Chapter 1: Introduction

Part of this chapter has been published in:

Rubber Chemistry and Technology, 81, 384 (2008).

1.1 General Introduction

Nanotechnology is recognized as one of the most promising fields of research of the 21st century. The beginning of nanotechnology and nanoscience research can be traced back over 40 years. However, it was in the last decade that the world witnessed bigger strides of this technology into various disciplines. Proliferating in the realm of interdisciplinary sciences, the prodigious growth of polymer nanocomposites has obliterated the boundaries of conventional academic disciplines of chemistry, biology, materials science and engineering.

The term, 'nanocomposite' refers to every type of materials having fillers in the nanometer size range, at least in one dimension.[1-16] More specifically, polymers that are reinforced with rigid inorganic/organic particles, which have at least one dimension in the nanometer size-range are termed as polymer nanocomposites. These organic-inorganic hybrid materials play important roles as structural composites and represent some of the finest examples of optimized interfacial interaction between matrix and filler particles via small-scale design.[17]

More often than not, lamellar fillers have been employed to form these nanocomposites. Thus, thorough knowledge of the morphological traits encountered in polymer nanocomposites with lamellar fillers is the first prerequisite of any attempt at comprehension and analysis of their performance and properties. Depending on strength of interfacial interactions, intra-lamellar composition and length scales of lamellar separation, lamellar nanocomposites can be divided into two distinct classes, intercalated and exfoliated. In the former, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intra-lamellar space. The result is a well ordered multilayer structure of alternating polymeric and inorganic layers, with a repeat distance between them.[5]

In exfoliated nanocomposites, delaminated structures are obtained when a large number of polymer chains are present between the layered platelets and the layers stand >10nm apart. Thus, the interlayer expansion is comparable to the radius of gyration of the polymer rather than that of an extended chain, as in the case of intercalated hybrids.[6,7]

When a polymer is unable to intercalate between the lamellae (for example, silicate sheets), a phase-separated (aggregated) composite is obtained, whose properties are in the same range as for traditional microcomposites. The two types of lamellar polymer nanocomposites are depicted in Scheme 1.1.
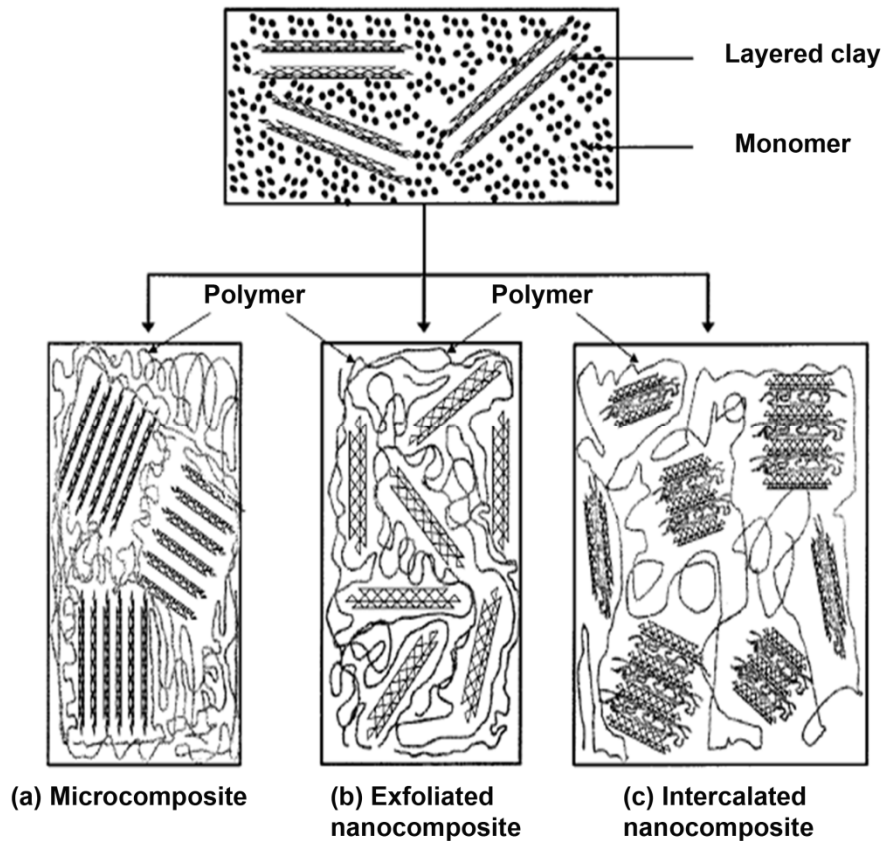
Scheme 1.1 Types of Lamellar Polymer-Nanocomposites

The exfoliation or delamination configuration is of particular interest because it maximizes the polymer–nanofiller interactions making the entire surface of nanofiller layers available for a polymer and thereby yields better properties than intercalated ones.

Depending on the level of interaction between these organic-inorganic phases, hybrid materials can either possess weak interaction between phases, such as van der Waals, hydrogen bonding or electrostatic interaction[18, 19] or be of strong, chemically bonded (covalent or coordinate) types.[20] Crucial parameters in determining the effect of nanofillers on the properties of composites are filler size, shape, aspect ratio and filler-matrix interactions. [21-28]

Nanofillers are necessarily nanoscopic and have a high specific surface area. The specific surface area is one of the reasons why the nature of reinforcement is

different in nanocomposites and is manifested even at very low filler loadings (<10 wt.%). In typical micro- and macro-composites, properties are dictated by the bulk properties of both matrix and filler. In the case of nanocomposites, the properties of the material are more tied to the interface. Interfacial structure is known to be different from bulk structure, and in polymers filled with nanofillers possessing extremely high available surface areas, most of the polymer is present near the interface, even in spite of the small weight fraction of filler. If the interaction at the interface is a strong one, or if the structure of the interfacial polymer is very different from the bulk, markedly different properties in the material as a whole can be observed. Thus, the properties have a fundamentally different origin than those found in micro- and macro-composites, where the volume of the interface is only a small fraction of the overall volume of the material.

1.2   Different Nanofillers

The nanofillers used in polymer nanotechnology are usually having different shapes and on that basis can broadly be categorized into the following classes:

- **Spherical/cubical** [e.g., nanosilica, polyhedral oligomeric silsesquioxanes (POSS), nano calcium carbonate, metal oxides etc.]
- **Rod/fiber** (e.g., synthetic whiskers, carbon nanotubes, carbon nanofibers, sepiolite, boehmite, nano calcium carbonate etc.)
- **Sheet/platelet** (e.g., layered silicates such as smectite group of clays, synthetic mica etc.).

The details about the nanofillers used in this research work are discussed below.

