD analysis was carried out with X-Ray Diffractometer, Bruker, D8 Advance model, employing CuKa radiation (λ =1.54 A^o) and Ni filter operating at

30 kV and 20 mA. The particle size was calculated using the Debye-Sherrer formula [2-3]

$$C_s = 0.9\,\lambda / \beta \cos\theta \qquad \text{...(2.4)}$$

where, C_s is the particle size, λ is the wavelength of the incident x-ray beam, β is the full width at half maximum (FWHM) of an *hkl* X-ray diffraction peak at θ value[4] and θ is half of the angle 2θ corresponding to the peak

2.2.2.4 *Infra red spectroscopy (IR)*

The IR spectra of the synthesized silica was recorded with Fourier Transform Infrared Spectroscope, Bruker, Tensor 27 model in ATR mode.

2.2.2.5 *Transmission electron microscopy (TEM)*

The morphology and particle size of nanosilica were observed using Transmission Electron Microscope (TEM). The TEM images were taken on Philips TEM CM 200 model.

2.2.2.6 *Scanning electron microscopy (SEM)*

The prepared silica surfaces were sputter- coated with gold and examined under SEM, Model No. S 360, Cambridge Instruments, U. K.

2.2.2.7 *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis of the silica sample was carried out in a Q50 Thermogravimetric Analyzer, TA Instruments at a heating rate of 10 °C/min, under nitrogen atmosphere.

2.2.3 Compounding

The formulations of the different mixes are given in the respective chapters. The mixing of NR, SBR, NBR and CR rubbers was done on a laboratory size two-roll mixing mill (150 mm x 300 mm) as per ASTM D 3184-89, ASTM D 3185-99, ASTM D 3187-001, and ASTM D 3190-001, respectively. A nip gap of 0.2 mm was set and the temperature was maintained at 70 ± 5 ºC for NR and 50 ± 5 ºC for SBR, NBR and CR rubbers. For the mixing of rubber with compounding ingredients, the rubber was passed through the rolls and it was banded over the front roll. After the nerve had disappeared, the compounding ingredients were added as per procedure given in relevant ASTM D standards. Chopped Nylon 6 fibers were added in small increment in order to obtain uniform dispersion. After the complete mixing, the stock was homogenized by passing through the tight nip for six times and finally sheeted out through the tight nip so as to orient fibers in one direction. Mixing time and temperature was controlled during the process. For NBR sulphur was added first since solubility of sulphur in NBR is poor.

2.2.4 Cure characteristics

Cure characteristics of the mixes were determined as per ASTM D 2084-1995 using Rubber Process Analyzer, RPA 2000®, which is a computer controlled torsional dynamic rheometer with a unique test gap design, an advanced temperature control system and fully automated operation modes. Testing environments employed in the present work are given in table 2.3.

Table 2.3. Testing parameters used for RPA

Sl.No.	Parameters	Limit
1	Frequency	50 cpm
2	Temperature	150 ºC
3	Time	30 min.
4	Die Type	Biconical
5	Die Gap	0.487 mm
6	Angle of oscillation of the Die	0.2 º

To determine the cure characteristics of the rubber compound, approximately 5 g of the sample was placed in a sealed biconical cavity under pressurized conditions and submitted to harmonic torsional strain by the oscillation of the lower die through a small deformation angle of about 0.2^0 and the transmitted torque is measured on the upper fixed wall [5]. The torque transducer on the upper die senses the force being transmitted through the rubber sample. A typical RPA cure curve is shown in the figure 2.2 and the following data can be obtained.

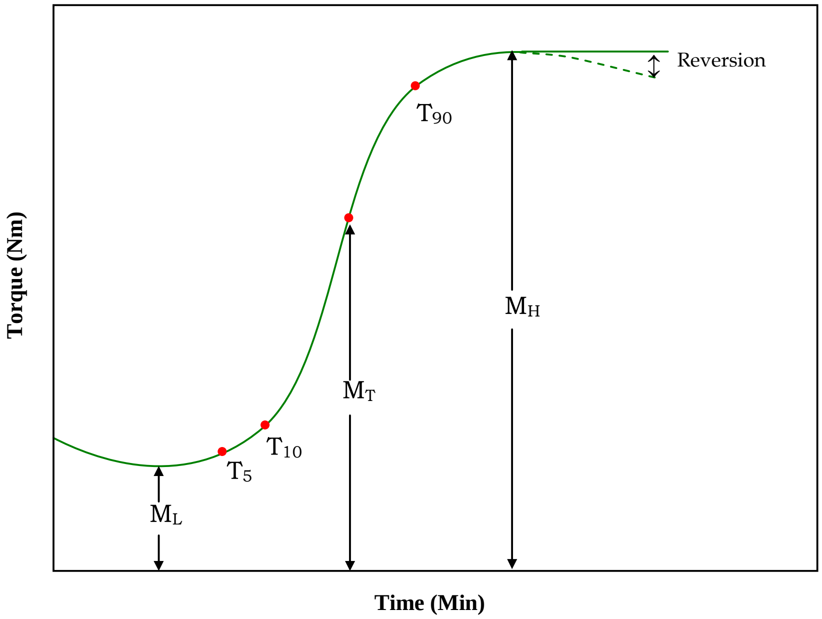

Figure 2.2. Schematic cure curve obtained from the Rubber Process Analyzer, RPA 2000

Minimum torque, M_L

Torque obtained by mix after homogenizing at the test temperature and before the onset of cure.

Maximum torque, M_H

Maximum torque recorded after the curing of the mix is completed.

Torque, M_T

Torque at any given time T

Optimum cure time, T_{90}

This is the time taken for obtaining 90% of the maximum torque

Scorch time, T_{10}

Time for attaining 10% of the maximum torque

Induction time, T_5

It is the time taken for about 5 % vulcanisation.

Cure rate index

Cure rate index is calculated from the following equation.

$$\text{Cure rate index} = 100 / T_{90} - T_{10} \qquad \text{.........(2.5)}$$

where, T_{90} and T_{10} are the times corresponding to the optimum cure and scorch respectively.

The computer software analyzes the cure curve and prints out the data after each measurement.

2.2.5 Molding

The thin sheet obtained from the mixing process was marked with the milling direction and cut in the required dimension and stacked one above the other to the desired volume for molding. The test specimens were molded in standard moulds by compression molding on an electrically heated hydraulic press having 45 cm x 45 cm platen at a pressure of 200 kg cm^{-2}. The rubber samples were vulcanized up to their respective optimum cure time at 150 °C. Moldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. Additional curing time based on the sample thickness for samples having thickness higher than 6 mm (compression set, resilience and hardness) was given to obtain satisfactory cure for the entire thickness of the sample.

2.2.6 Determination of physical properties

Tests such as tensile strength, tear strength, hardness, etc. were carried out on vulcanized composites. For each test at least six specimens were tested and the mean values were reported. In order to study the effect of fiber orientation on the physical properties of the composites, the samples with fibers oriented along the milling direction (longitudinal) and across the milling direction (transverse) were cut out. Schematic representation of fiber orientation in different test samples is given in the figure 1.5 (chapter 1). For ageing studies, the samples were kept in an air oven for 72 hours at 70 ^{o}C (ASTM 573 – 88). The properties were measured after 24 hours of ageing.

2.2.6.1 *Tensile properties.*

The tensile strength is defined as the force per unit area of cross section, required to break the test specimen, the condition being that the stress is substantially uniform over whole of the cross section. The elongation at break (EB) is the maximum value of elongation expressed as a percentage of the original length. The value of tensile stress (force/unit area) required to stretch the test piece from the unstrained condition to a given elongation is called modulus or more accurately tensile stress at a given strain.

The tensile properties of the composites were determined on a ‘Shimadzu Autograph AG-I series’ universal testing machine (UTM), at a crosshead speed of

500 mm/min as per ASTM D 412-1998 (Method A). All the tests were carried out at 28 ± 2^0C. Dumb bell specimens were punched out with fibers oriented along the mill direction (longitudinal) and across the milling direction (transverse) using a dumb bell die (C-type). The thickness of the narrow portion was measured using a digital thickness gauge. The sample was held tight by the two grips or jaws of the UTM, the lower grip being fixed. The tensile strength, elongation at break and modulus were determined.

2.2.6.2 *Tear strength*

The tear test was done on Shimadzu Universal Testing Machine Model AG-1, 10 KN according to ASTM D 624 (die C). The samples were punched from the molded sheets along and across the grain direction. The test speed was 500 mm/min.

2.2.6.3 *Hardness*

The hardness (Shore A) of the molded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 -1997. The tests were performed on unstressed samples of 30 mm diameter and 6 mm thickness. Readings were taken after 15 seconds of the indentation

2.2.6.4 *Abrasion resistance*

Abrasion resistance of the samples were measured using a DIN abrader based on DIN 53516. Molded samples of 6 ± 0.2 mm diameter and 12 mm thickness were placed on a rotating holder and a load of 10 N was applied. A pre run was given for conditioning the sample and the sample weight was taken. Weight after the test was also noted. The difference in weight is the weight loss of the test piece after its travel through 40 m on a standard abrasive surface.

$$\text{Abrasion loss} = \frac{Initial\ wt - Final\ wt}{Sp.Gravity} \times 27.27\ \text{cc/hr} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

Abrasion resistance is the reciprocal of abrasion loss.

2.2.6.5 *Compression set*

Compression set at constant strain was measured according to ASTM D 395-86 method B. Samples with 6.25 mm thickness and 18 mm diameter were compressed to constant strain and kept for 22 hours in an air oven at 70 ºC. At the end of the test period the test specimens were taken out, cooled to room temperature for 30 minutes and the final thickness was measured. The compression set in % was calculated as follows:

$$\text{Compression set (\%)} = \frac{T_i - T_f}{T_i - T_s} \times 100 \qquad \text{.......................................(2.7)}$$

where T_i and T_f are the initial and the final thickness of the specimen and T_s is the thickness of the spacer bar used.

2.2.6.6 *Rebound resilience*

Rebound Resilience was determined by vertical rebound method according to ASTM D 2832-88. In this method a plunger suspended from a given height above the specimen was released and the rebound height was measured. The resilience scale was marked in 100 equally spaced divisions and hence the rebound height was equal to the resilience (%).

2.2.7 Volume fraction of rubber, V_r

Contribution to the reinforcement effect arises from molecular interaction between the rubber and the filler. This interaction leads to an increase in the effective degree of crosslinking and can be evaluated by equilibrium swelling. The equilibrium swelling analysis of rubber vulcanizate is known to indicate the number of effective network chains per unit volume of rubber. For a filled vulcanizate it should reflect not only the effect of chemical linkages but also the polymer-filler attachments. V_r is dependent on the swelling power of the solvent (high swelling power means low V_r) and the crosslink density. Higher crosslink density results in lower swelling.

Circular specimens of diameter 20 mm. were punched out from the vulcanized sheets. Specimens of known weight were immersed in the solvents in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and the weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. V_r of the samples was determined from the equilibrium swelling data using the equation [6-7]

$$Vr = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0\rho_S^{-1}} \quad \text{..} (2.8)$$

where D is the de-swollen weight of the sample, F is the weight fraction of the insoluble component, T is the initial weight of the sample, ρ_r is the density of the rubber, ρ_s is the density of the solvent, and A_o is the weight of solvent absorbed.

2.2.8 Scanning electron microscopy (SEM)

In SEM, the electron beam incident on the specimen surface causes various phenomena of which the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is a one- to- one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen.

The tensile and tear fracture surfaces were sputter coated with gold and examined under Scanning Electron Microscope Model No. S 360 Cambridge Instruments, U. K.

2.2.9 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out on a Universal V4 2E TA instrument. It is a computer-controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample placed in a temperature programmed furnace was subjected to temperature in the range 30 ºC to 800 ºC with a heating rate of 10 ºC/minute and the corresponding weight changes were noted with the help of an ultra sensitive microbalance. Nitrogen was used as purge gase. The data of weight loss versus temperature and time was recorded online in the TA Instrument's Q series Explorer software. The analysis of the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were done using TA Instrument Universal Analysis 2000 software version 3.3B.

2.2.10 Dynamic mechanical analysis (DMA)

The dynamic mechanical thermal analysis was conducted using rectangular test specimens having a dimension of 30 mm x 5 mm x 2 mm under tension mode using a Dynamic Mechanical Thermal Analyzer, DMA Q-800, TA Instruments at a constant temperature of 70 °C. The frequency was varied from 1 to 50 Hz under frequency sweep mode at a rate of 2 Hz/min. The samples were subjected to dynamic strain amplitude of 0.1146 %. The dynamic storage modulus (E') and loss modulus (E") of the composites were monitored.

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Chapter 3

Synthesis and Characterization of Nanosilica

Contents

3.1 Introduction

Nano particles are small clusters of atoms about 1 to 100 nanometers in size. 'Nano' derives from the Greek word "nanos", which means dwarf or extremely small. Nano science has taken scientists around the world by storm. It claims to revolutionize the world we live in with radical break through in areas such as materials and manufacturing, electronics, medicine and healthcare, environment and energy, chemical and pharmaceutical, biotechnology and agriculture, computation and information technology. Due to the two unique phenomena which occur in nano particles, their properties (electrical, optical, chemical, mechanical, magnetic, *etc…*) can be selectively controlled by the size, morphology and composition of the particles. These new substances will have enhanced or entirely different properties from their parent materials. Nano particles are so small that they have different properties than the same substance in normal-sized pieces.

Studies on the effect of solid nanofillers on polymers are of much importance from the scientific and engineering points of view. Nanofillers, mostly based on clay [1- 3] and silica [4 - 5], impart enhanced physical and chemical properties to polymers even at low concentration. Understanding the interaction between a nanofiller and a polymer matrix is a key to explore the source of reinforcement by these fillers. A number of research publications are available, which deal with reinforcement of elastomers by conventional fillers like carbon black and silica [6 - 7]. However, there are only a few that describe reinforcement by nanofillers [8 - 10].

Particulate silica, so-called ‘white carbon black’ is now focused as an alternative of carbon black for rubber reinforcement [11-12]. The conventional silica by the precipitation method is, however, highly aggregated in the rubbery matrix due to filler-to-filler interaction resulting in a dispersion which is not favorable for reinforcement [13-15]. An alternative method of silica incorporation into rubbers is by an *in situ* sol-gel process [15-21]. This process involves the swelling of raw rubber [21] or rubber vulcanizate [20] in a silica precursor e.g. tetraethoxysilane [22]. To fasten the hydrolysis reaction, basic as well as acidic, catalytic systems could be added [23]. It is not easy to prepare homogeneous mix because of a difference in solubilities of both components. A full hydrolysis of precursors in polymer matrices is rather difficult. The same concerns the necessary separation of the hydrolysis product and residues of the catalytic systems applied. Therefore synthesis of nanosilica *in situ* is not a perspective method from the technological point of view.

The synthesis and characterization of nano scale silica is currently of great interest as silica has higher thermal tolerance and lower thermal conductivity, refractive index, dielectric constant and Young’s modulus. Such materials have tremendous potential application in the field of optoelectronics, nanocomposites, ceramics, rubber technology and biomedical materials, in addition to displaying great promise in applications involving catalysis and chemical separations.

Verónica Morote-Martínez and co workers [24] used nanosilica for improving the mechanical and structural integrity of natural stone by applying unsaturated polyester resin (UPR)-nanosilica hybrid thin coating. Different amounts (0.5-3 wt. %) of nanosilica was added to improve several properties, particularly the mechanical properties.Addition of nanosilica imparted pseudoplasticity and thixotropy to the UPR resin and an increase in viscosity was also produced. In the cured composites, improved thermal properties in UPR were reached by adding nanosilica due to the creation of a network between the filler and the polymer matrix. The improved properties in UPR obtained by adding nanosilica produced enhanced impact resistance to coated marble pieces, as both stiffness and toughness were also improved.

Achilias *et al.* [25] studied the effect of silica nanoparticles on solid state polymerization of poly(ethyleneterephthalate). From the experimental measurements and the theoretical simulation results, it was proved that nanosilica in small amounts (less than 1 wt %) enhances both the esterification and transesterification reactions at all studied temperatures acting as a co-catalyst. However, as the amount of nanosilica increases a number of inactive hydroxyl groups were estimated corresponding to participation of these groups in side reactions with the nanosilica particles. These side reactions lead initially to branched PET chains and eventually (5 wt% n-SiO_2 concentration) to crosslinked structures.

Epoxy–nanocomposite resins filled with 12-nm spherical silica particles improved their thermal and mechanical properties as a function of silica loading. [26]. The addition of small amounts of silica nanoparticles to the cement paste can **r**educe the calcium leaching rate of the cement paste [27]. Xiaowei Gao and co workers [28] has found that the antioxidant efficiency of the nanosilica-immobilized antioxidant was superior to the corresponding low molecular counterpart (AO), based on the measurement of the oxidation induction time (OIT) of PP/nanosilica-immobilized antioxidant and PP/AO compounds containing an equivalent antioxidant component. Nangeng Wen and co workers [29] used nanosilica for the preparation of raspberry-like organic–inorganic composite spheres with poly(vinyl acetate) (PVAc) as core and nanosilica particles as shell. The hydrogen bonds between nanosilica particles and PVAc were strong enough for the formation of long-stable composite spheres with raspberry-like morphology.

The introduction of nanosilica particle with a spherical diameter of about 20 nm into the Portland cement paste improved the performance of Portland cement-based composites. Portland cement composite with nanosilica had a more solid, dense and stable bonding framework [30]. The gas barrier properties of nanosilica filled latex membranes were very high [31]. Nanosilica has been used in different polymers as a reinforcing material and also as a special purpose additive to improve their properties for specific applications [32- 42].

Sol-gel technology has been used extensively in the synthesis of nanosilica [43 - 49]. Sol-gel synthesis of silica is based on the hydrolysis of alkoxy-silanes like tetra-ethoxy-silane or tetra-methoxy-silane, according to the reaction.

$$\mathbf{Si(OR)_4 + 4\,H_2O \xrightarrow{catalyst} Si(OH)_4 + 4\,R\text{-}OH} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.1)$$

$$\mathbf{Si(OH)_4 \rightarrow SiO_2 + 2\,H_2O} \quad \ldots\ldots\ldots\ldots\ldots(3.2)$$

Acidic or basic catalyst could be used. The proportion of Si-OH, Si $(OH)_2$ and Si $(OH)_3$ change during process, which first gives a swollen gel. It is then dried, heated and densified into final monolithic piece of silica. The gelation may correspond to a cross-linking process taking place between macromolecular species of polysiloxanes containing free Si-OH molecules. In the presence of acids, probability of formation of Si $(OH)_4$ is small and condensation reaction start before complete hydrolysis of $Si(OR)_4$ to $Si(OH)_4$ can occur. Under basic condition, $Si(OH)_4$ is easily formed by the preferential hydrolysis of the rest of the OR groups belonging to a partially hydrolyzed $Si(OR)_4$, and some silicon alkoxide molecules tend to remain non- hydrolyzed. Hydrolysis of tetra-ethoxy-silane is initiated with alcohol solvent in the presence of acid / basic catalyst and the gelation requires several days. Another method is exposing TEOS and water to ultrasound in the presence of acid catalyst and the gelling time for this 'Sonogel' was about 115-200 min. This gel is then heated at high temperatures to obtain fine powder of silica.

Nanosilica can also be produced in a form of a dry powder via pyrolysis of tetraalkoxysilanes or tetrachlorosilane in the presence of water as well as by direct hydrolysis of sodium methasilicate or tetraalkoxysilanes [50-51]. Several methods are used to produce nanosilica from different sources [52-54]. Saito *et al.* [55] have synthesized nano silica from Per-Hydro-Poly-Silazane (PHPS) with mild conditions using steam as catalyst. Density and refractive index of silica prepared from PHPS were close to silica glass. This work was carried out to study the effects of hydroxyl group and architecture of organic polymers on polystyrene /silica nano composites. Chrusoid and Slusarski [50] have prepared nano silica from a stable emulsion of alkoxysilanes by the addition of a surfactant and heating the emulsion to remove the residual materials. The addition of surfactant is necessary to lower the interfacial energy and minimize the surface energy between two liquids. Emulsion was formed with solution containing 60% mineral oil and 40% heptane and then they were heated to 450 ^{o}C to burn off residual mineral oil and un-reacted alkoxide group. Fujiwara et al [56] has modified the sol-gel method using acid anhydride instead of water for reacting with the organosilanes and condensation of alkoxy silane proceeded at a lower temperature of 150 ^{o}C. In this method, Diglycidyl ethers of bisphenol-A (DGEBA) was added as the precursor of epoxy resin into the alkoxy silane mixture to produce epoxy resin / silica nano composite. Kim, Liu and Zachariah [57] have suggested the aerosol-assisted sol-gel method to produce nanosilica. In this method, Tetraethoxysilane (TEOS), water and ethanol were allowed to react according sol-gel chemistry. Sufficient hydrolysis time was given and then the solution was aerosolized with sodium chloride. Sodium chloride was employed both as an agent to accelerate the kinetics of silica gelation and as a templating medium to support the formation and stability of pore structures.

Kotoky and Dolui [58] used sodium silicate with dilute hydrochloric acid as catalyst in poly (vinyl alcohol) to produce poly (vinyl alcohol) / silica nano composites. This is a sol-gel method in which the acid plays a catalytic role in enhancing sol-gel condensation of silicon alkoxides within the poly (vinyl alcohol). The reaction mixture was stirred for 30 minutes at 60 ^{0}C, pH maintained between 1 and 2. The sol-gel mixture was passed through cation exchange resin amberlite for the removal of Na^+ ions. After 24 hrs at ambient temperature the sample gelled and this was then dried for another 48 hrs at 47 ^{o}C.

A cocoon shaped nanosilica particles has been synthesised by Arai and co workers [59]. The particles were prepared from TMOS, water, ammonia and methanol by a sol–gel method. The method is to add the methanol solution of TMOS at a constant supply rate to a mixture of water, ammonia and methanol. Effects of various reaction conditions such as temperatures, supply rates of TMOS, and amounts of TMOS determined the diameter and shape of the particles. High temperature makes particles with high aspect ratio and small diameter. And the mechanism of forming the cocoon shaped particle was also discussed. It was concluded that the primary particles were generated at the beginning stage of reaction and two of them became the cocoon shaped particle. These cocoon shaped nanosilica particles is used for polishing applications. For high polishing efficiency, particles with the diameter between 40 nm and 210 nm are to be used. As a result, best diameter of particles for abrasive is 40–100 nm with respect to polishing efficiency and surface finish.

Nittaya *et al.* [60] have synthesized nanosilica from rice husk ash (RHA). Rice husk ash was washed with water and then burned at 700°C for 6 hrs. RHA samples were stirred with 3 N sodium hydroxide solutions and was heated in a covered Erlenmeyer flask for 3 hours. Pure silica was extracted by refluxing with 6 N HCl for 4 hours and then washed repeatedly using de-ionised water to make it acid free. It was then dissolved in 2 N NaOH by continuous stirring for 10 hrs on a magnetic stirrer and then concentrated H_2SO4 was added to adjust pH in the range of 7.5-8.5. The precipitated silica was washed repeatedly with warm de-ionised water till the filtrate was completely alkali-free. After the washing process silica powder was dried at 50°C for 48 h in the oven.

Jal and co workers [61] were synthesised nanosilica by precipitation method characterized it by various analytical tools. From transmission electron micrograph the silica particles were found to have almost spherical shape with a dimension of $\sim$50 nm. The surface area was found to be of 560 $m^2\ g^{-1}$ and density 2.2 $g\ cm^{-3}$. From thermogravimetric analysis the total silanol density in the silica was found to be 7.68 nm^{-2}. The number of reactive silanols that formed hydrogen bond with water molecules was found to be 2.48. The infrared spectral data suported the presence of hydrogen bonded silanol group and the siloxane groups in silica.

In this work we synthesised the nanosilica from a cost effective silica source, sodium silicate, and hydrochloric acid by precipitation method under controlled conditions using poly(vinyl alcohol), starch and carboxyl methyl cellulose as the dispersing agent. Sodium silicate is a cost effective silica source as compared to the more commonly used tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS). Moreover, by using a purely aqueous medium, the expensive and very often toxic, solvent could be avoided. The precipitation method was selected because of the following reasons:-

- It involves the use of commonly available sodium silicate and mineral acid.
- It is possible to produce nanosized silica particles under controlled conditions

- It does not require very long gelation and drying times as required for sol-gel process.
- The catalyst used in the sol-gel process may remain as impurities.
- Silica synthesized by the sol-gel process was observed to contain many lattice defects.
- The by products would be easily removed by washing with distilled water.

We have selected poly (vinyl alcohol), starch and carboxyl methyl cellulose as the dispersing agents because they are macromolecules which contain a large number of hydroxyl groups per molecule. It is expected that the addition of these dispersing mediums would produce a matrix into which synthesized silica would be incorporated, thus producing silica in the nanoscale. The interaction between the hydroxyl groups of dispersing medium and the hydroxyl groups of silica would results in co-condensation. The synthesized silica after complete drying is proposed to be calcined to remove the dispersing medium matrix and hence obtaining purer silica. If the end use of the synthesized silica is to produce nanocomposite with a polymer, no effort is proposed to be made to remove the dispersing agent matrix. The presence of organic molecule eliminate the need for the usage of coupling agent during nanocomposite preparation.

3.2 Experimental

15% sodium silicate solution was used for the synthesis. Hydrochloric acid of strength 1N was used. Poly (vinyl alcohol) (PVA), starch and carboxylmethyl cellulose (CMC) of 0 %, 1%, 1.5%, 2%, 2.5%, and 3% concentrations were used in the experiment.The experimental set up consists of a reactor, stirring cum heating arrangement, Filtration assembly and Drying assembly.

The reaction between sodium silicate and dil. HCl is given below:

$$\mathbf{Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.3)$$

$$\mathbf{H_2SiO_3 \rightarrow SiO_2 + H_2O} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.4)$$

The synthesized silica after complete drying was calcined in muffle furnace at 600 ^{o}C for six hrs to remove the dispersing agent's matrix. The purer silica particles obtained were then characterized by using various technique such as TEM, SEM, FTIR, BET, TGA etc..

The details of the synthesis and Characterization of nanosilica using varies technique are described in chapter 2.

3.3 Results and Discussion

3.3.1 Bulk density

Table 3.1. Bulk densities of the prepared silica samples

Sample	Bulk Density (g/cm ^{3})
Commercial silica	0.980
Silica prepared without dispersing medium	1.103
Silica prepared in 1 % PVA	1.131
Silica prepared in 1.5 % PVA	1.186
Silica prepared in 2 % PVA	1.292
Silica prepared in 2.5 % PVA	1.286
Silica prepared in 3 % PVA	1.284
Silica prepared in 1 % CMC	1.124
Silica prepared in 1.5% CMC	1.134
Silica prepared in 2 % CMC	1.134
Silica prepared in 2.5 % CMC	1.134
Silica prepared in 3 % CMC	1.135
Silica prepared in 1 % starch	1.113
Silica prepared in 1.5 % starch	1.125
Silica prepared in 2 % starch	1.128
Silica prepared in 2.5 % starch	1.129
Silica prepared in 3 % starch	1.130

The bulk density of the prepared samples is shown in table 3.1. It is found that the bulk density of synthesized silica is higher than the commercial silica. This may due to the smaller particle size of synthesized silica compared to that of commercial silica. Bulk density of the silica samples is higher when a dispersing medium is used during the synthesis. This may be due to the reduction in particle size and difference in structure.

It is expected that the addition of the dispersing agent would produce a matrix into which synthesized silica would be incorporated, thus producing silica with lower particle size and hence higher bulk density. Bulk density varies with the chemical nature of the dispersing agent. PVA gives higher bulk density than the other two types of dispersing mediums. Bulk density increases with the concentration of the dispersing agent. The optimum concentration is found to be 2 % for all the three mediums.

3.3.2 BET adsorption

Table 3.2 gives the BET adsorption results of the synthesized silica and that of commercial silica. From the table it is clear that synthesized silica has higher surface area than that of commercial silica and surface area of the synthesised silica increases when a dispersing medium is used.

Table 3. 2. Surface area of the silica samples.

Samples	Surface area (m^2/g)
Commercial silica	178
Silica prepared without dispersing medium	195
Silica prepared in 2 % PVA solution	295
Silica prepared in 2 % CMC solution	251
Silica prepared in 2 % starch solution	229

Higher the surface area, lower the particle size. It is clear that nanosilica synthesized by using dispersing medium has lower particle size. The highest surface area is obtained for 2% PVA solution. The surface area of the silica synthesized without the dispersing medium is found to be 195 m^2/g and that of commercial silica is 178 m^2/g.

3.3.3 X-Ray diffraction (XRD)

X-Ray diffraction patterns of the silica samples are shown in figures 3.1. Strong broad peaks centered around a 2θ of 22-23°, characteristics of amorphous SiO_2 [60, 62], are observed in all the cases. This shows that the synthesized silica and commercial silica are in an amorphous state. The full width at half maximum (β) is, however, different for different samples. The β is used to determine the particle size using the Debye-Sherrer formula. The average particle size, $C_{s,}$ of the silica samples (using the equitation 2.4) is given in the table 3.3.

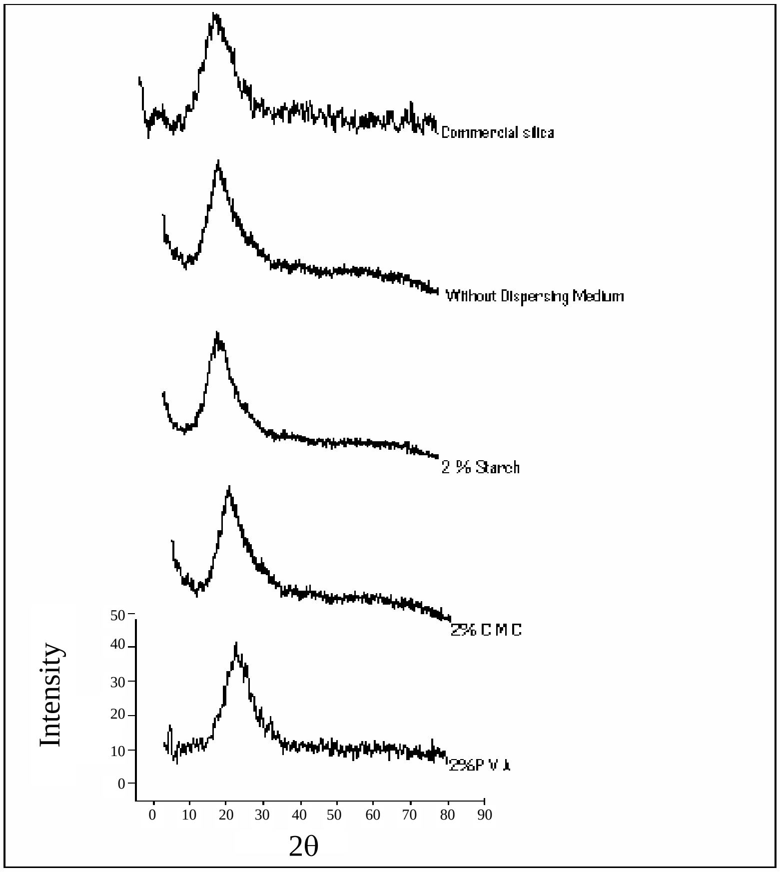

Figure 3.1. XRD patterns of the silica synthesized by using different dispersing agents

Table 3.3. Average particle size of the silica samples.

Sample	Average Particle size (nm)
Silica prepared in 2 % PVA solution	13
Silica prepared in 2 % CMC solution	16
Silica prepared in 2 % starch solution	18
Silica prepared without dispersing medium	22
Commercial silica	34

3.3.4 Infra red spectroscopy

Figures 3.2 is the IR spectra of the synthesized silica and commercial silica. The broad band between 2800 and 3750 cm^{-1} is due to silanol OH groups and adsorbed water. The predominant peak at 1080 cm^{-1} is due to siloxane bonds (Si-O-Si). The peaks between 1000 and 700 cm^{-1} are attributed to vibration modes of the gel net work [60-61]. It can be concluded that all samples consist predominantly of silicon oxide. In comparing the spectra of the synthesized silica and commercial silica it is found that there is a reduction in intensity of peak at 3437 cm^{-1} (of -OH stretching) in the case of the synthesized silica. Lesser number of hydroxyl groups in synthesized silica results in lower particle agglomeration.

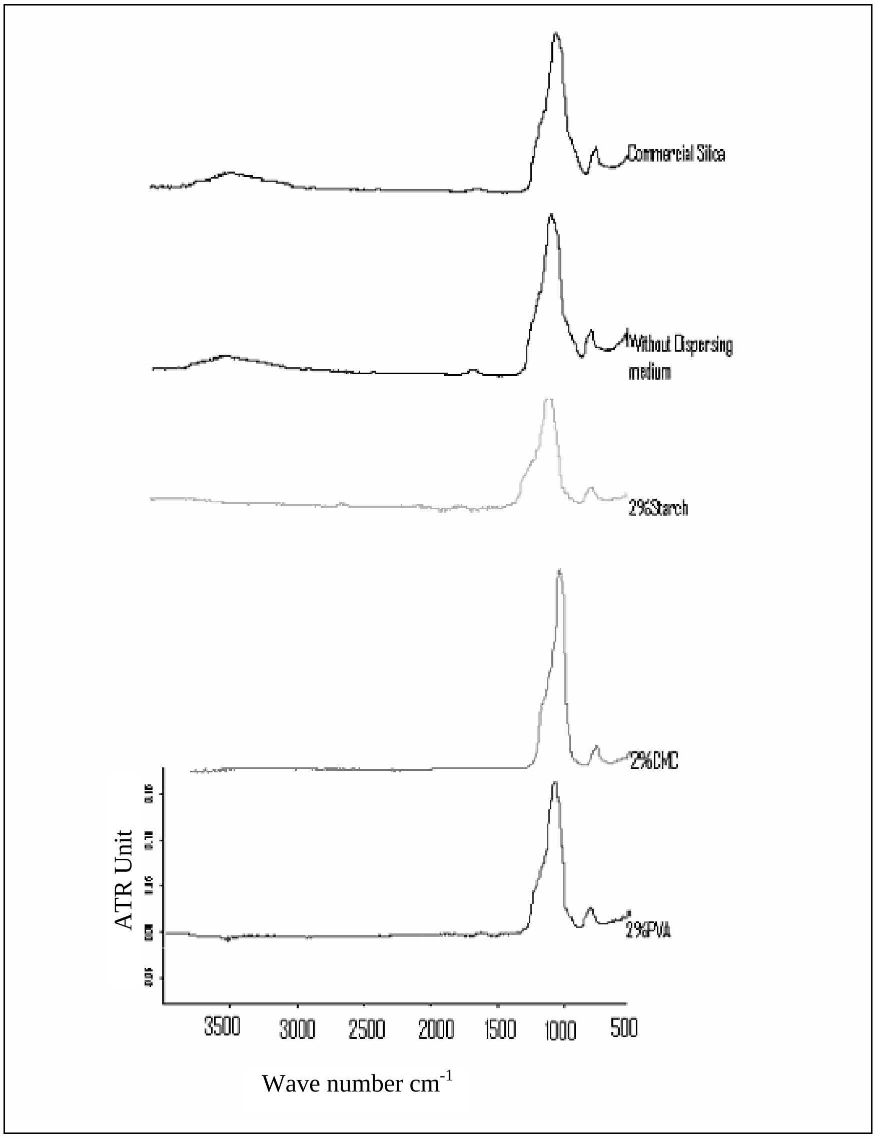

Figure 3.2. IR spectra of the silica synthesized by using different type of dispersing agents

3.3.5 Transmission electron microscopy

The TEM images of the synthesized silica samples are given in the figures 3.3 to 3.5

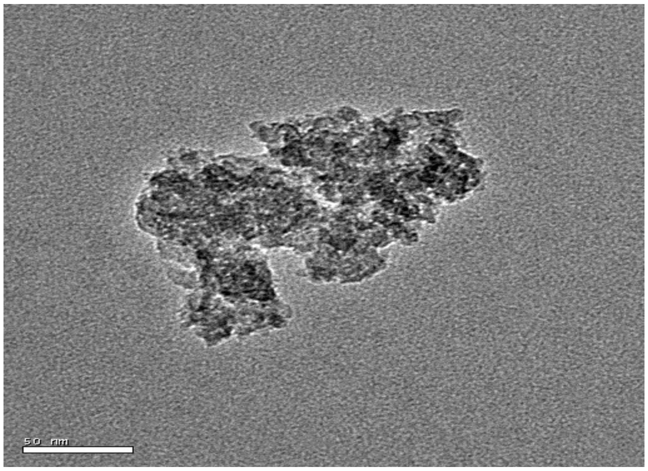

Figure 3.3. TEM image of the nanosilica synthesized by using 2 % PVA as the dispersing agent.

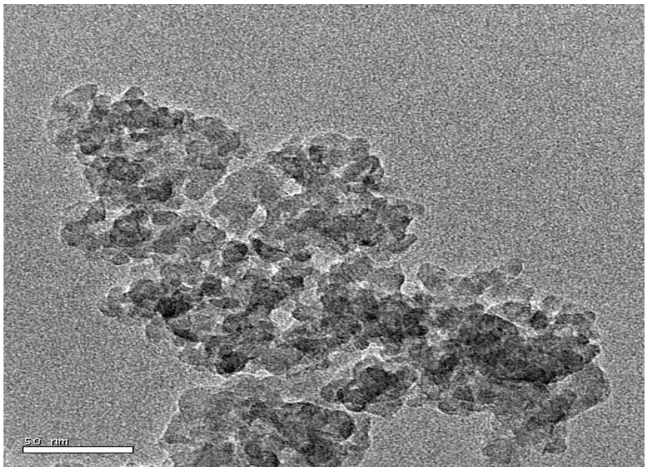

Figure 3.4. TEM image of the nanosilica synthesized by using 2 % CMC as the dispersing agent.

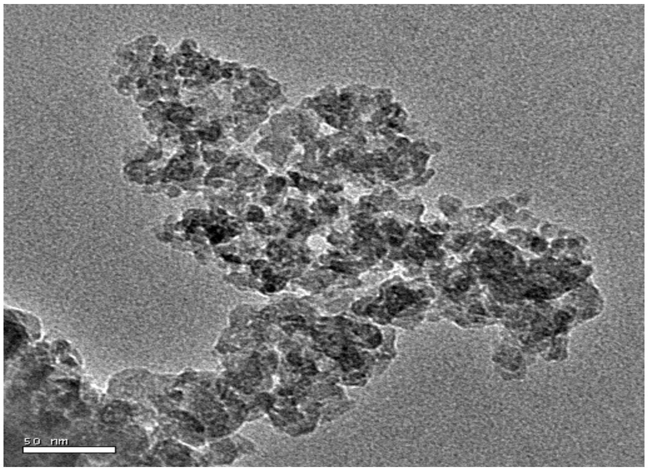

Figure 3.5. TEM image of the nanosilica synthesized by using 2 % starch as the dispersing agent.

From the TEM images it is clear that the size of the synthesized silica is in nanometer range. The corresponding diffraction pattern is shown in figure 3.6. This confirms the amorphous nature of the synthesized silca particles and it is identical to that of amorphous particles [60].

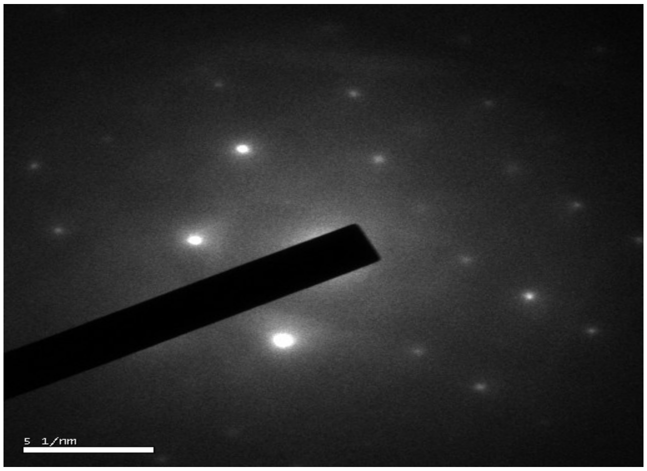

Figure 3.6. Diffraction pattern of the silica sample

3.3.6 Scanning electron microscopy (SEM)

Figures 3.7.(a) and (b) show the SEM micrographs of the silica synthesized by using 2% PVA as the dispersing agent and commercially available silica, respectively.

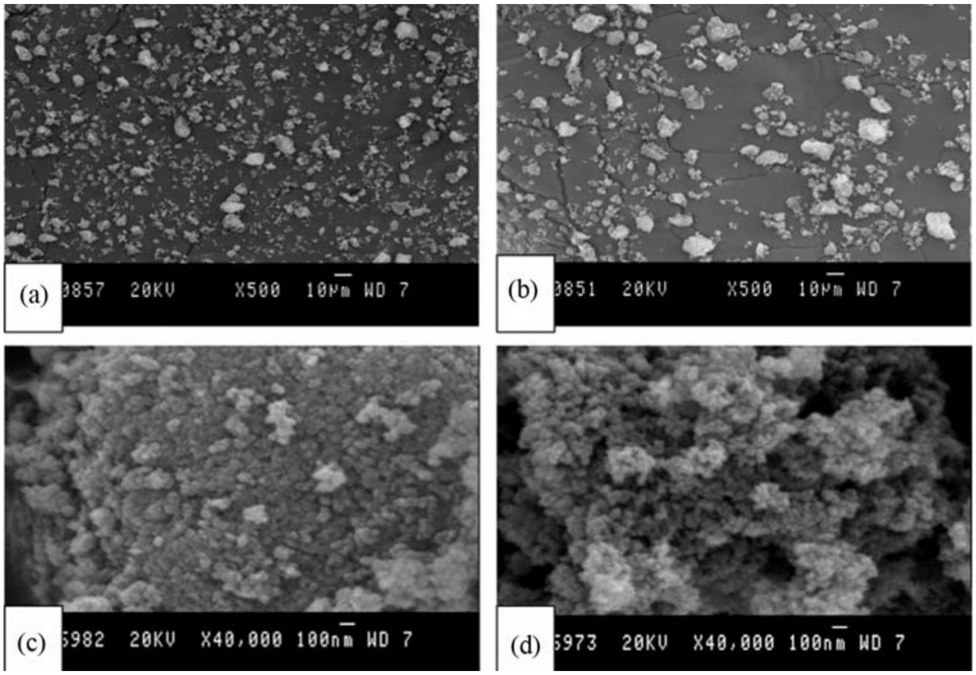

Figure 3.7.(a) and (c) SEM micrographs of nanosilica synthesized by using 2 % PVA as dispersing medium, (b) and (d) SEM micrographs of commercial silica

These micrographs show that the synthesized silica has lower particle size than the commercial silica. Figures (c) and (d) are the SEM of nanosilica and commercial silica, respectively at 40,000X magnification. It is seen that both the silica are of nanometer size. In the case of commercial silica the particles are agglomerated to a larger extent. Figures 3.8 and 3.9 are the SEM micrographs of nanosilica prepared by using 2 % CMC and 2 % starch as the dispersing agents, respectively. It is seen that both the silica are of nanometer size

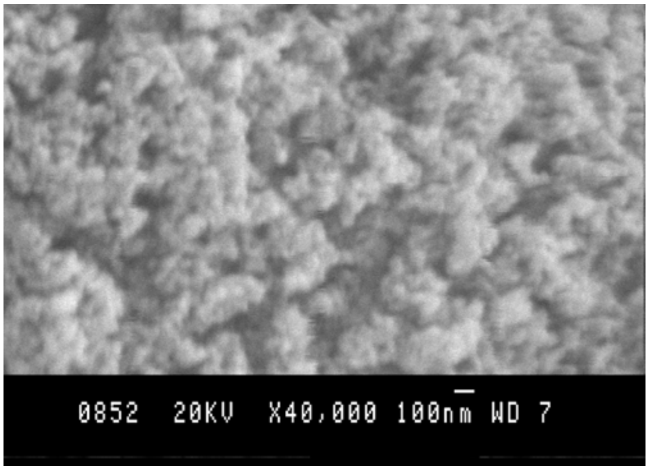

Figure 3.8. **SEM mircrograph of nanosilica synthesized by using 2 % CMC as dispersing medium**

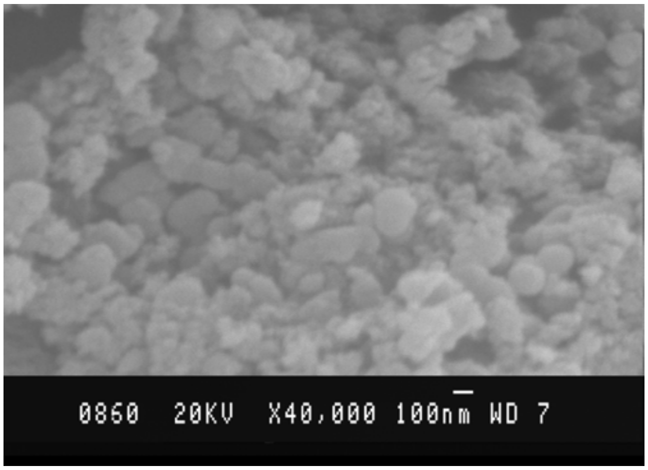

Figure 3.9. **SEM picture of nanosilica synthesized by using 2 % starch as dispersing medium**

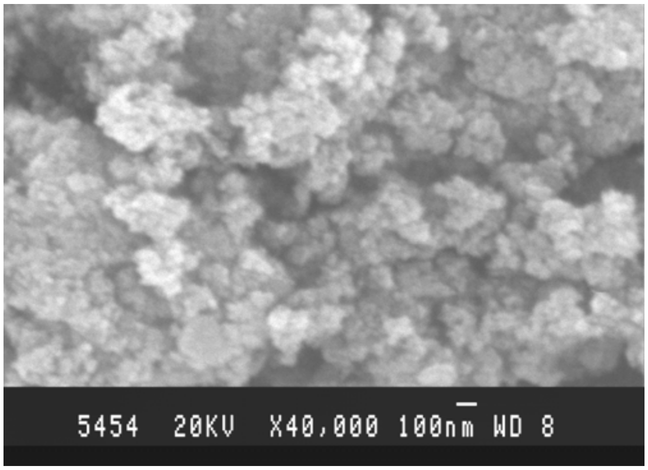

Figure 3.10. SEM micrograph of nanosilica synthesized without dispersing medium

The silica prepared without a dispersing agent is also found to be in nanometer range (Fig. 3.10) but it is relatively larger and more agglomerated. When the reaction is carried out under the controlled conditions this agglomeration is found to be less than that of commercial silica. From the SEM analysis it is evident that the introduction of dispersing agent in the reaction system gives silica samples with lower particle size and less agglomeration

3.3.7 Thermogravimetric analysis (TGA)

The TG-DTG curves of the synthesized silica is given in figure 3.11 and that of commercial silica is given in figure 3.12. The loss of weight below 100 ^{o}C is due to the moisture in the samples. Synthesized silica gives more residue at 800 ^{o}C than that of commercial silica indicating synthesized silica is purer than that of commercial silica and all the dispersing agent could be removed during the muffling process.

