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](image-url)
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 lose 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.

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 absence 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.
Introduction

- 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.

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 as 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\textsuperscript{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 \textit{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 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-aromatic 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.
Chapter-1

(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 caprolactum. 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

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

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 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].

\[ \varepsilon_c = \varepsilon_f = \varepsilon_m \] .................................(1.1)

where \( \varepsilon_c \), \( \varepsilon_f \) and \( \varepsilon_m \) 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.

\[ \sigma_f = E_f \varepsilon_f \] ...............................(1.2)
\[ \sigma_m = E_m \varepsilon_m \] ...............................(1.3)

Hence

\[ \frac{\sigma_c}{E_c} = \frac{\sigma_m}{E_m} = \frac{\sigma_f}{E_f} \] ...............................(1.4)

where \( \sigma_c \), \( \sigma_f \) and \( \sigma_m \) 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.

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

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**Figure 1.4. Effect of stretching force on the strain around long and short fiber in a low modulus matrix**
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 possess 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 ($l_c$).

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

where $d$ is the diameter of the fibre, $\sigma f_u$ is the ultimate fiber strength, and $\tau_y$ 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 Chakraborty [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.
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

\[
\text{Orientation} \% = \frac{S_L/S_G}{S_L/S_G + S_T/S_G}
\]

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
Introduction

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.

![Figure 1.6. Schematic representations of various fiber matrix adhesions.](image)

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 urethane 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].
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
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\textsubscript{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\textsubscript{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 SiO₄ (silicate) subunits show no regular lattice pattern in the structures. In silicon dioxide, silicon atom uses d orbitals for bonding and hence SiO₂ 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 SiO₂·nH₂O. 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 I. 8.

Figure I. 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].

\[ \text{Na}_2\text{SiO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SiO}_2 \] ........................................(1.7)

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

\[ \text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl} \] .............................................(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 \( \mu \)m and for fumed silica it is about 15 \( \mu \)m 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](image)

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](image)
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 \(^\text{4C}_1\) conformation. In amylose these are linked - (1\(\rightarrow\)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\(\rightarrow\)6) - forming branch-points. The relative proportions of amylose to amylopectin and - (1\(\rightarrow\)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%)
Poly (vinyl alcohol) is a water-soluble polymer having the following structure:

\[-(\text{CH}_2\text{—CH—})\text{—}\text{OH}\]

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 elastomers 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.
1.13 References


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