1.2.1   Clay Based Fillers

The silicates are the largest, the most interesting and the most complicated class of minerals by far (Scheme 1.2). Approximately 30% of all minerals are silicates and geologists estimate that 90% of the Earth's crust is made up of silicates. The basic chemical unit of silicates is the (SiO_4^{4-}) tetrahedron with a negative charge (-4). They can form single units, double units, chains, sheets, rings and framework structures. The silicates are divided into many subclasses by their structures [29] and the most common amongst them, *the layered silicates*, primarily belong to the phyllosilicate

subclass. In this subclass, tetrahedrons are linked by shared oxygens to other tetrahedrons in a two dimensional plane that produces a sheet-like structure. The typical crystal disposition of this subclass is flat, platy, book-like structure and displays good basal cleavage.
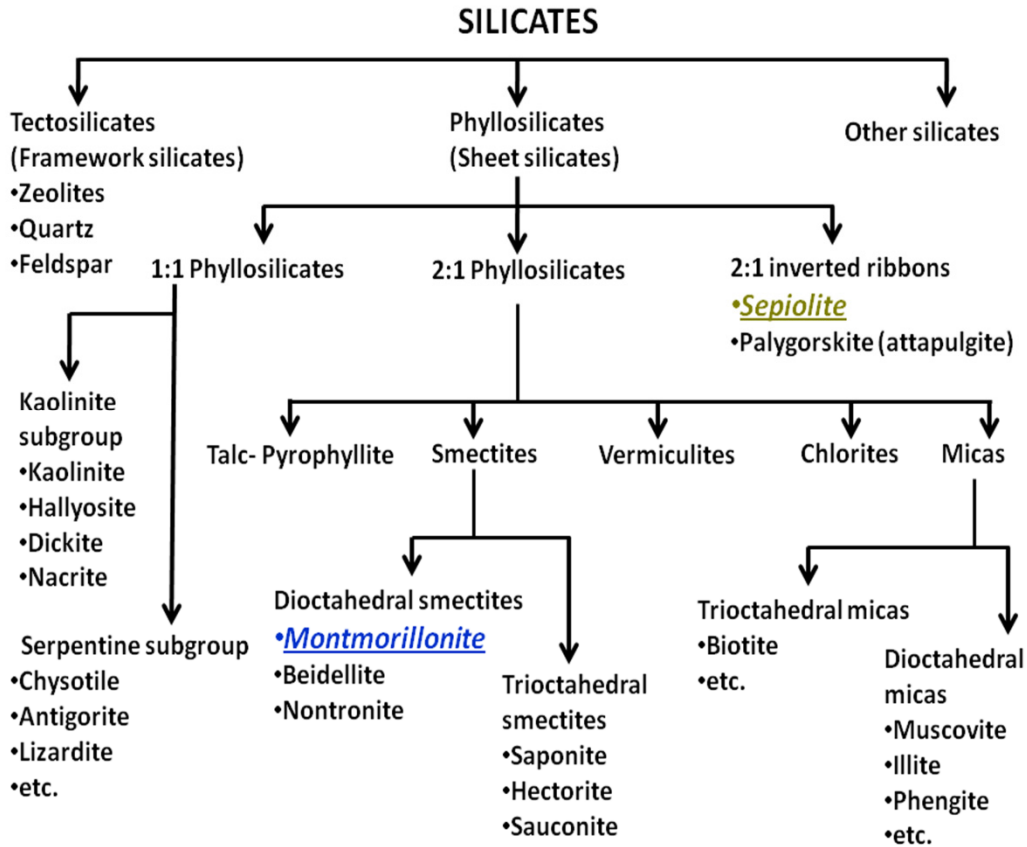
Scheme 1.2   Clay Group

Smectites are a member of this phyllosilicate subclass of the clay group. The smectite group is composed of several minerals including saponite, hectorite, bentonite, nontronite, beidellite, volkonskoite, sauconite, sobockite, vinfordite, and most important of them being montmorillonite (MMT). These silicates differ mostly in chemical content. The general formula is (Ca, Na, H) (Al, Mg, Fe, Zn)$_2$(Si, Al)$_4$O$_{10}$(OH)$_2$ - xH$_2$O, where x represents the variable amount of water that members of this group could contain. The structure of this group is composed of silicate layers sandwiching a gibbsite (or brucite) layer in between, in a silicate-gibbsite-silicate (s-g-s) stacking sequence. The variable amounts of water molecules would lie between the s-g-s sandwiches.

1.2.1.1 Structure and Properties of Montmorillonite -Physical Characteristics

Many varieties of clay are aluminosilicates with a layered structure, which consists of silica (SiO_4^{4-}) tetrahedral sheets bonded to alumina (AlO_6^{9-}) octahedral ones, arranged in a variety of ways. In smectite clays, a 2:1 ratio of the tetrahedral to the octahedral is observed.

The structure of montmorillonite $[(Na,Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2 - nH_2O]$ is derived from the original pyrophyllite structure by partial substitution of the trivalent Al-cation in the octahedral layer by divalent Mg/ Fe-cation or that of Si-cation by Al in the tetrahedrdral layer (Fig. 1.1). Because of deficit in charge arising out of the difference in charge between the Al and Mg/Fe ions (or, Si and Al), these 2:1 silicates are negatively charged and the negative charge is balanced by group I or II metal ions present between the 2:1 sheets. Montmorillonite (MMT) can absorb water between the charged layers because of the weak bonding and the large spacing and it is therefore a member of a group of water-expandable clay minerals known as smectites or smectite clays. As clearly shown in Fig. 1.1**,** in MMT, oxygen atoms from each alumina octahedral sheet also belong to the silica tetrahedral ones, the three of these s-g-s layers comprising ~1 nm thin layer.

These layers are in turn linked together by van der Waals bonds and organized in stacks with a regular gap between them called '*interlayer*' or '*gallery*'. Within the layers, isomorphic substitution of Al^{3+} with Mg^{2+} or Fe^{2+} (or, substitution of Si^{4+} with Al^{3+}) generates an excess of negative charge, the amount of which characterizes each clay type and is defined as the *cation exchange capacity* (CEC). The CEC value for smectites depends on its mineral origin and is typically 65-150 milliequivalents/100g. In natural clays, ions such as Na^+, Li^+ or Ca^{2+} in their hydrated form balance this excess negative charge; this suggests that natural MMT is only compatible with hydrophilic polymers. General characteristics of these materials include 20 layers of ~1 nm thickness and lateral dimensions ranging from ~25 nm to ~5 μm.[30]