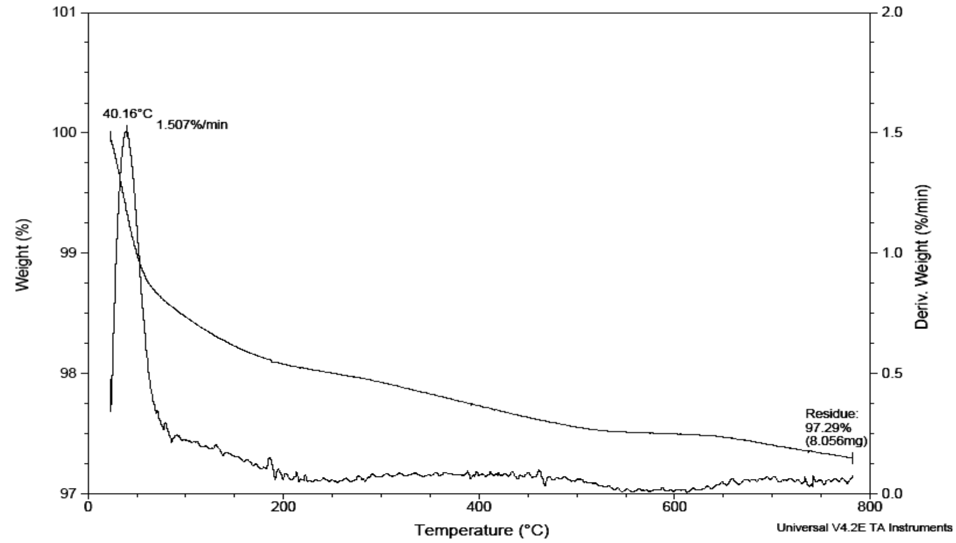

Figure 3.11. TG-DTG curves of the synthesized silica

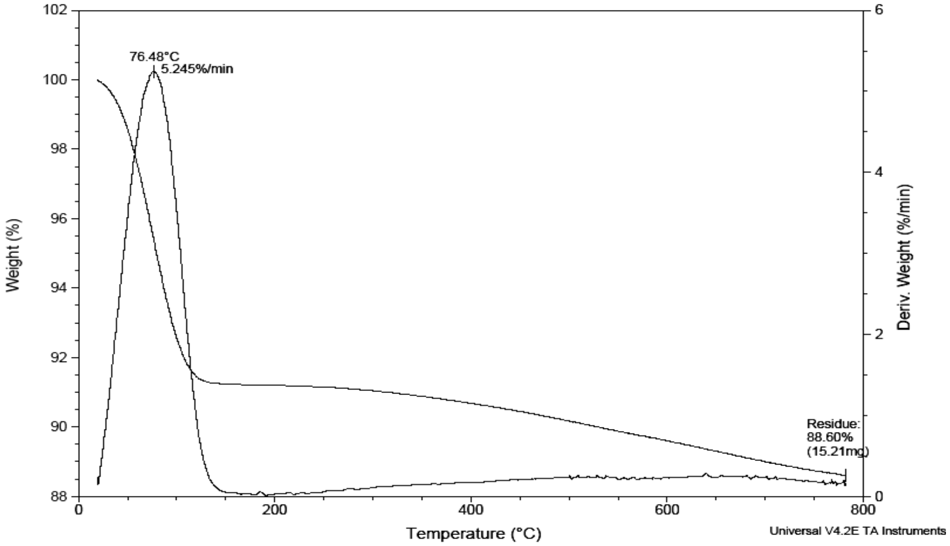

Figure 3.12. TG-DTG curves of the commercial silica

3.3 Conclusions

Nanosilica can be successfully prepared by precipitation methods under controlled conditions. Nanosilica prepared by this method has a particle size less than 18 nm which is lower than that of the commercially available silica. Using appropriate dispersing agents in the reaction, the particle size can be controlled. Nanosilica synthesized by using 2 % poly (vinyl alcohol) as a dispersing agent has a particle size lower than that prepared by using 2% carboxy methyl cellulose and 2 % starch. The particle size of silica was calculated to be 13 nm from the XRD results and the surface area was found to be $295m^2/g$ by BET method. The synthesized silica has lower hydroxyl number and hence reduced silica-silica agglomeration. XRD results show that the synthesized silica is predominantly amorphous. Nanosilica synthesized by using 2 % poly (vinyl alcohol) as a dispersing agent are used for further studies.

3.4 References

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* * *

Chapter 4

Nanosilica as a Filler in Natural Rubber Compound

Contents

4.1 Introduction

Polymer materials are used in a wide range of industrial applications such as the food industry, transportation, construction and aerospace. Elastomers comprise about 15-20 % of world wide polymer consumption, of which 35 % is natural rubber [1]. In 2005, world's NR consumption was 8.76 million tons. IRSG's recent forecast for the world's NR consumption was 15.2 million tons in 2020 [2]. In automotive application, approximately 10 % of total car weight is elastomer [3]. Raw elastomers are reinforced with fillers such as carbon black and precipitated silica to improve their physical and mechanical properties [4-10]. In recent years, synthetic precipitated silica has been replacing carbon black in rubber products offering significant beneficial properties. Precipitated silica which is of mineral origin reduces the rolling resistance and hence fuel consumption in automobile industry [11]. In green tyres i.e., eco-friendly tyres, silica is used as filler material for preparing high-performance tyres with low rolling resistance. Lower rolling resistance results in better fuel economy and lower impact on the environment. The fuel saving capacity of such a tyre is 3 % to 4 % compared to a tyre having treads made from compounds with carbon black, corresponding to a reduction of the rolling resistance of 2 % [12]. It is predicted that by 2010, the demand for precipitated silica in tyre applications will be around 430,000 metric tons per year [13]. The reinforcement of rubbers using particulate fillers such as carbon black or precipitated silica has also been studied at length [14-15]. In all these studies, conventional precipitated silica with particle size in microns has been used. The reinforcement effect of filler is mainly influenced by the size of filler particle and surface functionality [16]. If silica with reduced particle size and hence improved surface area can be prepared, composites with better properties can be obtained. Sufficiently small filler can give good reinforcement, even when matrix /domain bonding is poor [17-18].

Polymer nanocomposites containing nanometer sized fillers have received increasing attention of both scientific and industrial communities. The nano-scaled particles are suitable for micro-scaled reinforcement, thus achieving the macroscopic mechanical enhancement. Global polymer nanocomposite market is to exceed US $ 211 million by 2010 [19]. Because of their nanometer-size dispersion, the nanocomposites exhibits markedly improved properties when compared with the pure polymers or conventional composites. As lower size particles have higher surface area, nanosilica can be more effective in improving the mechanical properties of the vulcanizate. These include increased modulus and strength, decreased gas permeability, increased solvent and heat resistance and decreased flammability. A doubling of the tensile modulus and strength was achieved for nylon-layered silicate nanocomposite with as little as 2 volume % of inorganic content [20-22].

In this study the cure and mechanical properties of the natural rubber compounds containing the nanosilica are reported and the properties are compared with conventional silica composites.

4.2 Experimental

The formulation of mixes are given in the table 4.1. Natural rubber-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl)N'-phenyl-p-phenylenediamine)-1 phr, CBS-0.6 phr, TMTD- 0.2 phr, and sulphur-2.5 phr were common to all mixes.

Table 4.1. The formulation of mixes

Ingredient (phr)	Mix No							
	N_0	N_3	N_6	N_9	C_0	C_3	C_6	C_9
Nanosilica	-	3	6	9	-	-	-	-
Commercial silica	-	-	-	-	-	3	6	9

The mixing was done as per ASTM D-3184 (1989) on a two roll laboratory size mixing mill (150 mm×300 mm). After complete mixing, the stock was sheeted out at a fixed nip gap. The samples were kept for 24 hrs for maturation. The sheets were vulcanized in the hydraulic press at 150 ^{o}C and 200 kg/cm^2 pressure to their optimum cure time, as determined using a Rubber Process Analyzer (RPA – 2000, Alpha Technologies). The details of preparation of the mixes, molding and testing are given in chapter 2

4.3 Results and Discussion

4.3.1 Cure characteristics

Variation of minimum torque with silica loading of both sets of composites is shown in figure 4.1. The minimum torque increases with silica loading in both the cases. Mix N shows higher values at all silica loadings. The higher viscosity of the nanosilica composites may be due to a better dispersion of the filler particles in the matrix.

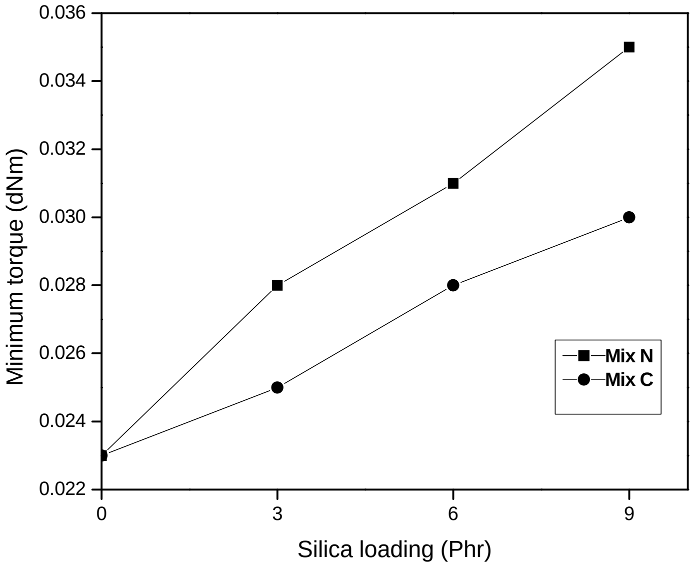

Figure 4.1. Variation of minimum torque with silica loading

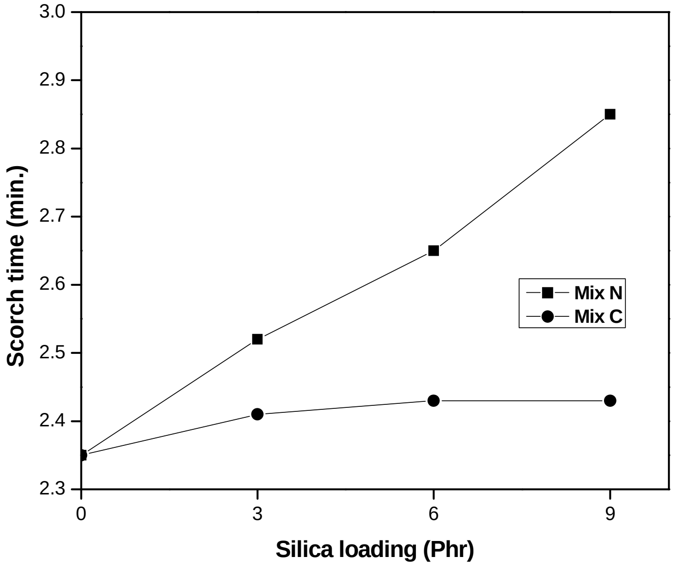

Figure 4.2. Variation of scorch time with silica loading

Figure 4.2 gives the variation of scorch time with silica content. While the scorch time remains more or less constant for commercial silica, it increases linearly for the nanosilica. Scorch time increases from 2.4 minute to 2.9 minute by the addition of 9 phr nanosilica in the gum compound. The corresponding change shown by the commercial silica is very less. The delayed start of cure reaction in the case of nanosilica may be attributed to the possible interaction of the silica with the accelerators, making it unavailable for cure reaction.

However, the cure time is found to be unaffected by this interaction, as indicated by the almost similar variation of the cure time with silica content in both the cases (Fig. 4.3). Cure time increases with silica content for both the cases. Cure time increases from 4.2 minute to 8.2 minute by the addition of 9 phr nanosilica in the gum mix. Commercial silica also shows an increment of 7.9 minute by the incorporation of 9 phr silica in the same mix.

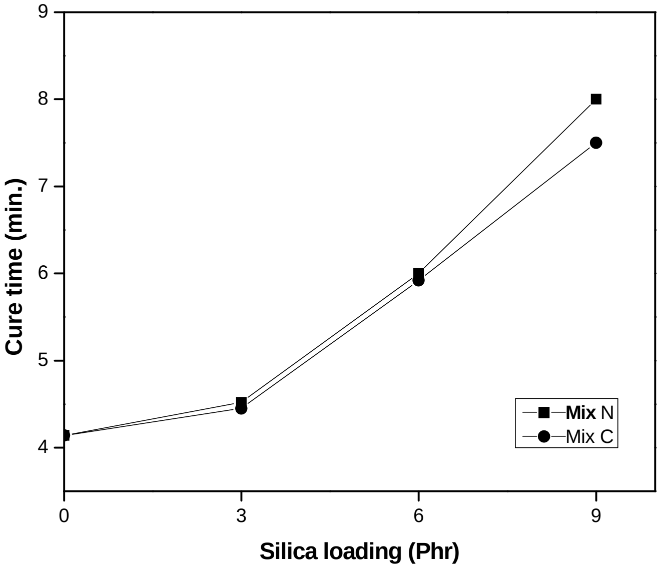

Figure 4.3. Variation of cure time with silica loading

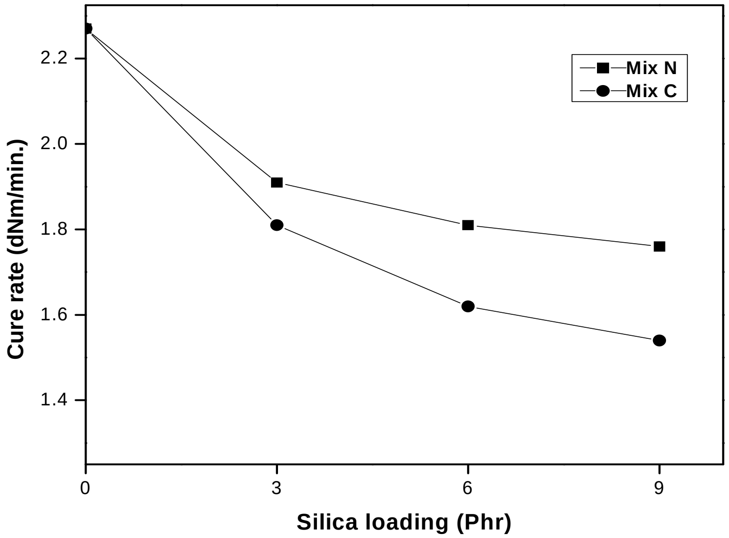

Figure 4.4. Variation of cure rate with silica loading

this indicates that the nanosilica-accelerator interaction is only short term and is reversible at elevated temperatures. With increasing silica content, however, the cure time increases. This may be attributed to the slight acidic nature of silica. Generally acids retard the cure reaction.

Figure 4.4 shows the rate of cure reaction with silica loading. In the case of cure rate, a similar trend is shown by both the silicas. As expected, the cure rate decreases with silica loading for both the cases. The cure rate is higher for the nanocompounds.

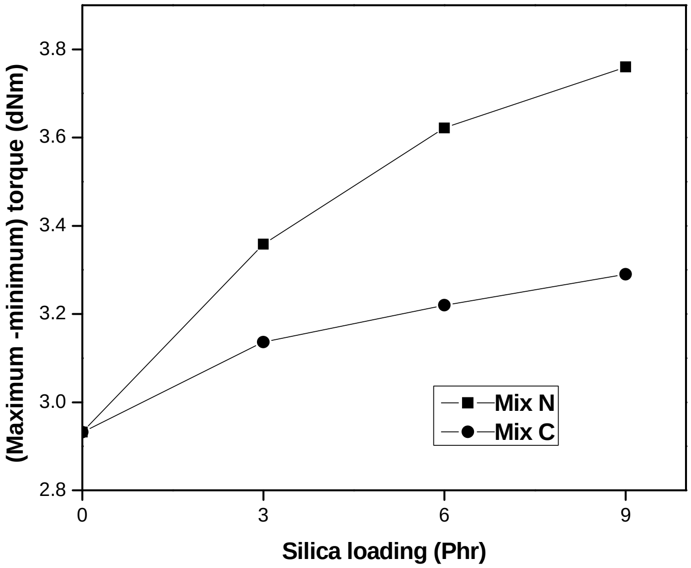

Figure 4.5. Variation of differential torque with silica loading

The differential torque i.e., the difference between the minimum and maximum torques developed during cure is found to be significantly higher for the nanosilica compounds (Fig.4.5). The differential torque increased to 3.8 dNm from 2.9 dNm by the addition of 9 phr nanosilica in the gum compound. The corresponding value obtained by the commercial silica is 3.2 dNm. The differential torque is a measure of the extent of the cross link formation and the filler –matrix interaction. The higher value for the nanosilica compounds indicates that it has higher cross link density and higher filler- matrix interaction. This is evident from the V_r values of the mixes.

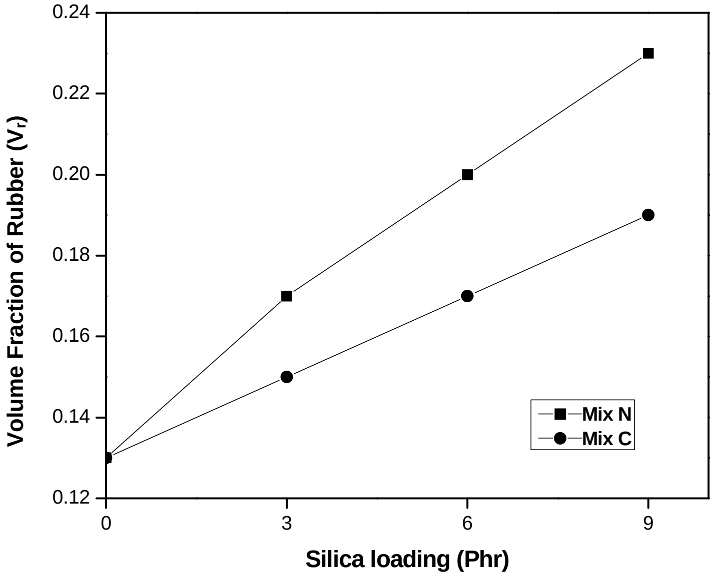

Figure 4.6. Variation of volume fraction of rubber with silica loading

Figure 4.6 shows that V_r of the nanosilica-containing mixes is higher at all silica loadings. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix due to their smaller size and hence higher surface area.

4.3.2 Mechanical properties

Figure 4.7 shows the variation of tensile strength with silica loading. As expected, the tensile strength drops at 3 phr for both the composites and then tends to regain at higher silica loadings. The initial drop at lower levels of reinforcing fillers is a result of dilution effect in a strain-crystallizing matrix such as natural rubber [23-24]. At 9 phr, the tensile strength is higher than the gum compound in the case of nanosilica compound whereas it is only half that gum strength in the case of commercial silica containing composite. It shows the better reinforcing efficiency of the nanosilica resulting from the higher surface area and better interaction of nanosilica with the matrix. SEM studies of the tensile fractured samples also support this view.

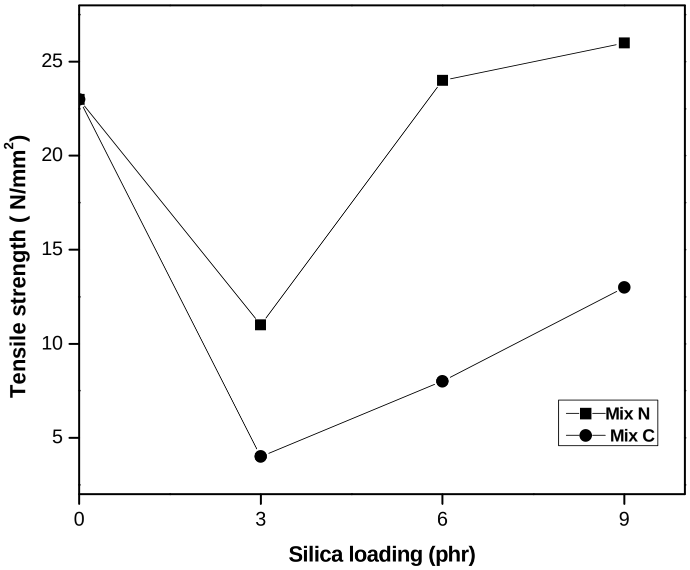

Figure 4.7. Variation of tensile strength with silica loading

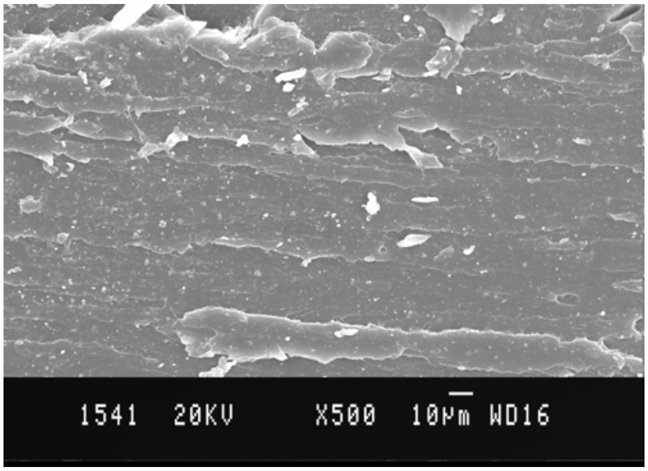

Figure 4.8. SEM picture of tensile fracture surface of Mix N_6

Figures 4.8 and 4.9 are the SEM pictures of the tensile fracture surfaces of Mixes N_6 and C_6, respectively. From the pictures it is clear that matrix is more restrained for nanosilica filled composite than the commercial silica.

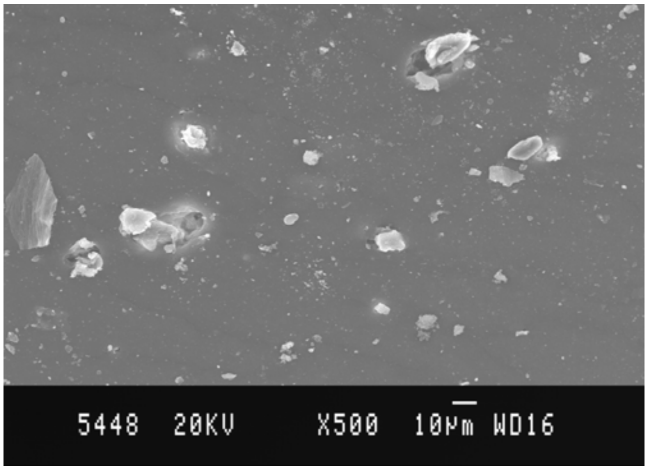

Figure 4.9. SEM picture of tensile fracture surface of Mix C_6

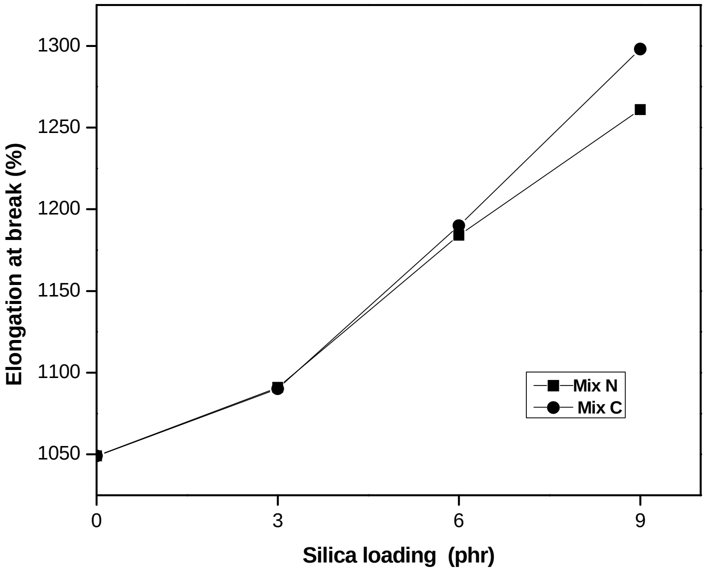

Figure 4.10. Variation of elongation at break with silica loading

Elongation at break varies almost similarly for both the composites. It increases with increasing filler loading (Fig.4.10).

The variation of tear strength with silica loading is also similar for both the cases. Figure 4.11 gives variation of tear strength of the composite with filler loading up to 9 phr. In both the cases, the tear strength drops to a lower value at 3 phr silica content. As in the case of tensile strength, the tear strength also tends to improve at higher filler loadings. The increase in tear strength in the case of nanosilica composite is 48 N/mm (9phr) from 23 N/mm (3phr) whereas for conventional silica composite, the shift is from 12 N/mm (3phr) to 30 N/mm (9phr).

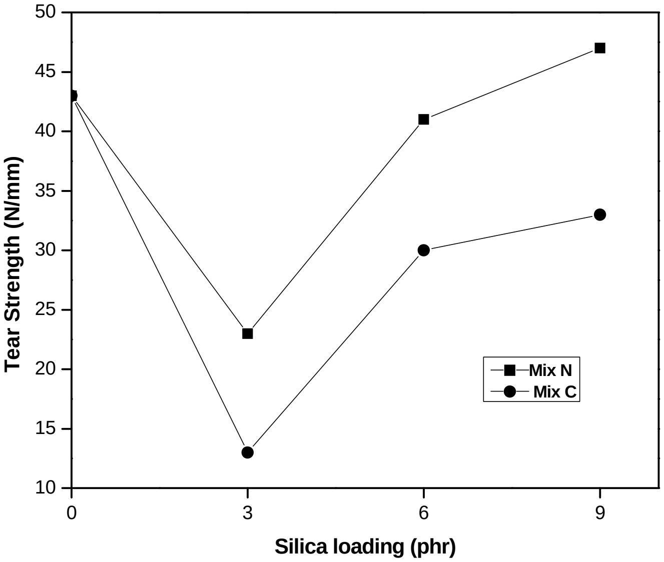

Figure 4.11. Variation of tear strength with silica loading

The higher tear strength value of nanosilica compound is due to better interaction of nanosilica with the matrix. The smaller particle size of the nanosilica helps it better arrest or deviate the tear cracks, resulting in higher tear resistance. SEM study of the tear fractured sample of the Mix N_6 also supports this view (Fig.4.12).

Modulus at 50 % strain shows an almost linear variation with silica loading (Fig.4.13). At 9 phr level, the improvement is about 43 % for nanosilica composite whereas it is only 20 % for the commercial silica composite. It indicates a more restrained matrix, resulting from better chances of filler –matrix interaction, in the case of nanosilica compounds.

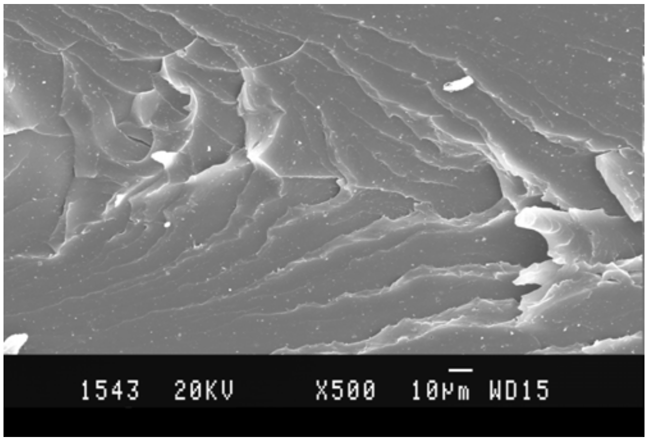

Figure 4.12. SEM picture of tear fracture surface of Mix N_6

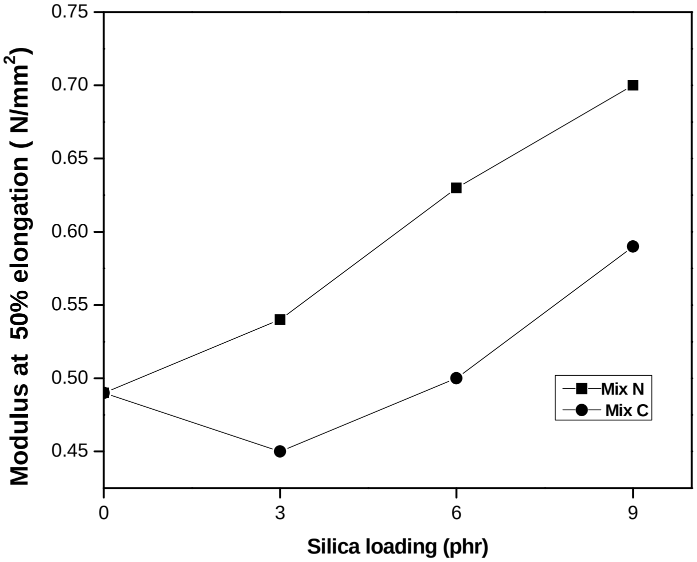

Figure 4.13. Variation of modulus with silica loading

Abrasion loss shows a continuous decrease with filler loading (Fig.4.14). The nanosilica composites shows significantly lower value for abrasion loss compared to the conventional silica composites. Nanosilica composite shows 67 % reduction at 9 phr loading, compared to 44 % in the case of compound with commercial silica.

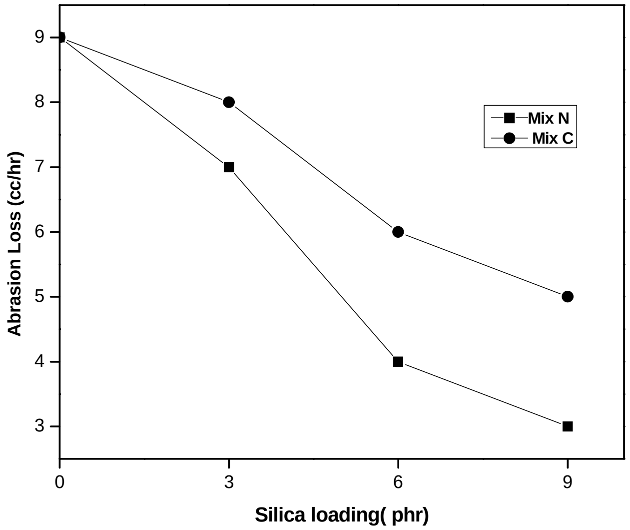

Figure 4.14. Variation of abrasion loss with silica loading

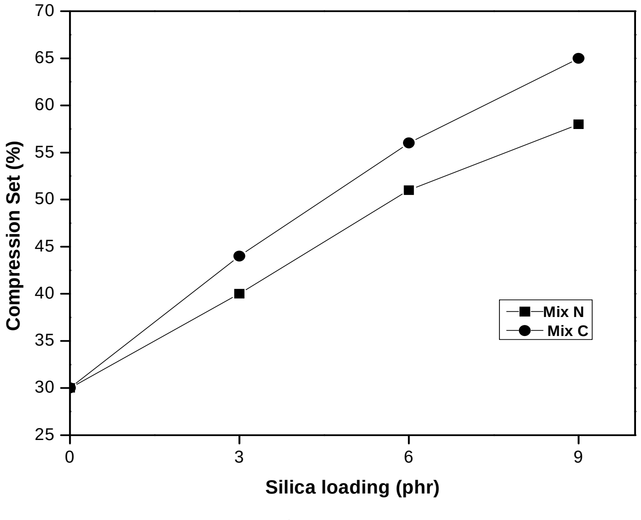

Figure 4.15. Variation of compression set with silica loading

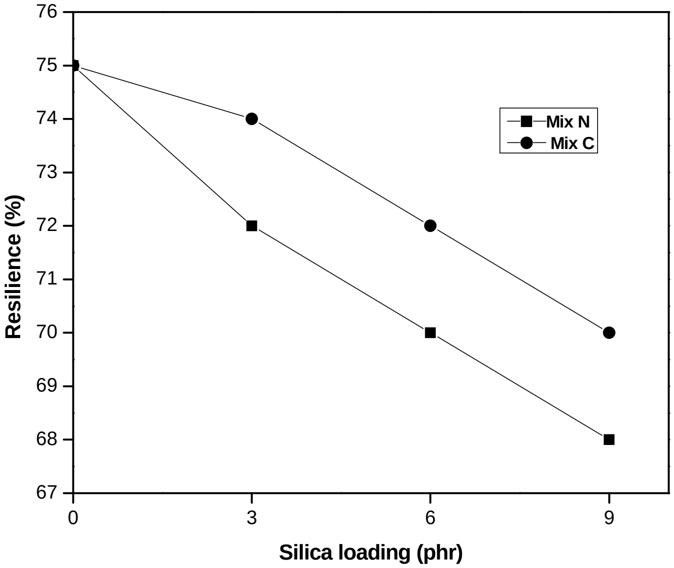

Figure 4.16. Variation of resilience with silica loading

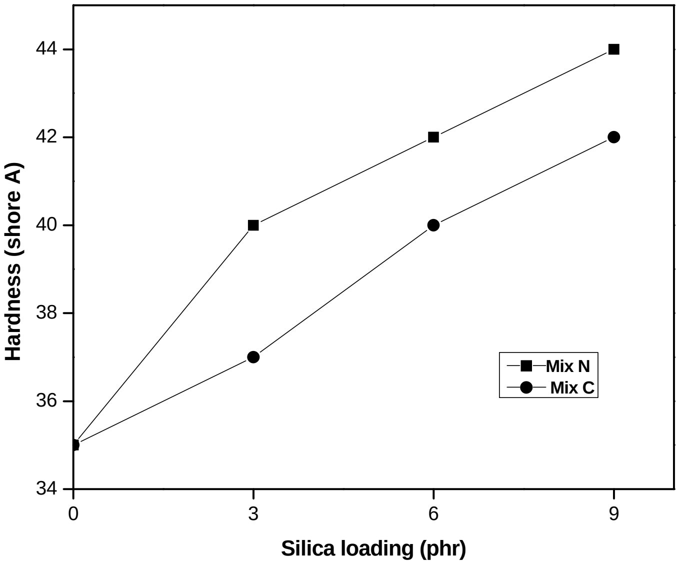

Figure 4.17. Variation of hardness with silica loading

Compression set, as expected, is higher at higher filler loadings (Fig.4.15). The fillers that are reinforcing in nature will adversely affect the elastic properties, especially at elevated temperatures. This is reflected as higher compression set of the composites. However, in the case of nanosilica composites the set is relatively lower compared to the conventional silica compounds, indicating that the extent of agglomeration in the case of nanosilica is lower. The reduced elasticity is also reflected in the resilience values. The resilience is reduced with increasing silica content (Fig.4.16).The nanosilica shows lower resilience. The hardness increases with filler loading and higher for nanosilica compound (Fig.4.17), again indicating a better efficiency of the nano filler.

4.4 Conclusions

Nanosilica is effective reinforcing filler in natural rubber compound. Minimum torque, maximum torque, scorch time and cure time increase with silica loading and are higher for nanosilica compounds. Filler-matrix interaction is better for nanosilica than the commercial silica. Volume fraction of rubber in a solvent-swollen sample is also higher for the nanosilica compounds. The introduction of the nanosilica in the rubber compound improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion loss, hardness and compression set properties are also better for the nanosilica compounds.

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Chapter 5

Nano Silica as a Dry Bonding Component in HRH Bonding System

Part – A

NATURAL RUBBER – SHORT NYLON 6 FIBER COMPOSITES

Contents

5A.1 Introduction

Short fiber reinforced composites are relatively a new class of materials that find applications in most general purpose and speciality products ranging from belts, hoses, diaphragms and seals to tyres. Since short fibers can be incorporated directly into the rubber compound along with other additives, the resulting composites are amenable to the standard rubber processing steps of extrusion, calendering and the various type of molding operations such as compression, injection and transfer molding [1]. Properties of short fiber elastomer composite critically depend upon the interfacial bonding between fiber and the matrix [2-6]. Conventionally, a tricomponent system based on hexamethylenetetramine (hexa), resorcinol and fine particle hydrated silica

(HRH system) is used to achieve good adhesion between short fiber and the rubber matrix. This is because, the constituents of the dry bonding system can be added to the rubber matrix like any other compounding ingredients and extra process like dipping and the drying can be avoided. Fiber-matrix adhesion in short fiber rubber composites has been a field of extensive research. Dunnom [7] observed a marked difference in the adhesion between the matrix and the fiber by adding silica to a compound containing resorcinol and hexa. Rajeev *et al.* [2], Sreeja *et al.* [5], Derringer [8], and De and co-workers [9-10] have described the various aspects of short fiber adhesion to rubber in the presence of the dry bonding system. In all these studies they have used conventional precipitated silica [2, 8, 10-13]. The role of silica is to improve wetting of the fiber surface [7-9, 12]. As small particles have higher surface area, nanosilica can be more effective in improving wettability of the fibers.

In this work the effect of nanosilica based tri-component dry bonding system on short Nylon 6 fiber - natural rubber composite is reported. The mechanical properties of Nylon 6 short fiber/natural rubber composites are presented.

5A.2 Experimental

NR-N6 composites were prepared using the prepared nanosilica and commercial silica based HRH bonding system. Formulation of the test mixes are given in the table 5.A.1. Natural rubber used in this study was ISNR-5 and Nylon 6 fiber, obtained from SRF Ltd., Chennai, India, was chopped to approximately 6 mm length. Fiber loading was varied from 0 to 30 phr. Hexa:Resorcinol:Silica (HRH) ratio was maintained as 2:2:1. HRH loading was adjusted as 16% of the fiber loading

Table 5 A.1. Formulation of the mixes

Ingredients (phr)[+]	Nanosilica HRH bonding				Commercial silica HRH bonding				Without HRH bonding			
Hexa	-	0.67	1.33	2	-	0.67	1.33	2	-	-	-	-
Resorcinol	-	0.67	1.33	2	-	0.67	1.33	2	-	-	-	-
Nanosilica	-	0.33	0.66	1	-	-	-	-	-	-	-	-
Commercial silica	-	-	-	-	-	0.33	0.66	1	-	-	-	-
Nylon 6 fiber	0	10	20	30	0	10	20	30	0	10	20	30

[+] phr- parts per hundred rubber.

Natural rubber-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3-dimethylbutyl)N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes.

The details of preparation of the mixes, molding and testing are given in chapter 2.

5A.3 Results and Discussion

Figure 5A.1 shows the variation of tensile strength with fiber loading in longitudinal direction for all mixes. The tensile strength increases with fiber content with an initial minor drop at 10 phr. This drop may be due to the dilution effect of the fibers at lower loadings [14-15]. At higher fiber loadings, however, the reinforcing effect takes over, resulting in an improved ultimate strength.

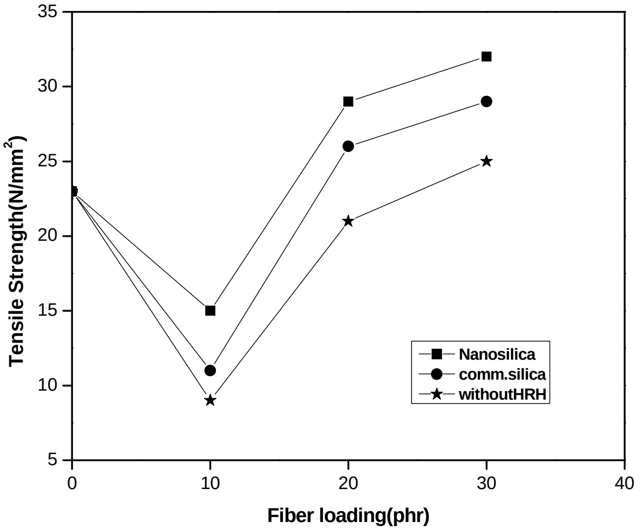

Figure 5A.1. Variation of tensile strength with fiber loading in longitudinal direction

The improvement in tensile strength of the composite containing 30 phr fiber loading with nanosilica as HRH bonding is 39 % compared to the gum compound. But the same mix containing commercial silica as HRH bonding shows only about 26 % improvement than the gum compound. The improvement in tensile strength of composite containing no HRH bonding system is only about 8 %. This implies that nanosilica is very effective in improving the efficiency of HRH bonding system in short nylon fiber – Natural rubber composites. Nanosilica contributes to effective interaction between the fiber and the matrix due to its small particle size and hence improves the interfacial adhesion between the fiber and the matrix. SEM studies of the tensile fractured samples also support this view.

Figures 5A.2 **is** the SEM picture of the tensile fracture surface of the composite containing nanosilica based HRH system. Fiber-surface is not smooth as the matrix is adhered on to the fiber. Fiber ends are seen to be broken. This indicates that there is a strong bond existing between the fiber and the matrix.

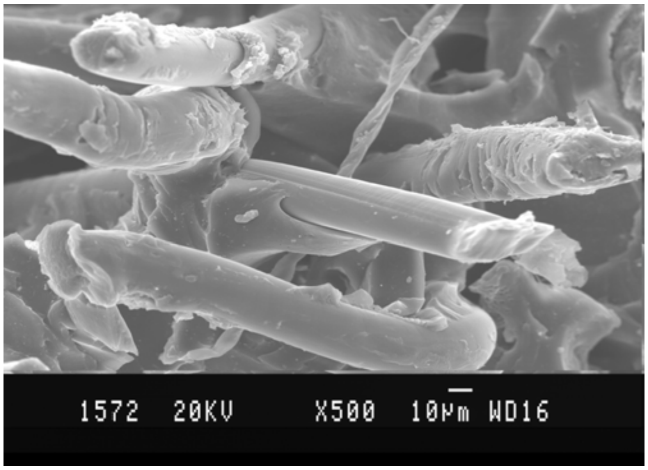

Figure 5A.2. Scanning Electron Micrographs of nanosilica HRH bonded composite.

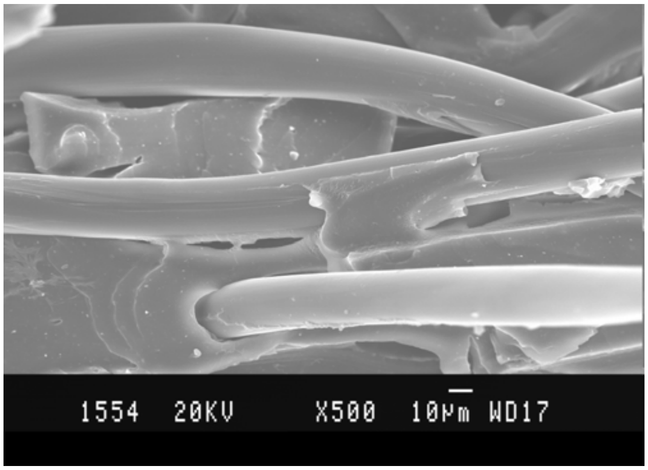

Figure 5A.3. Scanning Electron Micrographs of commercial silica HRH bonded Composite.

Figures 5A.3 is the micrograph of the tensile fracture surface of samples containing commercial silica based HRH bonding system. The fibers are pulled out from the matrix. No resin is adhered on to the fiber surface, as the bond is not as strong as in the case of nanosilica. The micrographs of the tensile fracture surface of samples without HRH bonding system also shows that the fibers are pulled out from the matrix (Fig.5A.4).

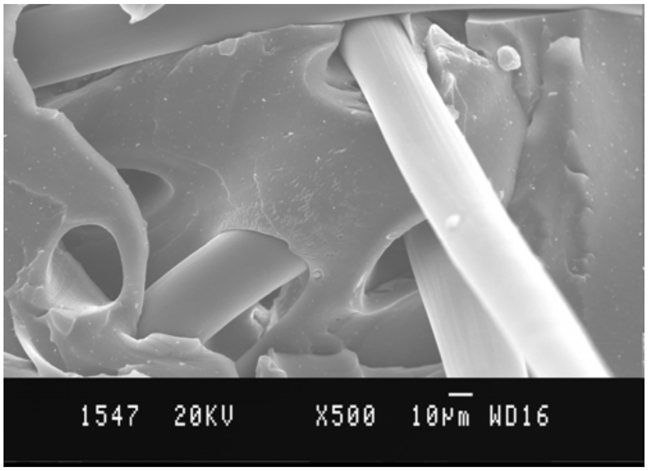

Figure 5A.4. Scanning Electron Micrographs of composite without HRH

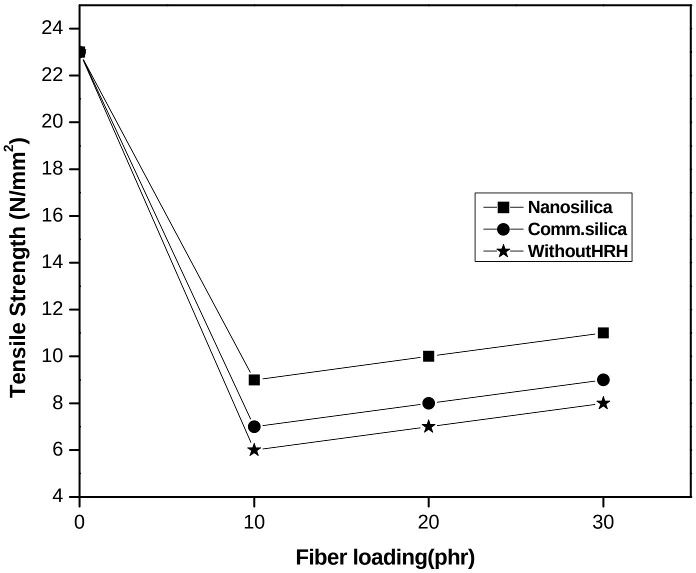

Figure 5A.5. Variation of tensile strength with fiber loading in transverse direction

The variation of tensile strength of the composites with fiber loading in transverse direction is shown in figure 5A.5. The strength drops drastically with 10 phr fiber. With further increase in fiber loading, the strength is not improved as in the case of longitudinal orientation of fibers. This is because the load is not effectively transmitted to the fibers as they are oriented across the direction of load. In this configuration growing crack can easily pass through the fiber- matrix interfaces facilitating the easy failure of the sample.

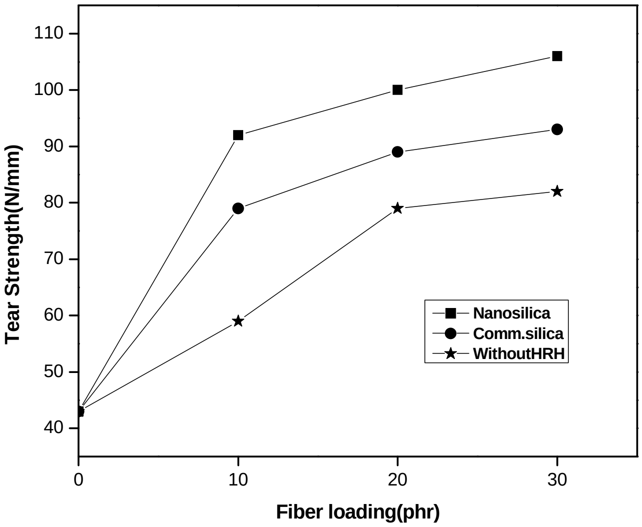

Figure 5A.6. Variation of tear strength with fiber loading in longitudinal direction

The variation of tear strength in longitudinal direction with fiber loading is shown in figure 5A.6. Tear strength increases with fiber loading. The higher tear strength of the composites is due to the obstruction of tear path by longitudinally oriented fibers. The composite containing synthesized nanosilica HRH system shows an improvement in tear strength from 43 N/mm for gum to 106 N/mm with 30 phr fiber loading. The composite containing commercial silica shows an improvement to 93 N/mm with the same fiber loading. Without HRH bonding system the corresponding value is 82 N/mm. The composite containing nanosilica shows a greater extent of improvement in tear strength than the other two types of composites. This may be attributed to the lower particle size of the synthesized silica. Due to this it improves the wettability of the fibers to the matrix.