The mechanical properties of a single silicate layer are often assumed to be similar to materials like glass and mica, and elastic moduli around 170 GPa are frequently mentioned in the literature.[31]
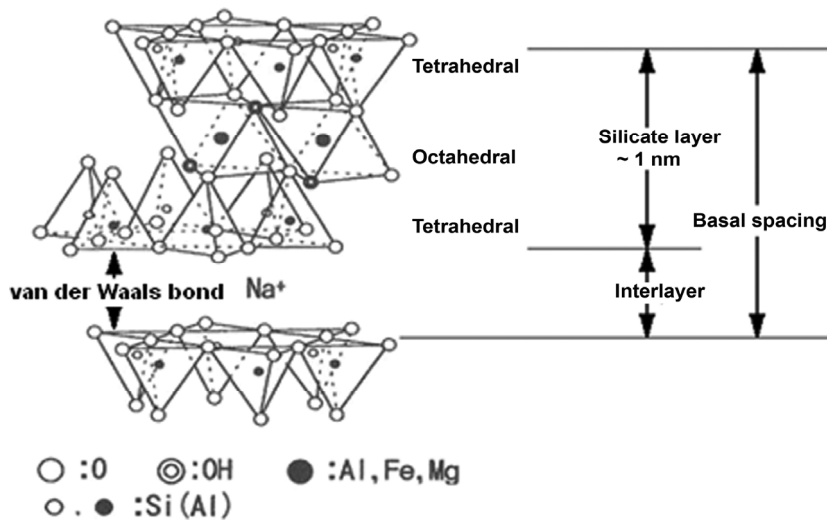
Fig. 1.1   Structure of a Typical MMT Layer

These silicate layers allow for the retention of aspect ratios in excess of 100-1000 during normal polymer processing, something that is exceedingly difficult to achieve with conventional fillers. Additionally, such systems also benefit from the extremely large amount of interface and interphase polymer produced due to full dispersion of nanometer thick silicate layers in the polymer matrix.

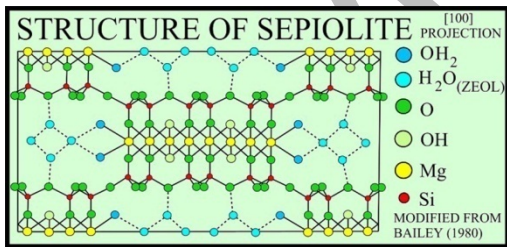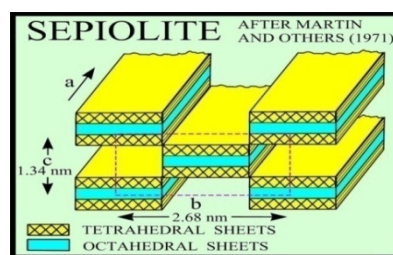### 1.2.1.2   Structure and Properties of Sepiolite -Physical Characteristics

Fig. 1.2   Crystalline Structure of Sepiolite [32]

Sepiolite, $Mg_4Si_6O_{15}(OH)_2$$_2$.6H$_2$O, is a phyllosilicate clay insofar as it contains a continuous two dimensional tetrahedral silicate sheet. However, sepiolite differs from other clays in that it lacks a continuous octahedral sheet structure. Instead, its structure can be considered to contain ribbons of 2:1 phyllosilicate structure, with each ribbon linked to the next by inversion of SiO_4 tetrahedra along a set of Si-O-Si bonds (Fig. 1.2). In this framework, rectangular channels run parallel to the X-axis between opposing 2:1 ribbons, which results in a fibrous morphology with channels running parallel to the fiber length. Channels are of 1.3 nm x 0.7 nm dimension (Fig. 1.3).[32,33] Individual fibers generally range from about 10 nm to 5 microns in length, 10-30 nm width, and 5-10 nm thickness (Figs. 1.2 and 1.3). Inside the channels are protons, coordinated

water, a small number of exchangeable cations, and zeolitic water (Fig. 1.3). Sepiolite is a non-expandable clay with a small CEC (about 15 meq/100g).

This unique structure imparts sepiolite a fibrous matrix, with channels oriented in the longitudinal direction of the fibers. The discontinuous nature of the octahedral sheet results in rectangular channels. These nanostructured tunnels account in large part for the high specific surface area and excellent sorption properties of

Fig. 1.3   Fiber Structure of Sepiolite[33]

sepiolite. In addition, it imparts good mechanical strength and thermal stability.[34,35]

These properties make sepiolite ideal for reinforcement of polymeric materials.   It differs from MMT in terms of the location of hydroxyl groups, as well. In MMT these groups are found only on the edge of the aluminosilicate platelets, whereas the silanol groups are present on the whole external surface of sepiolite, due to the discontinuous nature of the octahedral sheets.

1.2.1.3 Clay Characterization

X-ray diffraction (XRD) is commonly used for the characterization of the layered nanofillers like nanoclays. The characteristic peak of (001) plane of montmorillonite, hectorite and sepiolite is at 7.61°, 5.59° and 7.18°, respectively.
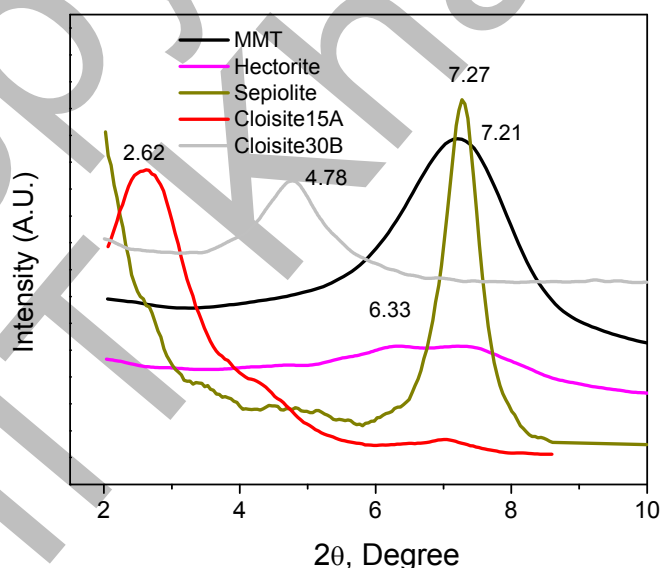
Fig. 1.4   XRD Pattern of Different Natural and Modified Clays Used in Rubber Nanocomposites (Cloisite 15A and 30B: organomodified MMTs procured from Southern Clay Products, USA)

The d-spacing of layered silicates can be calculated using Bragg's law. The X-ray diffractograms of various unmodified and modified montmorillonite, hectorite and sepiolite are shown in Fig. 1.4**.** After modification by organic amines, the d-spacing increases (Fig. 1.4).

Electron microscopy is another effective tool for characterizing nanofillers. Both scanning electron microscopy (SEM) [particularly recent generation SEMs like Field Emission SEM], and transmission electron microscopy (TEM) are extensively used these days for this purpose.

The transmission electron micrographs of natural montmorillonites[36] and sepiolite[37] are illustrated in Fig. 1.5a-b, respectively. Fig. 1.5a clearly depicts the layered platelet structure of the montmorillonitic clay, which is significantly different from the unexpandable layered ribbon type "bird's nest" structure of fibrous sepiolite. Unlike smectites, which have a layered structure, sepiolite has interstratified intergrowths. It can thus be regarded as a hybrid structure between layer- and ribbon-structures (Fig. 1.5b). The presence of longitudinal channels and the lath-like structure makes larger surface area available resulting in significant improvement of properties of its nanocomposites.
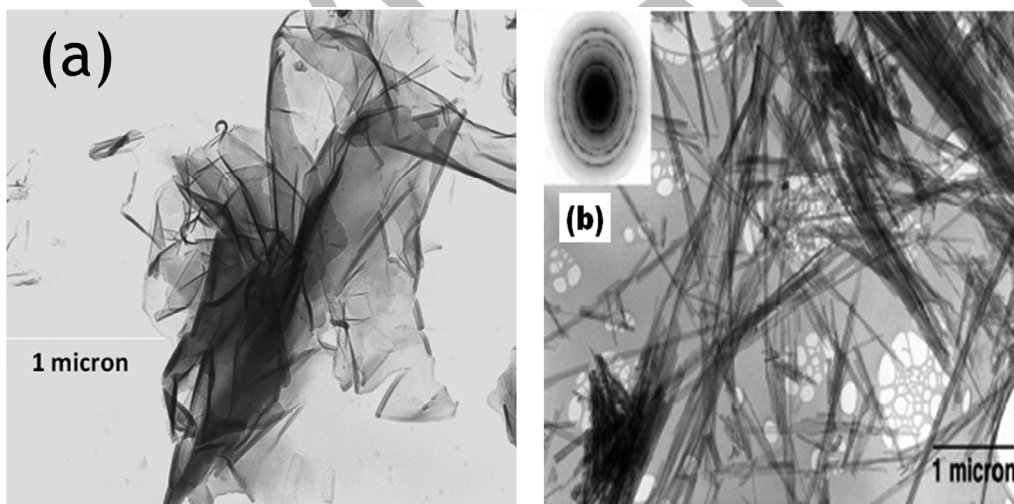

Fig. 1.5 TEM Images of (a) Natural Montmorillonite[36] and (b) Sepiolite [37]

1.2.2 Carbon Based Nanofillers

The carbon-based nanofillers are mainly layered graphite, nanotube and nanofibers. These carbon nanostructures differ greatly with regard to their aspect ratio, crystallinity, crystalline orientation, diameter, purity, entanglement, surface chemistry and straightness. These structural variations dramatically affect intrinsic properties, processing and behavior in composite systems. However, it is not yet clear which type of carbon based nanomaterial is most suitable for composite applications, nor is there much theoretical basis for rational design. Eventual selection depends on the matrix material, processing technology and the property enhancement required.[38]

1.2.2.1 Graphite

Graphite is an allotrope of carbon, the structure of which consists of graphene layers stacked along the c-axis in a staggered array.[39] Fig. 1.6 shows the layered structure of graphite flakes.
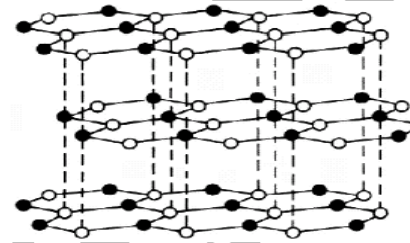

Fig. 1.6   3D Structure of Graphene Layers in Graphite [40]

1.2.2.2 Carbon Nanotubes (CNT)

Carbon nanotubes can be classified into single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT) depending on the number of graphitic cylinders with which they are formed. A single wall carbon nanotube is a hexagonal network of carbon atoms rolled up into a seamless, hollow cylinder of 1–2 nm diameter, with each end capped with half of a fullerene molecule. The diameter, chirality and form of the nanotube determine its eventual properties.[41] Chirality is a twist that determines whether the CNT behaves like a metal or a semiconductor. On the basis of chirality, SWNT can be further divided into three classes, i.e. armchair, zigzag and chiral, depending on the arrangement of hexagons in their structures.[42]

The discovery of multi-walled carbon nanotubes produced by arc evaporation of graphite in an atmosphere of helium by Iijima has attracted scientific and technological interest worldwide.[43] MWNT generally exists with diameter of 10-40 nm with length of few micrometers. SWNT and MWNT can be synthesized by means

of arc discharge,[44] laser ablation[45-48] and chemical vapor deposition (CVD) from hydrocarbons. [49-51]

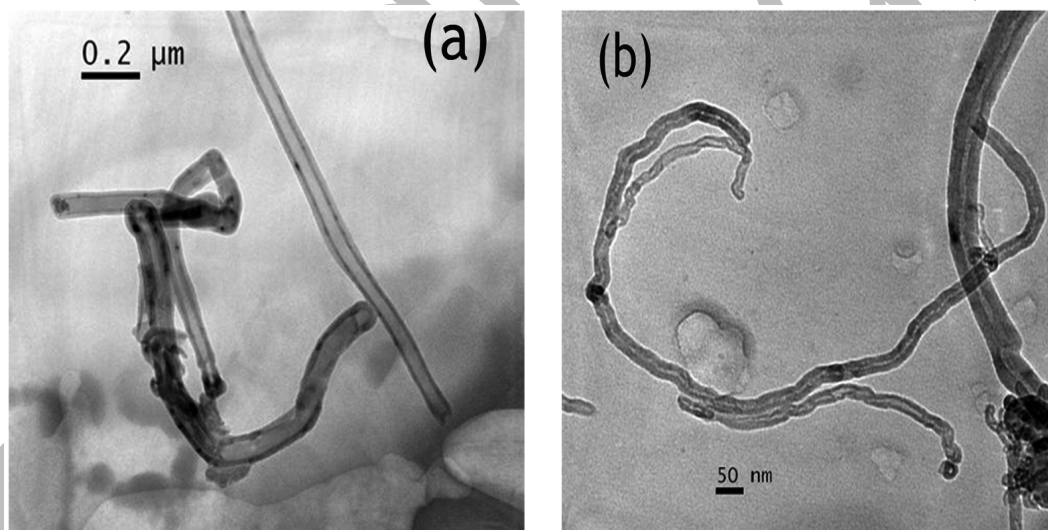### *1.2.2.3 Carbon Nanofiber (CNF)*

Vapor grown carbon nanofibers (VGCF) are another important member of this class of carbon based nanofillers. They possess graphitic structure similar to that of CNTs, with typical diameters of 50-200 nm. The inner diameter is 30-90 nm and the length is in the range of 50-100 μm, so that the aspect ratios are in the 100-500 range.[52]