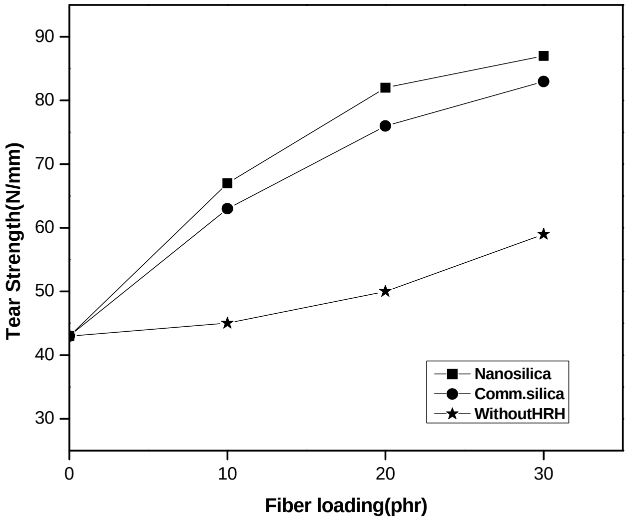

Figure 5.A.7. Variation of tear strength with fiber loading in transverse direction

Figure 5 A.7 shows the variation of tear strength with fiber loading in transverse direction. The increase in tear strength with increase in fiber loading is not as high as that in longitudinal direction. We can see that the composite with nanosilica HRH system shows an improvement from 43 N/mm for gum to 87 N/mm with 30 phr fiber loading. With commercial silica HRH system, the improvement is 83 N/mm with the same fiber loading. But the composites containing no HRH bonding system shows very little improvement in the presence of 30 phr fiber.

Figure 5A.8 and Figure 5A.9 show the variations of elongation at break with fiber loading in longitudinal and transverse directions, respectively. In both the cases there is a sudden drop in elongation at break with 10 phr fiber loading and after that it remains more or less constant with increase in fiber loading. The decrease in elongation at break of the composite with fiber loading may be due the restraining effect of the fibers.

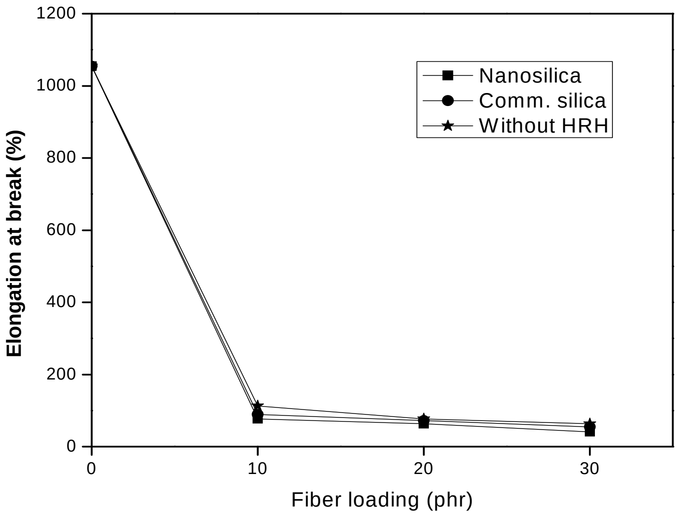

Figure 5A.8. Variation of elongation at break with fiber loading in longitudinal direction

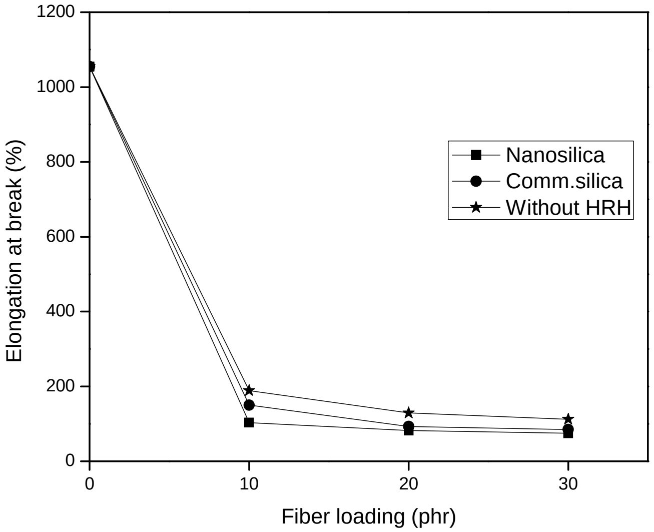

Figure 5A.9. Variation of elongation at break with fiber loading in transverse direction

The variation of Modulus at 50 % elongation for the composites with fiber loading in longitudinal direction is shown in figure 5A.10. There is marked improvement in modulus with increasing fiber content.

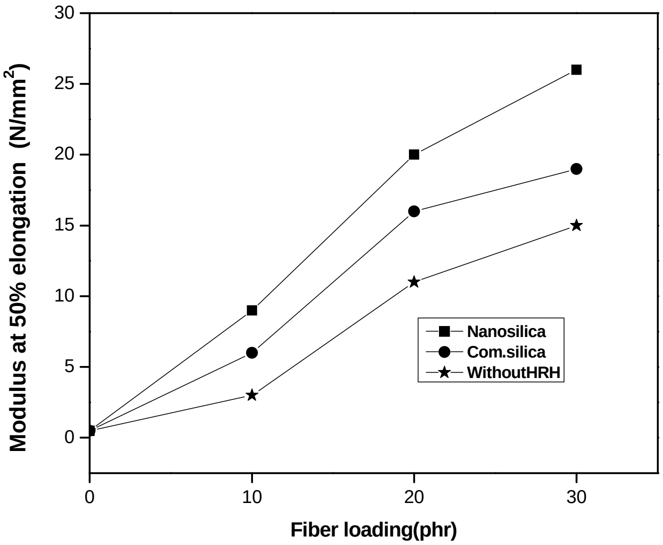

Figure 5A.10. Variation of modulus with fiber loading in longitudinal direction

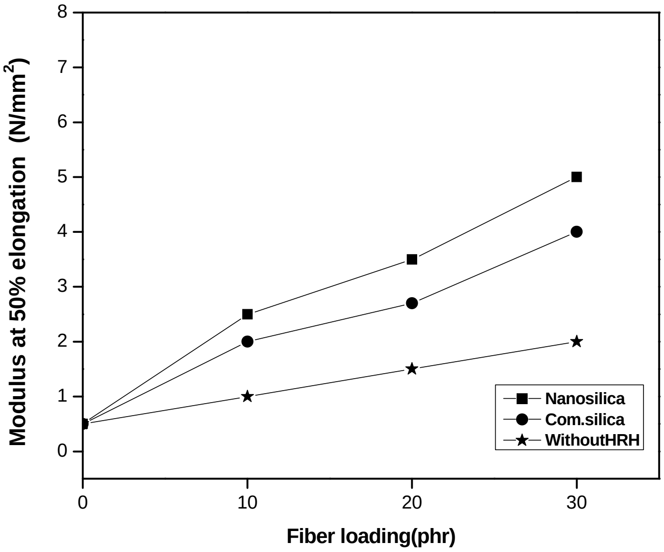

Figure 5A.11.Variation of modulus with fiber loading in transverse direction

The composite with synthesized nanosilica shows an improvement from 0.438 N/mm^2 for gum to 26 N/mm^2 with 30 phr fiber loading. With commercial silica the modulus is improved to 19 N/mm^2 at similar fiber loading. The corresponding improvement for the composite without HRH bonding system is to 15 N/mm^2. The lower particle size of the nanosilica helps in improving the adhesion of the fiber and matrix. A similar trend is observed in transverse direction also (Fig.5A.11).

The variation of abrasion loss with fiber loading is shown in figure 5A.12. Abrasion loss of all the composite samples is less than that of the gum compound. Samples with nanosilica show considerable decrease in the abrasion loss. In the case of samples without HRH bonding system, there is only marginal decrease in the abrasion loss. During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case, the presence of strong interfacial adhesion between the fiber and matrix makes the matrix stiffer and lowers the abrasion loss.

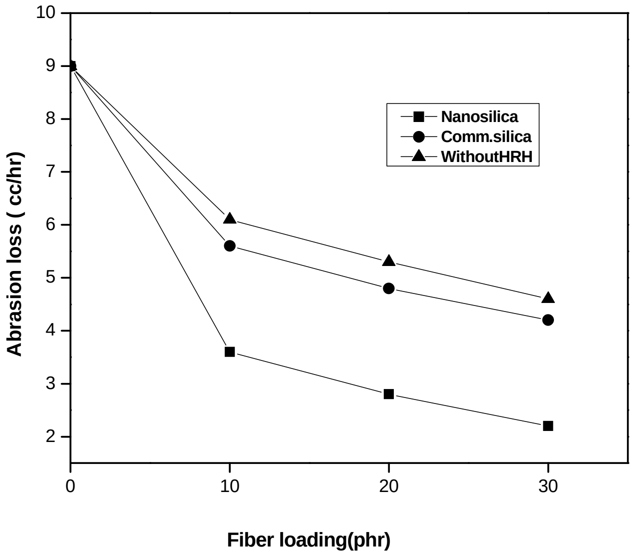

Figure 5A.12. Variation of abrasion loss with fiber loading

Figure 5A.13 shows the variation of compression set of all the mixes with fiber loading. Compression set increases with fiber loading. As the fiber loading increases the elastic property of the composite decreases. The composites containing nanosilica with 30 phr fiber loading shows higher compression set than the composite with commercial silica-HRH bonding and the composite without HRH bonding.

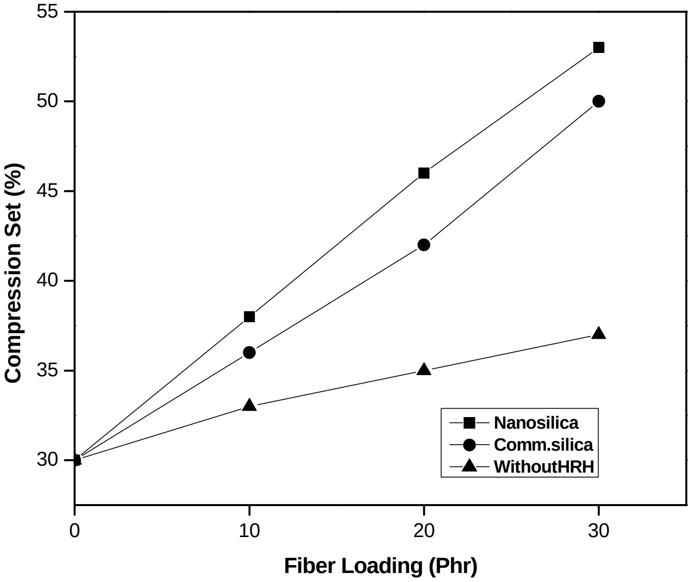

Figure 5A.13. Variation of compression set with fiber loading

The variation of rebound resilience with fiber loading is shown in figure 5A.14. A continuous decrease in resilience is observed with fiber loading. As more energy is dissipated at the fiber- matrix interface the resilience is reduced. The composite containing nanoscilica shows lower resilience than other two types of composites. Because in that composites the fiber- matrix adhesion is very strong.

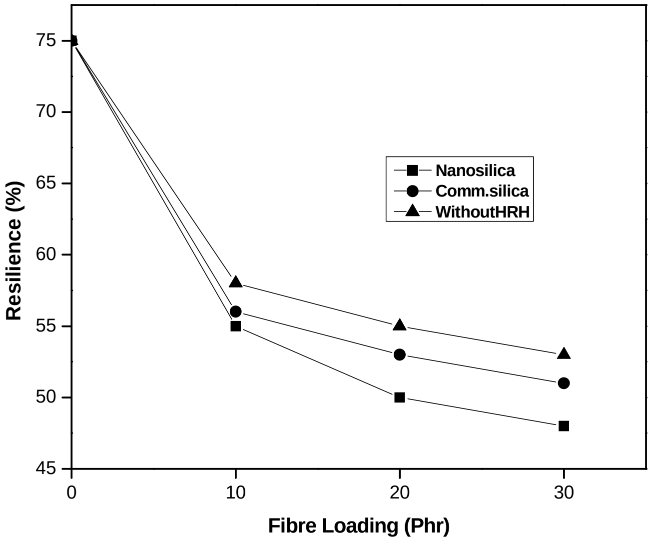

Figure 5A.14. Variation of resilience with fiber loading

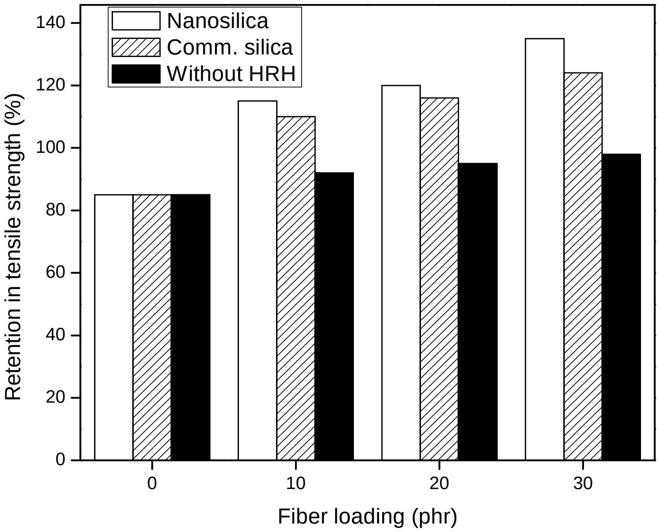

Figure 5A.15. Variation of percentage retention in tensile strength with fiber loading

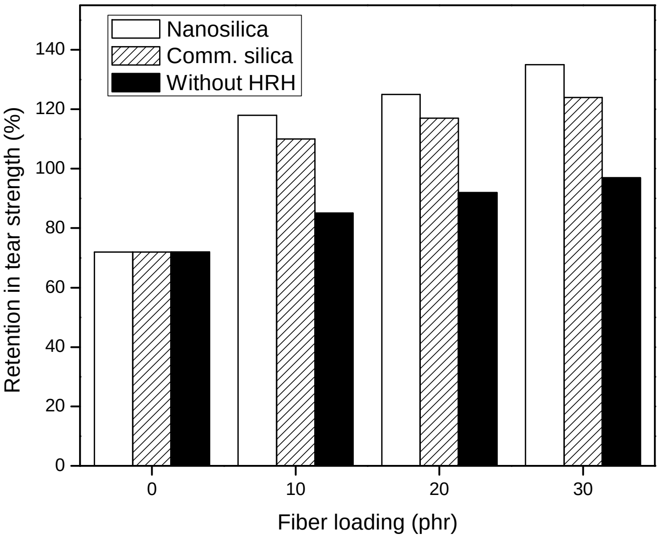

Figure 5 A.16. Variation of percentage retention in tear strength with fiber loading

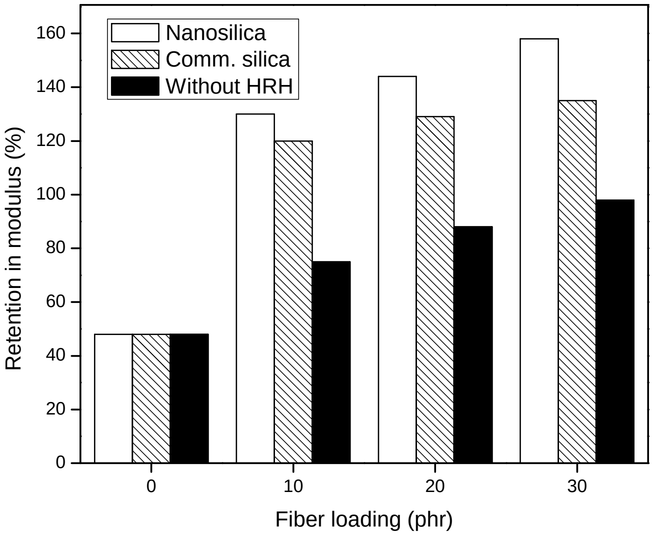

Figure 5A.17. Variation of percentage retention in modulus with fiber loading

Ageing of the composite at 70^o C for 72 hours causes a marginal increase in mechanical properties in the presences of HRH dry bonding system. (Fig.5A.15- Fig.5A.17).This may due to the improved fiber-matrix attachment by ageing. Similar result in the case of NBR composites has been reported earlier [16]. The percentage retention in ageing is higher for nanosilica bonded composites than that of commercial silica for the entire fiber loading.

5A.4 Conclusions

Dry bonding system comprising of resorcinol, hexamethylene tetramine, and silica causes significant improvement in the mechanical properties of the NR-short Nylon 6 fiber composites. The efficiency of HRH bonding system in NR-Nylon 6 short fiber composite is increased in the presence of synthesized nanosilica with particle size lower than the commercially available silica. Tensile strength, tear strength, modulus and abrasion resistance are increased by the use of nanosilica in HRH system which shows that the interfacial adhesion between the fiber and the matrix is improved. Compression set and resilience are adversely affected by the introduction of nanosilica. The composites show anisotropy in mechanical properties. Ageing of the composite at 70°C for 72 hours causes an increase in the tensile strength, tear strength and modulus in the presence of the dry bonding system. The retention in ageing is better for nanosilica composites.

5A.5 References

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* * *

Part – B

STYRENE BUTADENE RUBBER – SHORT NYLON 6 FIBER COMPOSITES

Contents

5B.1 Introduction

Styrene-butadiene rubber (SBR), a general purpose synthetic rubber is widely used in products such as tyres and belts, is much superior to NR with respect to ageing and ozone resistance. SBR exhibits significantly lower resilience than NR so that it has higher heat buildup on flexing. The oil resistance of SBR is poor and it is not resistant to aromatic, aliphatic or halogenated solvents. But the extrusion properties of SBR are superior to those of NR and its stocks have fewer tendencies to scorch in processing. The abrasion resistance of SBR is as good as that of NR or slightly better. The gum vulcanizates of SBR are generally weak and it is essential to use reinforcing fillers to produce products of high strength. Reinforcing SBR with short Nylon fibers will improve its mechanical properties. Interfacial bond is known to play an important role in short fiber composites since this interface is critical in transferring the load from the matrix to the fiber. Several methods are used to improve fiber matrix adhesion. The dry bonding system commonly used in rubbers is the HRH system consisting of hydrated silica, resorcinol and hexamethylene tetramine to create adhesion between the fiber and the rubber matrix. It has been reported by many authors that the HRH bonding system significantly improves the adhesion of various natural and synthetic fibers to rubber matrices [1-7]. In this work the effect of nanosilica based tri-component dry bonding system on the mechanical properties of short Nylon 6 fiber / styrene butadiene rubber composite is reported.

5B.2 Experimental

SBR/short Nylon 6 composites were prepared by using the newly prepared nanosilica and commercial silica based HRH bonding system. Styrene butadiene rubber (SBR) used was Techlen SBR 1502 grade and Nylon 6 fiber obtained from SRF Ltd., Chennai, India, was chopped to approximately 6mm length. Fiber loading was varied from 0 to 30 phr. Hexa:Resorcinol:Silica (HRH) ratio was maintained as 2:2:1. HRH loading was adjusted as 16% of the fiber loading. Formulation of the test mixes are given in the table 5B.1.

Table 5B.1. Formulation of the mixes

Ingredients (phr)$^{+}$	Nanosilica HRH bonding				Commercial silica HRH bonding				Without HRH bonding			
Hexa	-	0.67	1.33	2	-	0.67	1.33	2	-	-	-	-
Resorcinol	-	0.67	1.33	2	-	0.67	1.33	2	-	-	-	-
Nanosilica	-	0.33	0.66	1	-	-	-	-	-	-	-	-
Commercial silica	-	-	-	-	-	0.33	0.66	1	-	-	-	-
Nylon 6 fiber	0	10	20	30	0	10	20	30	0	10	20	30

$^{+}$ phr- parts per hundred rubber.

SBR-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.8 phr, TMTD- 0.2 phr and sulphur-2 phr were common to all mixes.

The details of preparation of the mixes, molding and testing are given in chapter 2.

5B.3 Results and Discussion

The variations of tensile strength with fiber loading in both the directions are shown in figure 5B.1 and figure 5B.2. Tensile strength varies linearly with the fiber loading. At any fiber content the tensile strength is higher for the nanosilica HRH bonded composites.

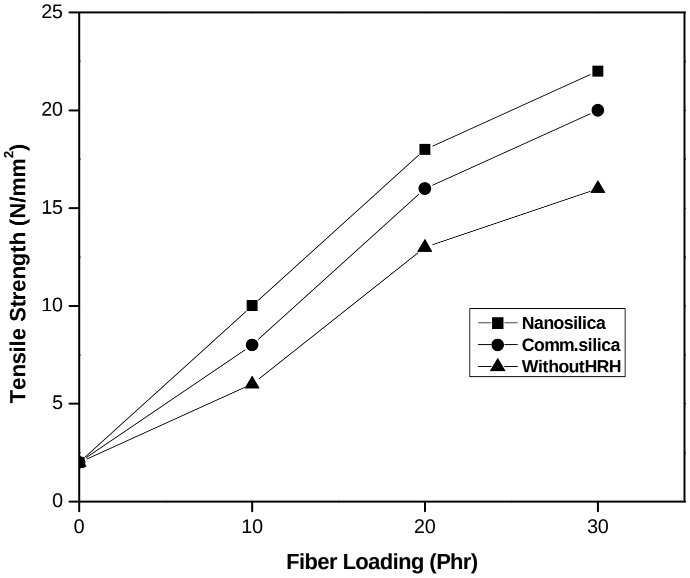

Figure 5B.1. Variation of tensile strength with fiber loading in longitudinal direction

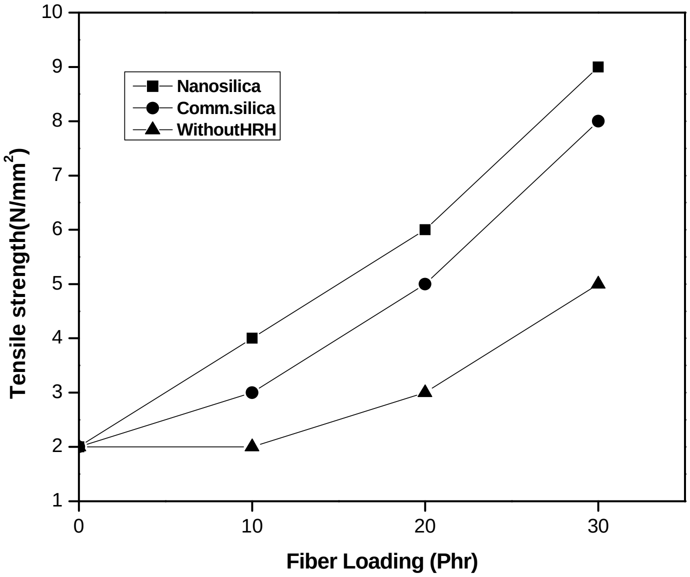

Figure 5B.2. Variation of tensile strength with fiber loading in transverse direction

The introduction of 10 phr fiber in the gum compound increases the tensile strength by 400% for nanosilica HRH bonded composites (Fig.5.B.1). The commercial silica HRH bonded composite shows an improvement of 300 % for the same mix. The corresponding improvement for the composite without HRH bonding system is only 200%. Similar improvements are also observed in 20 phr and 30 phr fiber loaded samples. This implies that the nanosilica has better interaction with the matrix and hence improves wettability of the short fibers, resulting in higher tensile strength. SEM studies of the tensile fractured samples also support this view. Figures 5.B.3 shows the tensile fracture surfaces of the composite with nanosilica HRH bonded system. Fiber surface is not smooth. Matrix is adhered on to the fiber surface. Broken fiber ends are also seen. This indicates that there is a strong bond existing between the fiber and the matrix.

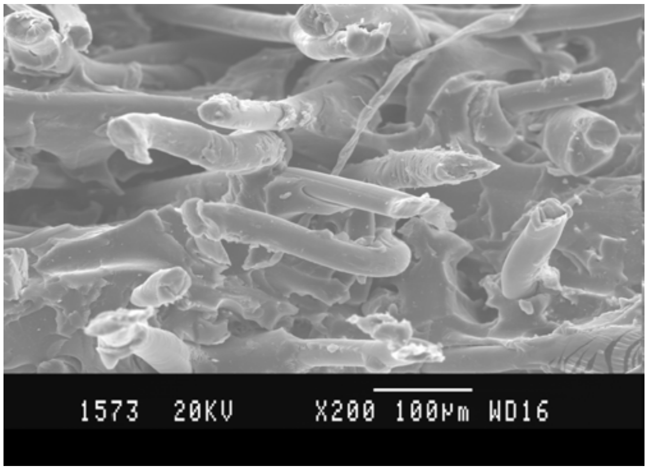

Figure 5B.3. Scanning Electron Micrographs of Nanosilica HRH bonded composite

Figures 5B.4 is the micrographs of the tensile fracture surface of composite containing commercial silica HRH bonding system. The fibers are pulled out from the matrix. No resin is adhered on to the fiber surface, as the bond is not as strong as in the case of nanosilica. The micrographs of the tensile fracture surface of samples without HRH bonding system shows that all the fibers are pulled out from the matrix (Fig.5 B.5). Comparing figures 5 B.1 and 5 B.2 it is clear that tensile strength is higher in longitudinal direction. This is because the transverse orientation of fibers is not effective in supporting the load as the growing crack can easily pass through the fiber-matrix interfaces facilitating easy failure of the composite.

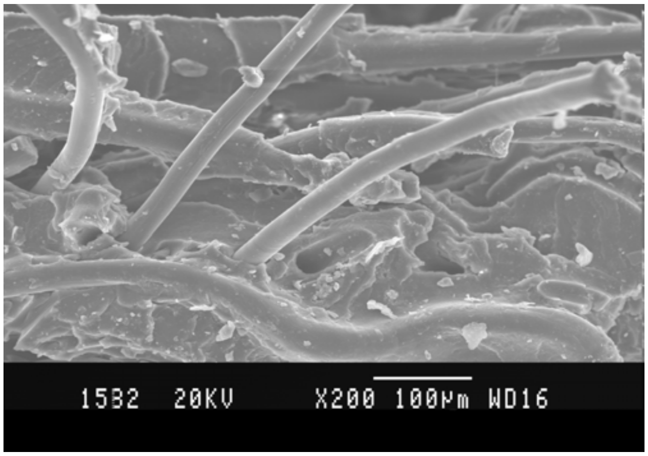

Figure 5B.4. Scanning Electron Micrographs of Commercial silica HRH bonded Composite

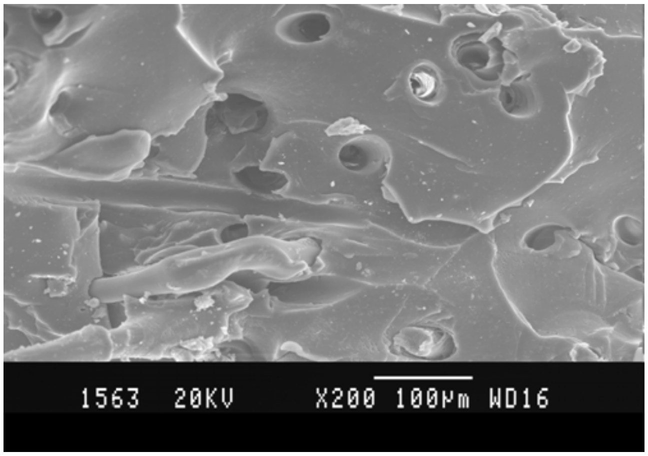

Figure 5B.5. Scanning Electron Micrographs of composite without HRH

Tear strength increases linearly with fiber loading for all the mixes (Fig.5 B.6 and 5 B.7). Tear strength increases to 111 N/mm from 14 N/mm in the presence of 30 phr fibers in the composite containing nanosilica based HRH bonding system. The corresponding values for the commercial silica based HRH system and without HRH are 106 N/mm and 101 N/mm, respectively. Like NR composite here also the tear strength is higher for the nanosilica HRH bonded composites.

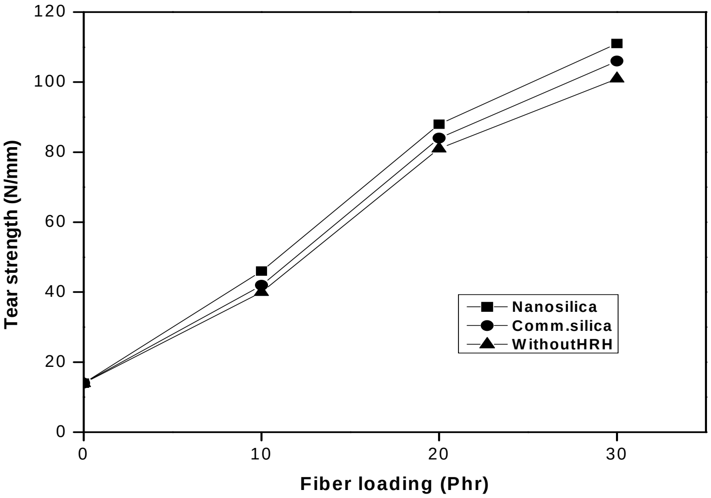

Figure 5B.6. Variation of tear strength with fiber loading in longitudinal direction

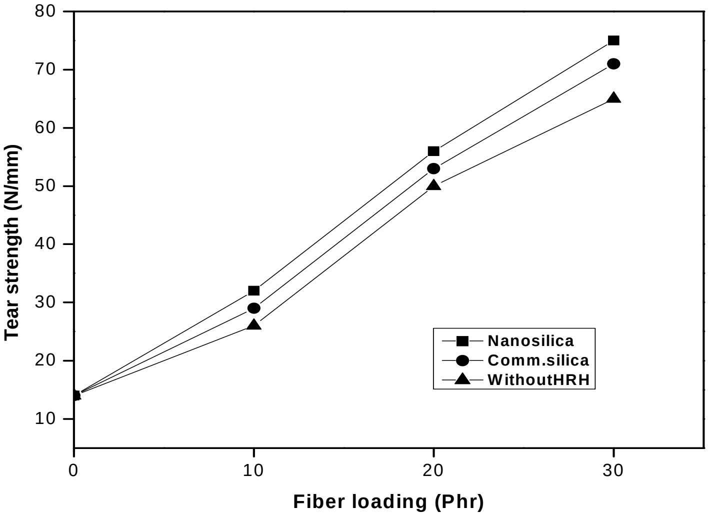

Figure 5 B.7. Variation of tear strength with fiber loading in transverse direction

The decrease in particle size of nanosilica improves dispersion of silica in the matrix and helps the better adhesion of the fiber and the matrix through the silica surface. A similar trend is observed in the transverse direction also (Fig.5 B.7). The tear strength values are higher in the longitudinal direction than the transverse direction. This is because transversely oriented fibers being parallel to the propagating crack front offers less resistance to propagating tear resulting in lower tear strength values.

The elongation at break decreases with fiber loading (Fig.5 B.8). The elongation at break undergoes a sharp fall on introduction of 10 phr of fibers in all the mixes. This is because the fibers inhibit the orientation and flow of molecular chains and hence the ultimate elongation decreases substantially on introduction of low concentration of fibers. With further fiber loading, the ultimate elongation remains almost constant. Since nanosilica improves the wettability of short fibers, there is better interaction between the matrix and the fiber occurs. Therefore composites having nanosilica-HRH bonding will have lower elongation at break. In transverse direction also elongation at break decreases with fiber loading and it is lower for composites containing nanosilica based HRH bonding system (Fig.5 B.9).

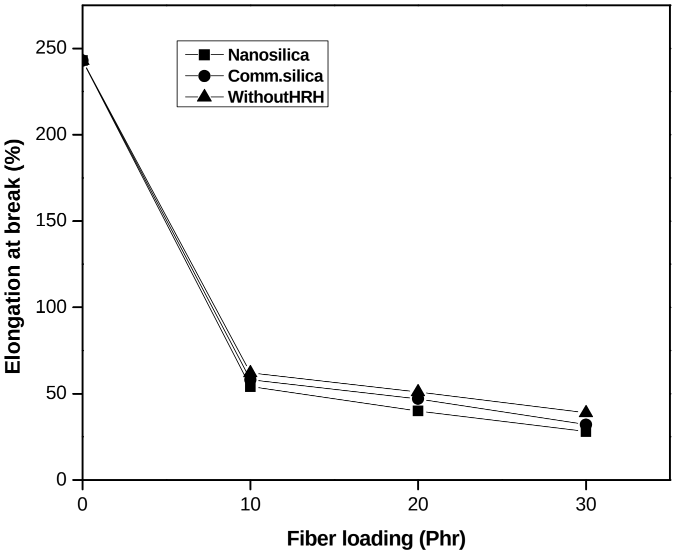

Figure 5B.8. Variation of elongation at break with fiber loading in longitudinal direction

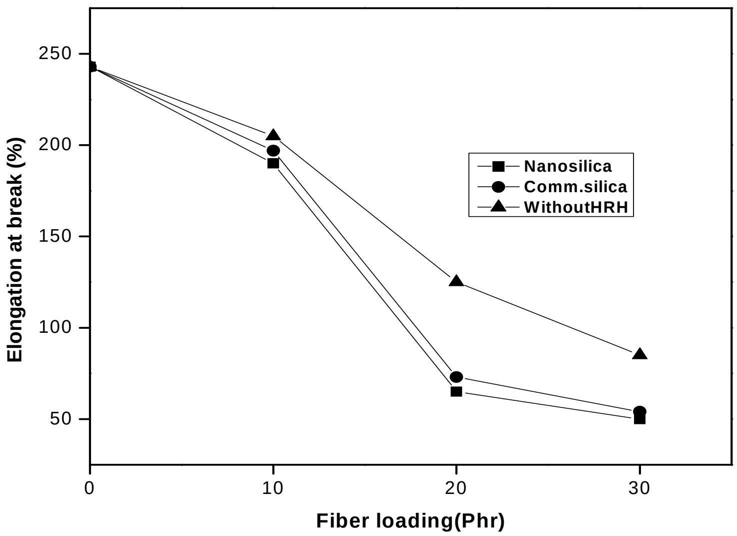

Figure 5B.9. Variation of elongation at break with fiber loading in transverse direction

Figures 5 B.10 and 5 B.11 show variation of modulus with fiber loading in the longitudinal and the transverse directions, respectively.

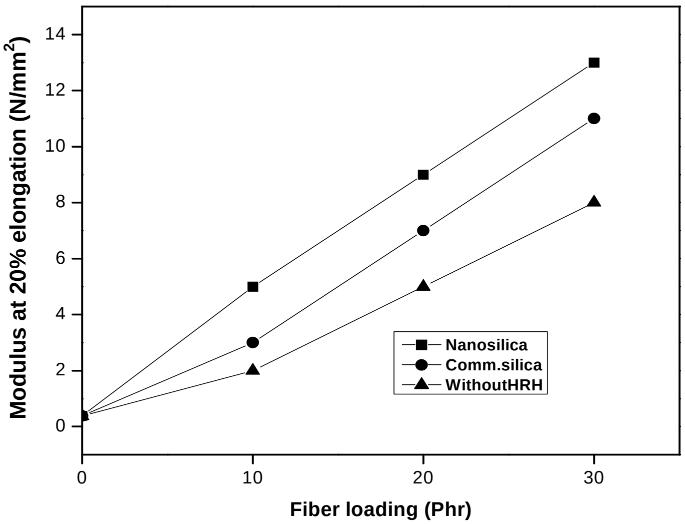

Figure 5B.10. Variation of modulus with fiber loading in longitudinal direction

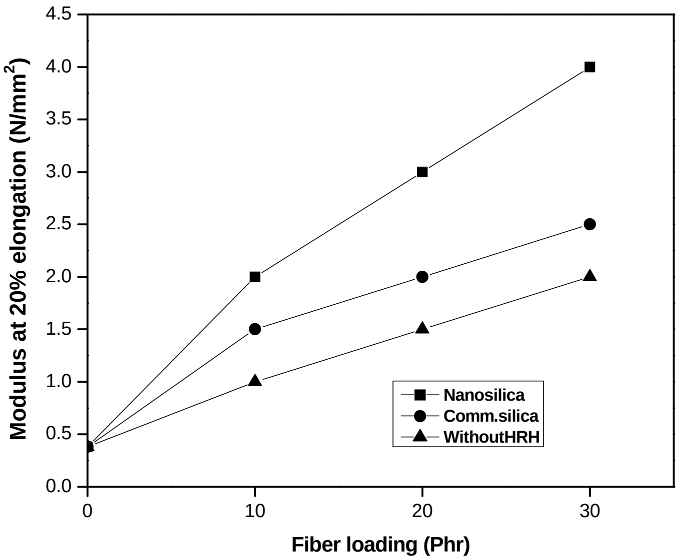

Figure 5B.11.Variation of modulus with fiber loading in transverse direction

The modulus increases with fiber loading for all the mixes in both the directions. But the improvement in modulus is low in the case of transverse direction. Here also the composite with nanosilica based HRH system gives the highest value. This implies that the nanosilica has better interaction with the matrix and hence improves the modulus values.

Figure 5 B.12 show that abrasion loss decreases with fiber loading. This may be attributed to the fact that as the fiber loading increases, reinforcement increases. The decrease in abrasion loss for 30 phr fiber loaded composites are 63.4%, 58.49% and 38.64% respectively for the composite with nanosilica, commercial silica and without HRH, respectively. Samples with nanosilica show a considerable decrease in the abrasion loss than the sample containing commercial silica. This is because of more restrained matrix of the composite. During abrasion test the matrix as well as the reinforcing fiber is worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case the presence of strong interfacial adhesion between the fiber and the matrix renders the matrix stiffer and lowers the abrasion loss.

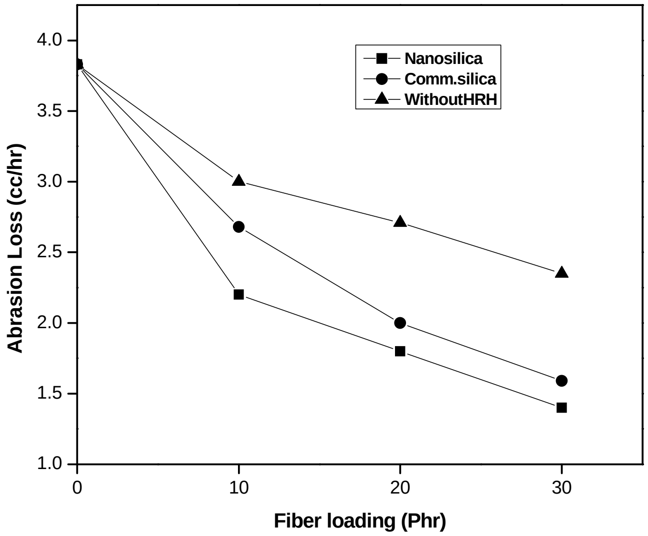

Figure 5B.12. Variation of abrasion loss with fiber loading

Figure 5B.13 shows the variation of compression set with fiber loading. The compression set increases with fiber loading.

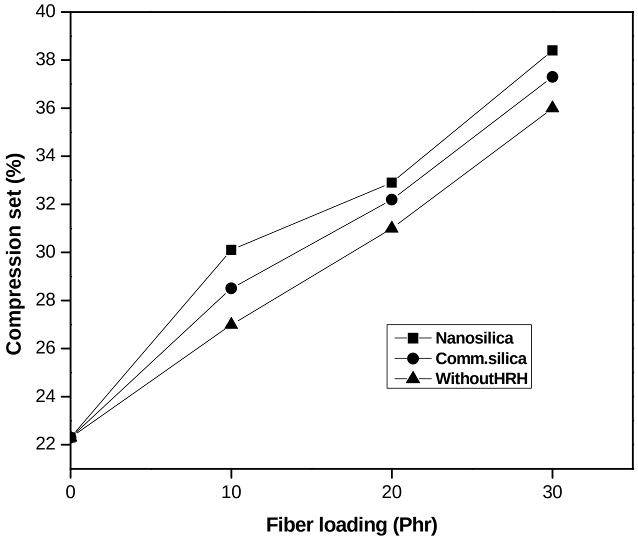

Figure 5B.13. Variation of compression set with fiber loading

This is because as fiber loading increases, the elastic characteristic of the matrix is reduced, giving high compression set values. The increases in compression set for 30 phr fiber loaded composites are 72%, 67% and 61% respectively for nanosilica based HRH bonding System, commercial silica based system and without HRH. Nanosilica bonded samples show a higher value of compression set. This may be due to probable breakage of fiber-matrix interfacial bond when subjected to prolonged effect of temperature and compressive force to the system.

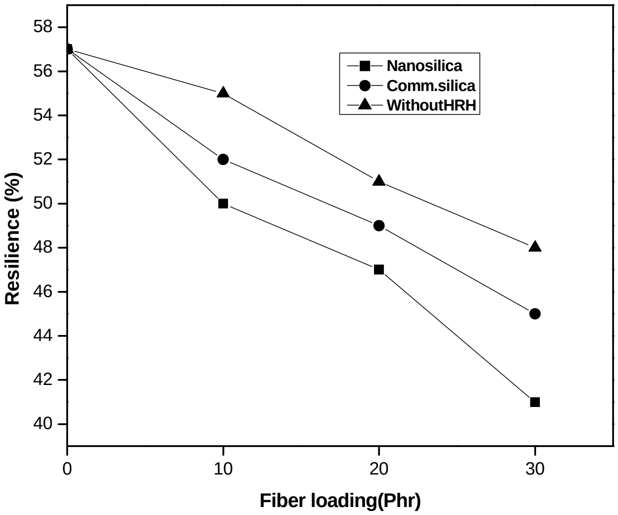

Figure 5B.14. Variation of resilience with fiber loading

Figure 5B.14 shows that there is a reduction in resilience with fiber loading. The dissipation of energy at fiber-matrix interface results in lower resilience value. For the 30 phr fiber- loaded composites, resilience shows a reduction of 39% for nanosilica based HRH system, 26% for commercial silica system and 19% for non-HRH system. Resilience, which is an indication of material elasticity is lowest for nanosilica composites. In presence of nanosilica, there is strong adhesion between the matrix and the fiber.

Ageing of the composite at 70° C for 72 hr. causes a marginal increase in mechanical properties in presences of HRH dry bonding system. (Fig.5 B.15, Fig.5 B.16 and Fig.5 B.17).This is due to the improved fiber-matrix attachment by ageing.

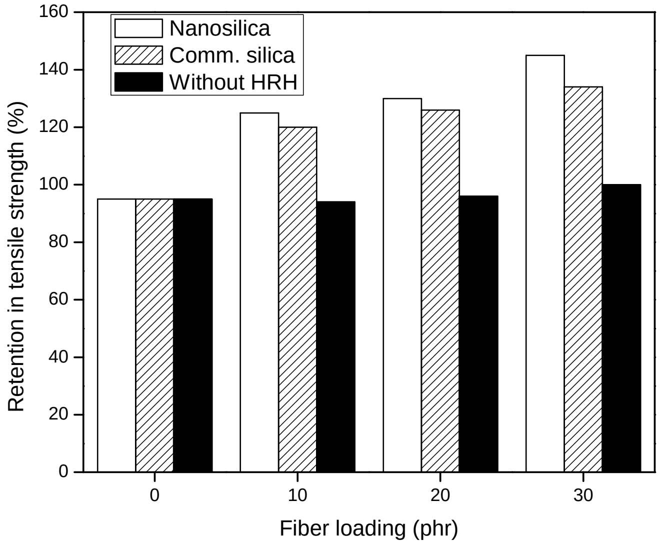

Figure 5B.15. Variation of percentage retention in tensile strength with fiber loading

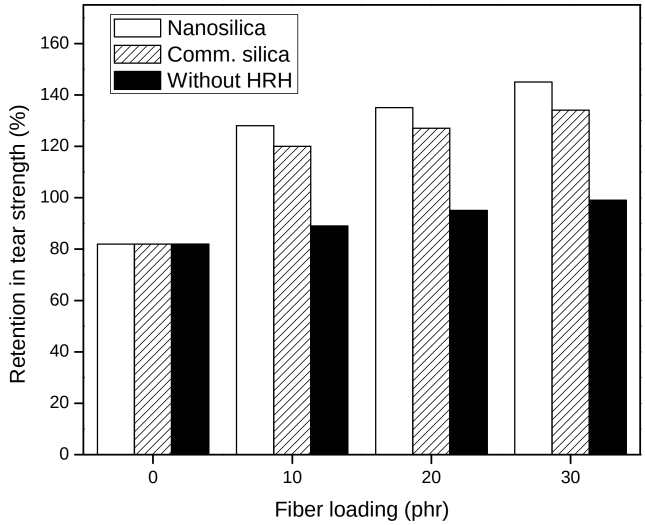

Figure 5B.16. Variation of percentage retention in tear strength with fiber loading

Similar effect in the case of melamine fiber reinforced EPDM rubbers has been reported in earlier [8]. The percentage retention in ageing is higher for nanosilica bonded composites than that of commercial silica for the entire fiber loading. This shows that the efficiency of nanosilica HRH bonding system is better than that of commercial silica HRH dry bonding system in SBR / short Nylon 6 fiber composites.

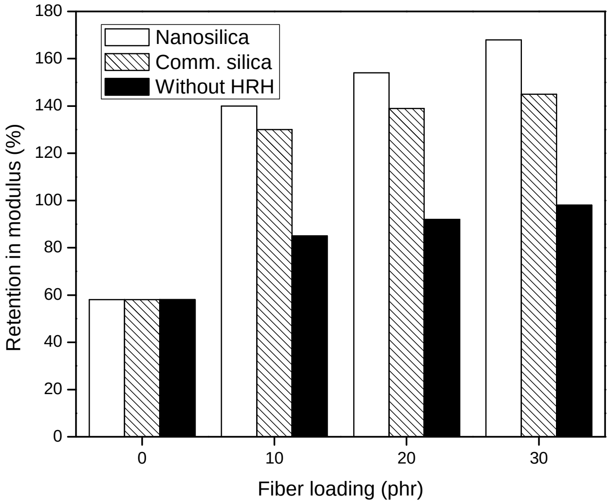

Figure 5B.17. Variation of percentage retention in modulus with fiber loading

5B.4 Conclusions

HRH bonding system in SBR / Nylon 6 short fiber composites causes a significant improvement in the mechanical properties of the composites. The efficiency of HRH bonding system in SBR / Nylon 6 short fiber composite is increased in the presence of synthesized nanosilica. Tensile strength, tear strength, modulus and abrasion resistance are increased by the use of nanosilica HRH system which shows that the interfacial adhesion between the fiber and matrix is improved in the presence of nanosilica. Compression set and resilience are adversely affected by the use of nanosilica based HRH bonding system. The composites show anisotropy in mechanical properties. Ageing of the composite at

70°C for 72 hr causes an increase in the tensile strength, tear strength and modulus in the presence of the dry bonding system. The improvement in properties by ageing is due to the improved fiber-matrix attachment. The retention in ageing is better for nanosilica composites.