CNFs are grown most efficiently from nanoscale metal catalyst particles (iron, nickel etc.) exposed to a carbon-containing feedstock at high temperature (Fig. 1.7).[50,53-55] Carbon is absorbed on to the particle and then participates to form a highly graphitic strand with a diameter somewhat larger than the catalyst particle. A CNF generally can be composed of two phases of carbon, designated as the "catalyst" phase and the "deposited" phase. The catalyst phase is that which is formed by the catalytic action of the metal seed particle from which the CNF grows. This phase tends to be highly graphitic. The deposited phase is formed by CVD of carbon on top of the catalyst phase. The CVD carbon tends to be disordered (turbostratic) unless subjected to high temperature, which tends to graphitize the carbon. CNFs are mainly differentiated from nanotubes by the orientation of the graphene planes: the graphitic layers are parallel to the axis in nanotubes, whereas nanofibers can show a wide range of orientations of the graphitic layers with respect to the fiber axis. They can be visualized as stacked graphitic discs or (truncated) cones and are intrinsically less perfect as they have graphitic edge terminations on their surface. Nevertheless, these nanostructures can be in the form of hollow tubes with an outer diameter as small as ~5 nm, although 70–200 nm is more typical. Also, the CNFs are more defective, while the CNTs possess highly crystallized tubular structures.[56] CNFs can be very inexpensive due to their size and the use of natural gas as the source of hydrocarbon gas.[57] The graphitic platelets are precipitated parallel to the faceted catalyst particle, and hence the angle between the planes and the fiber axis is determined by the shape of the catalyst particle.[58] Under certain conditions of gas composition, temperature and catalyst composition, the catalyst particles undergo surface reconstruction to form unique geometrical shapes which drive the formation of CNFs.[59]
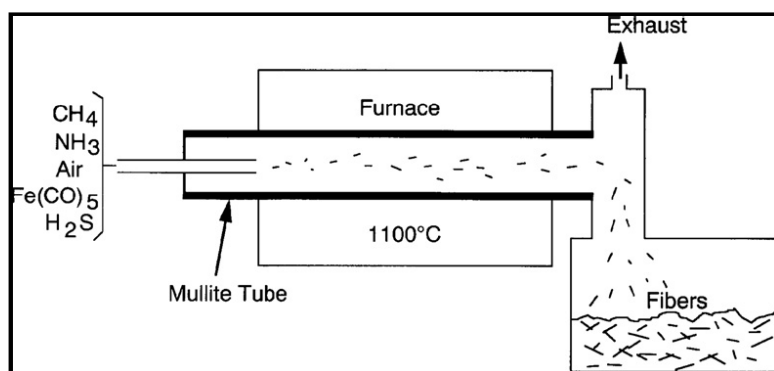
Fig. 1.7   Schematic of the Apparatus for Manufacturing CNF[59]

Fig. 1.8a shows the transmission electron micrographs of commercially available vapor grown carbon nanofiber. They have diameter in the range of 77±12 nm.[60] Fig. 1.8b represents commercial multiwall nanotube having 27±4 nm diameter.[61]

Fig. 1.8   TEM Photomicrograph of Commercially Available (a) Vapor Grown Carbon Nanofiber[60] and (b) Multiwall Nanotube[61]

1.2.3   Surface Area of Nanofillers

Brunauer-Emmett-Teller (BET) surface area of the nanoparticles highlighted in this study is tabulated in Table 1.1.

Table 1.1   Density and BET Surface Area of Some Nanoparticles[52, 62, 63]

Filler	Density, kg/m^3	Surface area, m^2/g
Cloisite 15A (Montmorillonite)	1660	147
Pangel B20 (Sepiolite)	2100	364
Pyrograf-III, PR 24 (Carbon nanofiber)	1950	60

1.3   Preparation of Nanocomposites

The reinforcement of rubber requires rigid entities, such as carbon black, clays, silicates, carbon nanofibers etc. and this important phenomenon has been discussed at length by various authors.[64-66] Thus, inclusion of fillers or reinforcement aids (in the nanoscale, in particular) to rubber formulations results in optimization of properties to meet given service application or sets of performance parameters.[67-72] Elastomer nanocomposites are currently prepared in the following ways:

1.3.1   Solution Blending

In this method, the elastomer is solubilized in a proper solvent and then the filler dispersion is added to it. In solution, the elastomer chains are well separated and can easily enter inside the layers of the layered nanofillers or can interact with the particulate nanofillers. Choudhury et al. [70] have established the importance of polymer-solvent and clay-solvent interaction on the optical and mechanical properties of rubber nanocomposites. They have found that the judicious choice of solvent combination on the basis of lowest difference in interaction parameter (rubber–solvent vs nanofiller–solvent) leads to the best dispersion and hence in improvement in mechanical properties.[70] After the nanofillers get dispersed, the solvent is evaporated usually under vacuum. The curatives may be added before solvent removal,[73] but they are usually compounded with the intercalated material after partial or complete solvent removal[74-76] and then vulcanized at a specific temperature.

Most of the elastomer-nanocomposites e.g., natural rubber (NR),[77-80] epoxidised natural rubber (ENR),[81-82] polybutadiene rubber (BR),[83] styrene-butadiene rubber (SBR), [76] butyl rubber (IIR),[84] ethylene propylene diene rubber (EPDM),[85] brominated poly(isobutylene-co-p-methylstyrene) (BIMS),[86] fluoroelastomer (FKM),[87] poly(ethylene-co-vinylacetate) (EVA),[61,73] acrylonitrile

butadiene rubber (NBR),[76,88] epichlorohydrin,[89] and chloroprene (CR)[90] have been synthesized by this method.

Carbon based nanofillers too have been dispersed in the above mentioned mode of solution blending, although often such a mixing process is preceded by certain pre-processing stages. Solution based methods provide an advantage through low viscosities, which facilitate mixing and dispersion of the CNTs. There are, however, limited examples of nanotube or nanofiber incorporation in rubber matrices. Solution mixing of MWNT in NR,[91-93] SBR,[92,94] and methyl vinyl silicone,[95] MWNT [61] and expanded graphite [96] in EVA have been reported. Frogley et al. discussed the ultrasonication and solution mixing of SWNT and VGCF in Room-Temperature-Vulcanizing (RTV) silicone rubber. [97] Isayev has patented an ultrasound assisted continuous process in this regard.[98]

1.3.2   Latex Compounding

Mostly layered silicate nanocomposites are made by this method. In this method the host medium is water because many elastomers are available in the form of latex, which is nothing but an aqueous dispersion of elastomer particles in the submicron–micron range. Pristine clay can be added to the elastomer latex directly or as its aqueous dispersion (slurry). The hydration of clays decreases the attractive forces between the silicate layers rendering their exfoliation easier under stirring. After mixing, the lattices are co-precipitated (coagulation) and dried. Suitable curatives, which can be dispersed in water, may also be mixed with the clay containing elastomer latex. After drying, the nanocomposites can be cured at a specific temperature.

Nanocomposites from NR,[99,100] SBR,[101-104] CR,[105] carboxylated styrene-butadiene rubber (XSBR) ,[106] carboxylated acrylonitrile-butadiene rubber (XNBR), [107] NBR [108] and polyurethane rubber (PU)[109] have been prepared by this route. There are also some patents on this method. [110,111]

Latex based nanocomposites having carbon nanotubes have been prepared from NR.[112] It has also been applied by Gauthier et al. [113] for dispersing VGCF in SBR. Recently, Bhowmick et al. have studied various latex blending techniques and also combined latex and melt blending techniques to enhance the dispersibility of unmodified MMT in NR.[114]

1.3.3 Melt Intercalation

From industrial stand point, the most economic mixing and environmental friendly technique used for preparing elastomer nanocomposites is melt compounding. This involves equipments like internal mixers and open two-roll mills. The intercalation/exfoliation phenomena are sometimes governed by the modification of elastomers and also the chemistry involved during compounding and curing in the case of elastomer nanocomposites. Mixing temperature and shear rate also influence the intercalation/exfoliation phenomena. [60,115-119]

There are a few papers on ENR and NR based nanocomposites prepared by melt mixing.[120-125] Schon and Gronski investigated the reinforcement of SBR by silica and organoclay as nanofillers.[126] Clay nanocomposites based on NBR [127-130] and EPDM [131-133] have also been reported in the literature.

Although melt mixing of MWNT has been carried out in NR[134], similar reports are not available on the utilization of VGCF in general purpose elastomers like NR and SBR. Preparation of NBR/expanded graphite nanocomposites by melt mixing has been studied by Liu et al. [135] There is a patent issued in this regard, as well. [136] Melt mixing is also the preferred mode of incorporation of hallyosite,[137] layered dihydrates[138, 139] and oxides like nano titanium dioxide[140] and nano zinc oxide[141]. Other miscellaneous fillers, for instance calcium sulphate[142] and zinc dimethylacrylate [143] too have been studied by melt mixing.

1.3.4 In-Situ Polymerization

In this method, monomers are added to the fillers and allowed to enter into the galleries of layered nanofillers or mix with the fillers in a proper solvent medium. Then they are polymerized using some initiator to get in-situ nanocomposite. This method requires a certain time period, which depends on polarity of monomer, surface treatment of filler and swelling temperature. There are a few elastomer-clay nanocomposites prepared by this way.[144,145]

There are also some silica based nanocomposites prepared by this way. In *in-situ* generated hybrids, the organic and the inorganic components are allowed to grow simultaneously. The monomers like acrylates and methacrylates or their derivatives are mostly used as the organic components.[144-147] Nanocomposites based on

multiblock polyester elastomers (PEE) and CNT have also been prepared by this method. [148]

1.4 Important Characterization Techniques for Nanocomposites

For appropriate structure-property correlation of nanocomposites, the knowledge of state and extent of nanofiller dispersion in the matrix is of paramount importance. Numerous methods have been reported in the literature in this regard, for instance, X-ray diffraction – wide angle X-ray scattering (WAXD), [149, 150] small angle X-ray scattering (SAXS), [151-153] ultra small angle X-ray scattering (USAXS), [154] small angle neutron scattering (SANS), [155, 156] electron microscopy – scanning electron microscopy (SEM), transmission electron microscopy (TEM), [150, 157] atomic force microscopy (AFM), [158, 159] and electron energy loss spectroscopy (EELS) techniques, [160] solid state nuclear magnetic resonance (SSNMR), [161-164] electron paramagnetic resonance (EPR), [165, 166] and spectroscopy [ultraviolet/visible/near infrared, Fourier transform infrared(FTIR), [167] Raman, [61] dielectric [168, 169]] and small angle light scattering (SALS) [170].

1.5 Health and Safety Aspects of Nanoparticles/Nanocomposites

Until recently, nanoparticles were widely accepted as beneficial and totally benign. But with the astonishing revelation in March 2002 that nanoparticles have shown up in the livers of research animals and perhaps get associated with bacteria to enter the food chain, concerns have been raised about potential health and environmental impacts of nanomaterials. [171] However, to date, there have been no confirmed reports of adverse effects to humans or the environment as a result of exposure to engineered nanomaterials. [172-175]

Almost all concerns are related to free, rather than fixed nanomaterials. The influences of physicochemical properties on the toxicological and eco-toxicological profile of nanomaterials are not yet fully understood. Factors determining human and environmental exposure include extent of use, exposure pathway and properties of the nanomaterials. There is potential for exposure to humans and the environment during manufacture, use and disposal of nanomaterials, but it is difficult to identify and quantify right now. Industry and academics are now facing the challenge to develop a

conceptual understanding of biological responses to nanomaterials, and use this know-how to develop safe, sustainable applications of nanomaterials.

1.6 Applications

Although little information is available on already commercialized rubber nanocomposite products, the thermoplastic and thermoset nanocomposites have seen some rapid growth and have already established a niche for themselves in the global consumer market. The plausible applications of elastomer nanocomposites are tremendous. In functionalities where a light weight but high strength elastomer product is of great significance, such as in space-shuttles, part substitution of conventional fillers (carbon black and silica) by nanofillers may be highly desirable. Superior barrier properties given by the platy/flake type nanofillers like, clay, in applications demanding low solvent and/or vapor permeability will always have scope for nanocomposites. Thus, in near future tire inner liners can be made of nanocomposites. As the silicate type of nanofillers can enhance the flame and fire retardancy, elastomer compounds containing nanoclays can be used in the cable industry. The zinc compounds are eco-toxic. Using nano-zinc oxide (ZnO), the loading of such zinc compounds can be reduced and thereby, the extent of eco-toxicity of such rubber compounds can be lowered.

1.7 Literature Survey of Polymer Nanocomposites- A Comprehen--sive Approach

1.7.1 Sepiolite Based Nanocomposites

This non-expandable clay, with its super adsorbent qualities, has only recently emerged in the horizon of polymer nanocomposites. Thus, only a handful of references are available in open and classified literature. Polyamides nanocomposites with sepiolite clays have been patented by Kobayashi and Jones[176] and Williamson[177], while Molitor et al.[178] patented a process for the production of polyester-sepiolite nanocomposites by melt mixing.

Bokobza and co-workers reported the use of sepiolite in poly (hydroxyethyl acrylate)[179] and NR[180] for reinforcement. Very recently, Choudhury et al.[181] reported the merits of sepiolite in improving the thermal, mechanical and dynamic mechanical properties of hydrogenated nitrile butadiene rubber nanocomposites prepared by

solution mixing. Its interaction with elastomers, the subsequent dispersion enhancement techniques and the science driving such beneficial associations have hitherto not been addressed.

1.7.2 Carbon Nanofiber Based Nanocomposites

Carbon nanofibers have been used in different polymer matrices like polyethylene,[182–184] polypropylene,[185–189] poly(methyl-methacrylate),[190,191] polystyrene,[192,193] polyester,[194] nylon 6,[195] epoxy[196] and poly (ether ether ketone)[197] to produce high performance nanocomposites.