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Chapter 6

Cure Characteristics and Mechanical Properties of Nanosilica / Short Nylon 6 Fiber Elastomeric Hybrid Composites

Part – A

NATURAL RUBBER BASED HYBRID COMPOSITES

Contents

6A.1 Introduction

Short fiber reinforced composites are finding ever-increasing applications in engineering and consumer products. Short fibers are used in order to improve or modify certain thermo mechanical properties of the matrix for specific applications or to reduce the cost of the fabricated article. The degree of reinforcement by the short fibers is governed largely by the fiber concentration, fiber aspect ratio, fiber adhesion to the matrix, fiber orientation and its dispersion in the matrix [1-5]. Many researchers have studied the effect of different fibers in natural and synthetic rubbers [6-8]. Murty and De reported the effect of bonding agents on short silk fiber reinforced natural rubber based composites [9]. Sreeja *et al.* studied the cure characteristics and mechanical properties of natural rubber / short Nylon 6 fiber composites [10]. The reinforcement of rubbers using particulate fillers such as carbon black or precipitated silica has also been studied at length [11-14]. Murty *et al.* [15] also reported the effect of particulate fillers on the processing characteristics and physical properties of jute fiber reinforced natural rubber composites. In all these studies they have used conventional precipitated silica with particle size in microns [16-20]. As small particles have higher surface area, nanosilica can be more effective in improving the properties of the hybrid composites. However hybrid composites based on particulate fillers, fiber and rubber matrices have not yet received much attention.

In this work the effect of nanosilica as reinforcement in short Nylon 6 fiber / natural rubber hybrid composites containing HRH dry bonding system is reported. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler. The cure and mechanical properties of nanosilica / short Nylon 6 fiber/natural rubber hybrid composites are presented.

6A.2 Experimental

Table 6A.1 Formulation of mixes

Mix No.		Ingredients (phr)+			
		Nylon 6	**Nanosilica**	**Commercial silica**	**HRH***
A series	A_0	-	-	-	-
	A_{10}	10	-	-	1.67
	A_{20}	20	-	-	3.33
	A_{30}	30	-	-	5
B series	B_0	-	3	-	-
	B_{10}	10	3	-	1.67
	B_{20}	20	3	-	3.33
	B_{30}	30	3	-	5
C series	C_0	-	6	-	-
	C_{10}	10	6	-	1.67
	C_{20}	20	6	-	3.33
	C_{30}	30	6	-	5
D series	D_0	-	9	-	-
	D_{10}	10	9	-	1.67
	D_{20}	20	9	-	3.33
	D_{30}	30	9	-	5
E series	E_0	-	-	6	-
	E_{10}	10	-	6	1.67
	E_{20}	20	-	6	3.33
	E_{30}	30	-	6	5

* Hexa:Resorcinol:Silica in the ratio 2:2:1. Total loading was 16% on fiber content.

+ phr- parts per hundred rubber.

Natural rubber-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3-dimethylbutyl)N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes.

Formulation of the test mixes is given in the table 6 A.2.1. Method of preparation and procedure adopted for the determination of cure characteristic and mechanical properties of the mixes are given in chapter 2.

6A.3 Results and Discussion

6 A.3.1 Cure characteristics

Variation of minimum torque with fiber loading at various silica contents are shown in figure 6 A.1. The minimum torque increases with fiber loading and nanosilica content for all the mixes, indicating that the processability becomes more energy intensive by the introduction of fiber and silica. Mixes B, C and D show higher viscosity than mix E. The higher viscosity of the nanosilica composites may be due to the better interaction between nanosilica and the rubber matrix. Lower particle size silica has higher surface area and hence can have improved interactions.

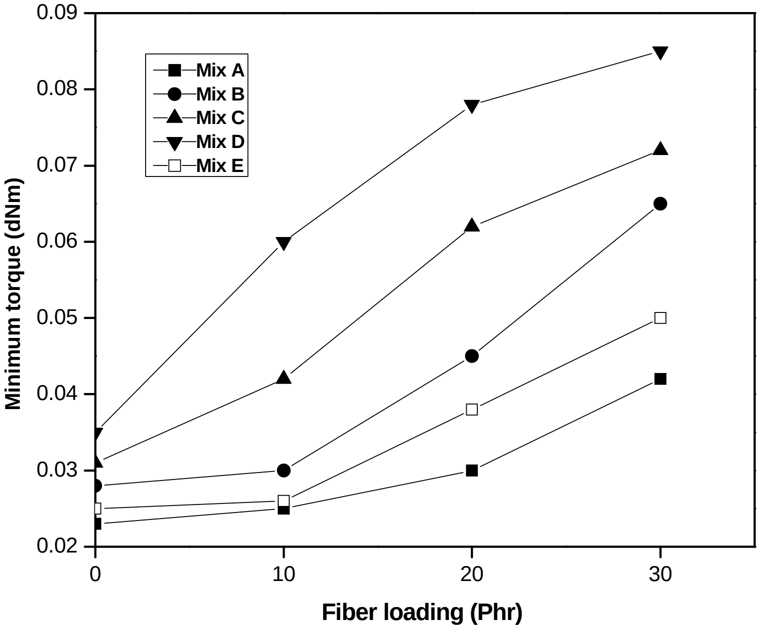

Figure 6A.1. Variation of minimum torque with fiber loading

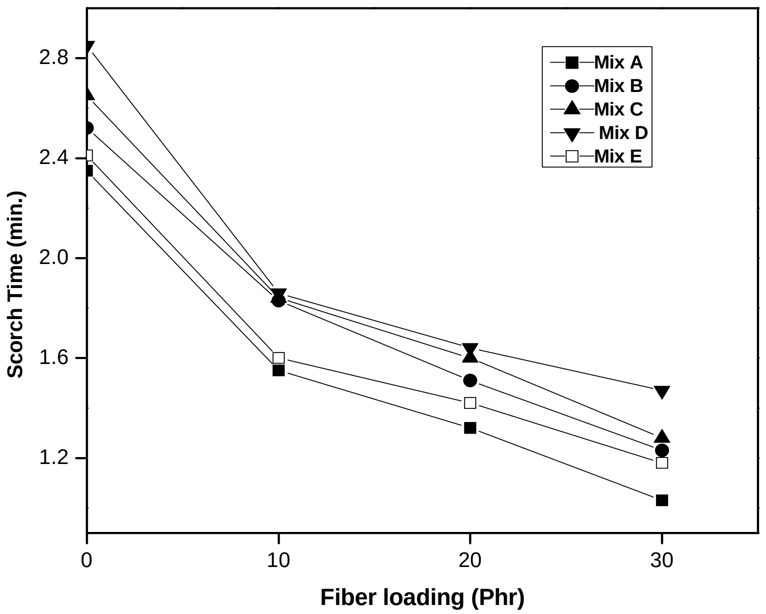

Figure 6A.2. Variation of scorch time with fiber loading

Figure 6 A.2 gives the variations of scorch time with silica content and fiber loading. Scorch time increases with silica content and decreases with fiber loading for all the mixes. Scorch time increases from 2.35 minute to 2.85 minute by the addition of 9 phr nanosilica in the gum compound (mixes A_0 to D_0). By the introduction of 9 phr silica in 10 phr fiber loaded sample the scorch time increases to 1.86 minutes from 1.55 minutes. Similar increments shown by 20 phr and 30 phr fiber loaded samples are from 1.32 minutes to 1.64 minutes and from 1.03 minutes to 1.47 minutes, respectively. The delayed start of cure reaction in the presence of silica may be attributed to the possible interaction of the silica with the accelerators, making it unavailable for cure reaction. Scorch time decreases from 2.35 minutes at 0 phr fiber loading to 1.47 minutes at 30 phr fiber loading for mix A (without silica). This indicates that nylon fiber has an accelerating effect on cure reaction. Similar results in the case of short nylon fiber reinforced NBR composite containing an epoxy-based bonding agent have been reported earlier [21].

Cure time increases with fiber content and silica loading for all the mixes (Fig.6 A.3). This may be due to the interaction of silica with the accelerators.

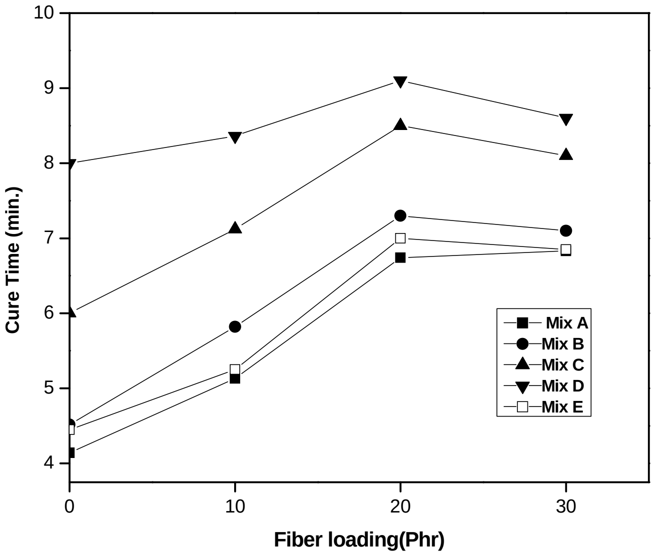

Figure 6A.3. Variation of cure time with fiber loading

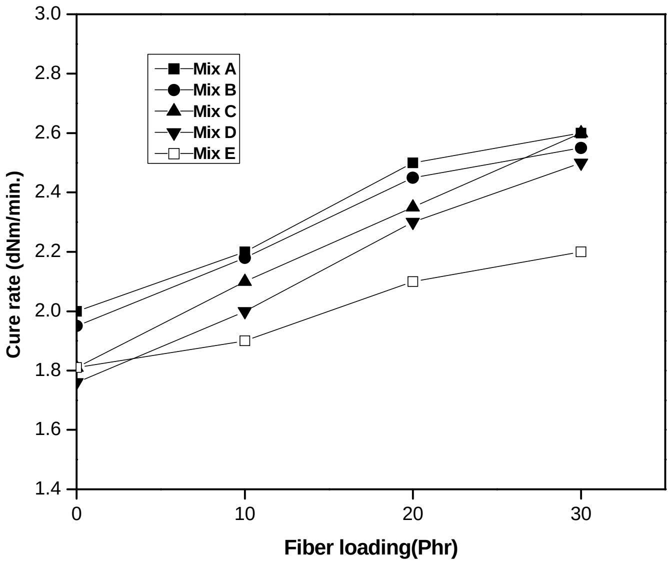

Figure 6A.4. Variation of cure rate with fiber loading

Figure 6 A.4 shows the rate of cure reaction with silica content and fiber loading. Cure rate increases with fiber loading and decreases with silica content. Increase in cure rate with fiber content is due to the accelerating effect of nylon fiber on the cure reaction. Decrease in cure rate with silica content may be due to the interaction of silica with the accelerators. The differential torque i.e., the difference between the minimum and maximum torque developed during cure is increased with fiber loading and silica content and it is higher for nanosilica composite (Fig.6A.5).

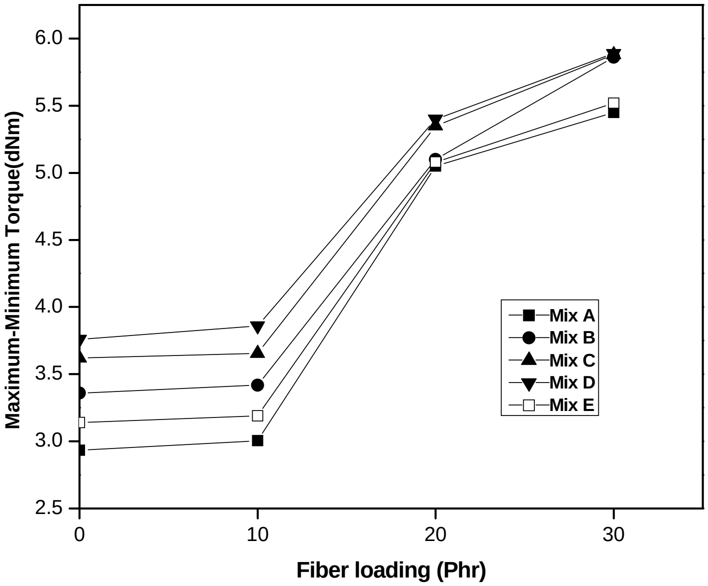

Figure 6A.5. Variation of differential torque with fiber loading

The differential torque is a measure of the extent of the cross link formation and the filler–matrix interaction. The higher values for the nanosilica compounds indicate that the matrix is more restrained. This is evident from the V_r values of the mixes. Figure 6.A.6 shows that V_r of the nanosilica-containing mixes is higher than that of commercial silica composite for all the mixes. This may be arising from improved silica-matrix interaction.

Nanosilica can interact better with the matrix due to their higher surface area. Volume fraction, V_r, increases with fiber loading, as expected. In the presence of fibers, the matrix gets more restrained and the diffusion of the solvent becomes limited.

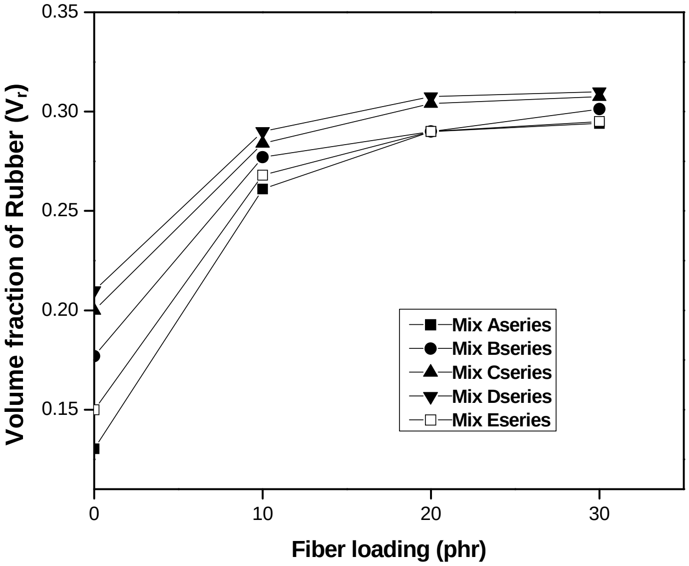

Figure 6A.6. Variation of volume fraction of rubber with fiber loading

6A.3.2 Mechanical properties

The tensile strength increases with fiber content with an initial minor drop at 10 phr fiber loading (Fig.6 A.7). This drop may be due to the dilution effect of the fibers at lower loadings [9, 22,]. At higher fiber loadings, however, the reinforcing effect takes over, resulting in an improved ultimate strength. At any fiber content the tensile strength is higher for the nanosilica filled samples. For the gum compound containing no fiber, the improvement is 13%, while for the 30 phr fiber-filled sample, 31 % improvement in tensile strength is obtained with 6 phr nanosilica. This may be attributed to better chances of interaction between the fiber and the matrix through silica surface. Silica is also known to improve the wetting of short fibers in natural rubber matrix [9]. Series E is the mixes containing 6 phr of conventional silica instead of nanosilica. It shows tensile strength values almost equal to the mixes without silica (Mix A). This implies that the nanosilica is better in improving the wettability of the short fibers, and thus improving the tensile strength.

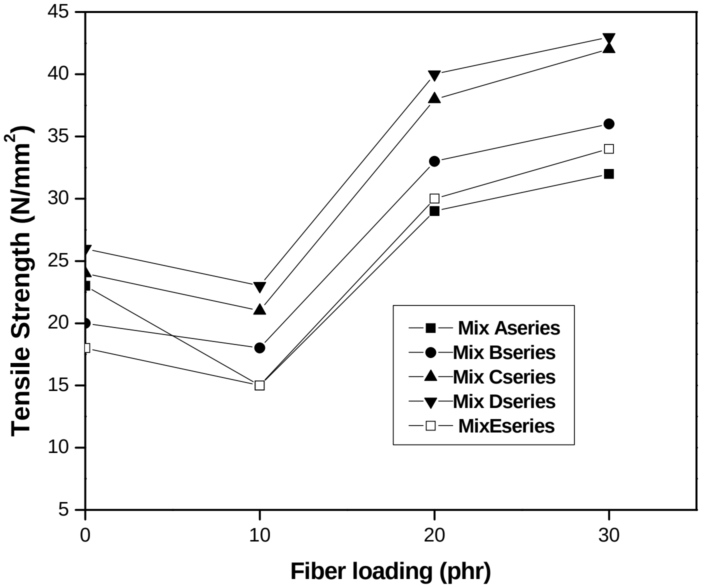

Figure 6A.7. Variation of tensile strength with fiber loading in longitudinal direction

SEM studies of the tensile fractured samples also support this view. Figures 6 A.8. (a) and (b) show the tensile fracture surfaces of the mixes C_{10} and C_{30}, respectively. Fiber surface is not smooth. Matrix is adhered on to the fiber surface. Fiber ends are seen to be broken. This indicates that there is a strong bond existing between the fiber and the matrix. Figures 6 A.8.(c) and (d) are the micrographs of the tensile fracture surface of samples containing commercial silica (Mixes E_{10} and E_{30}, respectively). The fibers are pulled out from the matrix. No resin is adhered on to the fiber surface, as the bond is not as strong as in the case of nanosilica.

For the samples with fibers oriented in the transverse direction (fibers oriented perpendicular to the direction of application of force), the variation is shown in figure 6.A.9. In all the cases, the tensile strength drops to a very low value and shows only a marginal recovery at 30 phr of fiber loading. With increasing silica content (Series A-E), the improvement is also very limited. The transverse orientation of fibers is not effective in supporting the load.

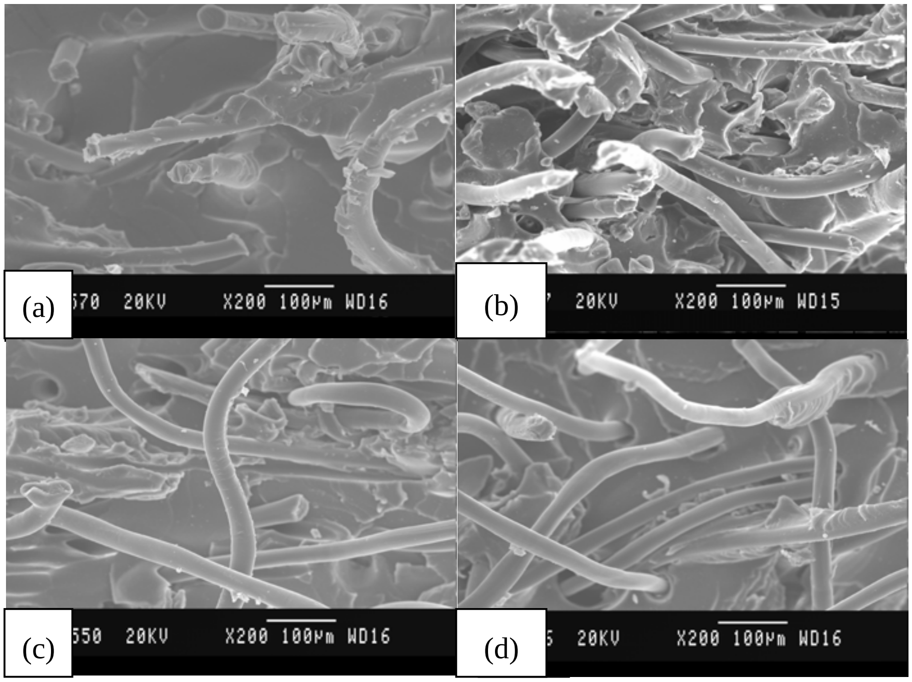

Figure 6A.8. Scanning Electron Micrographs of (a) Mix $C_{10,}$ (b) Mix C_{30}, (c) Mix E10,(d) Mix E_{30}

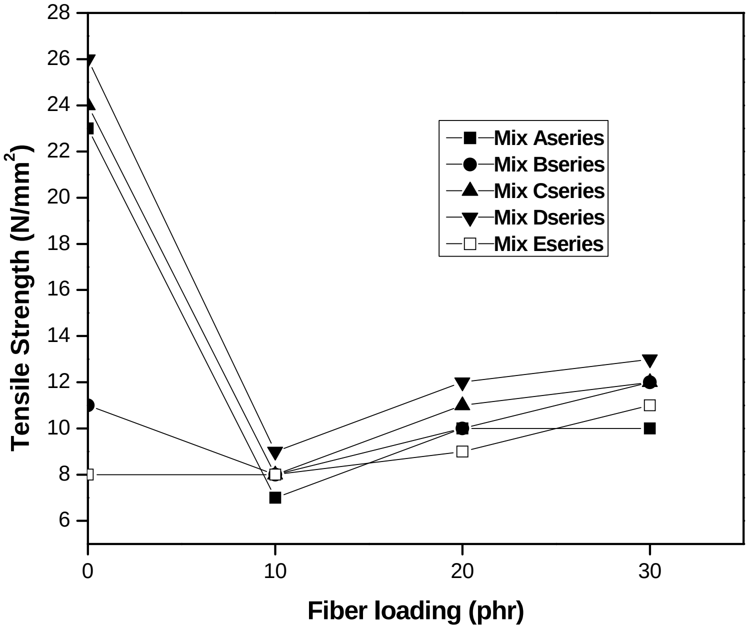

Figure 6A.9. Variation of tensile strength with fiber loading in transverse direction

The variation of tear strength with fiber loading is shown in figure 6 A.10. The tear strength registers a tremendous increase in the presence of short fibers. Tear strength increases from 43 N/mm to 106 N/mm by the addition of 30 phr fiber in the case of mix A. With nanosilica, the tear strength is further improved consistently for all the mixes. For 30 phr fiber loading the tear strength is improved from 106 to 118 N/mm in the presence of 6 phr of nanosilica. With the conventional silica the corresponding improvements in the tear strength is only 108 N/mm.

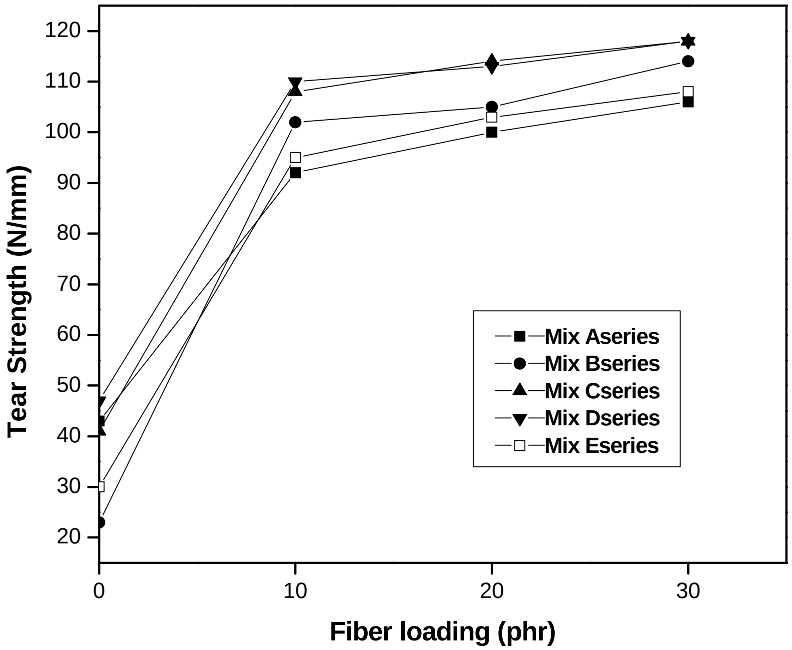

Figure 6A.10. Variation of tear strength with fiber loading in longitudinal direction

For transverse orientation of fibers, the variation of tear strength is shown in figure 6.A.11. The tear strength is improved to 81 N/mm with 30 phr fibers without added nanosilica filler. Incorporation of 6 phr of nanosilica raises the tear strength to 99 N/mm for 30 phr fiber loaded sample. For the commercial silica (Series E), the improvement is limited.

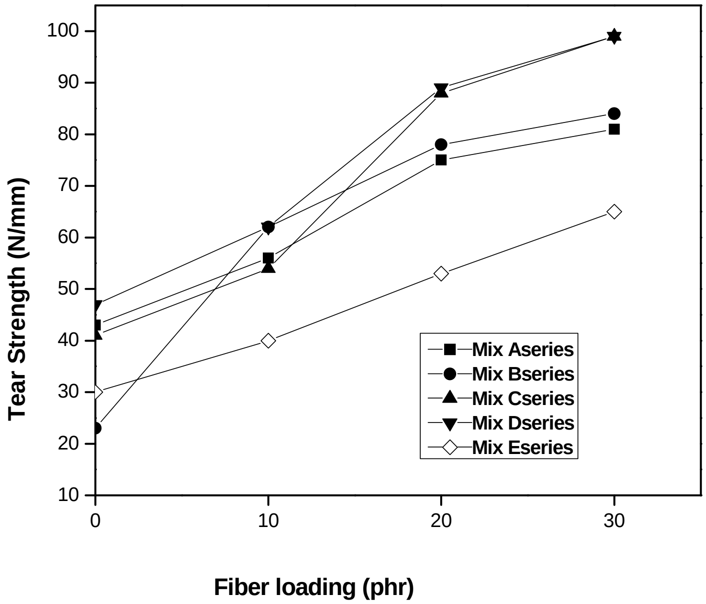

Figure 6A.11. Variation of tear strength with fiber loading in transverse direction

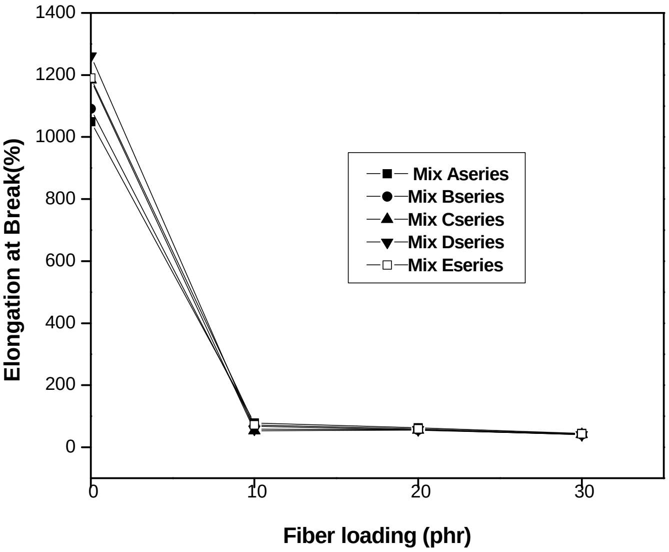

Figure 6A.12. Variation of elongation at break with fiber loading in longitudinal direction.

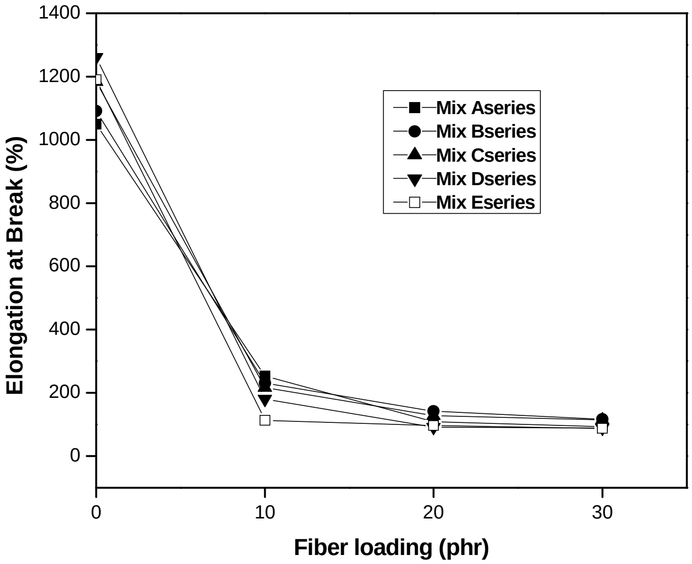

Figure 6A.13. Variation of elongation at break with fiber loading in transverse direction

Figures 6 A.12 and 6 A.13 show the variation of elongation at break with fiber loading in longitudinal and transverse directions, respectively. In both the cases there is a sudden drop in elongation at break with 10 phr fiber loading and after that it remains more or less constant with increase in fiber loading. With fibers distributed uniformly, the matrix becomes more restrained and hence fracture occurs at lower strains. The presence of silica does not seem to have a significant effect on the elongation at break of the fiber filled samples.

There is marked improvement in modulus values with added silica filler (Fig. 6 A.14). By the addition of 9 phr nanosilica, the modulus values increase by 55%, 33% and 28%, respectively for 10 phr, 20 phr and 30 phr fiber loaded samples. It indicates that the silica filler is very effective in improving the filler –matrix interaction. The Mixes A_0, B_0, C_0 and D_0 show very low modulus values. The silica improves the modulus only in the presence of fibers. Commercial silica mixes shows that the modulus values are lower than that of the mixes containing 3 phr nanosilica. The decrease in particle size of silica increases the modulus values of the composite. Similar trends also observed in the transverse direction (Fig. 6 A.15).

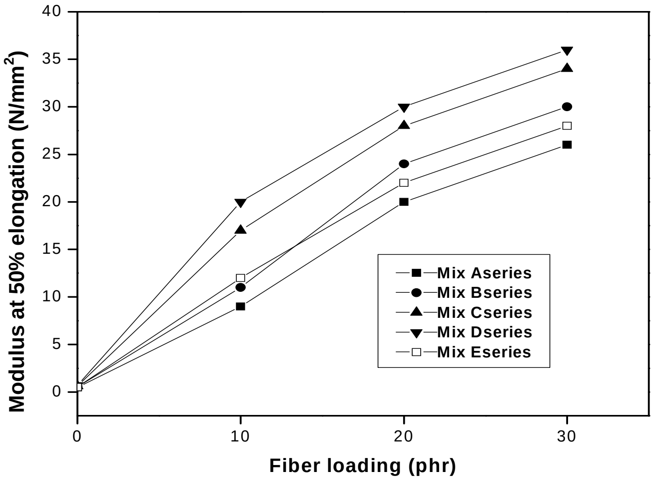

Figure 6A.14. Variation of modulus with fiber loading in longitudinal direction

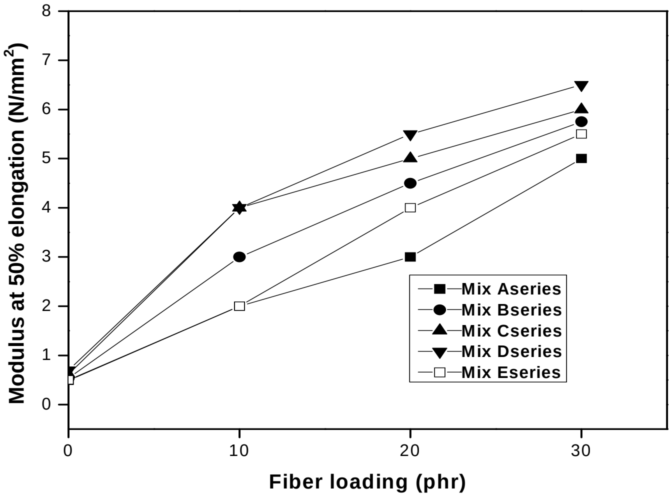

Figure 6A.15. Variation of modulus with fiber loading in transverse direction

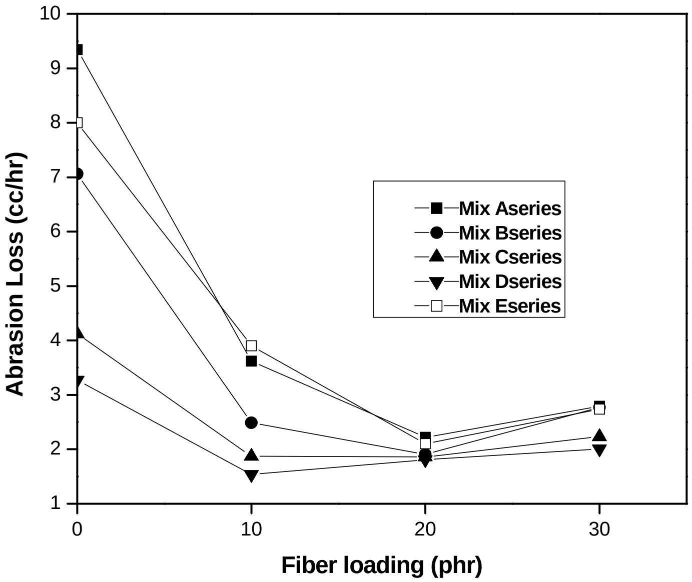

Figure 6A.16. Variation of abrasion loss with fiber loading

Variation of abrasion loss of mixes A-E is shown in figure 6 A.16. There is a drastic fall in the abrasion loss with increasing fiber loading. By the introduction of just 10 phr of fibers, the loss is reduced to approximately 50% in all the cases. With increasing loading of nanosilica, there is further reduction in the abrasion loss at any fiber loading. The composites containing commercial silica (Series E) show an abrasion loss almost equal to that of gum matrix, which is significantly higher than that of the nanosilica series. This is because of more restrained matrix of composite. During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case the presence of strong interfacial adhesion between the fiber and the matrix renders the matrix stiffer and lowers the abrasion loss.

Figure 6 A.17 shows the compression set of different mixes. Compression set increases with silica content and fiber loading. By the addition of 9 phr silica to the zero fiber loaded samples (Mix A_0-D_0), the compression set is increased to 27 %

and by the addition to 30 phr fiber filled samples (Mix D_{30}), it becomes 57 %. In the presence of reinforcing fillers, the viscoelastic dissipation of energy at the filler –matrix interface is increased.

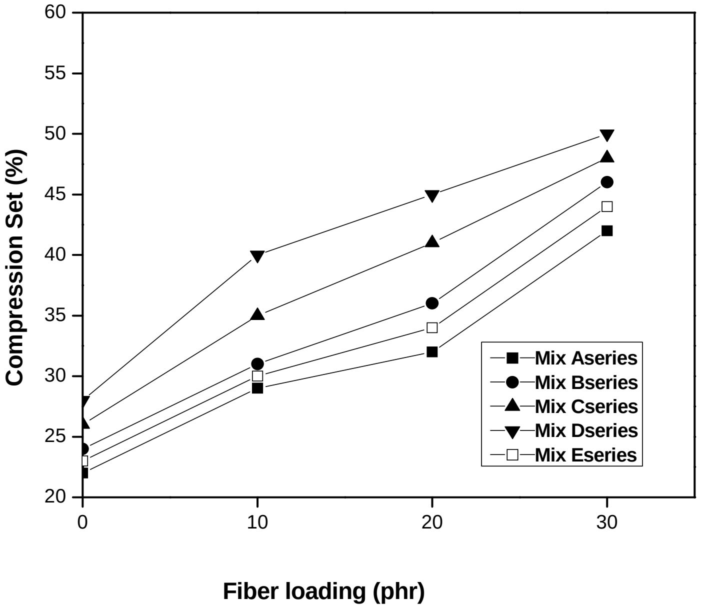

Figure 6A.17. Variation of compression set with fiber loading

At the elevated temperature of compression test, the matrix becomes soft and undergoes irreversible flow resulting in incomplete recovery on removal of the applied stress. This gives rise to higher compression set values in the case of reinforced matrices. In the presence of the nanosilica, the reinforcement is further enhanced and hence the viscoelastic dissipation is also more. This gives rise to higher compression set in the case of nanosilica composites. Hardness, as expected, is higher for the fiber- filled samples (Fig.6 A.18). With nanosilica the hardness is further enhanced. The resilience, an indication of the material elasticity, decreases with fiber loading and silica content for all the mixes, as expected (Fig.6 A.19).

Resilience shows a reduction from 75% at 0 phr fiber loading to 48 % at 30 phr fiber loading (Series A). With increasing silica content, the resilience is further reduced. With 9 phr nanosilica, the resilience of the 30 phr fiber loaded samples is lowered to 44 %. The dissipation of energy at the fiber-matrix interface results in lower resilience of the composites. With a lesser reinforcing commercial silica, the reduction in resilience is only marginal.

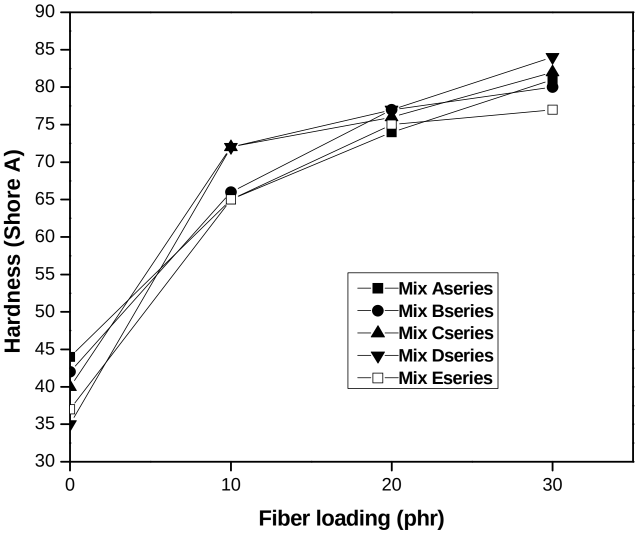

Figure 6A.18. Variation of hardness with fiber loading

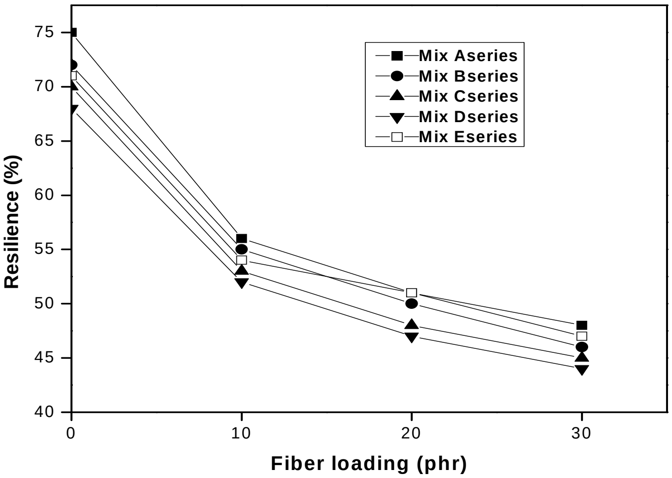

Figure 6A.19. Variation of resilience with fiber loading

6A.3.3 Ageing resistance

Ageing of the composite at 70^{o} C for 72 hours causes a marginal increase in mechanical properties of the hybrid composites (Fig.6 A.20 - Fig.6 A.22).This may be due to the improved fiber-matrix attachment by ageing. Similar effect has been reported in earlier [16].

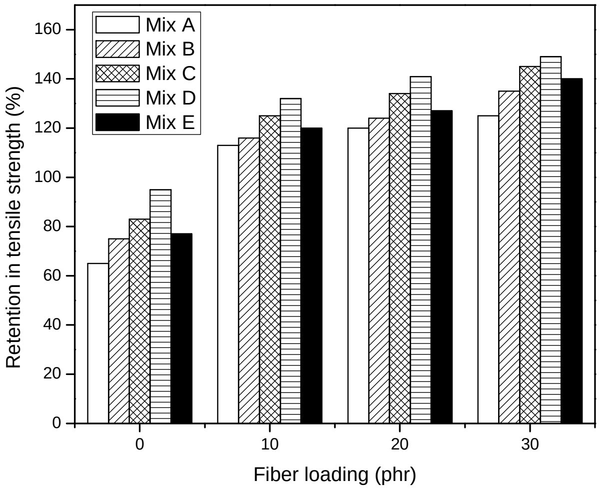

Figure 6A.20. Variation of percentage retention in tensile strength with fiber loading

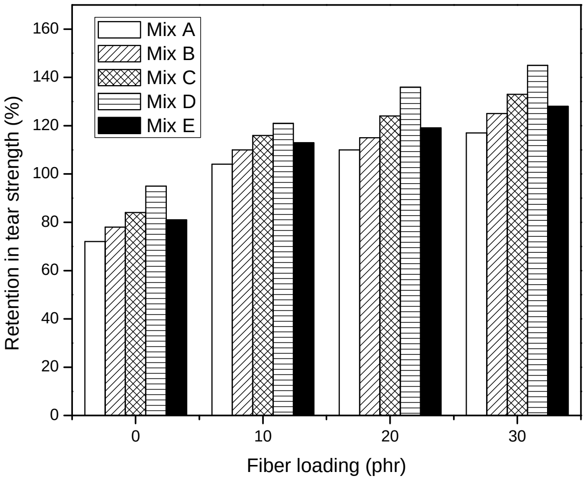

Figure 6A.21. Variation of percentage retention in tear strength with fiber loading

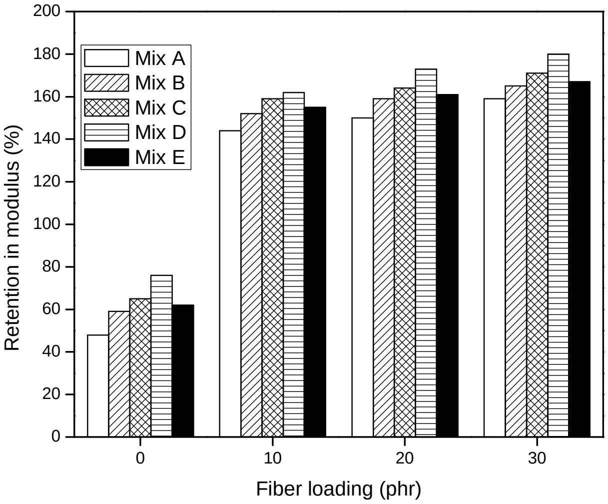

Figure 6A.22. Variation of percentage retention in modulus with fiber loading

The percentage retention in ageing is higher for nanosilica composites than that of commercial silica for all the fiber loading. This may be arising from a better interaction of nanosilica with the matrix.

6A.4. Conclusions

Cure and mechanical properties of natural rubber /short Nylon 6 fiber composite are improved by the introduction of nanosilica in the composites. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading and increases with silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Longitudinally oriented fiber composites have superior properties than transversely oriented ones. Volume fraction of rubber, a measure of the cross link density, in a solvent-swollen sample increases with nanosilica. Ageing resistance also better for nanosilica filled hybrid composites than that of commercial silica.

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Part – B

NITRILE RUBBER BASED HYBRID COMPOSITES

Contents

6B.1 Introduction

Nitrile rubber (NBR) is a special - purpose synthetic rubber having excellent oil and gasoline resistance due to the presence of polar acrylonitrile group. It is widely used in oil delivery hoses, gaskets, diaphragms and sealants. Because of its low gum strength and poor mechanical properties, NBR is usually reinforced with fillers. Synthetic fibers like glass, rayon, nylon, aramid and asbestos have been used by a number of scientists in natural and various synthetic rubbers and resins [1-11]. Short Nylon fibers with good strength make an excellent reinforcing material for NBR. Short fiber reinforced NBR composites were studied by Yoshiki and Sreeja [12-13]. Seema *et al.* also studied the effect of an epoxy-based bonding agent on the cure characteristics and mechanical properties of short nylon fiber reinforced NBR composite [6]. Thermal degradation of melamine fiber reinforced NBR composite was studied by Rajeev *et al.* [8]. Wazzan [11] studied the physico-mechanical properties of EPDM/ nylon 6 short fiber composite. Wang *et al.* [14] found that Nitrile rubber exhibited the highest interaction with silica probably through the hydrogen bond between the - CN group and silanol groups.

In this work the effect of nanosilica as reinforcement in short Nylon 6 fiber / Nitrile rubber hybrid composites containing HRH dry bonding system is reported. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler. The cure and mechanical properties of nanosilica/Nylon 6 short fiber/NBR hybrid composites are evaluated.

6B.2 Experimental

Formulation of the test mixes is given in the table 6 B.1 Method of preparation and procedure adopted for the determination of cure characteristic and mechanical properties of the mixes are given in the chapter 2.

Table 6B.1. Formulation of mixes

Mix No.		Ingredients (phr)$^+$			
		Nylon 6	Nanosilica	Commercial silica	HRH*
A series	A_0	-	-	-	-
	A_{10}	10	-	-	1.67
	A_{20}	20	-	-	3.33
	A_{30}	30	-	-	5
B series	B_0	-	3	-	-
	B_{10}	10	3	-	1.67
	B_{20}	20	3	-	3.33
	B_{30}	30	3	-	5
C series	C_0	-	6	-	-
	C_{10}	10	6	-	1.67
	C_{20}	20	6	-	3.33
	C_{30}	30	6	-	5
D series	D_0	-	9	-	-
	D_{10}	10	9	-	1.67
	D_{20}	20	9	-	3.33
	D_{30}	30	9	-	5
E series	E_0	-	-	6	-
	E_{10}	10	-	6	1.67
	E_{20}	20	-	6	3.33
	E_{30}	30	-	6	5

* Hexa:Resorcinol:Silica in the ratio 2:2:1. Total loading was 16% on fiber content.

$^+$ phr- parts per hundred rubber.

NBR-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes.

6B.3 Results and Discussion

6B.3.1 Cure characteristics

Variation of minimum torque with fiber loading at various silica contents are shown in figure 6 B.1. The minimum torque increases with fiber loading and silica content for all the mixes, indicating that the processability of the composite is adversely affected by the introduction of fiber and silica. Mixes B, C and D show higher viscosity than mix E. The higher viscosity of the nanosilica composites may be due to the better interaction between the silica and the rubber matrix. Lower particle size silica has higher surface area and hence can have improved interactions.

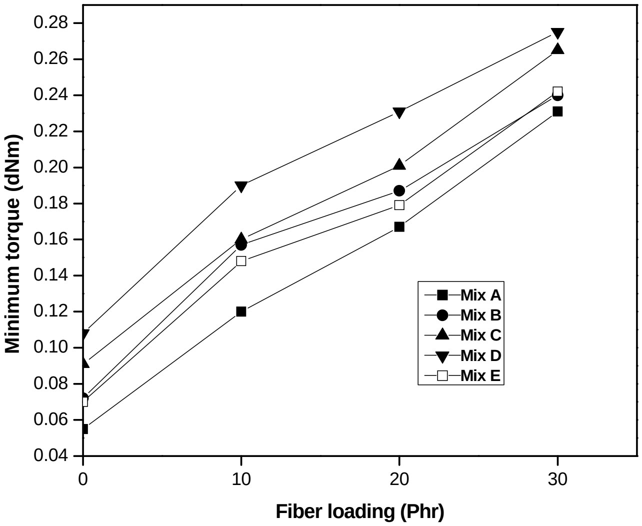

Figure 6B.1. Variation of minimum torque with fiber loading

Figure 6 B.2 gives the variation of scorch time with silica content and fiber loading. Scorch time decreases with fiber loading and silica content for all the mixes.

Scorch time decreases from 3.3 minute at 0 phr fiber loading to 1.7 min. at 30 phr fiber loading for mix A (without silica). This indicates that nylon fiber has an accelerating effect on cure reaction. Similar results in the case of short nylon fiber reinforced NBR composite using an epoxy-based bonding agent have been reported earlier [6].

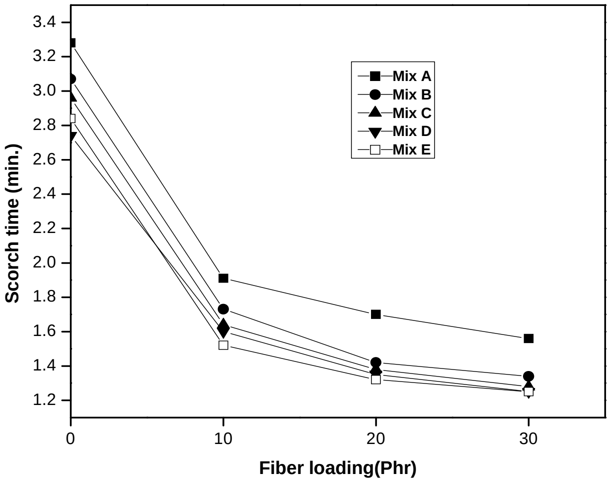

Figure 6B.2. Variation of scorch time with fiber loading

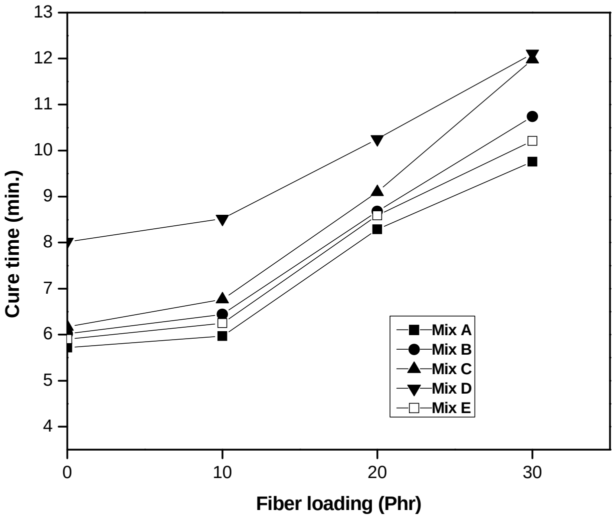

Figure 6B.3. Variation of cure time with fiber loading

Cure time increases with fiber content and silica loading for all the mixes (Fig.6.B.3). Cure time increases from 5.72 minute to 8.02 minute by the addition of 9 phr nanosilica in the gum compound (Mix Ao-Do). This is due to the interaction of silica with the accelerators, making it unavailable for cure reaction and this interaction is found to be more for nanosilica.

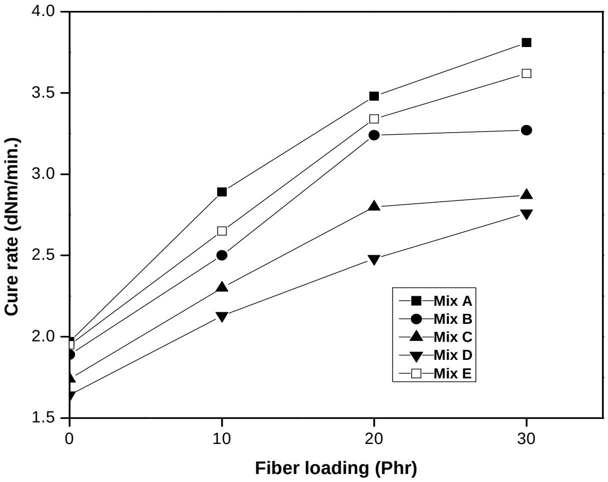

Figure 6B.4. Variation of cure rate with fiber loading

Figure 6 B.4 shows the variation of rate of cure reaction with silica content and fiber loading. Cure rate increases with fiber loading and decreases with silica content. Increase in cure rate with fiber content points to accelerating effect of Nylon on the cure reaction. The silica appears to have some interaction with the accelerators because of which the rate of cure reaction is slowed down.

The differential torque i.e., the difference between the minimum and maximum torque developed during cure is increased with fiber loading and silica content and the effect is higher for nanosilica composites (Fig.6 B.5). The differential torque is a measure of the extent of the cross link formation and the filler–matrix interaction. The higher values for the nanosilica compounds indicate that the matrix is more restrained. This is evident from the V_r values of the mixes.

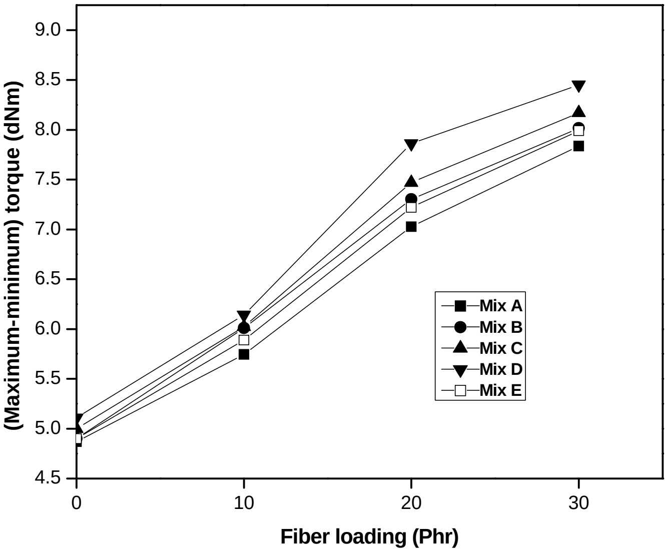

Figure 6B.5. Variation of differential torque with fiber loading

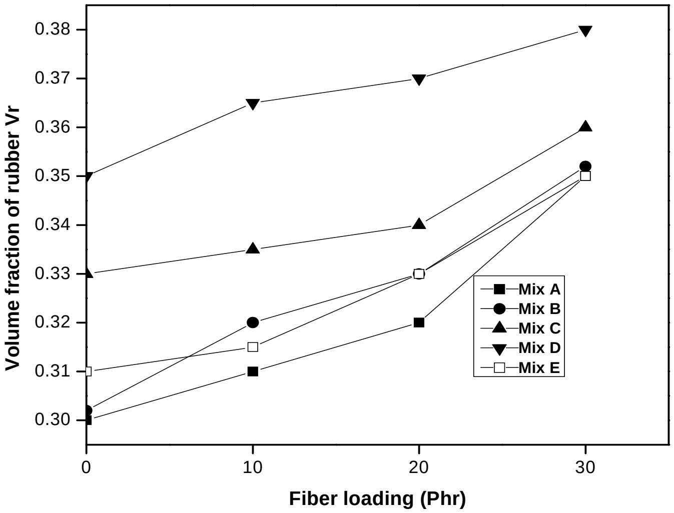

Figure 6B.6. Variation of volume fraction of rubber with fiber loading

Figure 6 B.6 shows that V_r of the nanosilica-containing mixes is higher than that of the commercial silica composite. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix due to their higher surface area.

6B.3.2 Mechanical properties

Figure 6 B.7 shows variation of tensile strength with different fiber loading and silica content. The tensile strength increases significantly for all the mixes.

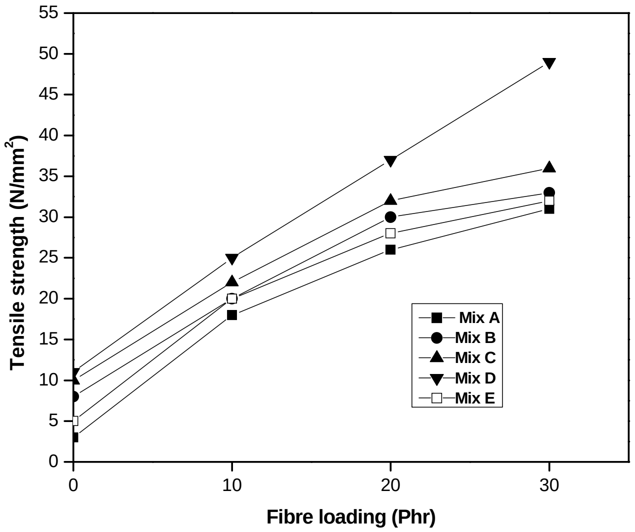

Figure 6B.7. Variation of tensile strength with fiber loading in longitudinal direction

The improvement in tensile strength for 30 phr fiber loaded composites is 58 % in the presence of 9 phr of silica. At 10 phr fiber loading, the improvement is about 38 %. It shows that the efficiency of nanosilica is increased in the presence of short fibers. This may be attributed to better chances of interaction between the fiber and the matrix through silica surface. Silica is also known to improve the wetting of short fibers in the rubber matrix. Mix E contains 6 phr of conventional silica instead of nanosilica. It shows tensile strength values almost equal to that of mixes without silica (Mix A). This implies that the nanosilica has better interaction with the matrix and hence it can improve the tensile strength.

For the samples with fibers oriented in the transverse direction (fibers oriented perpendicular to the direction of application of force), the variation is as shown in figure 6 B.8

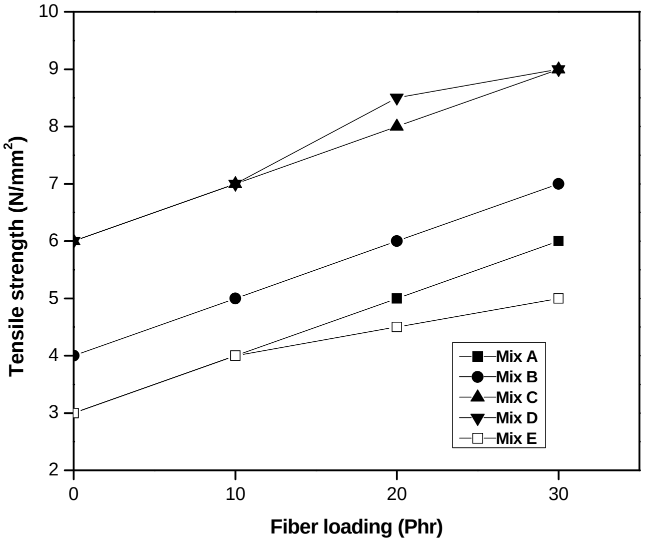

Figure 6B.8. Variation of tensile strength with fiber loading in transverse direction

In all the cases, the tensile strength shows only a marginal improvement at 30 phr fiber loading. With increasing silica content (Mix A-E), the improvement is also limited. The transverse orientation of fibers is not effective in supporting the load. The fibers fail to arrest or deviate crack paths as it propagates through the fiber-matrix interface.

The variation of tear strength with fiber loading is shown in figure 6 B.9. Tear strength increases with silica content and fiber loading for all the mixes. The tear strength is improved from 16 N/mm to 30 N/mm by the addition of 9 phr of nanosilica in the gum compound (without fiber). By the incorporation of 30 phr fiber in the gum mix, the tear strength is improved to 121 N/mm (Mix A_{30}) and by the addition of 6 phr nanosilica in the mix A_{30} the tear strength is increased to 132

N/mm (Mix C_{30}). The tear strength obtained by using commercial silica is only 120 N/mm (Mix E_{30}). It shows the better reinforcing efficiency of the nanosilica

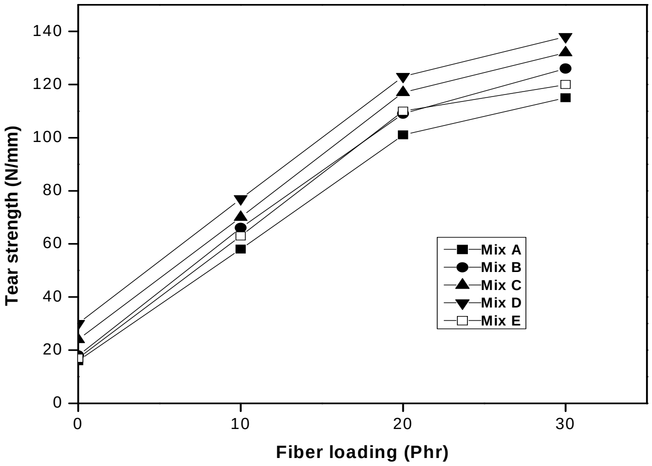

Figure 6B.9. Variation of tear strength with fiber loading in longitudinal direction

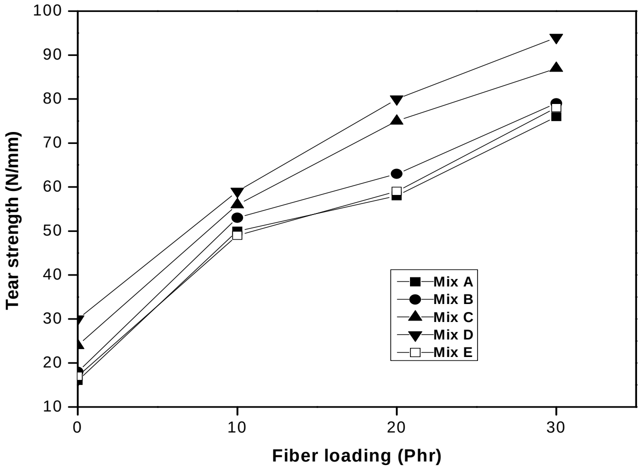

Figure 6B.10. Variation of tear strength with fiber loading in transverse direction

For transverse orientation of fibers, the variation of tear strength is shown in figure 6 B.10. The tear strength is improved to 76 N/mm with 30 phr fibers in the gum compound. Incorporation of 6 phr of nanosilica further raises the tear strength to 94 N/mm. For the commercial silica (Mix E), the tear strength is almost equal to that of gum compounds. Longitudinally oriented fiber composites have superior properties than transversely oriented ones.

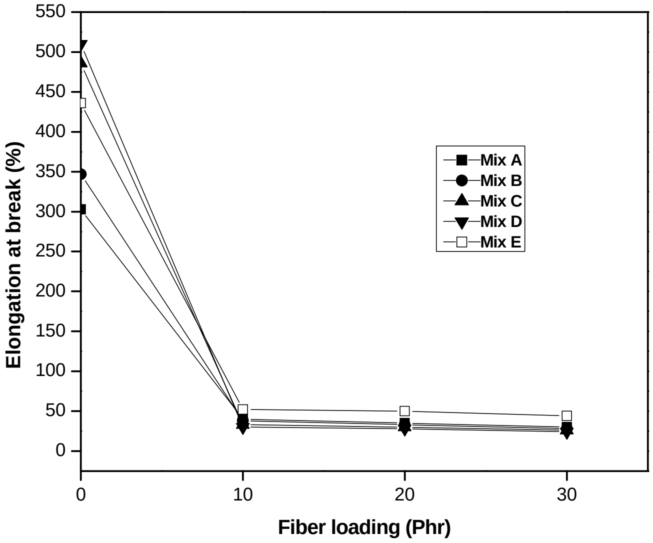

Figure 6B.11. Variation of elongation at break with fiber loading in longitudinal direction

Figure 6 B.11 shows the elongation at break for the mixes. There is a sudden drop at 10 phr fiber loading and then it remains almost constant for all the mixes. With fibers distributed uniformly, the matrix becomes more restrained and hence fracture occurs at lower strains. The presence of silica does not seem to have a significant effect on the elongation at break of the fiber filled samples. The same effect is observed in the transverse direction also (Fig.6 B.12).

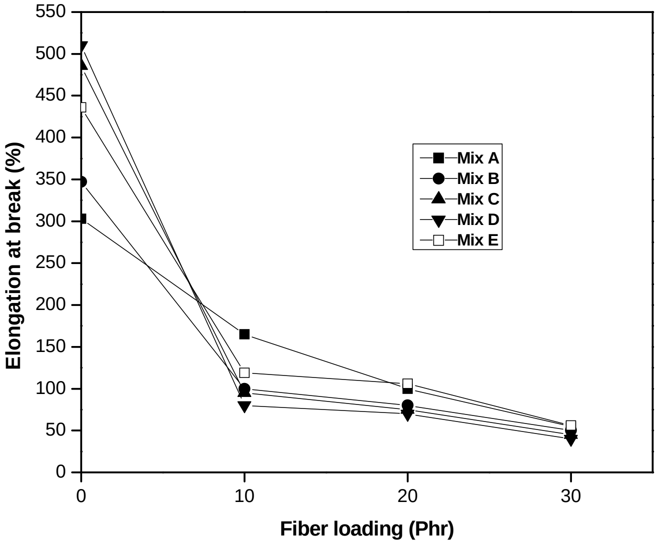

Figure 6B.12. Variation of elongation at break with fiber loading in transverse direction

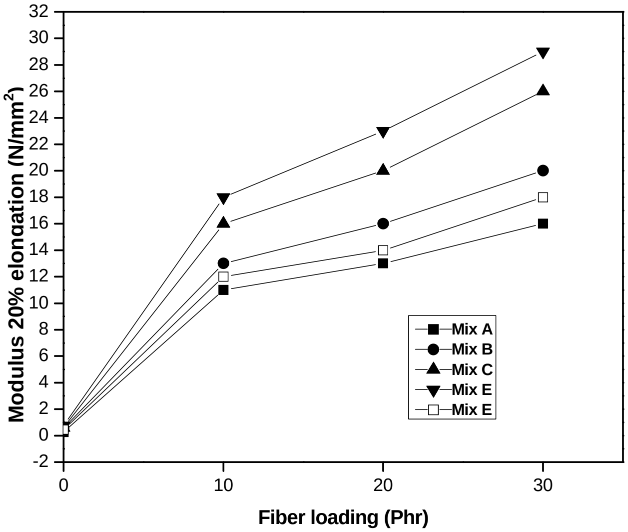

Figure 6B.13. Variation of modulus with fiber loading in longitudinal direction

There is a very good improvement in modulus values with silica content (Fig.6 B 13). By the addition of 9 phr nanosilica, the modulus values increase by 63%, 76% and 81% for 10 phr, 20 phr and 30 phr fiber loaded samples, respectively. It indicates that the silica filler has a significant effect on the modulus value of the hybrid composites. The non-fiber mixes ,containing increasing amounts of silica (Mixes A_0, B_0, C_0 and D_0),show very low modulus values. The silica improves the modulus only in the presence of fibers. Commercial silica mixes show that the modulus values are lower than that of the mixes containing 3 phr nanosilica. The decrease in particle size of silica increases the modulus values of the composite. The same trend is observed in transverse direction also (Fig.6 B.14).

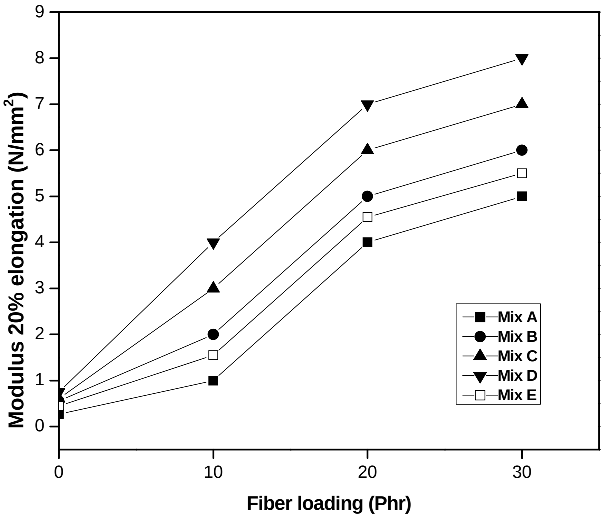

Figure 6B.14. Variation of modulus with fiber loading in transverse direction

Variation of abrasion loss of mixes A-E is shown in figure 6 B.15. There is a fall in the abrasion loss with increasing fiber loading. For mixes B and C the change is very limited. But in the case of 9 phr nanosilica filled samples (Mix D) it significantly decreases with fiber loading. The composites containing commercial silica (Mix E) show an abrasion loss in between that of the gum compound and 3 phr nanosilica mixes. During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case the presence of strong interfacial adhesion between the fiber and the matrix renders the matrix stiffer and lowers the abrasion loss.

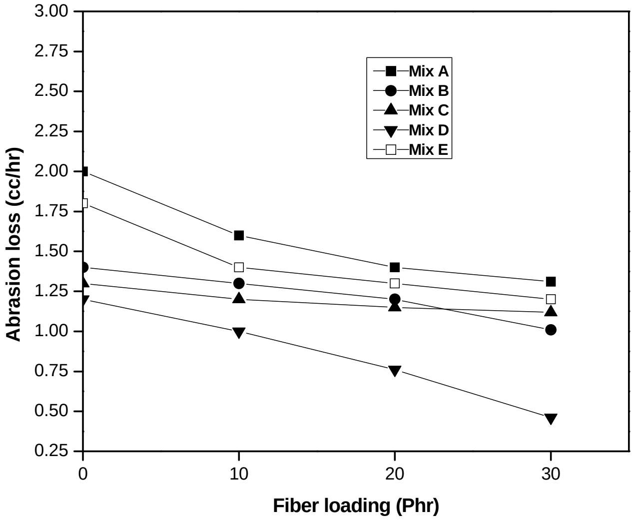

Figure 6B.15. Variation of abrasion loss with fiber loading

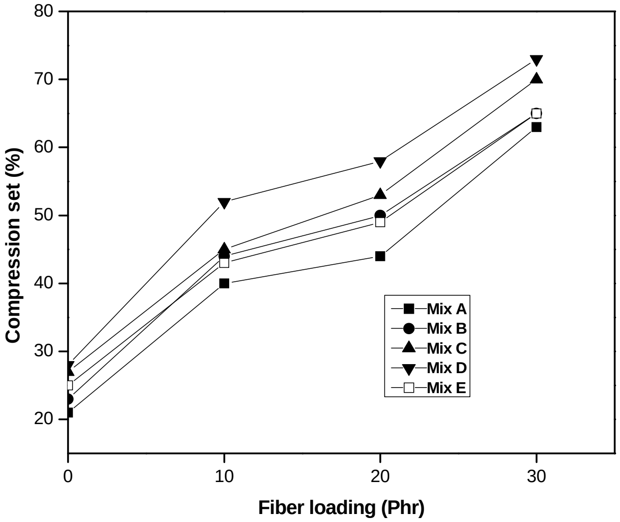

Figure 6B.16. Variation of compression set with fiber loading

Figure 6 B.16 shows the compression set of the different mixes. Compression set increases with silica content and fiber loading. By the addition of 9 phr silica to samples containing no fiber (Mix A_0-D_0), the compression set increases to 33 % and by the addition to 30 phr fiber filled samples (Mix D_{30}), it becomes 247 %.This is due to the reinforcing effect of the silica and the Nylon fiber. The mix E which contains 6 phr commercial silica instead of nanosilica shows the set value almost equal to that of mix B which contains only 3 phr nanosilica.

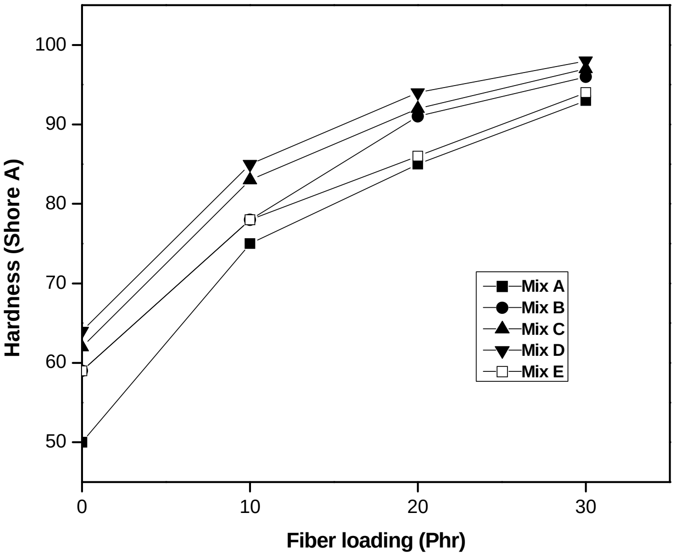

Figure 6B.17. Variation of hardness with fiber loading

Hardness improves significantly with silica content and fiber loading for all the mixes (Fig.6 B.17). With commercial silica, the hybrid composites show only limited increase in hardness. This also points to better efficienty of the nanosilica.

Resilience, an indication of the material elasticity, decreases with silica content for all the mixes (Fig.6 B.18). Incorporation of the fiber also decreases the resilience value. The dissipation of energy at the fiber-matrix interface results in lower resilience values of the composites. Reduction in the resilience of the composite is less for commercial silica filled hybrid composite. Due to the higher surface area of the nanosilica, there will be more interfacial bonds which may undergo changes and breakage leading to more loss and lower resilience.

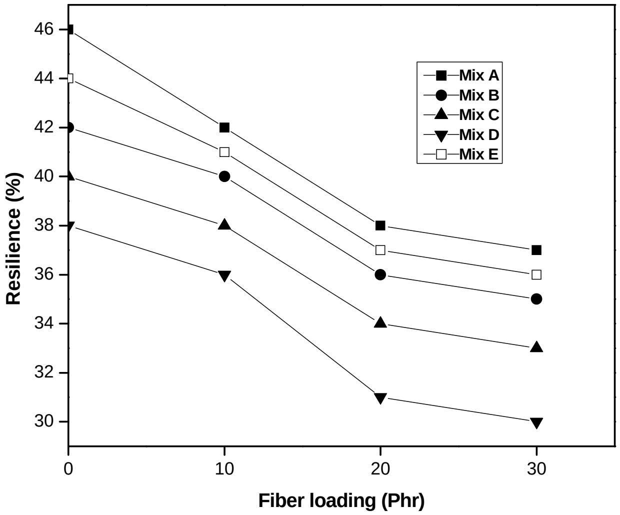

Figure 6B.18. Variation of resilience with fiber loading

6B.3.3 Ageing resistance

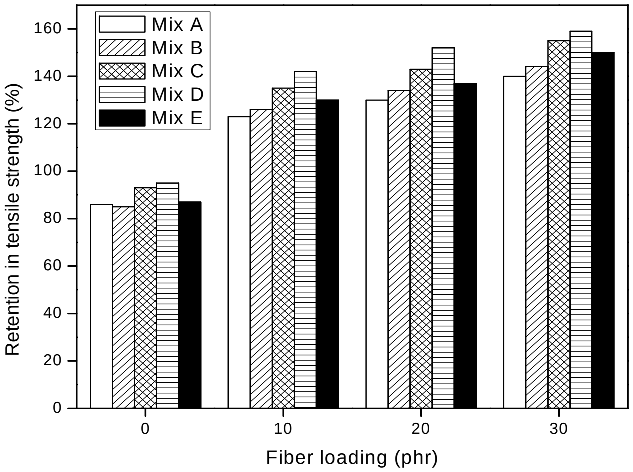

Figure 6 B.19. **Variation of percentage retention in tensile strength with fiber loading**

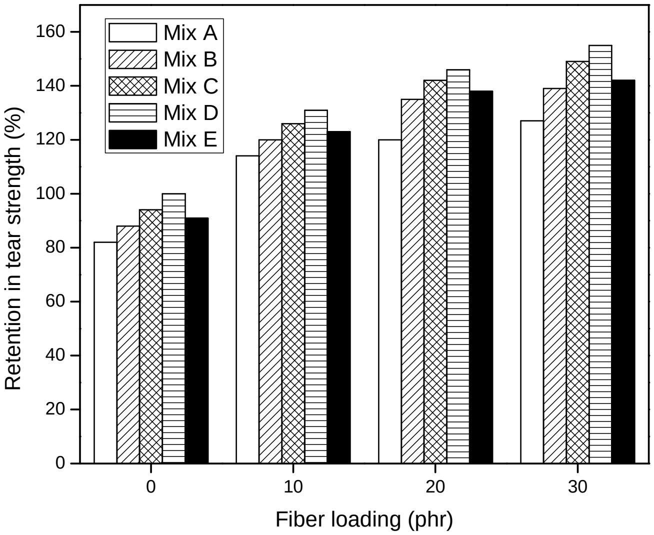

Figure 6B.20. Variation of percentage retention in tear strength with fiber loading

Percentage retention in tensile strength (Fig.6 B.19), tear strength (Fig. 6 B.20) and modulus (Fig.6 B.21) of the composites is improved substantially on the introduction of fibers and is further increased with the nanosilica content.

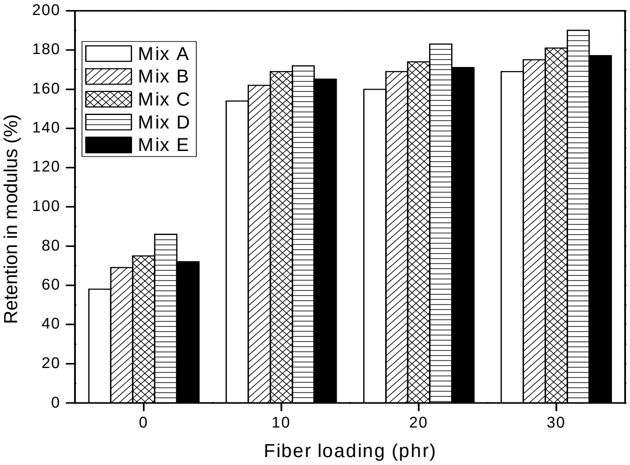

Figure 6B.21. Variation of percentage retention in modulus with fiber loading

The mechanical properties of the composite without fiber is deteriorated after ageing. All the fiber -containing hybrid composite show more than 100% retention in the mechanical properties. This is due to the better fiber- matrix interface formation during ageing. The percentage retention in ageing is higher for nanosilica composites than that of commercial silica for all the fiber loading. This is due to the better interaction of nanosilica with the matrix and hence improves the fiber-matrix adhesion better than that of commercial silica.

6B.4 Conclusions

Nitrile rubber /short Nylon 6 fiber composite shows a very good improvement in cure and mechanical properties by the introduction of nanosilica. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading and silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Hybrid composites show anisotropy in mechanical properties. Volume fraction of rubber in a solvent-swollen sample increases with nanosilica. Retention in ageing is improved with fiber loading and it is better for nanosilica- filled hybrid composites.

6B.5 References

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Part – C

STYRENE BUTADIENE RUBBER BASED HYBRID COMPOSITES

Contents

6C.1 Introduction

Short- fiber- reinforced polymers were developed largely to fill the property gap between continuous fiber laminates used as primary structures by the aircraft and aerospace industry and unreinforced polymers used largely in non-load bearing applications. In some respects the short fiber systems couple advantages from each of these property bounding engineering materials. Short-fiber-reinforced rubber composites have attracted much attention because of better processability, improved physical and mechanical properties and economic advantage. SBR is much like natural rubber in most of its properties and the lowest-cost and highest-volume elastomer available. In some properties like heat build up and tackiness, SBR is inferior to those of NR. Abrasion resistance and resistance to degradation under heat are better for SBR than NR. The major draw back of SBR is its poor gum strength. Reinforcing SBR with short Nylon fibers will improve its mechanical properties. SBR is widely used in the production of tyres, moulded goods, floorings, belting and hose, etc. Many researches have studied the effect of different fibers in styrene butadiene rubbers. Dielectric properties and interfacial adhesion of short sisal fiber reinforced SBR composite were studied by Kumar *et al.* [1-2]. Ismail [3] studied the effect of the adhesion system on the physico-mechanical and electric properties of SBR/polyester short fiber composite. Radiation vulcanization of short carbon fiber /SBR composites was studied by Abdul-

Aziz *et al.* [4]. Sreeja and Kutty [5] reported the effect of a urethane resin based bonding agent on styrene-butadiene rubber- whole tire reclaim -short nylon fiber composites. Hybrid composites based on SBR/ polyester short fiber/ carbon black are studied by Ward [6 - 7].

In this chapter the effect of nanosilica as reinforcement in short Nylon 6 fiber / Styrene butadiene rubber hybrid composites containing HRH dry bonding system is reported. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler. The cure and mechanical properties of nanosilica/Nylon 6 short fiber / SBR hybrid composites are also reported.

6C.2 Experimental

Table 6C.1. Formulation of mixes

Mix No.		**Ingredients (phr)$^+$**			
		Nylon 6	**Nanosilica**	**Commercial silica**	**HRH***
A series	**A_0**	-	-	-	-
	A_{10}	10	-	-	1.67
	A_{20}	20	-	-	3.33
	A_{30}	30	-	-	5
B series	**B_0**	-	3	-	-
	B_{10}	10	3	-	1.67
	B_{20}	20	3	-	3.33
	B_{30}	30	3	-	5
C series	**C_0**	-	6	-	-
	C_{10}	10	6	-	1.67
	C_{20}	20	6	-	3.33
	C_{30}	30	6	-	5
D series	**D_0**	-	9	-	-
	D_{10}	10	9	-	1.67
	D_{20}	20	9	-	3.33
	D_{30}	30	9	-	5
E series	**E_0**	-	-	6	-
	E_{10}	10	-	6	1.67
	E_{20}	20	-	6	3.33
	E_{30}	30	-	6	5

* Hexa:Resorcinol:Silica in the ratio 2:2:1. Total loading was 16% on fiber content.
$^+$ phr- parts per hundred rubber.

SBR-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.8 phr, TMTD- 0.2 phr and sulphur-2 phr were common to all mixes.

Formulation of the test mixes are given in the table 6.C.1. Method of preparation and procedure adopted for the determination of cure characteristic and mechanical properties of the mixes are given in the chapter 2.

6C.3 Results and Discussion

6C.3.1 Cure characteristics

Variation of minimum torque with fiber loading at various silica contents are shown in figure 6 C.1. The minimum torque increases with silica loading for all the mixes. It is due to better dispersion of silica particle in the matrix. Mixes B, C and D series show higher viscosity than mix E series. The higher viscosity of the nanosilica composites may be due to the better interaction between the silica and the rubber matrix. Lower particle size silica has higher surface area and hence can have improved interactions.

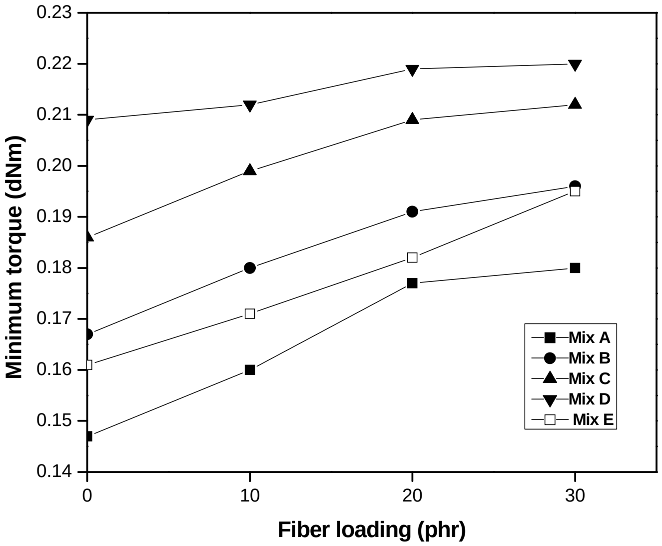

Figure 6C.1. Variation of minimum torque with fiber loading

Figure 6 C.2 gives the variation of scorch time with silica content and fiber loading. Scorch time decreases with fiber loading for all the mixes up to 20 phr fiber loading and then remains more or less constant. Scorch time decreases from 6.9 minute at 0 phr fiber loading to 1.4 min. at 30 phr for mix A series (without silica). This indicates that Nylon fiber has an accelerating effect on the cure reaction of SBR, like in the case of other rubbers. Similar results in the case of short Nylon fiber reinforced NBR composite using an epoxy-based bonding agent have been reported earlier [8].

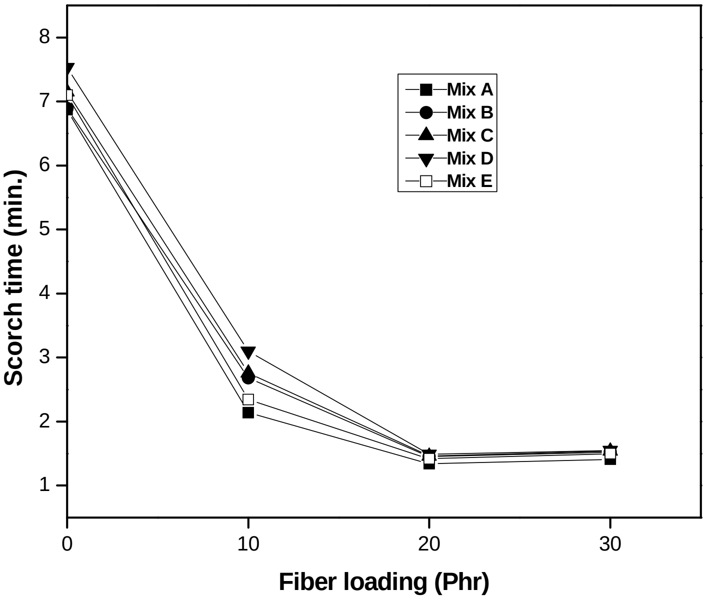

Figure 6C.2. Variation of scorch time with fiber loading

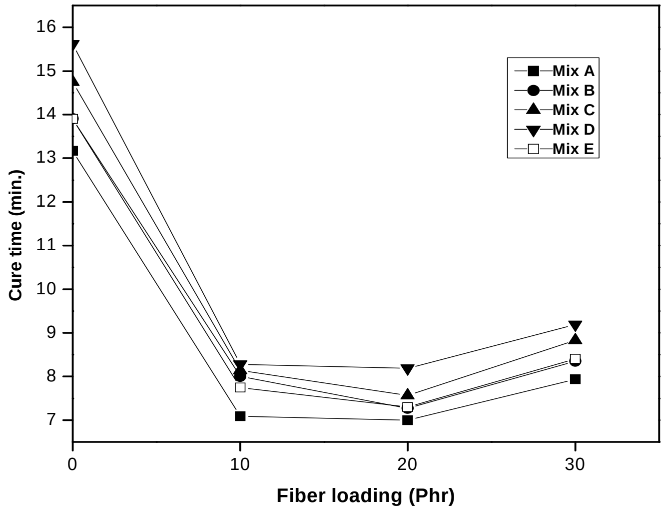

Figure 6C.3. Variation of cure time with fiber loading

The variation of cure time with filler loading is shown in figure 6 C.3. Cure time decreases with fiber loading. This cure accelerating effect is more up to 10 phr fiber loading and after that the effect is less pronounced. With increasing silica content, however the cure time increases. This may be attributed to the slight acidic nature of silica. Generally acids retard the cure reaction.

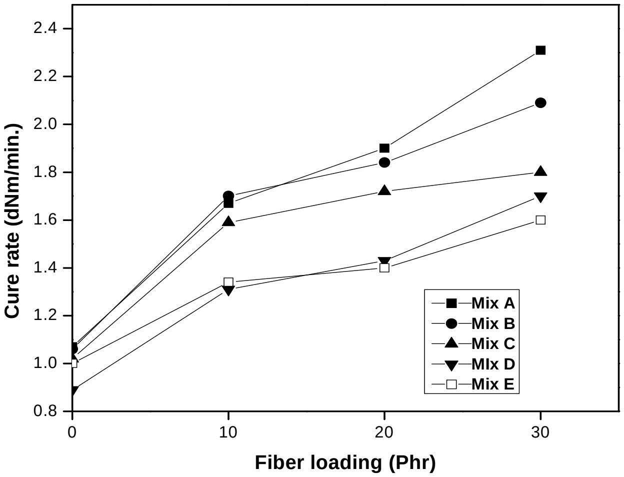

Figure 6C.4. Variation of cure rate with fiber loading

Figure 6 C.4 shows the rate of cure reaction with silica content and fiber loading. As expected, cure rate increases with fiber loading and decreases with silica content. Increase in cure rate with fiber content is due to the accelerating effect of Nylon fiber on the cure reaction. Decrease in cure rate with silica content is due to the interaction of silica with the accelerators

The differential torque i.e., the difference between the minimum and maximum torques developed during cure is increased with fiber loading and silica content and it is higher for nanosilica composite (Fig.6 C.5). The differential torque is a measure of the extent of the cross link formation and the filler–matrix interaction. The higher torque values of the nanosilica compounds indicate that the matrix is more restrained. Due to the lower particle size and higher surface area, nanosilica is more effectively dispersed in the rubber matrix than the commercial silica.

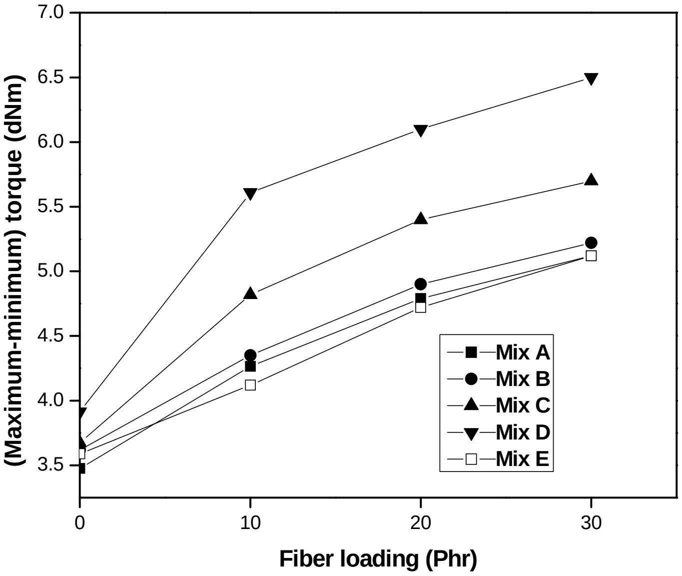

Figure 6C.5. Variation of differential torque with fiber loading

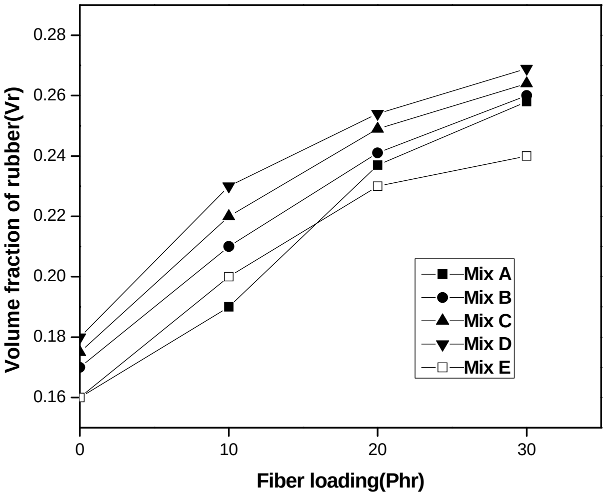

Figure 6C.6. Variation of volume fraction of rubber with fiber loading

Figure 6 C.6 shows that V_r of the nanosilica-containing mixes is higher than that of commercial silica composites. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix because of their higher surface area. Volume fraction, V_r, increases with fiber loading, as expected. In the presence of fibers, the matrix gets more restrained and the diffusion of the solvent becomes limited.

6C.3.2 Mechanical properties

Figure 6 C.7 shows variation of tensile strength with fiber loading and silica content. The tensile strength increases almost linearly with fiber loading. At any fiber content the tensile strength is higher for the nanosilica filled samples. For the gum compound containing no fiber, the improvement is 250 % while for the 30 phr fiber-filled sample, a 32 % improvement in tensile strength is obtained with 6 phr nanosilica. With the conventional silica the corresponding improvements in the tensile strength are 100 % and 10 %, respectively. In the case of conventional silica (Mix E series) the tensile strength values are almost equal to that of mix A series which contains no additional silica. The improved efficiency of nanosilica may be attributed to its higher surface area which gives better interaction between the silica particles and the matrix.

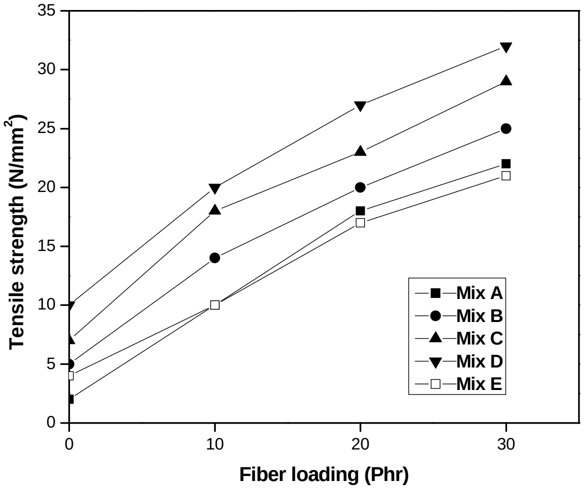

Figure 6C.7. Variation of tensile strength with fiber loading in longitudinal direction

For the samples with fibers oriented in the transverse direction (fibers oriented perpendicular to the direction of application of force), the variation is as shown in figure 6 C.8

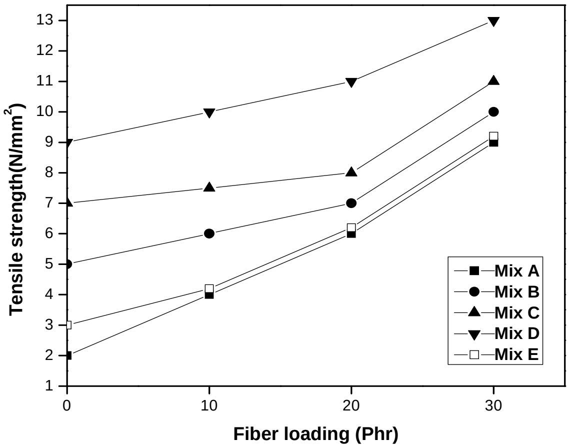

Figure 6C.8. Variation of tensile strength with fiber loading in transverse direction

In all the cases, the tensile strength shows an improvement less than that of the composites with fibers oriented longitudinally. The transverse orientation of fibers is not effective in supporting the load and the ultimate strength is the strength of the matrix. The fibers fail to arrest or deviate crack paths as it propagates through the fiber-matrix interface. With increasing nanosilica content the tensile strength is improved (Series B-D). Tensile strength increases from 8 N/mm^2 to 13 N/mm^2 by the incorporation of 9 phr nanosilica in 30 phr fiber loaded composites. This shows that the nanosilica is effective in restricting easy propagation of the crack by possible interaction with matrix. For the 6 phr conventional silica mixes (Series E), the values are almost equal to that of mix A series which contains no additional silica.

The variation of tear strength with fiber loading is shown in figure 6 C.9. The tear strength registers a tremendous increase in the presence of short fibers.

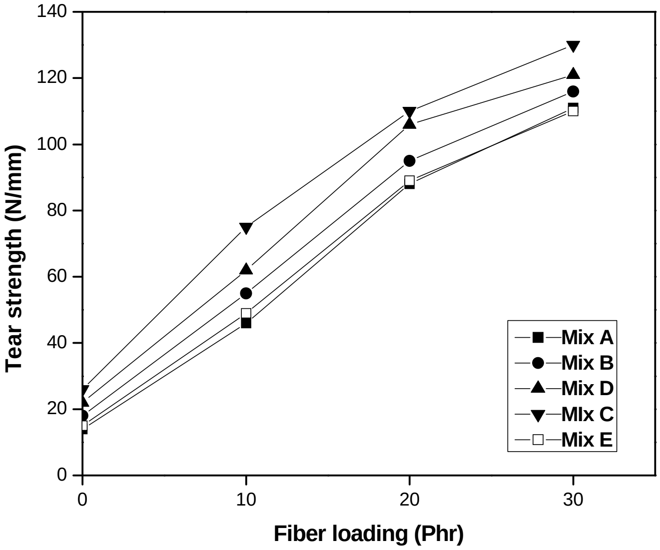

Figure 6C.9. Variation of tear strength with fiber loading in longitudinal direction

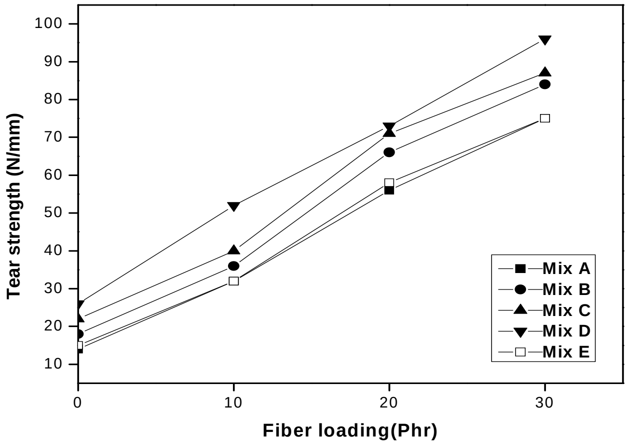

Figure 6C.10. Variation of tear strength with fiber loading in transverse direction

Tear strength increases from 14 N/mm to 111N/mm by the addition of 30 phr fiber in the case of Mix A. With nanosilica, the tear strength is further improved consistently for all the mixes. At 9 phr loading the tear strength is improved by 86 % for the gum compound (Mix Ao) and by 17 % for the 30 phr fiber filled sample (Mix A_{30}). The smaller particle size of the nanosilica helps it better arrest or deviate the tear cracks, resulting in higher tear resistance. For the commercial silica series (Series E), the improvement is very limited and is equal to that of the series A.