Uniaxial deformation of the nanocomposite studied by in situ synchrotron X-ray diffraction by Kelarkis et al. revealed that CNF acts as an effective nucleating agent for isotactic polypropylene crystallization in an elastomeric ethylene-propylene rubber (84.3 wt.% propylene).[198] The presence of CNFs provides a physical crosslinking network to the matrix, which facilitates strain induced crystallization. At elevated temperatures, pronounced deviations from the ideal melt behavior in the low frequency domain indicated the formation of a three-dimensional percolated network with bridge formation of polymer segments between two adjacent nanofillers in concentrated nanocomposites.[199] Gauthier et al. achieved good properties in epoxy-CNF nanocomposites, but failed to do so in the case of SBR due to poor dispersion.[113]

The morphology, thermophysical and flammability properties of thermoplastic polyurethane elastomer nanocomposites compounded using twin-screw extrusion for preparing internal insulation for solid rocket motors have been studied by Ho et al.[200] Utilizing the side electron emission configuration, highly efficient, indium-tin-oxide free, flexible field emission device from carbon nanofiber/elastomer nanocomposite sheet has also been reported.[201]

Patents exist on the preparation of ethylene copolymer ionomeric nanocomposite compositions for covers of golf balls[202] and tire liner rubber compositions containing carbon nanofiber/carbon black composites with good air permeability and bending resistance.[203] The electrical properties of CNF filled rubber nanocomposites have also been carried out.[204, 205] George and Bhowmick have studied EVA/CNF nanocomposites in great details. They have modified and characterized the fiber surface and subsequently studied their effect on thermal, physico-mechanical

and electrical properties.[206, 207] Various kinds of surface treatments have been performed on CNFs in order to induce functionalities and thereby improve the fiber-matrix adhesion.[208, 209] Reports in the area of polymer grafting on to the nanofiber surfaces by various chemical methods are also available.[210] However, Valentin et al. observed that chemical treatment of CNFs hardly changes the properties of the NBR nanocomposites due to the degradation that the nanofibers suffer after treatment.[211] Non-invasive chemical and physical modification techniques, for instance, variation in nanofiber incorporation time, speed and temperature have not been explored in this regard.

1.7.3 Elastomer Nanocomposites Containing Carbon Black (CB)

Due to the presence of VGCFs, the properties of the single-layer gas diffusion layers, including electronic resistivity, mechanical characteristic, gas permeability and water repellency improved the performance of the proton exchange membrane fuel cell made from carbon black/poly(tetrafluoroethylene) composite.[212]

In spite of its technological importance, dual filler systems comprising of carbon black have not often been reported in rubber nanocomposites. In a study, on SBR latex (styrene-butadiene rubber: solid content: 25%) nanocomposites reinforced with carbon/octadecyl amine modified MMT, good dispersion and improved mechanical properties were reported.[213] Butyl rubber-EPDM blend nanocomposite containing silica and nanoclay has been patented for tire sidewall applications.[214] Amongst others, it showed excellent barrier properties. Jia et al. studied the combined effect of nanoclay and carbon black on properties of NR nanocomposites and observed that there is a synergistic effect of the two fillers.[215] They formed the initial NR nanocomposites by co-coagulating clay aqueous solution and NR latex, which were subsequently melt-mixed with CB. Such a tedious three step process (solution, latex and melt mixing) involving solvents precludes chances of favorable nanofiller-CB interaction. Hence, it is necessary to devise an entirely melt mixed process that would impart stability to the microstructure and facilitate formation of nanofiller-CB based nano-architecture.

SBR/BR-based rubber nanocomposites filled with carbon black and nanoclay were radiation-cured by a 60Co gamma-radiation source. Reinforcement effect derived from the nanoclay addition to the composite was exhibited both in the

radiation-cured compounds and in the sulphur-cured compounds.[216] There exists ample scope to explore the cause of such synergy at the nanoscales. The effect of such synergy on abrasion and other properties important for wear resistant application has not been investigated as well.

1.7.4 Natural Rubber Nanocomposites

Natural rubber (NR) is the most widely used naturally occurring rubber. Literature search shows that several research groups have prepared nanocomposites based on this rubber.[78 ,115,120,124,217-219] Most of the studies have been carried out on the effect of nanoclay dispersion (particularly that of montmorillonite) on the properties of NR. Mechanical properties and cure characteristics of NR nanocomposites have been studied by several researchers.[220,221]

However, only a few references are available on melt processed NR nanocomposites. Some researchers found that only organomodified clays yielded best results in melt mixed NR nanocomposites.[222-227] Varghese et al. prepared NR based nanocomposite by melt intercalation method. They also studied the properties of NR-ENR blend nanocomposite.[120] Effects of epoxidized natural rubber as a compatibilizer in melt compounded natural rubber-organoclay nanocomposites, were investigated by Teh et al. [123,125]

Avalos et al.[224] observed that aliphatic quaternary phosphonium salts could only enforce exfoliation, while aromatic counterparts yielded intercalated nanocomposites. Similarly, octadecylamine modified-bentonite[226] and fluorohectorite[223] resulted in exfoliated morphology and improved properties. Vulcanization kinetics of natural rubber-organoclay nanocomposites were studied by Lopez-Manchado et al. [122], but literature lacks any report describing the transition of RNCs through *uncured* to *cured* state, especially in terms of their viscoelastic properties, which yield a measure of their processability and applicability.

Effect of carbon nanoparticles, nanotubes and graphite nanoparticles on the mechanical and physical properties of NR nanocomposites has also been studied. [93,112,221] For NR/MWCNT prepared by mechanical mixing method, the tensile strength, fatigue life and elongation at break decreased due to agglomeration of MWCNT. Also, these studies have been carried out in the unvulcanized state, that is in absence of common rubber curatives. NR, CNT and cotton yarns were mixed to

give a uniformly mixed composite and they exhibited heat resistance temperature ≥ 300 °C.[136] Although different filler systems have been studied in NR, the role and effect of fibrous nanofillers, modification agents like titanate, filler incorporation and dispersion techniques in NR have not received their due attention.

1.7.5 Theories/Modeling on Polymer-Filler Interaction in RNCs

Till date, some theoretical efforts have addressed the structural changes of polymer chains due to the addition of spherical nanoparticles. The variables like particle size, particle loading, chain length and particle–polymer interaction have been studied. However, multiscale modeling and simulation strategies need to evolve further for the fundamental understanding of their hierarchical structures and behaviors necessary for development of such nanocomposites.

Sharaf and co-workers[228–230] found that the volume fraction and the size of nanoparticles as well as their spatial arrangement in a polymer matrix significantly affect the end-to-end chain distance. Buxton and Balazs[231] used lattice spring model to investigate the effects of filler geometry and intercalation–exfoliation of clay platelets. They attributed the reinforcement efficiency to the volume of polymer matrix constrained in the proximity of the particles.

In order to understand the effects of filler loading and filler–filler interaction on the viscoelastic behavior, Chabert et al.[232] proposed two micromechanical models (a self-consistent scheme and a discrete model) to account for the short range interactions between fillers, which led to a good agreement with the experimental results. The effect of polymer-filler interaction on solvent swelling and dynamic mechanical properties of the sol-gel derived acrylic rubber (ACM)/silica, ENR/silica, and poly (vinyl alcohol) (PVA)/silica hybrid nanocomposites was described by Bandyopadhyay et al.[233] Wu et al.[234] verified the modulus reinforcement of rubber-clay nanocomposites using composite theories based on Guth, Halpin–Tsai and the modified Halpin–Tsai equations. On introduction of a modulus reduction factor for the platelet-like fillers, the predicted moduli were found to be closer to the experimental measurements.[234] In this direction, the spatial statistics of carbon nanotube polymer composites have been discussed by Pegel et al. by means of statistical analysis of TEM images.[235] There still exists good scope to understand polymer-nanofiller interaction and its effect on nanocomposites properties.