For transverse orientation of fibers, the variation of tear strength is shown in figure 6 C.10. The tear strength is improved to 75 N/mm from 14 N/mm with 30 phr fibers. Incorporation of 9 phr of nanosilica raises the tear strength to 98 N/mm. For the commercial silica (Mix E series), the tear strength is almost equal to that of compounds with no additional silica. In comparing figure 6.C.9 and figure 6 C.10, it is found that the hybrid composite also shows anisotropy in tear strength.

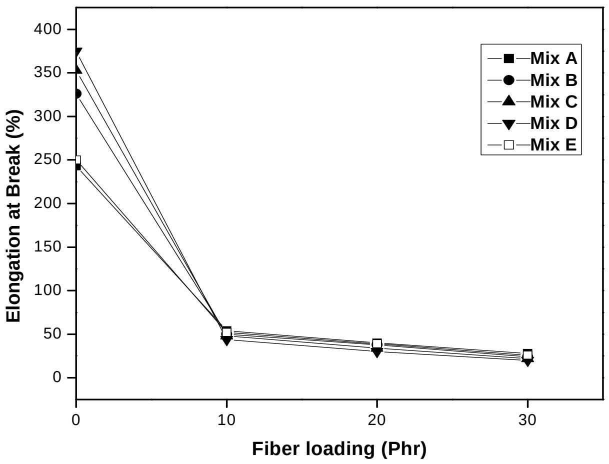

Figure 6C.11. **Variation of elongation at break with fiber loading in longitudinal direction**

Figure 6 C.11 shows the elongation at break [EB] for the mixes. There is a sudden drop at 10 phr fiber loading and then it remains almost constant for all the mixes. With fibers distributed uniformly, the matrix becomes more restrained and hence fracture occurs at lower strains. But in the transverse direction the stabilization is beyond 20 phr fiber loading (Fig.6 C.12).

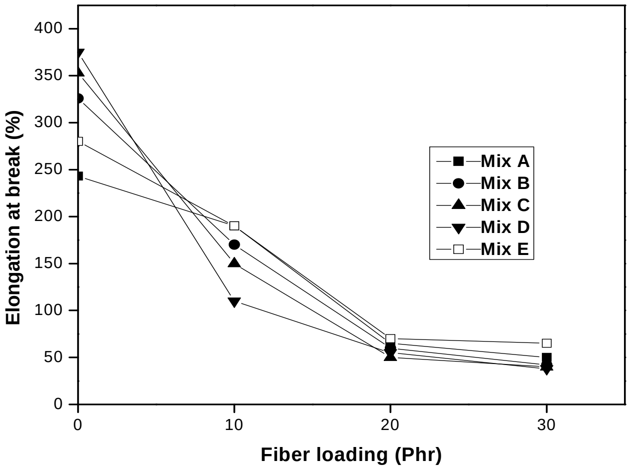

Figure 6C.12. **Variation of elongation at break with fiber loading in transverse direction**

The modulus at 20% elongation is found to increase linearly with fiber content. At all fiber loading, addition of nanosilica further improves the modulus (Fig.6.C.13).

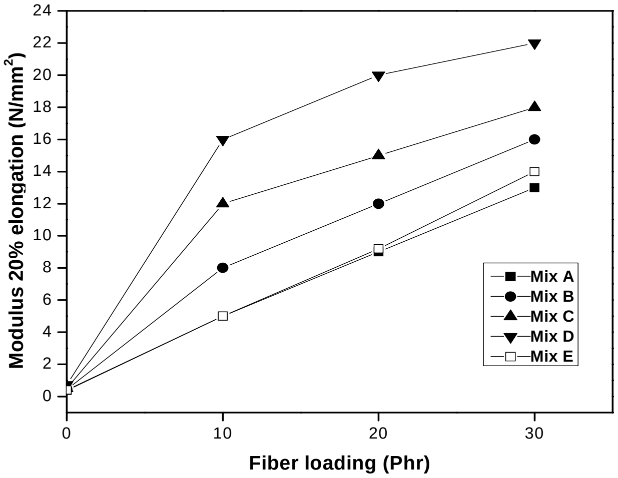

Figure 6C.13. Variation of modulus with fiber loading in longitudinal direction

Though the improvement for the gum compound (Mix Ao) with 6 phr nanosilica is only 34 %, for the 30 phr fiber composite (Mix A_{30}) the modulus is improved by 39 %, in the presence of 6 phr nanosilica. For the commercial silica, the corresponding value is only 18 %. This shows that the nanosilica improves the fiber-matrix interaction better than the commercial silica. This may be attributed to relatively higher surface area of the nanosilica. The silica improves the interaction between the fiber and the rubber matrix through hydrogen bonding [3]. With no fibers in the matrix the silica is not effective in improving the modulus, as evident from the very low modulus of the gum compound. Similar trend is observed in transverse direction also (Fig. 6 C.14). The modulus obtained in the transverse direction is less than that of longitudinal direction. This is because transversely oriented fibers being parallel to the propagating crack front offers less resistance to propagating tear and hence has lower tear strength values.

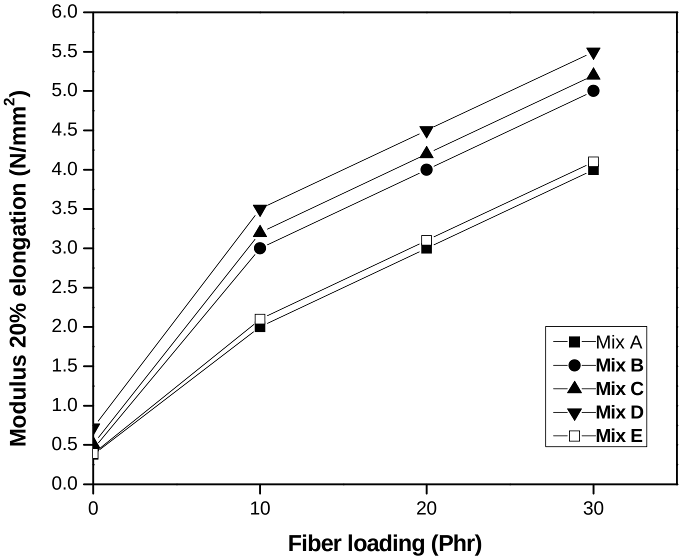

Figure 6C.14. Variation of modulus with fiber loading in transverse direction

Variation of abrasion loss of mixes A-E series is shown in figure 6 C.15. There is a significant reduction in the abrasion loss with increasing fiber loading.

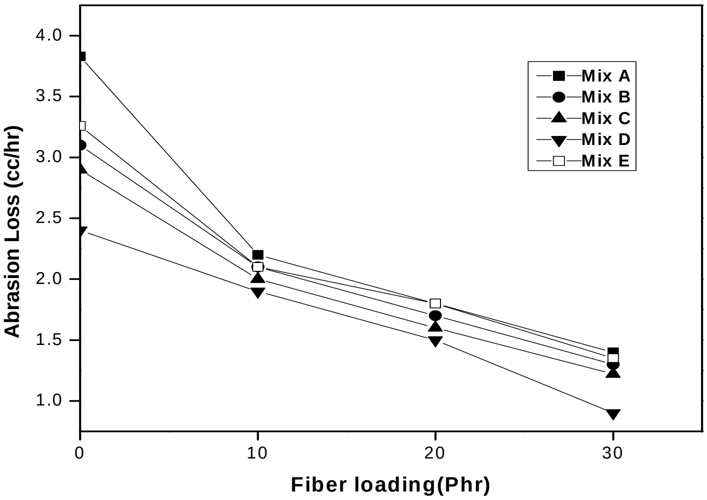

Figure 6C.15. Variation of abrasion loss with fiber loading

The composites containing commercial silica (Mix E series) show an abrasion loss in between that of the gum compound and 3 phr nanosilica mixes. This is because of more restrained matrix of composite. During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case the presence of strong interfacial adhesion between the fiber and matrix renders the matrix stiffer and lowers the abrasion loss.

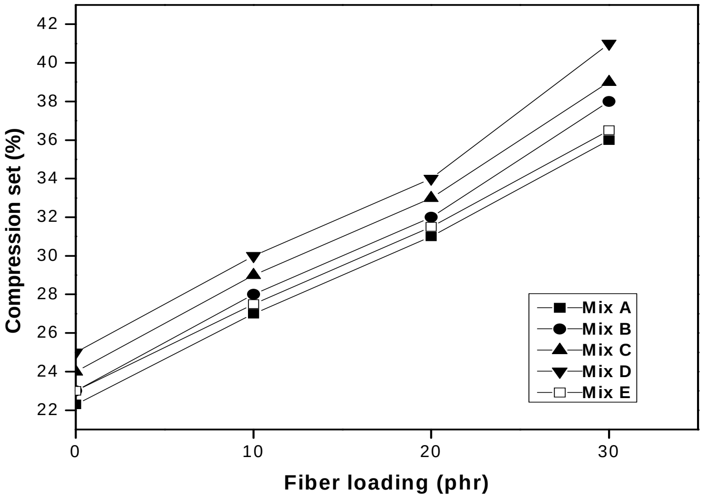

Figure 6C.16. Variation of compression set with fiber loading

Figure 6 C.16 shows the compression set of the different mixes. Compression set increases linearly with silica content and fiber loading. By the addition of 9 phr silica to samples containing no fiber (Mix A_0-D_0), the compression set increases to 14 % and by the addition to 30 phr fiber filled samples (Mix D_{30}), it becomes 84 %. The introduction of reinforcing fillers into the matrix reduces its elasticity which in turn increases the compression set. This is in agreement with observed resilience values.

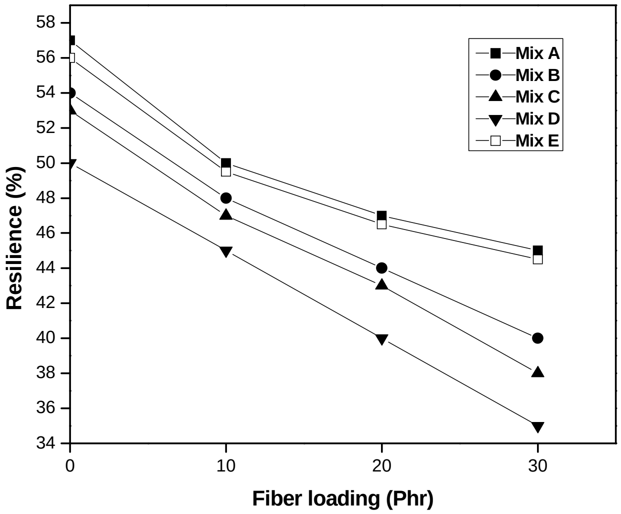

Figure 6C.17. Variation of resilience with fiber loading

Resilience decreases with silica content for all the mixes (Fig. 6 C.17). Incorporation fiber also decreases the resilience value. The dissipation of energy at the fiber-matrix interface results in lower resilience values of the composites. Resilience shows a reduction from 57 % at 0 phr fiber loading to 41 % at 30 phr of fiber loading (Series A). With increasing silica content, the resilience is further reduced. With 9 phr nanosilica, the resilience of the 30 phr fiber loaded samples is lowered to 34 %. The dissipation of energy at the fiber-matrix interface results in lower resilience of the composites. With a lesser reinforcing commercial silica, the reduction in resilience is only marginal.

Hardness, as expected, is higher for the fiber- filled samples (Fig.6 C.18). With nanosilica the hardness is further enhanced. For the gum compound (Mix Ao), the hardness is improved with increasing nanosilica content. With 6 phr commercial silica (Mix E series) the improvement is only limited and is close to that of the series B.

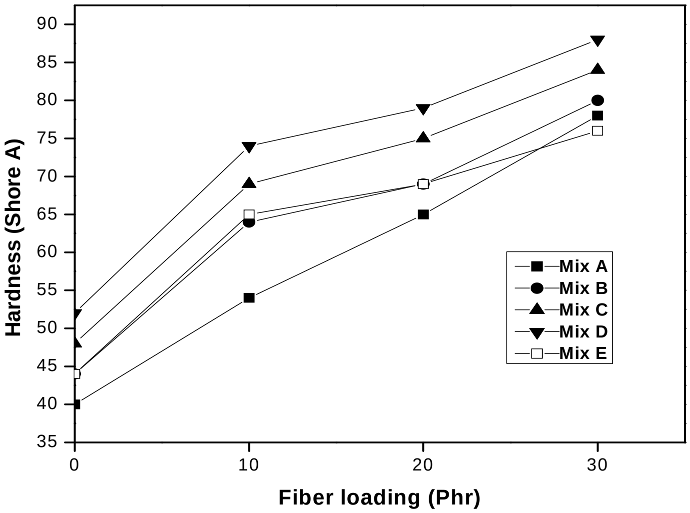

Figure 6C.18. Variation of hardness with fiber loading

6C.3.3 Ageing resistance

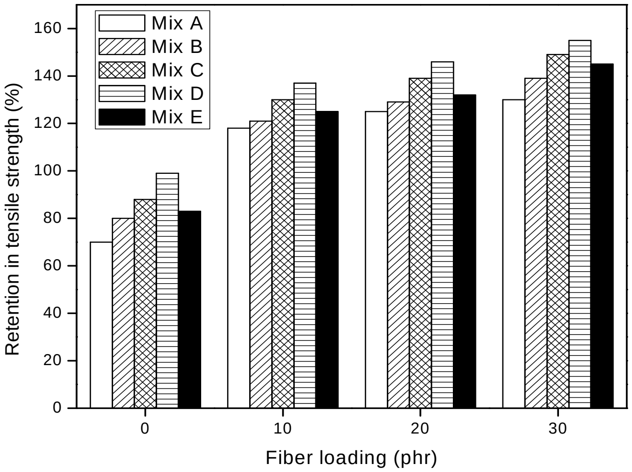

Figure 6.C.19. Variation of percentage retention in tensile strength with fiber loading

Ageing of the composite at 70° C for 72 hrs causes a marginal increase in mechanical properties in the presences of short fibers and silica (Fig.6 C.19 - Fig.6 C.21).

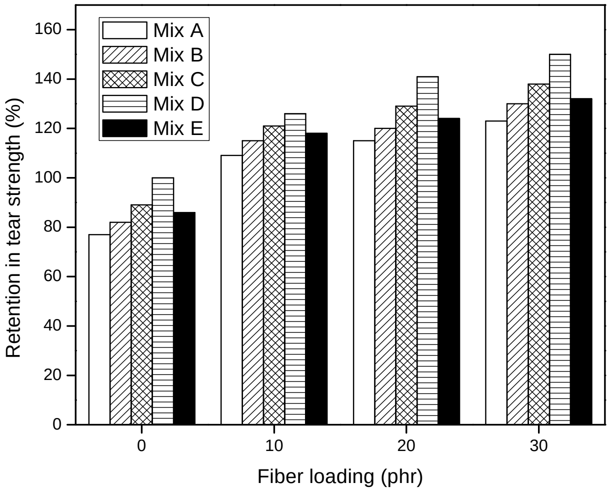

Figure 6C.20. **Variation of percentage retention in tear strength with fiber loading**

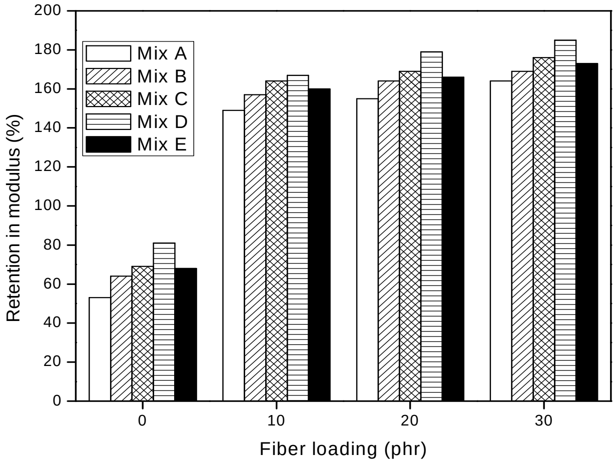

Figure 6C.21. **Variation of percentage retention in modulus with fiber loading**

In absence of fibers there is deterioration taking place during ageing of the mixes (Mix A_0 –D_0). Introduction of fibers improves the retention in tensile strength, tear strength and modulus of the hybrid composite. This is due to the improved fiber-matrix attachment by ageing. Similar effect has been reported in earlier [9]. The percentage retention in ageing is higher for nanosilica composites than that of commercial silica for all the fiber loading. Due to the higher surface area of the nanosilica, better interaction of the silica with the matrix occurs in the hybrid composites.

6C. 4. Conclusions

SBR /short Nylon 6 fiber composite shows a good improvement in cure and mechanical properties by the introduction of nanosilica. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading. Volume fraction of rubber, a measure of the cross link density, in a solvent-swollen sample increases with nanosilica. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Hybrid composites show anisotropy in mechanical properties. Retention in ageing is improved with fiber loading and it is better for nanosilica filled hybrid composites.

6C.5 References

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Part – D

CHLOROPRENE RUBBER BASED HYBRID COMPOSITES

Contents

6D.1 Introduction

Short fiber reinforced elastomers combine the rigidity of fiber with the elasticity of rubber. Short fiber reinforced rubber composites offer a great advantage over traditional composites in manufacturing and processing operations. In comparison with particulate filler composites, short fiber reinforced systems possess a high degree of reinforcement even at relatively low fiber content. Chloroprene rubber (CR) is the world's first commercial synthetic rubber. CR has some inherent flame resistance because of the presence of chlorine in the molecule. Chloroprene rubber is somewhat inferior to the nitrile rubbers in oil resistance but it is substantially better in this respect than the other diene rubbers. Short fibers can impart many desirable properties to rubber articles, up to now unobtainable with traditional reinforcements. Short fibers can improve thermomechanical properties of the composites and reduce the cost of fabrication. Chloroprene rubbers are mainly used in heat resistant and flame resistant beltings, industrial hoses, wires and cables, gaskets and O - rings, rubber rollers, coated fabrics, etc. Many researchers have studied the effect of different fibers in Chloroprene rubbers. Cure characteristic and mechanical properties of short Nylon fiber- Neoprene rubber composite containing epoxy resin as bonding agent was studied by Seema *et al.* [1]. Park and co – workers [2] studied the effect of fiber loading and matrix strength on the physical properties of short aramid fiber reinforced chloroprene rubber composites.

In this chapter the effect of nanosilica as reinforcement in short Nylon 6 fiber / Chloroprene rubber hybrid composites containing HRH dry bonding system is presented. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler. The cure and mechanical properties of nanosilica/ Nylon 6 short fiber/CR hybrid composites are discussed here.

6D.2 Experimental

Formulation of the test mixes are given in the table 6 D.1. Method of preparation and procedure adopted for the determination of cure characteristic and mechanical properties of the mixes are given in the chapter 2.

Table 6D.1. Formulation of mixes

Mix No.		**Ingredients (phr)[+]**			
		Nylon 6	**Nanosilica**	**Commercial silica**	**HRH***
A series	**A_{0}**	-	-	-	-
	A_{10}	10	-	-	1.67
	A_{20}	20	-	-	3.33
	A_{30}	30	-	-	5
B series	**B_{0}**	-	3	-	-
	B_{10}	10	3	-	1.67
	B_{20}	20	3	-	3.33
	B_{30}	30	3	-	5
C series	**C_{0}**	-	6	-	-
	C_{10}	10	6	-	1.67
	C_{20}	20	6	-	3.33
	C_{30}	30	6	-	5
D series	**D_{0}**	-	9	-	-
	D_{10}	10	9	-	1.67
	D_{20}	20	9	-	3.33
	D_{30}	30	9	-	5
E series	**E_{0}**	-	-	6	-
	E_{10}	10	-	6	1.67
	E_{20}	20	-	6	3.33
	E_{30}	30	-	6	5

* Hexa:Resorcinol:Silica in the ratio 2:2:1. Total loading was 16% on fiber content.

[+] phr- parts per hundred rubber.

CR-100 phr, zinc oxide-5 phr, stearic acid-0.5 phr, N-(1, 3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, magnesium oxide -4 phr, ethylene thiourea-0.5 phr were common to all mixes.

The compounded sheets were vulcanized in a hydraulic press at 160 ^{o}C and 200 kg/cm^2 pressure to their optimum cure times, as determined using a Rubber Process Analyzer (RPA – 2000, Alpha Technologies).

6D.3 Results and Discussion

6D.3.1 Cure characteristics

Variation of minimum torque with fiber loading at various silica contents is shown in figure 6 D.1 The minimum torque increases with fiber loading up to 20 phr. At 30 phr, however, the values are lower. This may be attributed to probable entanglement of the fibers at higher concentrations. Mixes B, C and D series show viscosity higher than the E series.

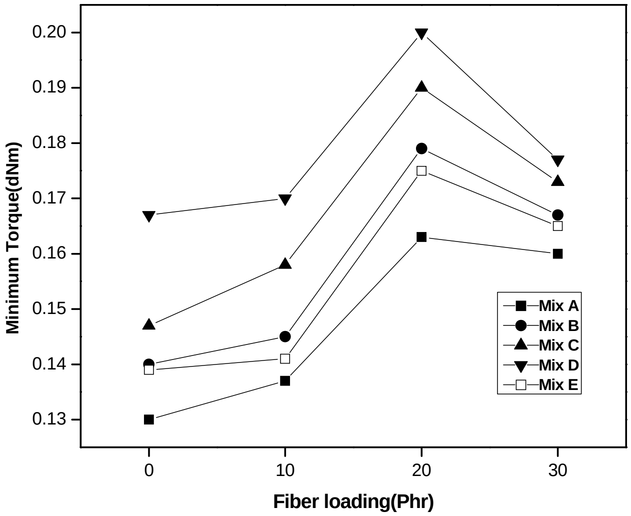

Figure 6D.1. Variation of minimum torque with fiber loading

The higher viscosity of the nanosilica composites may be due to the better interaction between silica and the rubber matrix. Lower particle size silica has higher surface area and hence can have improved interactions. The higher viscosity indicates that the processability of the composite is affected in the presence of fibers.

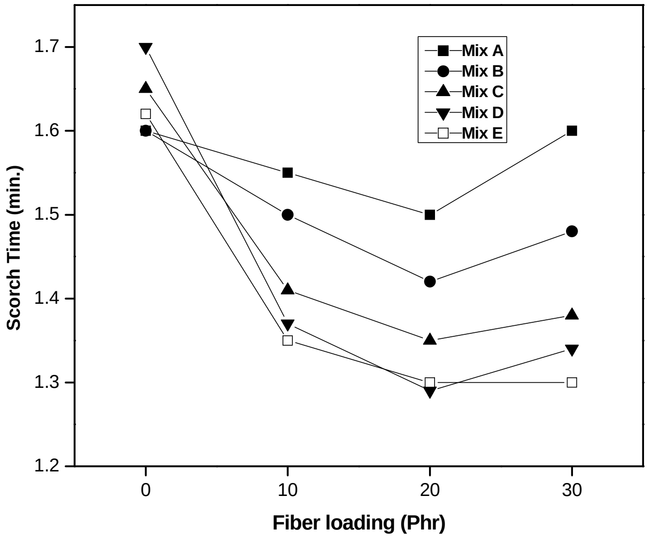

Figure 6D.2. Variation of scorch time with fiber loading

Figure 6 D.2 gives the variations of scorch time with silica content and fiber loading. Scorch time decreases with fiber loading for all the mixes up to 20 phr fiber loading and then slightly increases for all the mixes except the mix E. For mix E containing commercial silica it remains more or less constant. Scorch time increases from 1.55 minutes to1.7 minutes by the addition of 9 phr nanosilica to the gum compound (without fiber) i.e. mixes A_0 and D_0.The delayed start of cure reaction in the case of nanosilica composites may be attributed to the possible interaction of the silica with the accelerators, making it unavailable for cure reaction. By the introduction of Nylon fiber in the mixes the scorch time decreases. The scorch time is decreased from 1.70 minutes to 1.29 minutes in the presence of 20 phr Nylon fiber in mix containing 9 phr nanosilica i.e. for the mixes D_0 and D_{20}. This indicates that Nylon fiber has an accelerating effect on cure reaction. Similar results in the case of short Nylon fiber reinforced NBR composite using an epoxy-based bonding agent have been reported earlier [3]. The variation of cure time with filler loading is shown in figure 6 D.3. Cure time shows the same tendency for all the mixes. Cure time increase with silica content and decreases with fiber loading. Cure time increases from 15.17 minute to 16.24 minute by the introduction of 9 phr nanosilica in the gum compound (Mix A_0-D_0). This is due to the interaction of silica with the accelerators and this interaction is more for nanosilica than that of commercial silica. Cure time decreases from 15.17 minute to 14 minute (A_0 to A_{30}) by the addition of 30 phr fiber in the gum composites. The decrease in cure time with fiber loading is due to the accelerating effect of Nylon fiber in the cure reaction.

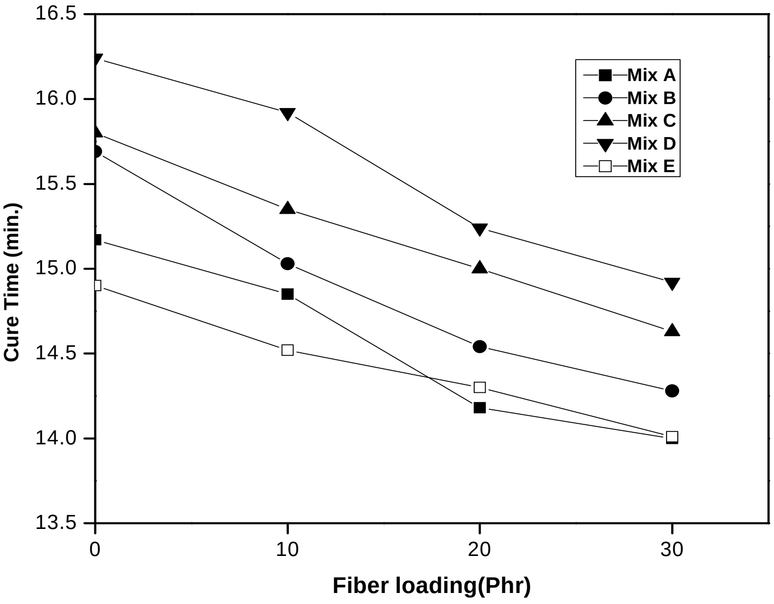

Figure 6D.3. Variation of cure time with fiber loading

Figure 6 D.4 shows the rate of cure reaction with silica content and fiber loading. As expected, cure rate increases with fiber loading and decreases with silica content. Increase in cure rate with fiber content is due to the accelerating effect of Nylon fiber on the cure reaction, as explained earlier. Decrease in cure rate with silica content may be due to the interaction of silica with the accelerators.

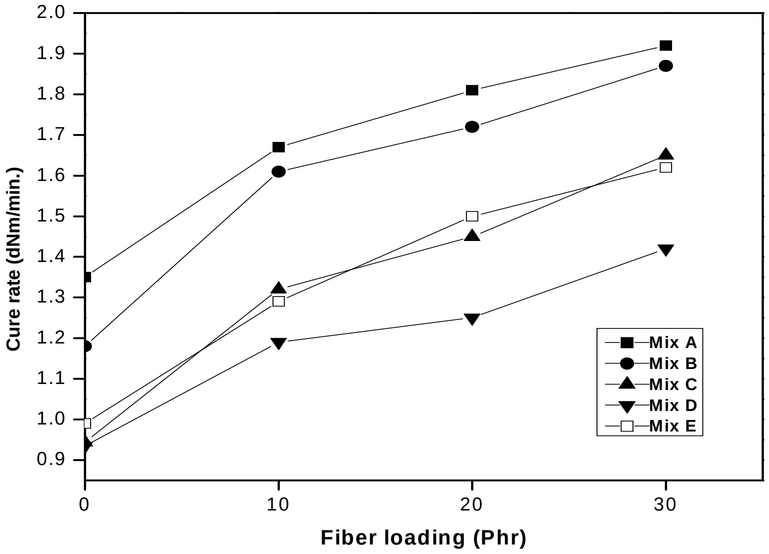

Figure 6D.4. Variation of cure rate with fiber loading

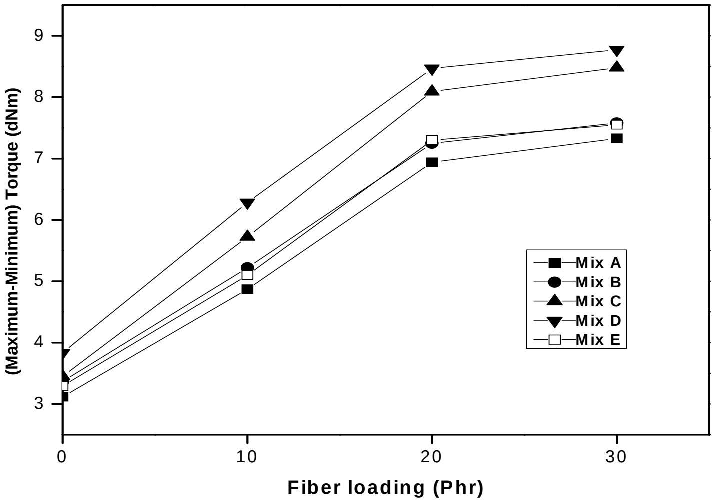

Figure 6D.5. Variation of differential torque with fiber loading

The differential torque i.e., the difference between the minimum and maximum torque developed during cure is marginally increased with fiber loading and silica content and it is higher for the nanosilica composite (Fig.6 D.5). The differential torque is a measure of the extent of the cross link formation and the filler–matrix interaction. The higher values for the nanosilica compounds indicate that the matrix is more restrained. This is in agreement with the V_r values of the mixes.

Figure 6 D.6 shows that V_r of the nanosilica-containing mixes is higher than that of commercial silica composite for all the mixes. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix due to their higher surface area. Volume fraction, V_r increases with fiber loading, as expected. In the presence of fibers, the matrix gets more restrained and the diffusion of the solvent becomes limited.

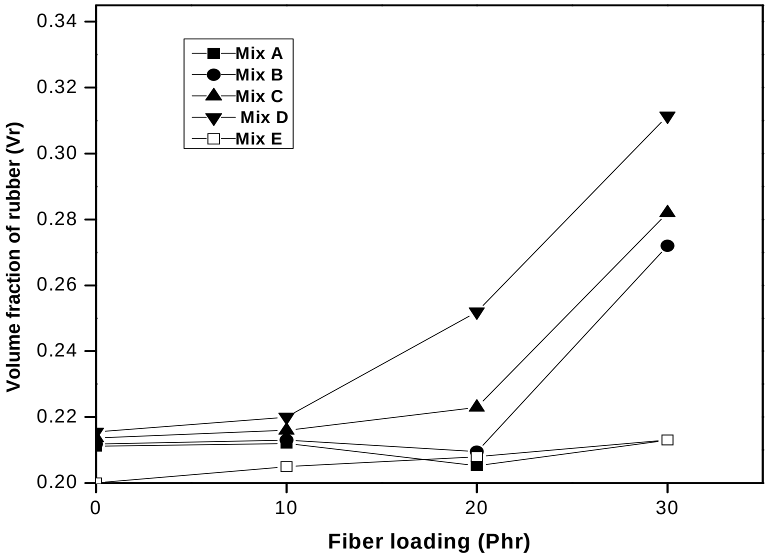

Figure 6D.6. Variation of volume fraction of rubber with fiber loading

6D.3.2 Mechanical properties

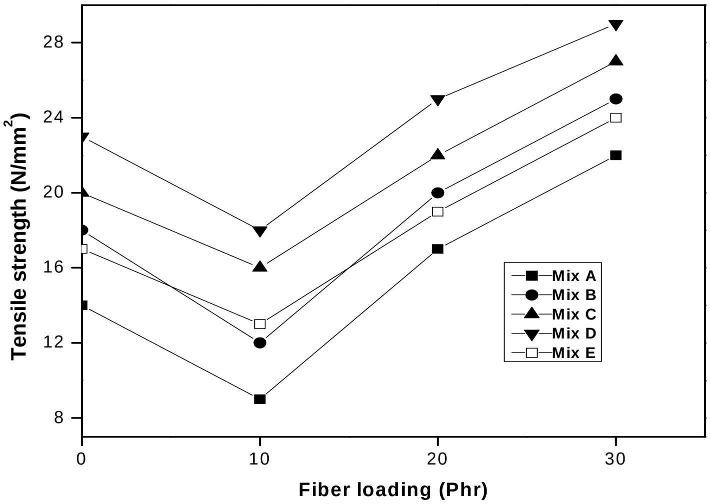

Figure 6D.7 Variation of tensile strength with fiber loading in longitudinal direction

The tensile strength increases with fiber content with an initial minor drop at 10 phr (Fig.6 D.7). This drop may be due to the dilution effect of the fibers at lower loadings [4- 5]. At higher fiber loadings, however, the reinforcing effect takes over, resulting in an improved ultimate strength.

At any fiber content the tensile strength is higher for the nanosilica filled samples. For the gum compound containing no fiber, the improvement is 43 % while for the 30 phr fiber-filled sample, a 93 % improvement in tensile strength is obtained with 6 phr nanosilica. With the conventional silica the corresponding improvements in the tensile strength are 21% and 71%, respectively. The tensile strength values of the E series mixes containing the conventional silica are close to that of B series mixes which contain only 3 phr nanosilica. The improved efficiency of nanosilica may be attributed to its higher surface area which gives better interaction between the fiber and the matrix.

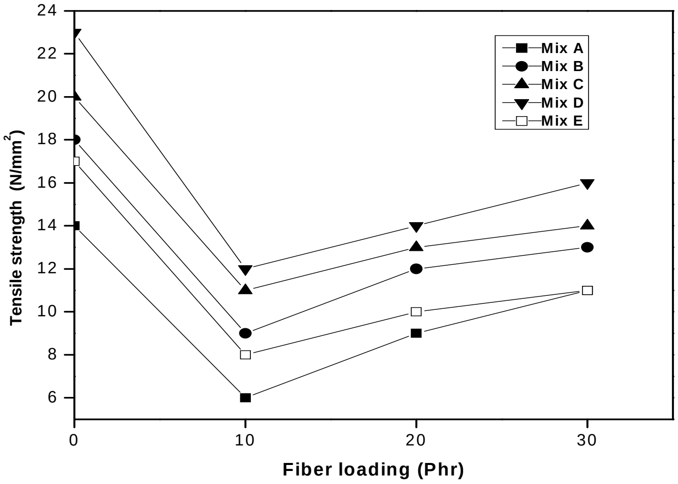

Figure 6D.8. Variation of tensile strength with fiber loading in transverse direction

For the samples with fibers oriented in the transverse direction (fibers oriented perpendicular to the direction of application of force), the variation is shown in figure 6 D.8. In all the cases, the tensile strength drops to a low value at 10 phr fiber loading and then recovers marginally. Even at 30 phr fiber loading the tensile strength is lower than that of the corresponding non-fiber composites. The transverse orientation of fibers is not effective in supporting the load. As the crack can propagate easily with the fibers oriented parallel to its propagation, the samples fail easily, resulting in lower tensile strength. With increasing nanosilica content the tensile strength is improved (Series B-D). Tensile strength increases from 11 N/mm^2 to 16 N/mm^2 by the incorporation of 9 phr nanosilica in 30 phr fiber loaded composites. This shows that the nanosilica is effective in restricting easy propagation of the crack by possible interaction with matrix. For the 6 phr conventional silica mixes (Series E), the values are lower than that of the Series B containing 3 phr nanosilica.

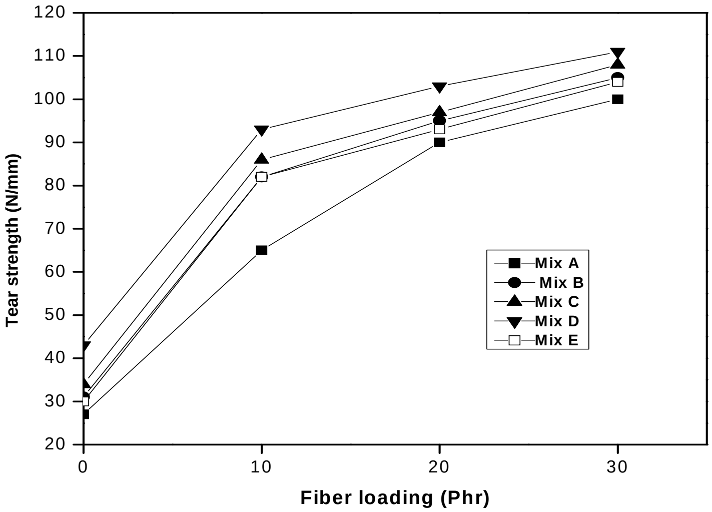

Figure 6D.9. Variation of tear strength with fiber loading in longitudinal direction

The variation of tear strength with fiber loading is shown in figure 6 D.9. The tear strength registers a significant increase in the presence of short fibers. Tear strength increases from 27 N/mm to 95 N/mm by the addition of 30 phr fiber in the case of mix A. With nanosilica, the tear strength is improved consistently for all the mixes. At 9 phr loading the tear strength is improved by 59% for the gum compound (Mix A_0) and by 11 % for the 30 phr fiber filled sampled (Mix A_{30}). The smaller particle size of the nanosilica helps it better arrest or deviate the tear cracks, resulting in higher tear resistance. For the commercial silica series (Series E), the improvement is only limited and is close to that of the Series B.

For transverse orientation of fibers, the variation of tear strength is shown in figure 6 D.10. Here also the tear strength increases with fiber loading, though to a limited extent, compared to the mixes where the fibers are oriented longitudinally. The non-silica mixe (Series A) shows an improvement of 203 % in tear strength with 30 phr fiber loading which is further improved in the presence of 9 phr nanosilica (Mix D_{30}). In the case of the gum compound (Mix A_0) the corresponding improvement with 9 phr nano silica is 59 %. With the conventional silica the improvement is only marginal at all concentrations.

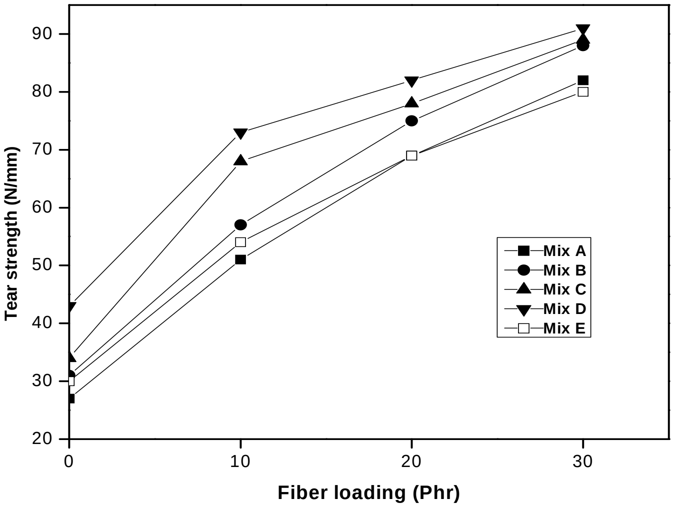

Figure 6D.10. Variation of tear strength with fiber loading in transverse direction

Figure 6 D.11 shows the variation of the elongation at break (EB) with fiber loading. There is a sudden drop in the EB at 10 phr fiber loading and then it remains almost constant for all the mixes. With fibers distributed uniformly, the matrix becomes more restrained and hence fracture occurs at lower strains.

With fibers oriented in the transverse direction as well, the EB is reduced beyond 10 phr loading (Fig.6 D.12). The presence of silica does not seem to have a significant effect on the EB of the fiber-filled samples. In the case of the gum compound (Mix A_0), the EB is reduced marginally with increasing silica content.

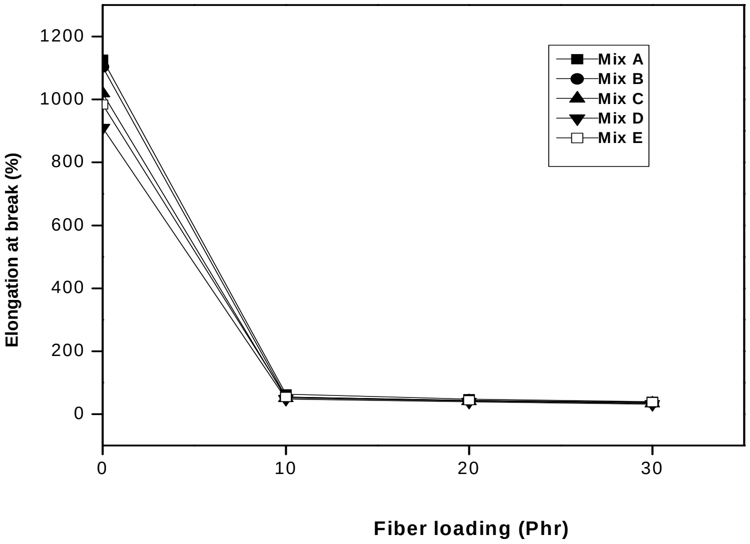

Figure 6D.11. Variation of elongation at break with fiber loading in longitudinal direction

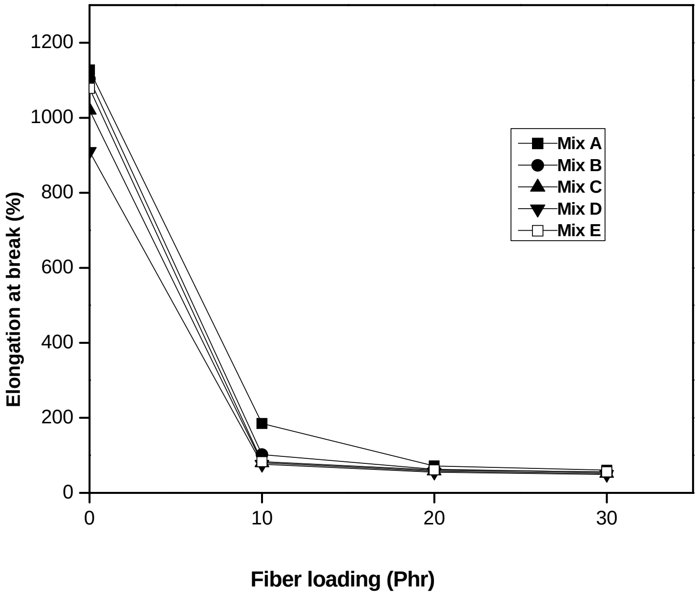

Figure 6D.12. Variation of elongation at break with fiber loading in transverse direction

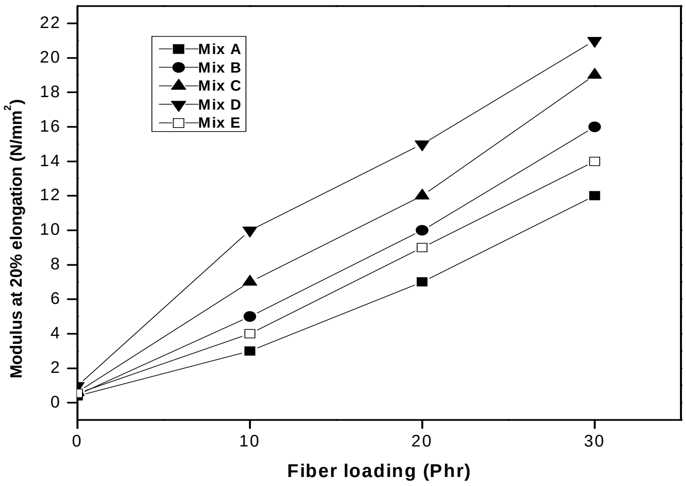

Figure 6D.13. Variation of modulus with fiber loading in longitudinal direction

The modulus at 20% elongation increases linearly with fiber content. At all fiber loading, addition of nanosilica further improves the modulus (Fig.6.D.13).

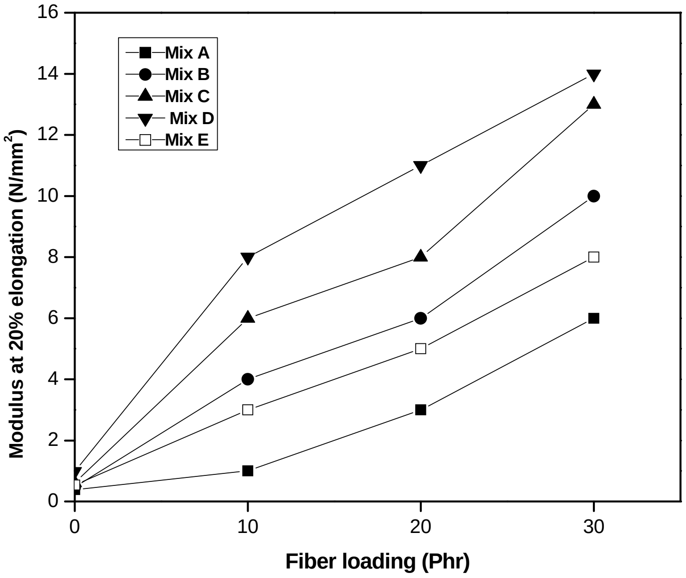

Figure 6D.14 Variation of modulus with fiber loading in transverse direction

Though the improvement for the gum compound (Mix A_0) with 6 phr nanosilica is only 56 %, for the 30 phr fiber composite (Mix A_{30}) the modulus is improved by 58 %, in the presence of 6 phr nanosilica. For the commercial silica, the corresponding value is only 16%. This shows that the nanosilica improves the fiber-matrix interaction better than the commercial silica. This may be attributed to relatively higher surface area. The silica has been reported to improve the interaction between the fiber and the rubber matrix through hydrogen bonding [6]. With no fibers in the matrix the silica is not effective in improving the modulus, as evident from the very low modulus of the gum compound. Similar trend is observed in transverse direction also (Fig. 6 D.14).

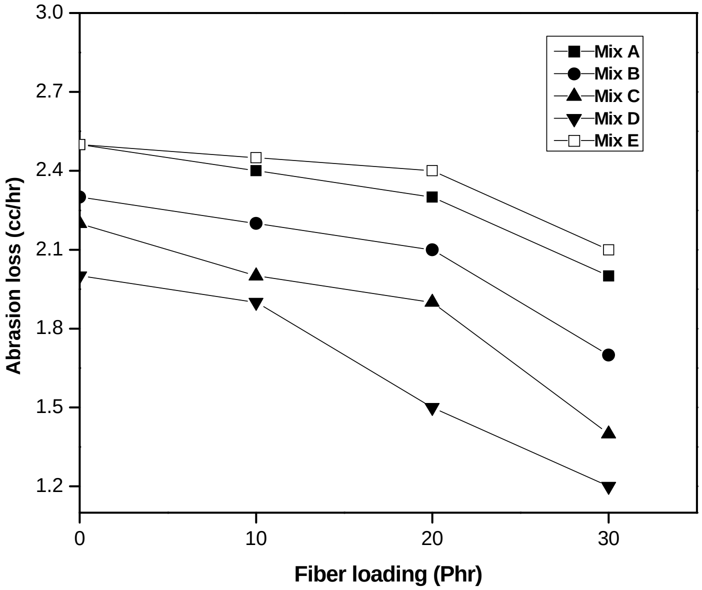

Figure 6D.15. Variation of abrasion loss with fiber loading

Variation of the abrasion loss of the Series A - E is shown in figure 6 D.15. The abrasion loss decreases with both fiber content and nanosilica loading. The mixes containing commercial silica (Series E) show higher abrasion loss compared to the non-silica mixes (Series A). This again indicates that the commercial silica is not effective in restraining the matrix, like the nanosilica. During an abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In the case of nanosilica hybrid composites a strong interfacial adhesion between the fiber and matrix renders the matrix stiffer and lowers the abrasion loss.

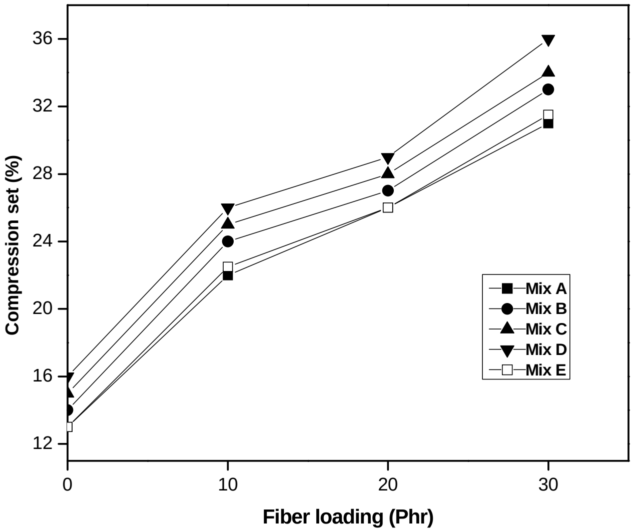

Figure 6D.16. Variation of compression set with fiber loading

Figure 6 D.16 shows the variation of compression set with fiber loading of the different mixes. Compression set increases with fiber content. The compression set registers 138 % increase at 30 phr fiber loading (Series A). In the presence of reinforcing fillers, the viscoelastic dissipation of energy at the filler – matrix interface is increased. At the elevated temperature of compression test, the matrix becomes soft and undergoes irreversible flow resulting in incomplete recovery on removal of the applied stress. This gives rise to higher compression set values in the case of reinforced matrices. In the presence of the nanosilica, the reinforcement is further enhanced and hence the viscoelastic dissipation is also more. This gives rise to higher compression set in the case of nanosilica composites. In the presence of 9 phr of nanosilica, the compression set of the 30 phr fiber loaded sample (Mix A_{30}) is increased by 16 %. Since the commercial silica is not effective as reinforcing filler, the set values are almost equal to that of the Series A composites.

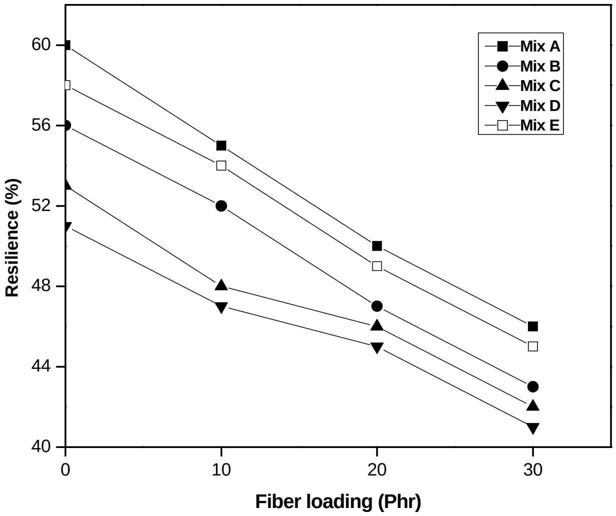

Figure 6D.17. Variation of resilience with fiber loading

The resilience, an indication of the material elasticity, decreases with fiber content and silica content for all the mixes, as expected (Fig.6 D.17). Resilience shows a reduction from 60% at 0 phr fiber loading to 46 % at 30 phr fiber loading (Series A). With increasing silica content, the resilience is further reduced. With 9 phr nanosilica, the resilience of the 30 phr fiber loaded samples is lowered to 41 %. The dissipation of energy at the fiber-matrix interface results in lower resilience of the composites. With a lesser reinforcing commercial silica, the reduction in resilience is only marginal.

Hardness, as expected, is higher for the fiber- filled samples (Fig.6 D.18). With nanosilica the hardness is further enhanced. For the gum compound (Mix A_0), the hardness is improved with increasing nanosilica content. With 6 phr commercial silica (Mix E_0) the hardness is only marginally improved. It is less than that of the mix with 3 phr nanosilica (Mix B_0)

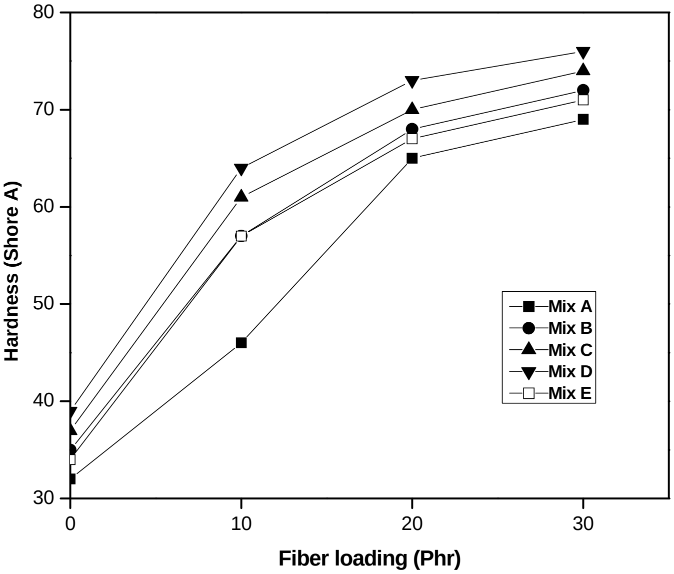

Figure 6D.18. Variation of hardness with fiber loading

6D.3.3 Ageing resistance

Ageing of the composite at 70^{o} C for 72 hr causes a marginal increase in mechanical properties of the hybrid composites (Fig.6 D.19 - Fig.6 D.21).

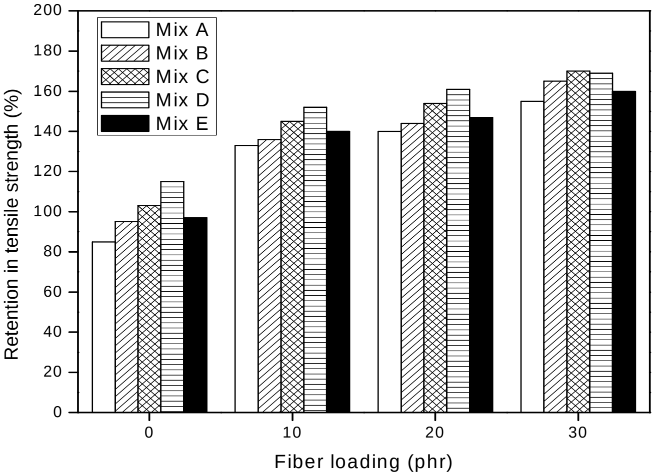

Figure 6D.19. Variation of percentage retention in tensile strength with fiber loading

This is due to the improved fiber-matrix attachment by ageing. Similar effect is reported in earlier [7]. The percentage retention in ageing is higher for nanosilica composites than that of commercial silica for all the fiber loading. This may be due to the better interaction of nanosilica with the matrix and hence improve the fiber- matrix adhesion than that of commercial silica.

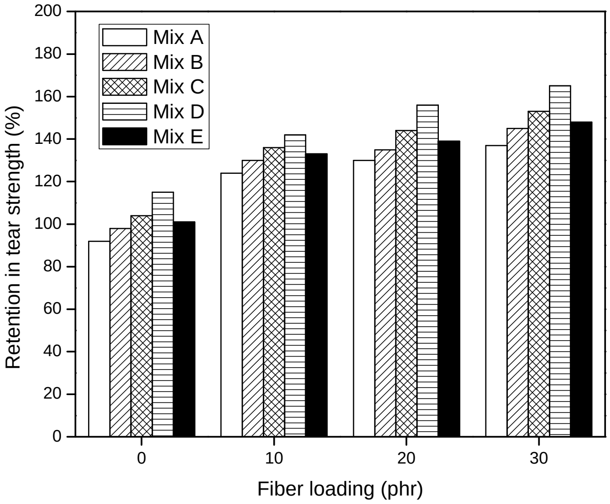

Figure 6D.20. Variation of percentage retention in tear strength with fiber loading

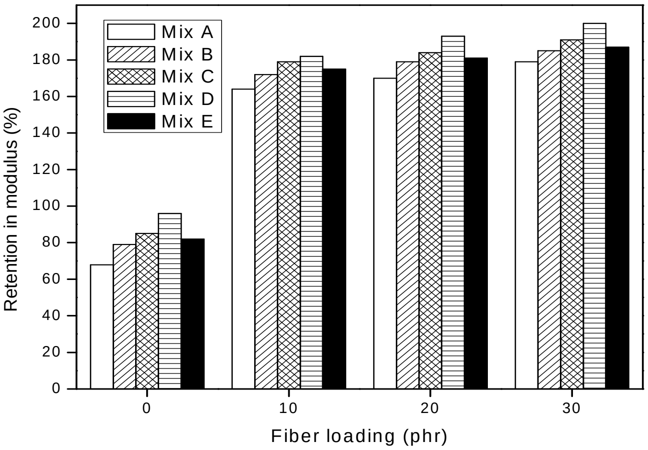

Figure 6D.21. Variation of percentage retention in modulus with fiber loading

6D.4 Conclusions

Cure and mechanical properties of Choloprene rubber / short Nylon 6 fiber composite are improved by the introduction of nanosilica in the composites. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading and increases with silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Longitudinally oriented fiber composites have superior properties than transversely oriented ones. Volume fraction of rubber, a measure of the cross link density, in a solvent-swollen sample increases with nanosilica. Ageing resistance also is better for nanosilica filled hybrid composites than that of commercial silica.

6D.5 References

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Chapter 7

Thermal Characterisation of Elastomeric Hybrid Composites

Contents

7.1 Introduction

Thermal analysis is considered as an important analytical method in understanding the structure- property relationship and mastering the technology for the industrial production of different polymeric materials. It is well known that thermal stability of a polymeric material can be improved by adding short fibers [1-4] and inorganic nanofillers [5-9]. Strong interaction between the polymer and the filler particles is essential for achieving good mechanical properties and thermal stability [10-14]. Silica with fine particle size will be effective in improving the interactions. The use of nanosilica as a component of the dry boding system is expected to improve the thermal stability of the composites based on short Nylon fiber and elastomers. Correa *et al.* [15] studied the influence of short fibers on the thermal resistance of the matrix and Tg and kinetic parameters of the degradation reaction of thermoplastic polyurethane and found that thermal resistance of aramid fiber-reinforced composite was greater than that of carbon fiber-reinforced composites. The thermal degradation characteristics of short Kevlar fiber-reinforced thermoplastic polyurethane was reported by Kutty *et al.* [1] Younan *et al.* [2] studied the thermal stability of natural rubber - polyester short fiber composites. Suhara *et al.* [3] studied thermal degradation of short polyester fiber-polyurethane elastomer composite and found that incorporation of the short fiber enhanced the thermal stability of the elastomer. Rajeev *et al.* [4] studied thermal degradation of short melamine fiber-reinforced EPDM, maleated EPDM, and nitrile rubber composite with and without bonding agent and found that the presence of melamine fiber in the vulcanizates reduced the rate of decomposition, and the effect was pronounced in the presence of the dry bonding system. Shield *et al.*[16] used thermogravimetric technique to study the blends of acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR). The compositions of NBR/SBR blends were estimated by TGA from the linear correlation between the polymer composition and temperature required to pyrolyze a sample to a specific ‘‘% weight loss.’’ Thermal studies on sulphur, peroxide, and radiation-cured NBR and SBR vulcanizates containing carbon black and silica fillers were carried out by Ahmed *et al.* [17] and they found that radiation-cured vulcanizates had better thermal stability. Thermal degradation of short Nylon 6 fiber reinforced SBR composite was studied by Seema *et al.* [18]. Seema and Kutty [19] also reported the effect of epoxy resin bonding agent on the thermal degradation of short Nylon 6 NBR composite. However, a systematic study on the effect of nanosilica on the degradation of hybrid composite has not been reported.

The objective of the present study is to analyze the effect of nanosilica and short Nylon 6 fiber on the thermal degradation properties of NR, NBR and SBR rubber based hybrid composite containing HRH dry bonding system. The nanosilica filler is used both as a component of HRH dry bonding system and as a filler.

7.2 Experimental

The formulations of mixes are given in table 7.1, table 7.2, and table 7.3 for NR composites, NBR composites and SBR composites, respectively. The mixing was done as per ASTM D-3184 (1989) standard on a two-roll laboratory size mixing mill (150mm×300mm). Nylon 6 fibers were added in small increments in order to obtain uniform dispersion. Dry bonding system components resorcinol, hexamethylene tetramine (hexa) and silica, were added during the milling operation. The sheets were vulcanized in the hydraulic press at 150 °C and at 200 kg/cm^2 pressure to their optimum cure times, as determined using a Rubber Process Analyzer (RPA – 2000), Alpha Technology.

Table 7.1. Formulation of the NR composites.

Ingredient (phr)$^+$	**Mix No.**					
	A	**B**	**C**	**D**	**E**	**F**
NR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	30
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	5

Zinc oxide-5phr, Stearic acid-2phr, N-(1, 3-dimethylbutyl) N'-phenyl-p-phenylene diamine) -1phr, CBS-0.6phr, TMTD- 0.2phr and sulphur-2.5phr were common to all mixes of the NR composites.

Table 7. 2. Formulation of the mixes of NBR based composites.

Ingredient (phr)$^+$	**Mix No.**					
	G	**H**	**I**	**J**	**K**	**L**
NBR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	30
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	5

Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl)N$'$-phenyl-p-phenylenediamine) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes of the NBR composites.

Table 7.3. Formulation of the mixes of SBR based composites.

Ingredient (phr)$^+$	**Mix No.**					
	M	**N**	**O**	**P**	**Q**	**R**
SBR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	30
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	5

Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl)N$'$-phenyl-p-phenylenediamine) -1 phr, CBS-0.8 phr, TMTD- 0.2 phr and sulphur-2 phr were common to all mixes of the SBR composites.

* Hexa: Resorcinol: Silica in the ratio 2:2:1. Total loading was 16% on fiber content.

$^+$ part per hundred rubber

Thermogravimetric analysis were carried out on a Universal V4 2E TA instrument at a heating rate of 10 ^{o}C/minute under nitrogen atmosphere. The data of weight loss versus temperature and time were recorded online in the TA Instrument's Q series Explorer software. The analysis of the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves was done using TA Instrument's Universal Analysis 2000 software version 3.3B. In the present study, the onset temperature (Ti), temperature corresponding to the maximum value in the derivative thermogram (Tmax), peak rate of decomposition (Rmax) and residue at 800^{o}C were recorded.

7.3 Results and Discussion

7.3.1 Natural rubber based composites

The TG-DTG curves of the neat Nylon 6 fiber is given in Figure 7.1 and that of raw natural rubber and gum compound (Mix A) are given in Figures 7.2 and 7.3, respectively. The derivative TGA (DTG) curves of the hybrid composites are shown in Figure 7.4.

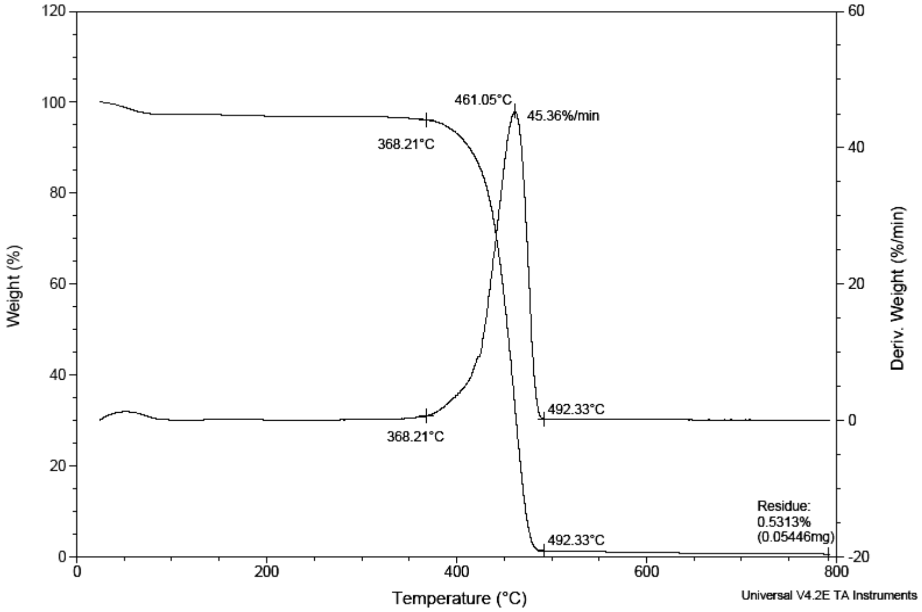

Figure 7.1. TG-DTG curves of the neat Nylon fiber

The temperature of onset of degradation (Ti), the temperature at which the rate of decomposition is maximum (Tmax), the peak degradation rate (Rmax) and the residue weight at 800 ^{o}C are given in Table 7.4. Neat nylon fiber degrades at 461^{o}C in single step with a maximum rate of degradation 45.3 %/min. The residual weight at 800 ^{0}C is only 0.53%. This is in agreement with the values reported by Seema *et al.*[18- 19] for the Nylon 6 fiber.

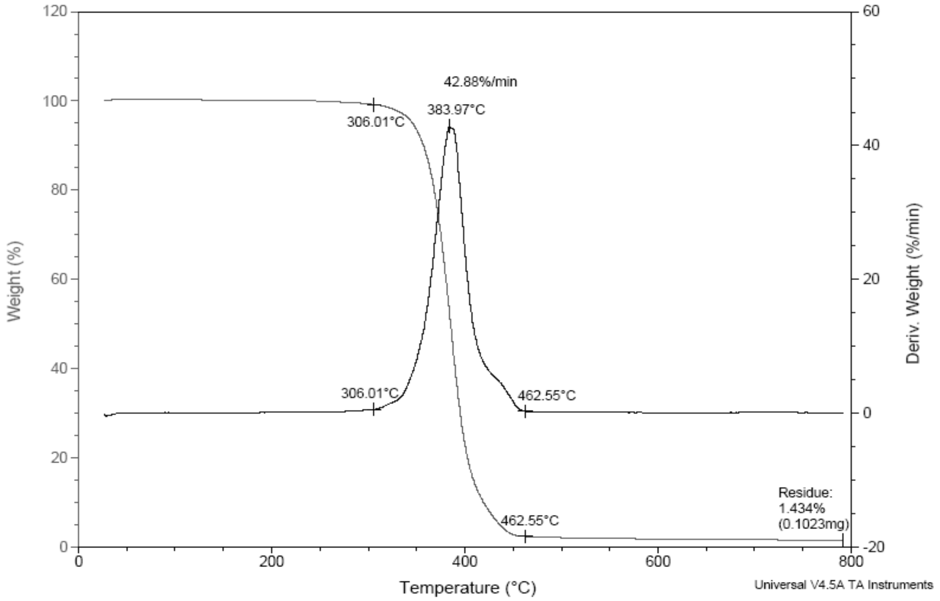

Figure 7.2. TG-DTG Curves of raw NR

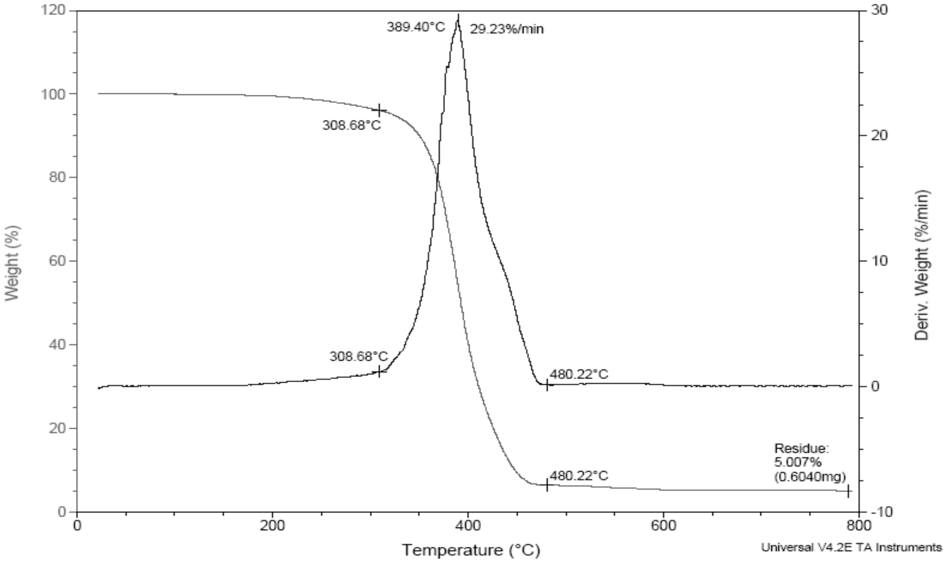

Figure 7.3. TG-DTG curves of unfilled NR composite

Table 7. 4. Thermal degradation characteristic of Natural rubber based Composites

Parameters	Nylon 6 fiber	Raw NR	Mix No.					
			A	B	C	D	E	F
Temp. of initiation (Ti)^{o}C	368	306	309	315	325	319	329	322
First Peak Degradation Temp (Tmax)^{o}C	461	384	389	387	389	387	389	388
First Peak rate of decomposition (Rmax) %/^{o} min.	45.3	42.88	29.2	28	25.5	24	22.5	27
Second Peak Degradation Temp (^{o}C)	-	-	-	461	463	462	464	462
Second Peak rate of decomposition (Rmax) %/^{o} min.	-	-	-	9	8	12	11	11.5
Residue at 800^{o}C (%)	0.53	1.434	5.00	5.7	10.54	6.28	11	9.72

The raw NR degrades at 384^o C in a single step with maximum rate of degradation 42.88 %/min. The residual weight at 800 ^{0}C is 1.434 %. The unfilled NR compound (Mix A) also degrades in a single step (Fig.7.3). The degradation starts at a temperature of 309 ^{o}C and the maximum rate of degradation is 29.23 %/min. The residue remaining at 800 ^{o}C is 5.0 %. This higher residual weight may be attributed to the presence of ZnO, incorporated as cure activator.

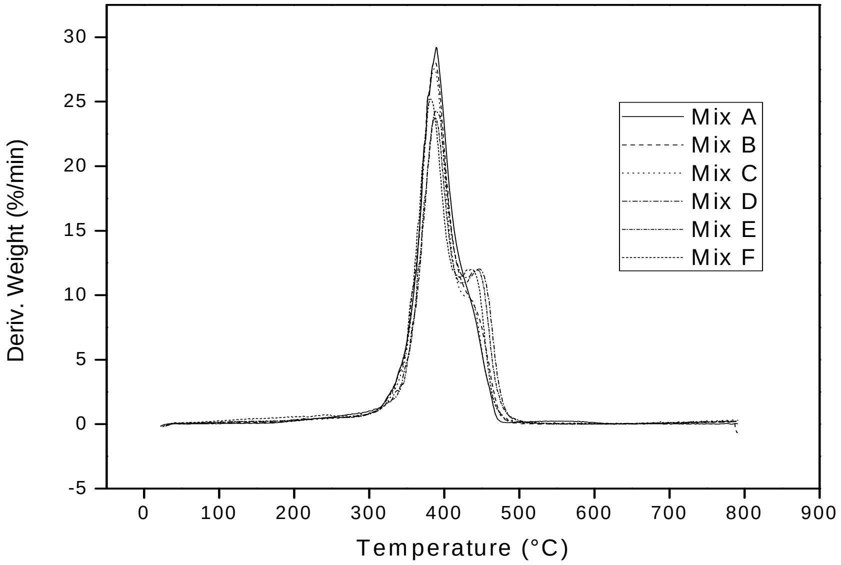

Figure 7.4. DTG curves of NR hybrid composite

It can be seen from the figure 7.4 that the composites undergo two-step degradation. The first degradation at around 387 ^{0}C corresponds to the degradation of the natural rubber and the second peak at 462 ^{0}C corresponds to the degradation of the Nylon fiber. By the introduction of 10 phr fiber in to the gum compound, the temperature of onset of degradation is shifted to higher side. ie from 309 ^{o}C to 315 ^{o}C. For the 30 phr fiber loaded samples, the degradation starts at 319 ^{o}C. This indicates the improved thermal stability of the composites (Table 7.4). Similar results have been reported earlier by Kutty *et al.* [1] and Seema *et al.* [18- 19]. There is not much change in the peak degradation temperature for the mixes with respect to the fiber loading. The maximum rate of degradation decreases with fiber concentration, and 30 phr fiber-loaded composite has the lowest peak rate of degradation.

In the presence of HRH (Mix B) the char yield is slightly increased to 5.7 %. Even though the char yield of the neat fiber at 800 ^{o}C is very low (0.53%), the residue remaining for the composites is more than that of the raw rubber (1.43 %) and gum compound (5.0 %) at the same temperature. This is due to the formation of strong interphase between the fiber and matrix in the presence of HRH bonding system in the fiber filled composite preventing the complete decomposition of the composite. For Mix C, the residue weight is 10.5 %. Residue values of the nanosilica-containing mixes are higher than that of other mixes. This may be arising from improved silica-matrix interaction. Nanosilica can interact better with the matrix due to their smaller size and hence higher surface area. This makes the matrix stiffer and the diffusion of heat and gases through the bulk more difficult prevented the complete degradation of the composite.

In the presence of 9 phr silica, the temperature of initiation increases from 315 ^{0}C to 325 ^{0}C for 10 phr fiber loading and 329 ^{0} C for 30 phr fiber loading. The peak rate of decomposition, Rmax, decreases with silica content. The Rmax decreases to 22.5 %/min. from 24 %/min. by the addition of 9 phr nanosilica in the 30 phr fiber loaded composite. This indicates that the material becomes thermally more stable by the addition of nanosilica. In the case of the mix containing commercial silica,(Mix F), the temperature of initiation (322 ^{0}C) and peak degradation temperature (388 ^{0}C) are lower than that of the mixes containing nanosilica and the peak rate of decomposition is higher. i.e., 27 %/min. This may attributed to the poor interfacial interaction between the fiber and the matrix in the case of the commercial silica mixes. Nanosilica contributes to effective interaction between the fiber and the matrix due to its small particle size and hence improves the interfacial adhesion between the fiber and the matrix. Strong interface renders the matrix stiff and makes the diffusion of heat and gases through the bulk more difficult. This makes the matrix thermally more stable in the presence of nanosilica.

The kinetics of the degradation reaction was studied by using the Freeman-Carroll Method [20]. According to this method

$$\Delta \log (dW/dt) = n. \Delta \log Wr - (\Delta E/2.3 R) \Delta (1/T) \text{.........................} (7.1)$$

where dW/dt is the rate of reaction, n is the order of reaction, R is the gas constant, T is the absolute temperature, and Wr is proportional to the amount of reactant remaining.

The above equation can be rearranged to

$$\frac{(\Delta \log (dW/dt))}{\Delta \log Wr} = n - \frac{(\Delta E/2.3 R) \Delta (1/T)}{\Delta \log Wr} \quad \text{................................} (7.2)$$

The order of the reaction and activation energies can be obtained from the intercept and gradient of the plot of the left side of Equation (7.2) versus Δ(1/T) / Δlog Wr and such a plot is given in Figure 7.5. That a common line with an intercept of one can be drawn to represent all the data points shows that the degradation of gum mix and the composites follow first-order kinetics. The role of silica and the short fibers seems to be very limited. This is because the degradation under nitrogen proceeds primarily by the thermal decomposition of the backbone chain. In the molecular level where the degradation is thermally initiated the reactant is primarily the rubber hydrocarbon and hence the rate is dependant only on its concentration. Similar results in the case of short fiber composites have been reported earlier [18- 19].

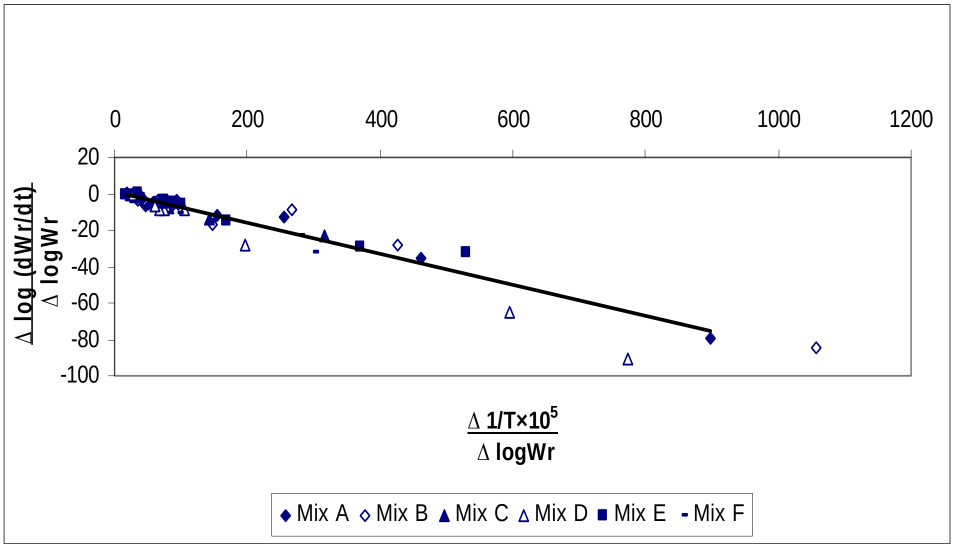

Figure 7. 5. Freeman –Carroll Plot of NR composite

The activation energies of the decomposition of the composites obtained from the gradient (fig. 7. 5) are given in table 7.5.

Table 7. 5. Activation energy of the decomposition of the NR composites

Parameters	Neat fiber	Raw NR	Mix No					
			A	B	C	D	E	F
Activation Energy(kJ/mole)	284	148	152	156	178	172	189	174

Activation energy increases with fiber content and silica loading. Higher the activation energy of the decomposition of the composite, better will be the thermal stability of the composite. Activation energy of the gum compound increases from 152 kJ/mole to 156 kJ/mole by the addition of 10 phr fiber; it further increases to 178 kJ/mole in presence of 9 phr nanosilica. In the case of 30 phr fiber loaded sample the corresponding values were 172 kJ/mole and 189kJ/mole. The mix F, which is the composite containing commercial silica, has an activation energy that is less than that of nanosilica composite. This also supports the view that nanosilica is more effective in improving the thermal stability of hybrid composite based on natural rubber and short Nylon fibers.

7.3.2 NBR based composites

Unlike NR, the virgin NBR degrades in two steps (Fig.7.6) with one minor peak at 428 ^{0}C and a major peak at 458 ^{0}C. The residual weight at 800 ^{0}C is 5.474 %. This higher residue compared to that of the natural rubber may be due to the formation of stable structures through probable cyclisation reaction that acrylonitrile can undergoes at elevated temperature. The unfilled NBR also (Mix G) degrades in two steps (Fig7.7) with one minor peak at 435 ^{0}C and a major peak at 460 ^{0}C. This is due to the multiple degradation steps of the butadiene component present in the raw rubber. Similar results in the case of polybutadiene rubber have been reported earlier [21]. Because of the lower diene content and also the presence of –CN group the nitrile rubber starts degrading at a higher temperature than that of NR. The degradation starts at a temperature of 328 ^{o}C and the maximum rate of degradation of 27.9 %/min occurs at a temperature of 460 ^{0}C. The residue remaining at 800 ^{o}C is 8.95 %. The DTG curves of the hybrid composite are shown in figure 7. 8. Thermal degradation characteristic of NBR based composites is given in table 7. 6.

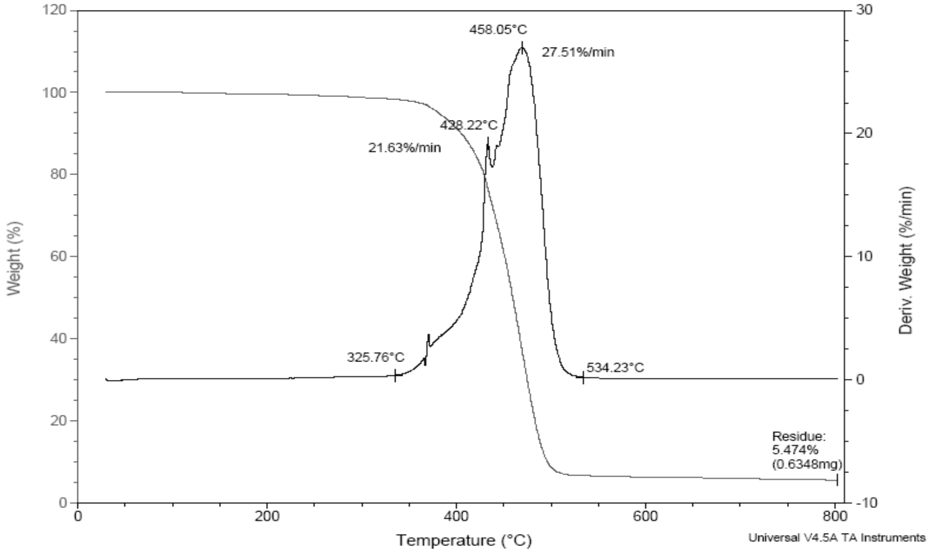

Figure 7.6. TG-DTG curves of raw NBR

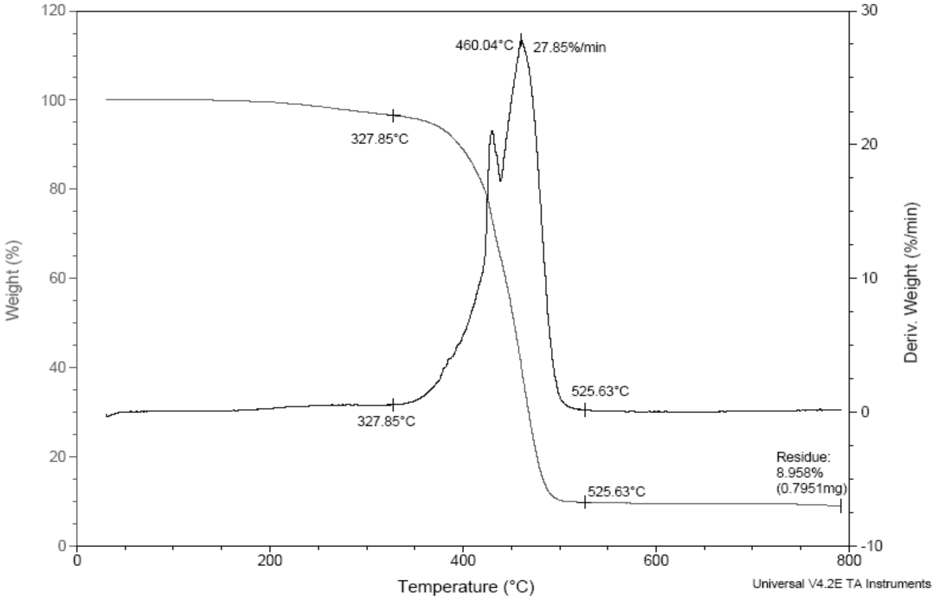

Figure 7.7. TG-DTG curves of unfilled NBR composite

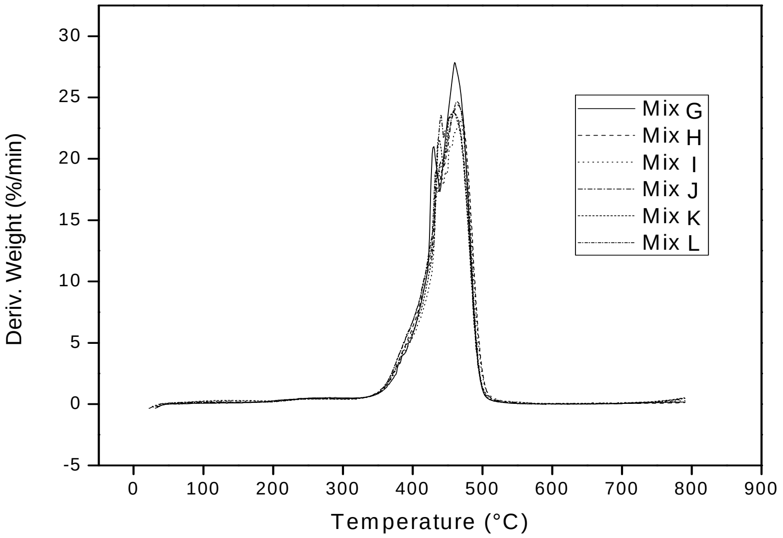

Figure 7.8. DTG curves of NBR hybrid composites

The figure shows that the degradation pattern of NBR composites is also similar to that of the unfilled rubber with one minor peak around at 440 ^{0} C and a major peak approximately at a temperature of 465 ^{0}C. The two peaks may be assigned to the degradation of the NBR matrix. The degradation of the fiber coincides with second peak of the matrix degradation. Both the temperature of initiation and the peak degradation temperature are improved in the presence of short fibers and also with nanosilica.

By the introduction of 10 phr fiber in the gum compound (Mix G), the temperature of onset of degradation is shifted to 331 ^{o}C from 328^{o} C and for 30 phr fiber loading it is 334 ^{o}C, indicating improved thermal stability of the composites. The major degradation temperature increases from 460^{o} C to 465^{o} C and to 467^{o} C for 10 phr and 30 phr fiber loaded composites, respectively. The maximum rate of degradation decreases with fiber concentration, and the 30 phr fiber loaded composite has the lowest maximum rate of degradation. Similar to NR composite, NBR composite also gives high residue content than that of gum composite at 800°C. The higher residual values of the NBR composites is due the high residue of the raw NBR and also due to the better interaction of the NBR with the silica and also with the fiber.

Table 7.6. Thermal degradation characteristic of NBR based composites

Parameters	Raw NBR	Mix No.					
		G	H	I	J	K	L
Temp. of initiation (Ti)°C	326	328	331	337	334	338	332
First Peak Degradation Temp (Tmax)°C	428	430	434	439	440	443	438
First Peak rate of decomposition (Rmax) %/° min.	21.63	21	18.6	18	23	21.5	18.9
Second Peak Degradation Temp (°C)	458	460	465	468	467	468	466
Second Peak rate of decomposition (Rmax) %/° min.	27.51	27.9	24.4	23	23.8	23	24.7
Residue at 800°C (%)	5.474	8.95	9.96	15.27	9.95	14.13	13.63

In presence of 9 phr silica, the onset temperature increases from 331 ^{0}C to 337 ^{0}C for 10 phr fiber loading and 338 ^{0}C for 30 phr fiber loading. The peak rate of decomposition decreases to 23 %/min. from 24.4. %/min. by the addition of 9 phr nanosilica in 10 phr fiber loaded composite. This indicates that the material becomes thermally more stable by the addition of nanosilica. In the Mix L i.e., the mix containing commercial silica the temperature of initiation (332 ^{0}C) and peak degradation temperature (466^{0}C) are lower than the mixes containing nanosilica and peak rate of decomposition is higher. i.e., 24.7 %/min. Peak rate of decomposition of NBR composites is less than that of the gum compound. All these show that the effect of these fillers is more pronounced in NBR composites compared to the natural rubber based composites. This may be attributed to the fact that the interaction of the fillers with the NBR matrix is better due to its the polar nature

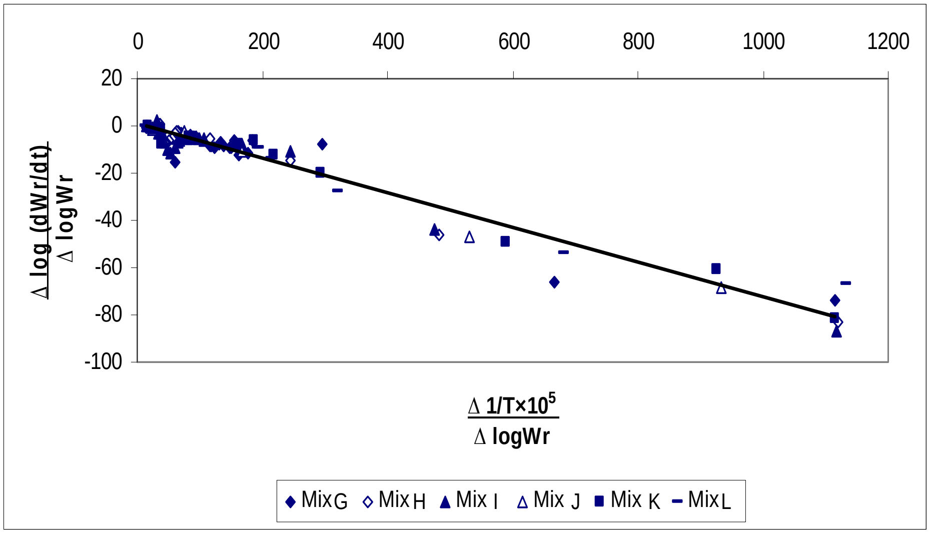

Figure 7.9. Freeman-Carroll plot of NBR composites

Freeman-Carroll plot of the NBR composites is shown in Figure 7.9. The intercepts show that the degradation of gum mix and the composites follows first-order kinetics. The activation energy of the decomposition of the composite is obtained from the gradient of the Figure 7.9 and is given in the Table 7.7 Activation energy increases with fiber content and silica loading. The higher the activation energy, the better will be the thermal stability. Activation energy of the gum compound increases from 249 kJ/mole to 254 kJ/mole by the addition of 10 phr fiber; it further increases to 258 kJ/mole in the presence of 9 phr nanosilica. In the case of the 30 phr fiber loaded sample the corresponding values are 256 kJ/mole and 260 kJ/mole. Mix L, which contains commercial silica, has an activation energy less than that of the nanosilica composite. The activation energy of the decomposition of the NBR composites is found to be higher than that of the NR composites.

Table 7.7 Activation energy of the decomposition of the NBR composites

Parameters	Neat fiber	Raw NBR	Mix No.					
			G	H	I	J	K	L
Activation Energy(kJ/mole)	284	245	249	254	258	256	260	255

7.3.3 SBR based composites

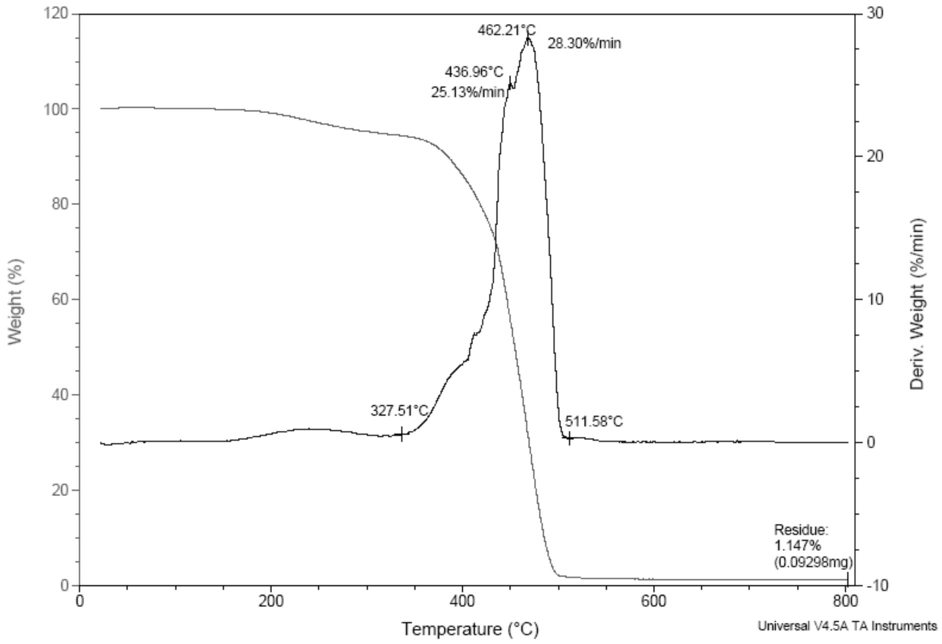

Figure 7.10. TG-DTG Curves of raw SBR

Similar to NBR, the raw SBR and the unfilled SBR (Mix M) also undergo two-step degradation (Fig.7.10 and Fig.7.11) due to the presence of butadiene [21].