1.7.6 Wear Resistance of Elastomer Nanocomposites

Movahed et al. compared the dynamic behavior of several rubbers filled with silanized silica nanofiller with regard to tire tread application[236] and found that SBR along with BR based rubber compounds had the highest rolling resistance, while IR based ones had the least. Moreover, it was found that SBR filled rubber had the best skid resistance. They also observed that elongation at break, stored energy density at break, tearing energy and abrasion resistance benefited from increases in the mass fraction of the interphase in cured silanized silica-filled SBR/BR blends for use in passenger car tire treads.[237] The abrasion resistance of nanocomposites has been shown to be superior to that of conventional composites.[238,239] Nah et al.[238] immersed crosslinked NR sheets in tetraethoxyorthosilicate for 48 hr and then dried them in vacuum oven, before measurement of wear. These vulcanizates containing in-situ formed nanosilica particles were reported to have demonstrated low frictional coefficients and superior abrasion resistance compared to that of melt-mixed composites.[238]

Tire tread rubber compositions containing core-shell nanosilica with good abrasion resistance have been patented.[240] Viscoelastic and abrasion behaviors of carbon black/silica/ organically modified layered silicate filled SBR nanocomposites were found to improve, especially in presence of calcium stearate.[241] Karger-Kocsis and co-workers have studied the wear resistance of carbon-nanofiber-modified Santoprene thermoplastic elastomer[242] and HNBR/ FKM/ CNT compounds under dry sliding and fretting conditions against steel.[243] Kim et al. reported melt-compounded butadiene rubber/Cloisite20A nanocomposites with improved mechanical properties and abrasion resistance.[244]

Gatos et al. observed that the organoclay modified clay containing HNBR and EPDM rubbers exhibited low resistance to wear, as the alignment of the clay platelets in planes parallel to the sliding direction may be disadvantageous.[245] Although modulus and tear strength increased, but poor abrasion resistance and tensile strength have been reported for fibrillar silicate/SBR nanocomposites.[246] It can be inferred that the subject is not properly understood, as highlighted by the high specificity of elastomer-nanofiller combinations with regard to enhancement in abrasion resistance.

Furthermore, there is no report on melt mixing of fibrous nanofillers, like sepiolite and carbon nanofiber, in NR to investigate, improve and quantize the tribological behavior of such nanocomposites, both in presence and absence of carbon black at conventional loadings.

1.8 Scope and Objectives

In the last two decades, the omnipresence of nanomaterials in polymeric systems has ushered in a new era of interdisciplinary sciences of nanostructured materials. However, the development of elastomeric nanocomposites has been delayed due to the multivariate nature of the systems. For instance, it is necessary to recognize and utilize the best mixing technique for dispersing judiciously chosen nanofillers specific to different rubber matrices. Extensive literature search also highlights that the sorptive prowess of nanofillers with fibrous morphology, for instance, sepiolite (SP) and carbon nanofiber (F), has not been fully utilized in the field of elastomer nanocomposites. Hence, it is imperative to study the effects of morphological constitution and varying gallery-spacing of different nanofillers on their dispersion in the matrix and eventual properties of the nanocomposites.

No synthetic material has yet equaled the overall engineering characteristics and consequent wide latitude of applications available with NR. Especially in high-performance tires (e.g., radial, truck, snow and aircraft tires) there exist other prerequisites; for instance, greater need for green strength, building tack and better low-temperature flexibility which can be met only by NR.

When one drives a car, the engine burns fuel which creates a certain amount of carbon dioxide (CO_2), thereby producing a carbon footprint. Typically, tire rolling resistance (RR) accounts for a fifth of a vehicle's fuel consumption. According to conservative estimates, a 20 per cent reduction in RR coefficient can reduce CO_2 emissions by as much as 820 kg, over a ten year life span. Another ecological threat imposed by automotive tires is that of waste handling and disposal. According to the Rubber Manufacturing Association, USA, 4.5 million tonnes of tire waste was generated in USA in 2007.[247] Rubber nanocomposites may have a major role to play in design of low RR, high abrasion resistant and longer lasting tires. It has been observed that the replacement of CB by silica could lower the RR, but at the expense

of poor abrasion properties. Surprisingly, dual filler systems combining CB and nanofillers have not been investigated.

The role and effect of fibrous nanofillers, non-invasive chemical and physical modifications using modifiers like titanate, filler incorporation and dispersion techniques such as variation in nanofiller incorporation time, speed and temperature, have not been studied critically. The interactions of such nanofillers with NR and the science driving their beneficial associations have not been addressed as well. There is a pertinent need to understand and quantize polymer-nanofiller interaction and its effect on nanocomposite properties. Literature search reveals that abrasion behavior of RNCs and the high specificity of elastomer-nanofiller combinations in this regard are not well understood. There also exists ample scope to explore and exploit the cause and effect of CB-nanofiller synergy, with an eye on wear resistant applications.

In order to address the above gaps in the literature, natural rubber (NR) has been used as base matrix in this thesis. Different commercially available nanofillers have been used to attain demanding and at times contradictory performance properties required in the rigorous present day applications. The nanocomposites have been prepared by industrially viable conventional mixing process. A couple of fillers were chosen from the entire gamut, on the basis of mechanical, swelling and dynamic mechanical properties of the nanocomposites. Subsequently, their loading was optimized and their incorporation technique was modified to enhance their dispersion. Extensive morphological studies have been done by using the state-of-the–art tools, transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) for the establishment of structure-property correlations. The results obtained have been explained with the help of surface energetics.

New insights into polymer-nanofiller interfacial interactions have been derived by replacing the spherical filler in Kraus's rubber swelling model by elliptical nanofiller. A generalized, dimensionless factor has been used to modify the Kraus's plot to render it suitable for application in nanocomposites. The theoretical and experimental findings were found to be in good agreement.

The cure and rheological properties in shear mode have been studied to characterize processability vis-à-vis morphological developments in these nanocomposites. The wear behavior of these nanocomposites has been investigated using an orthogonal Taguchi design array. Extensive microscopy, surface metrology

and statistical analysis have been exercised to characterize and quantify the tribological behavior of these nanocomposites targeted at wear resistant application. Finally, their performance has been critically studied in the presence of carbon black at loadings generally associated with tire tread compounds and the sustenance of improvement in various properties has been ascertained. For the first time, the synergistic effects of favorable CB-nanofiller interaction have been critically explored on various static and dynamic mechanical, and wear properties of these RNCs.