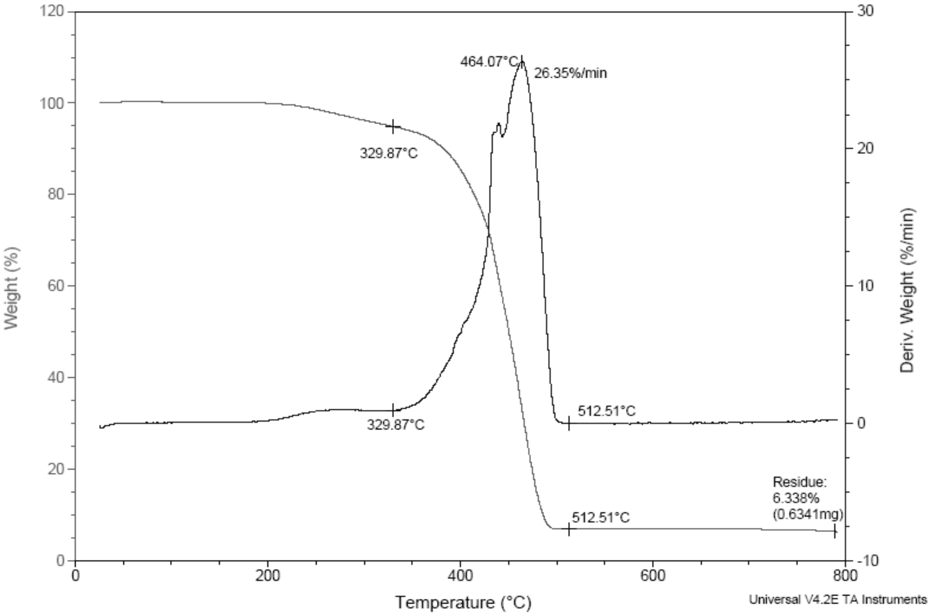

Figure 7.11. TG-DTG curves of unfilled SBR composite

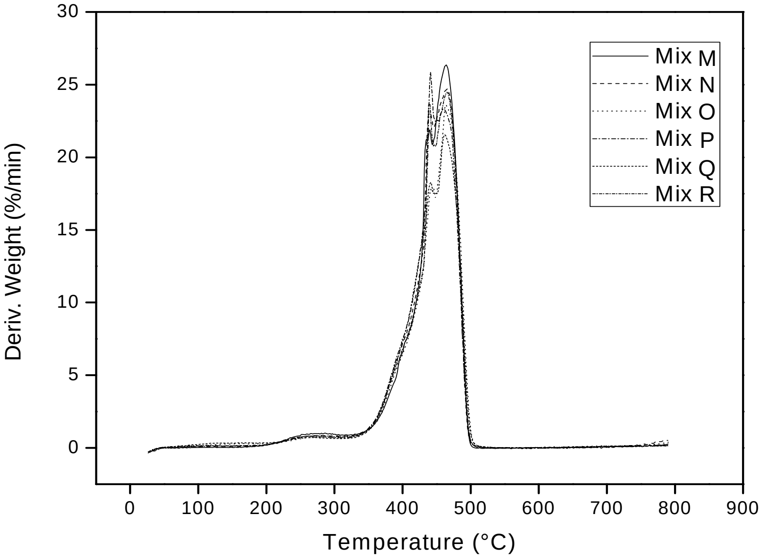

Figure 7.12. DTG curves of SBR hybrid composites

In the case of virgin SBR the degradation begins at a temperature of 328 ^{o}C. The two peaks appear at 437 ^{0}C and at 462 ^{0} C The peak rate of degradation is 28.3 %/min. The residue remaining at 800 ^{o}C is only 1.147 %.

Table 7.8. Thermal degradation characteristic of SBR based composites

Parameters	**Raw SBR**	**Mix No.**					
		M	**N**	**O**	**P**	**Q**	**R**
Temp. of initiation (Ti)^{o}C	328	330	332	339	342	347	335
First Peak Degradation Temp (Tmax)^{o}C	437	440	441	446	441	448	442
First Peak rate of decomposition (Rmax) %/^{o} min.	25.13	21.89	23	17	25	18	23.73
Second Peak Degradation Temp (^{o}C)	462	464	464	465	464	466	465
Second Peak rate of decomposition (Rmax) %/^{o} min.	28.3	26.4	24.7	23.6	23.3	21.6	24.5
Residue at 800^{o}C (%)	1.147	6.33	6.20	12.37	6.72	12.25	9.01

For unfilled SBR, degradation begins at a temperature of 330 ^{o}C and two peaks appear at 440 ^{0}C and at 464 ^{0} C. The peak rate of degradation is 26.4 %/min. The residue remaining at 800 ^{o}C is 6.33 %. The DTG curves of the hybrid composite are shown in Figure 7.12. The figure shows that the degradation pattern of SBR composites is similar to that of unfilled rubber, with a minor peak approximately at 442 ^{0} C and a major peak at around 465 ^{0} C. The two peaks may be assigned to the degradation of the SBR matrix. The degradation of the fiber coincides with second peak of the matrix degradation. Thermal degradation characteristics of SBR based composites are given in Table 7.8. The temperature of onset of degradation of the gum compound (Mix M), is increased to 342^{o} C from

330° C by the addition of 30 phr fiber in the mix, it is further increased to 347 ° C in presence of 9 phr nanosilica in the same mix. There is not much change in the peak degradation temperature of the composites with respect to the fiber and silica loading.

The peak rate of degradation decreases from 26.4 %/min. to 24.7%/min. and 23.3%/min, respectively in the presence of 10 phr and 30 phr Nylon fiber. By the addition of 9 phr silica into these mixes, (Mix O and Mix Q) the rate of degradation is further decreased. The improvement in the thermal stability of the SBR composites is limited compared to the natural rubber composite.

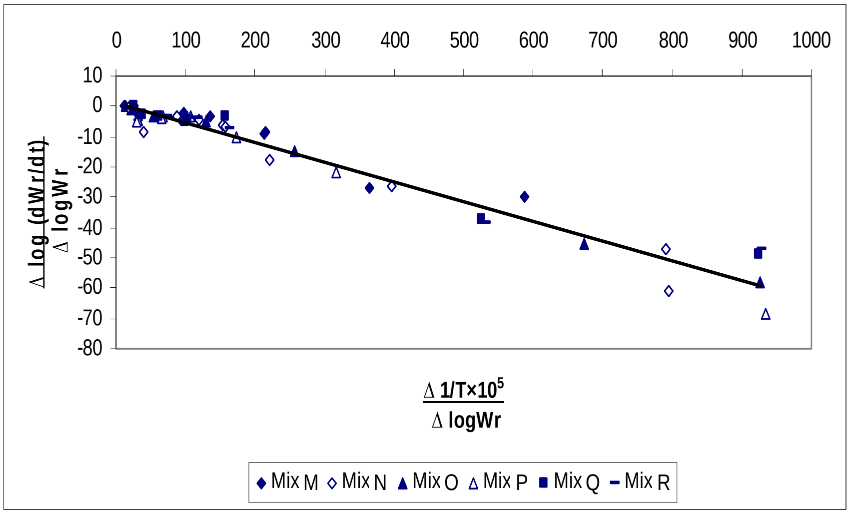

Figure 7.13. Freeman-Carroll plot of SBR composites

Freeman-Carroll plot of the SBR composites is shown in Figure 7.13. The intercepts show that the degradation of gum mix and the composites follows first-order kinetics, as in the case of the other two matrices. The activation energy of the decomposition of the composite is obtained from the gradient of Figure 7.13 and is given in Table 7.9.

Table 7.9. Activation energy of the decomposition of the SBR composites

Parameters	Neat fiber	Raw SBR	Mix No.					
			M	N	O	P	Q	R
Activation Energy(kJ/mole)	284	222	226	229	232	230	233	230

Activation energy increases with fiber content and silica loading. Activation energy of the gum compound increases to 229 kJ/mole from 226 kJ/mole by the addition of 10 phr fiber; it further increases to 232 kJ/mole in presence of 9 phr nanosilica. In the case of 30 phr fiber loaded sample the corresponding values are 230 kJ/mole and 233 kJ/mole. The mix R which is the composite containing commercial silica has activation energy less than that of the nanosilica composite.

7. 4 Conclusions

The present study shows that short Nylon fiber improves the thermal stability of rubber-fiber composites based on natural rubber, styrene butadiene rubber and nitrile rubber. The introduction of nanosilica improves the thermal stability of the hybrid composite better than the commercial silica. Natural rubber composites undergo two-step degradation. The first degradation corresponds to the degradation of the natural rubber and the second peak corresponds to the degradation of the Nylon fiber. The degradation of NBR and SBR composites also follows two- step degradation patterns. The two peaks may be assigned to the degradation of the matrix. The degradation of the fiber coincides with second peak of the matrix degradation. The temperature at onset of degradation (Ti) of NBR and SBR based composite are almost in the same range. NR composites show lower Ti values than that of the other two composites. Among the three types of elastomeric composites NR based composites show lower peak degradation temperature (Tmax.). Kinetic studies show that the degradation of the all the three elastomeric composites follows first-order kinetics.

7. 5 References

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Chapter 8

Dynamic Mechanical Analysis of Elastomeric Hybrid Composites

Contents

8.1 Introduction

The dynamic mechanical properties of a composite material depend on the type and loading of filler, apart from the matrix material. The extent of filler–matrix interaction and the type of filler dispersion can be evaluated by studying the time dependant properties of the composite system. The dynamic properties are also of direct relevance to a range of unique polymer applications, concerned with the isolation of vibrations or dissipation of vibrational energy in engineering components. Rubber is used as the base material in a product if it requires rubber-like elasticity and flexibility. In certain cases, rubber products require stiffness along with flexibility, often in specific directions. This can be achieved by reinforcing rubbers with long or short fibers to form composites. Short fiber reinforced rubber composites are more advantageous due to their ease of processing and flexibility in product design.

Several studies have been reported on the dynamic mechanical properties of polymeric composites [1-6]. Varghese *et al.* [7] studied the DMA of acetylated short sisal fiber reinforced NR composites and found that composite with poor interfacial bonding dissipated more energy than that with good interfacial bonding. DMA of short pineapple fiber reinforced polyethylene and oil palm fiber reinforced phenol formaldehyde resin composites has been conducted by George *et al* [8]. Thomas and co-workers [9-10] have reported the dynamic mechanical response of various natural fiber filled polymer composites. It was observed that addition of natural fibers into the polymer improved the viscoelastic properties to a greater extent. Otaigbe [11] reported that incorporation of solid elastic filler into polymer matrix increased the mechanical damping of the polymer. Nielson [12] observed that incorporation of reinforcing fillers usually decreased damping. Ibarra *et al.* [13] reported that the loss modulus values increased with loading of short PET fibers in NR, CR, NBR and SBR compared to their respective gum compounds. Dynamic viscoelastic properties of PET fiber reinforced styrene-isoprene and styrene-butadiene copolymers have been studied by Guo and Ashida [14]. Nano sized fillers are increasingly being used in rubber compounds and composites. By virtue of their smaller particle size and higher surface area they interact differently with the matrix compared to the conventional particulate fillers and fibers. Much of the work done so far on nano- filler composites were limited to nanoclays [15-16].

In the present work a study on a hybrid composite based on nanosilica and short Nylon 6 fiber is presented. The dynamic mechanical property of the composite was studied over a frequency range of 1Hz to 50 Hz at 70 ^{0}C. The strain was limited to 0.1146 %.

8.2 Experimental

The formulations of mixes are given in table 8.1, table 8.2, table 8.3 and table 8.4 for NR composites, NBR composites, SBR composites and CR composites, respectively.

Table 8.1. Formulation of the NR composites.

Ingredient (phr)$^+$	**Mix No.**					
	A1	**B1**	**C1**	**D1**	**E1**	**F1**
NR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	10
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	1.67

Zinc oxide-5phr, Stearic acid-2phr, N-(1,3-dimethylbutyl) N$^{'}$-phenyl-p-phenylene diamine) -1phr, CBS-0.6phr, TMTD- 0.2phr and sulphur-2.5phr were common to all mixes of the NR composites.

Table 8.2. Formulation of the NBR composites.

Ingredient (phr)$^+$	**Mix No.**					
	A2	**B2**	**C2**	**D2**	**E2**	**F2**
NBR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	10
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	1.67

Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl)N$^{'}$-phenyl-p-phenylenediamine) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes of the NBR composites.

Table 8. 3. Formulation of the SBR composites.

Ingredient (phr)⁺	Mix No.					
	A3	B3	C3	D3	E3	F3
SBR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	10
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	1.67

Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl)N'-phenyl-p-phenylenediamine) -1 phr, CBS-0.8 phr, TMTD- 0.2 phr and sulphur-2 phr were common to all mixes of the SBR composites.

Table 8.4. Formulation of the CR composites.

Ingredient (phr)⁺	Mix No.					
	A4	B4	C4	D4	E4	F4
CR	100	100	100	100	100	100
Nylon 6	0	10	10	30	30	10
Nanosilica	0	0	9	0	9	0
Commercial silica	0	0	0	0	0	9
HRH*	0	1.67	1.67	5	5	1.67

CR-100 phr, zinc oxide-5 phr, stearic acid-0.5 phr, N-(1, 3- dimethylbutyl) N'-phenyl-p-phenylenediamine) -1 phr, magnesium oxide - 4 phr, ethylene thiourea- 0.5 phr were common to all mixes.

* Hexa: Resorcinol: Silica in the ratio 2:2:1. Total loading was 16% on fiber content.

$^{+}$ part per hundred rubber

The mixing was done as per ASTM D-3184 (1989) standard on a two-roll laboratory size mixing mill (150mm×300mm). Nylon 6 fibers were added in small increments in order to obtain uniform dispersion. Dry bonding system comprising of resorcinol, hexamethylene tetramine (hexa) and silica (HRH), was used as the bonding system to achieve improved bonding between the fiber and the matrix. The sheets were vulcanized in the hydraulic press at 150 °C and 200 kg/cm^2 pressure to their optimum cure times, as determined using a Rubber Process Analyzer (RPA – 2000), Alpha Technology.

The dynamic mechanical thermal analysis was conducted using rectangular test specimens having a dimension of 30 mm x 5 mm x 2 mm under tension mode using a TA Instruments DMA Q-800 at a constant temperature of 70 °C. The frequency was varied from 1 to 50 Hz under frequency sweep mode at a rate of 2 Hz/min. The samples were subjected to dynamic strain amplitude of 0.1146 %.

8.3 Results and Discussion

Variation of storage modulus E’ and loss modulus E” with frequency at 70 ^{0}C of the gum compounds of NR, NBR, SBR and CR rubbers are shown in the figures 8.1 and 8.2.

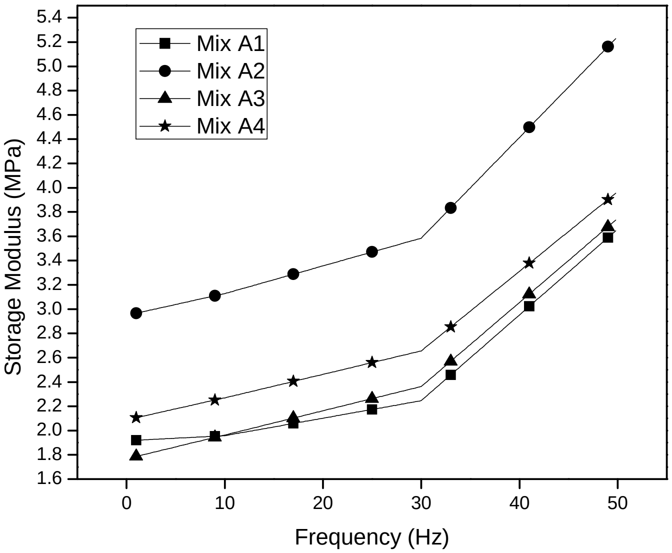

Figure 8.1. Variation of storage modulus (E’) with frequency of gum compound

E' and E" increase linearly with frequency irrespective of the matrix used. For all the mixes the E' and E" increase marginally up to 30 Hz and beyond this the rate is high. Among the four matrices, NBR compound (Mix A2) shows the highest E' values over the frequency range studied. It also shows the highest rate of increase. In the case of NR compound the storage modulus increases at 0.01 MPa/ Hz upto 30 Hz and after that the rate is 0.07 MPa / Hz. SBR and CR compounds show almost the same rate of increase. They show a rate of 0.02 MPa / Hz upto 30 Hz and after that it increases to 0.07 MPa/Hz. In the case of NBR compound the rate is slightly higher than that of other matrix beyond 30 Hz. The increase in modulus with frequency may be arising from the viscoelastic nature of the matrix. There is a definite time lag between an external stimulus and response of a viscoelastic matrix. Increasing frequency is, in effect, giving lesser time for response. This results in the material behaving like a stiffer matrix which is manifested as increased modulus.

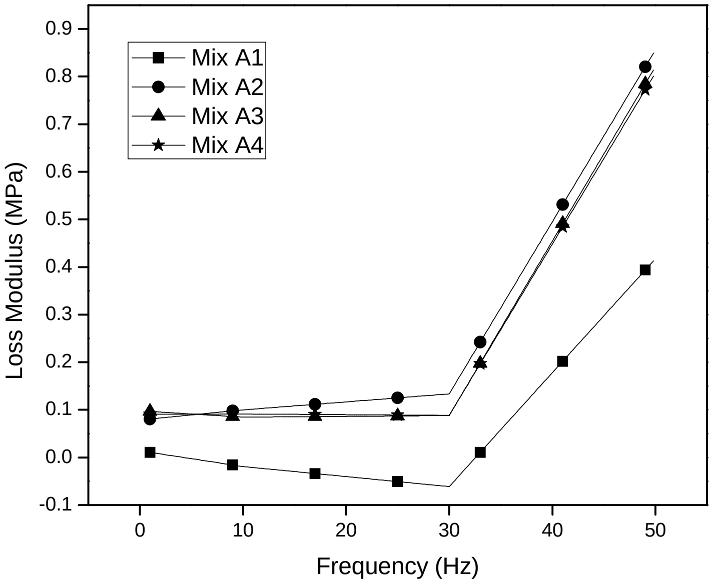

Figure 8.2. Variation of loss modulus (E") with frequency of gum compound

A frequency of 30 Hz seems to be a critical value. Beyond this, the rate of increase is high. The loss modulus E” remains almost independent of frequency up to 30 Hz except for mix A1 which shows a marginally negative initial slope. Beyond 30 Hz the modulus increases at 0.04 MPa/Hz for SBR, NBR and CR compounds and for NR it increases at 0.02 MPa/Hz.

Figures 8.3 and 8.4 show the variation of storage modulus E’ and loss modulus E” of NR based composites with frequency. E’ and E” show linear increase with frequency. For the gum compound (Mix A1) the E’ remains almost independent of frequency up to 30 Hz. Beyond this, the E’ tends to increase marginally. For 10 phr fiber-filled samples, (Mixes B1 &C1), the variation is found to be linear with a moderate slope of 0.04 MPa /Hz. For the silica-containing samples (Mixes C1, E1 and F1), the E’ is found to be significantly higher than the corresponding non -silica mixes, with the nanosilica sample (Mix C1) showing consistently higher values than the corresponding commercial silica filled samples (Mix F1).

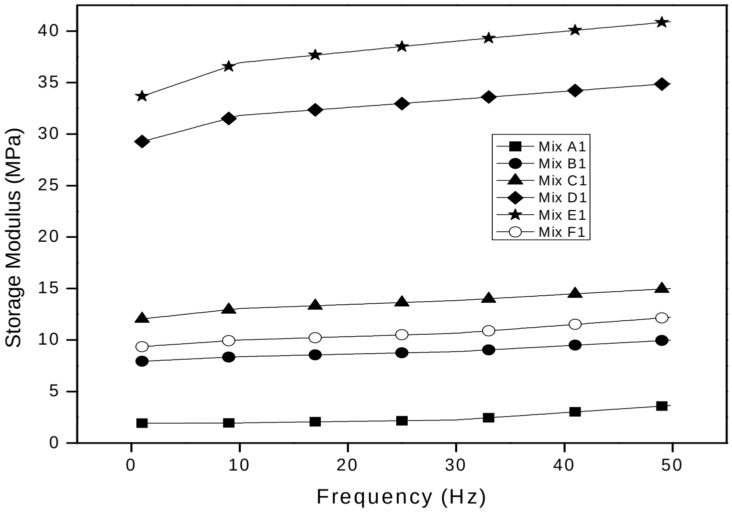

Figure 8.3. Variation of storage modulus (E’) with frequency of NR composite

Silica is known to have even a tertiary structure formed by the agglomeration of the primary agglomerates. After an initial structure break down further increase in frequency does not seem to have profound influence on the E'. Compared to mix C1 with nanosilica, mix F1 containing commercial silica shows lower E' over the frequency range studied. It may be attributed to the higher structure of the commercial silica compared to the nanosilica.

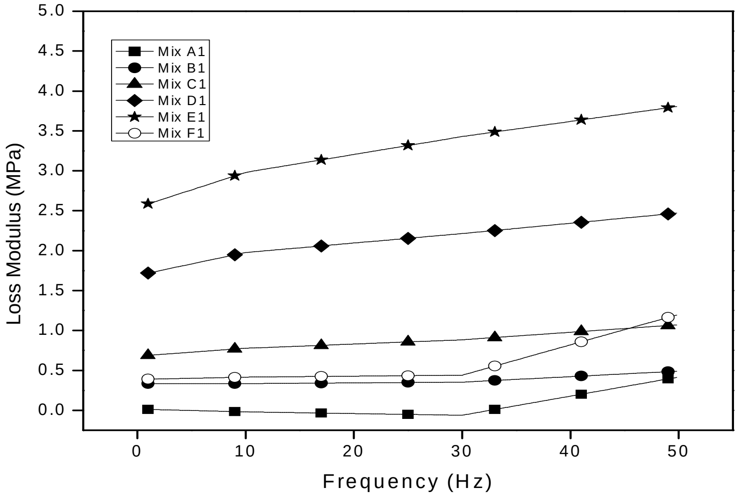

Figure.8.4. Variation of loss modulus (E”) with frequency of NR composite

The higher fiber loaded samples show a two-step increase of E' with frequency (Mix D1 and E1). Up to a frequency of 10 Hz the E' increases at a rate 0.3 MPa/ Hz and then it grows at a lower rate of 0.09 MPa/ Hz. The rate of increase of these two regions of mixes D1 and E1 are indicated in the figure 8.3. The initial higher slope followed by a region of lower slope may be attributed to the surface features of the hybrid composite. A steeper increase in E' with frequency indicates relatively more viscoelastic nature of the matrix resulting from the breakage of the filler – matrix bonds and filler structure.

It can be seen that with the incorporation of 10 phr of short nylon fiber in the NR gum composite (mix A1), E' is uniformly improved over the frequency range studied. At lower frequencies, the improvement is 242 % (mix B1). E' is further improved by 415 % by the incorporation of just 9 phr of nanosilica (mix C1). By the incorporation of commercial silica instead of nanosilica in 10 phr fiber filled composite (mix F1) the corresponding increment is only 300 %. This may be due to the improved interaction of nanosilica with the matrix. By increasing the fiber content from 10 to 30 phr, E' is improved by 172 % (between mixes B1 and D1). The storage modulus of the composite is highly influenced by the incorporation of nanosilica.

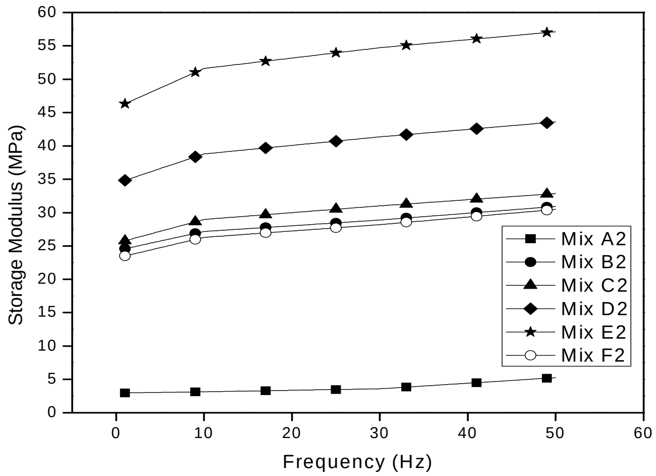

Figure 8. 5. Variation of storage modulus (E') with frequency of NBR composite

The variation of E' with frequency of composites based on NBR, SBR and CR is similar to that of natural rubber (Figures 8.5, 8.6 and 8.7). The storage moduli of NBR and CR are the highest. This may be attributed to the difference in polarity of these matrices. NBR and CR being more polar than NR and SBR, the chances of interaction of the fillers with the matrix is more. This renders the composites stiffer.

The NBR composites also show a two- stage increment in E’ with respect the frequency. All the fiber loaded samples have a higher rate of modulus upto 10 Hz. Beyond this the rate is lower and almost linear. The effect of nanosilica in the 10 phr fiber loaded samples is less than that in the 30 phr fiber loaded sample (Mix D2 and E2).

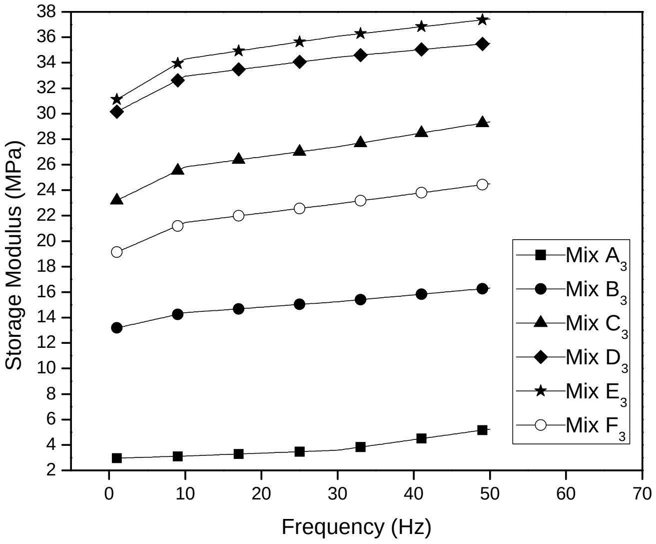

Figure 8.6. Variation of storage modulus (E’) with frequency of SBR composite

The SBR composites show a linear increase with frequency. SBR composite also shows two -step change in modulus in the cases of E’. Up to 10 Hz the E’ increases at a higher rate of 0.3 MPa / Hz and after that the rate is much lower (0.05 MPa / Hz). From the graph it is clear that E’ is increases with fiber loading and silica content for all the frequency range studied. But there is not much variation in the rate of change of E’ by the incorporation of nanosilica or fiber and the rate is higher at lower frequencies. i.e. the storage modulus of SBR matrix is independent of frequency over the frequency range studies. The maximum E’ recorded for SBR based composites (Mix E3) is equal to that of naturual rubber.

The effect of commercial silica is also found to be matrix-dependant. In the NBR composites, the E' of the commercial silica samples (Mix E2) is almost equal to that of the 10 phr fiber loaded samples (Mix B2) where as in SBR and CR composites, the commercial silica composites lie in between that of mixes B and C. ie. 10 phr fiber loaded samples with and without silica. The highest value of E' is recorded for the NBR based composites. In all the cases, the composites containing commercial silica show lower storage modulus than the nanosilica based composites.

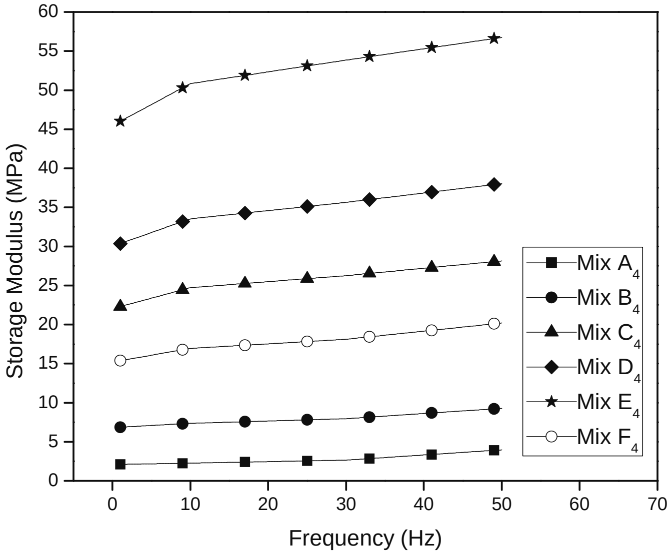

Figure 8.7. Variation of storage modulus (E') with frequency of CR composite

In the case of CR composite the rate of change of E' with frequency occurs only the addition of silica or higher fiber loading (Fig.8.7). Similar to all the other composite, silica filled CR composite also shows a two step change in E' with frequency and the rate is higher at lower frequencies up to 10 Hz and beyond this the rate decreases.

Figure 8.4 shows the E” of the different NR composites. The E” at any frequency is greater than that of the gum compound. Fiber incorporation increases the E”, which indicates a higher heat dissipation (heat build-up) in the case of short Nylon fiber reinforced NR composites compared to that of gum compound arising from a possible breakdown of filler – matrix bonds. Similar results in the case of short coir fiber / natural rubber composite have been reported earlier [9]. The E” is also found to increase by increasing the silica content. At lower frequencies, the increases are 118 % and 255% for 10 and 30 phr samples (Mixes B1 and D1) respectively with respect to the gum compound. By the incorporation of 9 phr nanosilica in the mix B1, the E” is increased by 300 % and for 30 phr fiber loaded sample the corresponding improvement is 66 %. E’and E” are found to increase with fiber content. As the reinforcing fillers contributes to increase in stiffness the storage modulus (E’) is expected to increase. The increase in loss modulus (E”) may be due to loss at interfaces. The fiber-matrix interface bonds break irreversibly, contributing to the E”. It has been reported that the mechanical damping of polymer increases when compounded with solid elastic filler [11, 13]. The E” of butyl rubber has been found to increase with increase in loading of HAF black filler [18]. The nanosilica loading is also having a significant effect on the frequency-dependency of the E’ and E”. Loss modulus E” shows a two- step increase with respect to frequency except for 10 phr fiber filled composite. For 10 phr fiber filled samples (Mix B1 & C1), E” remains linear with a moderate slope of 0.006 MPa /Hz over the frequency range studied. Higher fiber loaded composite (Mix D1 and E1) shows a higher rate of increase up to 10 Hz and after that it remains linear with a moderate slope of 0.02 MPa/ Hz. Compared to the nanosilica loaded samples, the commercial silica sample (Mix F1) shows higher rate of increase beyond 30 Hz. But for nanosilica filled composite it remains independent of frequency. Due to the lower particle size and less agglomeration nanosilica interact better with the matrix and matrix remains more restrained.

The variation of E” in the case NBR, SBR and CR composites is shown in figures 8.8, 8.9 and 8.10 respectively. For NBR composites also, the loss modulus E” shows two step increase in modulus with respect to the frequency (Fig.8.8). For gum and 10 phr fiber loaded samples E” increases slightly up to 30 Hz and beyond this the rate of increase is higher. But in the case of nanosilica filled samples this change is observed below 10 Hz. Up to 10 Hz the rate of increase is high for the mixes C2, D2 and E2. This is due to the variation of viscoelastic response of the compound in the presence of nanosilica.

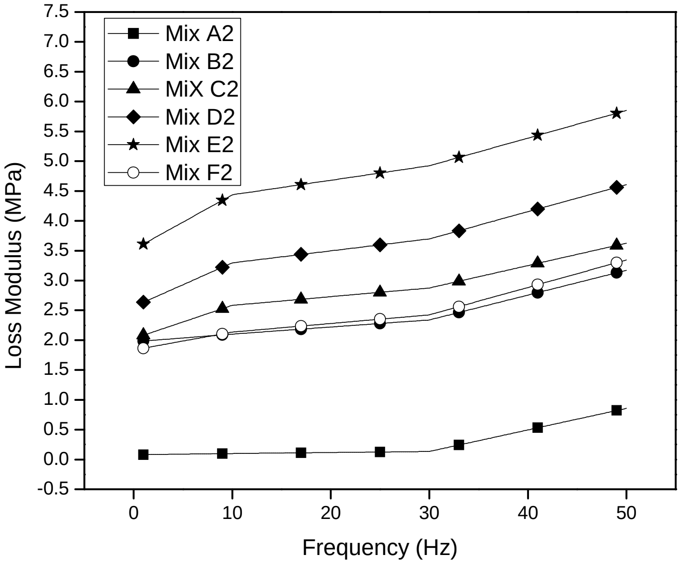

Figure 8. 8. Variation of loss modulus (E”) with frequency of NBR composite

In the case of commercial silica mix (Mix F2) E” values are equal to that of mix B2 i.e. the mix containing 10 phr fiber only. This indicates that the role of commercial silica on the damping properties of NBR composite is limited.

In SBR composites the rate of change of modulus of the composite occurs at 30 Hz (Mix A3, Mix B3and Mix D3). The incorporation of silica shifts this point to a lower frequency of around 10 Hz (Mix C3, E3 and F3). 30 phr fiber loaded samples show a three step change in the rate of E”. Up to 10 Hz the E”changes by a higher rate of 0.03 MPa/ Hz and after that the rate remains unaffected by the frequency up to 30 Hz. Beyond this the rate again increases at 0.03 Mpa/Hz.

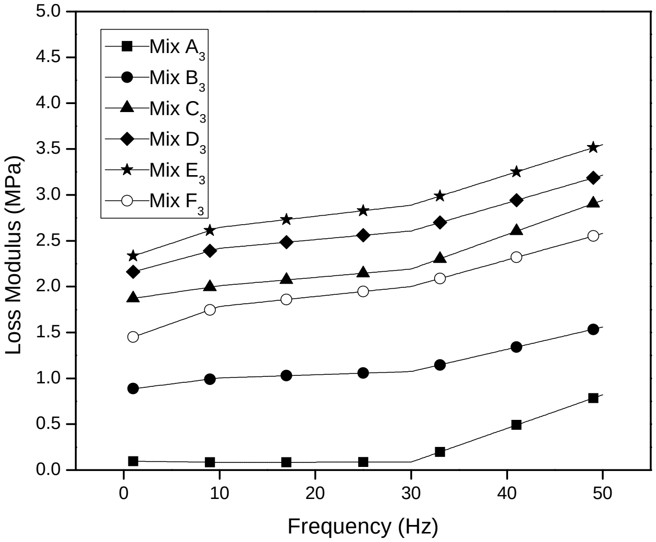

Figure 8.9. Variation of loss modulus (E”) with frequency of SBR composite

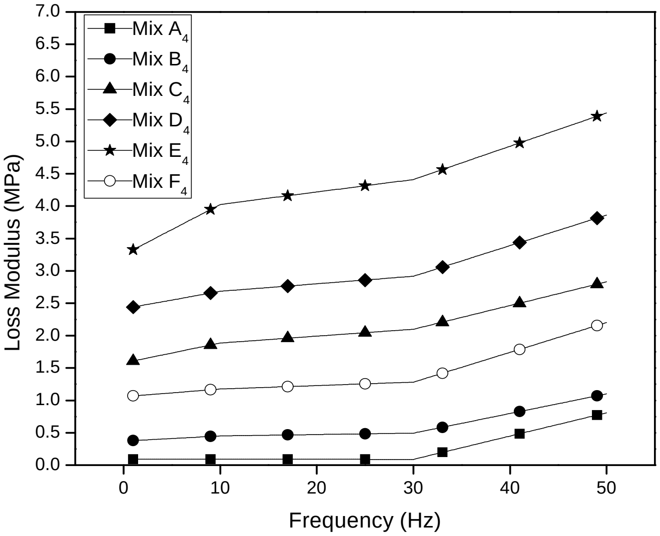

Figure 8.10. Variation of loss modulus (E”) with frequency of CR composite

Fiber incorporation increases the E”, which indicates the higher heat dissipation (heat build-up) in the short Nylon fiber reinforced composites compared to that of gum compound. The increase in damping at the interface with fiber loading can be explained by the fact that the larger the interfacial area, the more energy loss there is [9]. In all the cases, the nano silica based composites show higher E” values.

E” of the CR composites varies linearly with frequency for all the frequency range studied (Fig.8.10). Compared to gum compound (Mix A4) E” increases with fiber content and silica loading. Commercial silica filled composites (Mix F4) shows E” values in between that of mix B4 and mix C4. Mixes A4, B4 and commercial silica (Mix F4) mixes shows an increase in the rate of change of E” at 30 Hz. But in the case of higher filler loaded composites there is a two step change in E” values i.e at 10 Hz and 30 Hz. Mix E4, the composite containing 30phr fiber and 9 phr nanosilica shows a higher rate of increases in E” values both at 10 Hz and 30 Hz. Being more polar the chances of interaction of the fillers with the CR matrix is more. Filler incorporation increases the E”, which indicates a higher heat dissipation (heat build-up) arising from a possible breakdown of filler – matrix bonds.

8.4 Conclusions

The dynamic mechanical analysis of short Nylon 6 fiber / nanosilica reinforced Natural rubber, Nitrile rubber, Styrene butadiene rubber and Chloroprene rubber based elastomeric hybrid composites has been done with reference to the fiber content, silica content and frequency. Storage modulus E’ and loss modulus E” show linear increase with frequency for all the composites irrespective of the matrix. The highest rate of increase was registered for NBR rubber. With the incorporation of short fiber, E’ is uniformly improved over the frequency range studied. Fiber incorporation increases the E” of these composites indicating the higher heat dissipation of the composites compared to that of the gum. The storage modulus of the composite is highly influenced by the incorporation of nanosilica for all the mixes. Similar trends are shown by E” also. Compared to nanosilica the effect of commercial silica is limited. The rate of increase of E’ and E” with silica for different samples shows that the slope is higher for samples containing nanosilica than that of commercial silica. The silica filled composites show a two-step increase of E’ with frequency. The frequency of 10 Hz and 30 Hz seems to be the critical values. Loss modulus (E”) varies linearly with the frequency and also shows a two step increase.

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Chapter 9

Summary and Conclusion

In recent years there has been a tremendous advancement in the field of science and technology of short fiber reinforced polymer composites. The low density, high strength, high stiffness to weight ratio, excellent durability and design flexibility are the major reasons for their use in many diversified fields such as air crafts, automobiles, marine industry etc. Polymer nanocomposites containing nanometer sized fillers have received increasing attention of both scientific and industrial communities. Sufficiently small filler can give good reinforcement, even when matrix /domain bonding is poor. Of late, the interest in green composites based on silica is gaining momentum. The nanosized silica is a filler with untapped potential. The nanosilica can be used to make hybrid composites based on short fibers and elastomers. The nanosilica can also be used as a component in hexa-resoricinol (HRH) dry bonding system. The present study is primarily on the preparation and characterization of nano sized silica and its utilization in hybrid composites based on short Nylon 6 fiber and elastomers. A summary of the thesis is given below.

A review of the earlier studies on short fiber / polymer composites, a brief discussion on the classification of composites, various types of matrices and reinforcing materials, factors influencing the performance of short fiber elastomer composites are outlined. The principal objectives of the present study are pointed out briefly at the end of the chapter.

In the first stage of the work, we synthesized the nanosilica from a cost effective silica source, sodium silicate, and hydrochloric acid by precipitation method under controlled conditions using polyvinyl alcohol, starch and carboxy methyl cellulose as the dispersing agents. This synthesized silica was characterized by using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), BET Adsorption and Infrared Spectroscopy (IR). Nanosilica prepared by this method had particle size lower than that of the commercially available silica. Use of a dispersing agent in the reaction reduced the particle size of the silica produced. This synthetic nanosilica had lower hydroxyl number and hence reduced agglomeration. XRD results showed that the synthesized silica was in amorphous state. Nanosilica synthesized by using 2 % poly vinyl alcohol as a dispersing agent had the lowest particle size.

The performance of this synthesized nanosilica as a reinforcing filler in natural rubber compound was investigated. Nanosilica is, an effective reinforcing filler in natural rubber compound. Minimum torque, maximum torque, scorch time and cure time increase with silica loading and are higher for nanosilica compounds. Filler-matrix interaction is better for nanosilica than the commercial silica. Volume fraction of rubber in a solvent-swollen sample is also higher for the nanosilica compounds. The introduction of the nanosilica in the rubber compound improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion loss, hardness and compression set properties are also better for the nanosilica compounds.

An investigation on the effect of nanosilica on the mechanical properties of short Nylon 6 fiber - natural rubber and styrene butadiene rubber composites shows that the role of silica is to improve wetting of the fiber surface. As small particles have higher surface area, nanosilica can be more effective in improving wettability of the fibers. The dry bonding system comprising of resorcinol, hexamethylene tetramine, and silica improves the mechanical properties of the short Nylon 6 fiber composites. The efficiency of HRH bonding system in the composite increases in the presence of synthesized nanosilica. Tensile strength, tear strength, modulus and abrasion resistance increase by the use of nanosilica HRH system which shows that the interfacial adhesion between the fiber and the matrix can be improved. Compression set and resilience are adversely affected by the introduction of nanosilica in HRH bonding system. The composites show anisotropy in mechanical properties. Ageing of the composite at 70°C for 72 h increases the tensile strength, tear strength and modulus in the presence of the dry bonding system. The retention in ageing is better for nanosilica composites.

Evaluation of the nanosilica as a reinforcing filler in short Nylon 6 fiber / elastomeric composites based on natural rubber, nitrile rubber, styrene butadiene rubber and chloroprene rubber shows that the synthesized silica is more effective in the presence of short fibers The nano silica is also effective as a component of the HRH dry bonding system

The cure and mechanical properties of natural rubber / short Nylon 6 fiber composite are improved by the nanosilica. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading and increases with silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Longitudinally oriented fiber composites have superior properties than transversely oriented ones. Volume fraction of rubber, a measure of the cross-link density, in a solvent-swollen sample, increases with nanosilica. Ageing resistance of nanosilica filled hybrid composites is better than that of the commercial silica-based composites.

The hybrid composites based on nanosilica, Nylon 6 short fiber and NBR show improved mechanical properties in the presence of nanosilica. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading and silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Hybrid composites show anisotropy in mechanical properties. Volume fraction of rubber increases with nanosilica. Retention in ageing is improved with fiber loading and it is better for nanosilica filled hybrid composites.

SBR /short Nylon 6 fiber composites also show improved mechanical properties in the presence of nanosilica. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time also decreases with fiber loading. Volume fraction of rubber increases with nanosilica. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Hybrid composites show anisotropy in mechanical properties. Retention in ageing is improved with fiber loading and it is better for nanosilica filled hybrid composites.

Nanosilica is a good reinforcing filler in short Nylon 6 fiber / chloroprene rubber hybrid composites containing HRH dry bonding system. Cure and mechanical properties of chloroprene rubber /short Nylon 6 fiber composite are improved by the introduction of nanosilica in the composites. Minimum torque, maximum torque and cure time increase with silica loading. Cure rate increases with fiber loading and decreases with silica content. Scorch time decreases with fiber loading and increases with silica content. The nanosilica improves the tensile strength, modulus and tear strength better than the conventional silica. Abrasion resistance and hardness are also better for the nanosilica composites. Resilience and compression set are adversely affected. Longitudinally oriented fiber composites have superior properties than transversely oriented ones. Volume fraction of rubber increases with nanosilica. Ageing resistance also better for nanosilica filled hybrid composites than that of commercial silica.

Thermal characterization of elastomeric hybrid composite based on nanosilica and short nylon 6 fiber shows that the short Nylon fiber improves the thermal properties of rubber-fiber composites based on natural rubber, styrene-butadiene rubber and nitrile rubber. The nanosilica is more effective in improving the thermal stability of the hybrid composites than the commercial silica. Natural rubber composites undergo two-step degradation. The first degradation corresponds to the degradation of the natural rubber and the second peak corresponds to the degradation of the Nylon fiber. The degradation of NBR composite and SBR composites also follows two- step degradation pattern. The first degradation is due to the partial degradation of the raw rubber and second peak is due to the degradation of the matrix and also the fiber. The temperature at the onset of degradation (Ti) of NBR and SBR based composite is almost in the same range. NR composites show a lower Ti values than that of the other two composites. Among the three types of elastomeric composites NR based composites show the lowest peak-degradation temperature (Tmax.). Kinetic studies show that the degradation of the all the three elastomeric composites follows first-order kinetics.

The dynamic mechanical behavior of elastomeric hybrid composites based on short Nylon 6 fiber/nanosilica reinforced natural rubber, nitrile rubber, styrene butadiene rubber and chloroprene rubber has been studied with reference to the fiber content, silica content and frequency. The test was conducted using rectangular test specimens having a dimension of 30 mm x 5 mm x 2 mm under tension mode using a TA Instruments DMA Q-800 at a constant temperature of 70 °C.

The frequency was varied from 1 to 50 Hz under frequency sweep mode at a rate of 2 Hz/min. The samples were subjected to dynamic strain amplitude of 0.1146 %. Storage modulus E' and loss modulus E"show linear increase with frequency for all the composites. The highest rate of increase is registered for NBR rubber. With the incorporation of short fiber, E' improves uniformly over the frequency range studied. Fiber incorporation increases the E" of these composites indicating higher heat dissipation of the composites compared to that of the gum. The storage modulus of the composite is highly influenced by the incorporation of nanosilica for all the mixes. Similar trends are shown by E" also. Compared to nanosilica the effect of commercial silica is limited. The rate of increase of E' and E" of different samples is higher for samples containing nanosilica. The silica filled composite show a two-step increase of E' with frequency. The frequencies 10 Hz and 30 Hz seem to be critical. Loss modulus E"varies linearly with the frequency and also shows a two -step increase for all the composite in the presence of nanosilica.

The study shows that we can synthesize low particle size, less agglomerated silica by less expensive and ecofriendly method. Nanosilica is an efficient reinforcing filler in polar and non-polar rubbers, especially in the presence of short Nylon 6 fibers.

* * *

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List of Abbreviations

ASTM	American society for testing and materials
AFM	Atomic Force microscopy
BET	Brunauer, Emmett and Teller
CBS	N-cyclohexyl-2-benzothiazyl sulphenamide
CR	Chloroprene rubber
CMC	Carboxy (methyl cellulose)
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Derivative thermogravimetry
E'	Storage modulus
E"	Loss modulus
EB	Elongation at break
FTIR	Fourier Transform Infra Red
HAF	High abrasion furnace carbon black
Hrs	Hours
Hexa	Hexa methylene tetramine
Hz	Hertz
HRH	Hexa methylene tetramine- resorcinol- hydrated silica
l_c	Critical fibre length
IR	Infra Red Spectroscopy
ISNR	Indian standard natural rubber
L	Longitudinal
μm	Micrometer
min	Minutes
mm	millimetre
mol	Mole
M_H	Maximum torque
M_L	Minimum torque
Mpa	Mega Pascal
MMC	Metal matrix composite
ML(1+4)	Mooney viscosity using large rotor (1’ preheating and 4’ testing time)
NBR	Acrylonitrile butadiene rubber
Nm	Newton meter

NR	Natural rubber
PET	Polyethylene terephthalate
PMC	Polymer matrix composite
PMMA	poly methyl methacrylate
PP	poly propylene
phr	Parts per hundred rubber
PU	Polyurethane
PVA	Poly (vinyl alcohol)
R	Universal gas constant
RFL	Resorcinol formaldehyde latex
Rpm	Revolutions per minute
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TEOS	Tetraethoxysilane
TMOS	Tetramethoxysilane
$T_{max} - T_{min}$	Difference between maximum and minimum torque
T_i	Temperature of intiation
tan δ	Loss factor
T	Transverse
TG	Thermogravimetry
T_g	Glass transition temperature
TGA	Thermo gravimetric analysis
TMTD	Tetramethylthiuram disulphide
TS	Tensile strength
t_{90}	Optimum cure time
t_{10}	Scorch time
UPR	Unsaturated polyester resin
UTM	Universal Testing Machine
V_f	Volume fraction of fibre
V_m	Volume fraction of matrix
V_r	Volume fraction of rubber
XRD	X- ray diffraction
ZnO	Zinc oxide

BIO- DATA

LENY MATHEW
Lecturer in Polymer Engineering
Mahatma Gandhi University College of Engineering,
Muttom, Thodupuzha. 685 587.

Phone No. +91 9495469173 (cell)
E-mail - geoleny@gmail.com

Personnel Details

Date of Birth	:	20-04-1970
Sex	:	Female
Religion	:	Christian, R.C.S.C
Qulification	:	B.Tech. (Polymer Science & Rubber Technology) M.Tech. (Polymer Technology)
Present Job	:	Working as Lecturer in Polymer Engineering, Mahatma Gandhi University College of Engineering, Thodupuzha. 685 587. (1997 onwards)
Teaching Experience	:	11 Years
Industrial Experience	:	3 Years

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