Chapter 1

INTRODUCTION

Abstract

This chapter deals with the various aspects of nanoscience, nanotechnology and nanocomposites. In this chapter, the properties of nanocomposites including the mechanical, thermal, biological, optical and chemical properties will be addressed. An updated survey of literature covering nanocomposites with special reference to chlorobutyl rubber based nanocomposites is presented. Last part of the chapter covers the major objectives as well as the motivation for this work.

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Introduction

Nanotechnology, in its traditional sense, means building things from the bottom up, with atomic precision. The application of nanomaterials can be historically traced back to even before the generation of modern science and technology [1]. Systemic experiments conducted on nanomaterials had also been started from the known Faraday experiments [2] in 1857. The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics. This would include microelectronics (which could now be referred to as nanoelectronics) as the critical dimension scale for modern devices is now below 100 nm. Other areas include polymer-based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibers, imprint lithography, polymer blends and nanocomposites. Even in the field of nanocomposites, many diverse topics exist including composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties. Nanotechnology is not new to polymer science as prior studies before the age of nanotechnology involved nanoscale dimensions but were not specifically referred to as nanotechnology until recently. Phase separated polymer blends often achieve nanoscale phase dimensions; block copolymer domain morphology is usually at the nanoscale level; asymmetric membranes often have nanoscale void structure, miniemulsion particles are below 100 nm; and interfacial phenomena in blends and composites involve nanoscale dimensions. While the reinforcement aspects of nanocomposites are the primary area of interest, a number of other properties and potential applications are important including barrier properties, flammability resistance, electrical/electronic properties, membrane properties, polymer blend compatibilization. The synergistic advantage of nanoscale dimensions (“nano-effect”) relative to larger scale modification is an important consideration [3]. Nano
investigations, being widely interdisciplinary by their very nature, promote the joining and merging of the various science and technology fields such as powder technology, colloid chemistry, surface chemistry and physics, clusters and aerosols, tribology, catalysis, simulation and modeling, computer technique, etc [4]. The field of nanotechnology has changed the face of research in polymer chemistry. Polymer–nanocomposites, in last few decades, have become worldwide research interest for developing polymeric materials with improved/desired properties by incorporation of these nanoscale materials into polymer matrix.

1.2 Nanomaterials

The term of nanomaterials covers various types of nanostructured materials which posses at least one dimension in the nanometer range. Figure 1.1 summarizes the typical nanomaterials, which include zero dimension nanostructures such as metallic, semiconducting and ceramic nanoparticles; one dimension nanostructures such nanowires, nanotubes and nanorods; two dimension nanostructures such as thin films. Besides this individual nanostructures, ensembles of these nanostructures form high dimension arrays, assemblies, and superlattices. Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them, (i) large fraction of surface atoms; (ii) high surface energy; (iii) quantum confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials [5]. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials [6,7]. This in turn may enhance or modify the properties of the bulk materials. For example,
metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. However, if the size of a semiconductor crystal becomes small enough that it approaches the size of the material's Exciton Bohr Radius, then the electron energy levels can no longer be treated as continuous - they must be treated as discrete, meaning that there is a small and finite separation between energy levels. Nanoparticles can be viewed as a zero dimension quantum dot while various nanowires and nanotubes can be viewed as quantum wires. The quantum confinement of nanomaterials as shown in figure 1.1 has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk count part and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelectronics. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials. Nanostructures and nanomaterials favor a self-purification process in that the impurities and intrinsic material defects will move near to the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials arose from these novel properties have also been proposed. However, due to broad coverage of the nanomaterials and related applications, it is nearly impossible to cover all the aspects of the nanomaterials properties in one chapter [8-10].
Fig 1.1. Quantum confinement in nanostructures
1.3 Polymer composites

Polymer composites are prepared by mixing polymers with inorganic materials such as reinforcing fibers (e.g., glass, carbon, aramid etc.) and particulate solids (e.g., talc, carbon black, calcium carbonate, mica etc.). Such composites exhibit physical properties synergistically derived from both the organic and inorganic components, for example, they show superior mechanical properties and higher heat deflection temperature compared to the pristine polymers while maintaining processibility [11]. Fiber reinforced polymer (FRP) composites were first developed in the 1940’s mainly for military applications. Polymer composites since then have replaced metals and have found applications in diverse areas like construction, electronics and consumer products. However, the improvement in properties is typically achieved at the expense of optical clarity and surface gloss, and often results in increased weight. This is because conventional reinforcing agents and fillers are required to be added at a higher loading level (typically >10-wt %) in order to achieve significant improvement in the properties. The replacement of traditional composites with a new class of more effective composites that use nano fillers is today an active field of industrial and academic research.

1.4 Polymer nanocomposites

In recent years the advances in synthesis techniques and the ability to characterize materials on atomic scale has lead to a growing interest in nanometer-size materials. The invention of Nylon-6/clay nanocomposites by the Toyota Research Group of Japan heralded a new chapter in the field of polymer composites. Polymer nanocomposites combine these two concepts, i.e., composites and nano-sized materials. Polymer nanocomposites are materials containing inorganic components that have nano-dimensions. In this thesis the discussion is restricted to polymer nanocomposites made by dispersing two-dimensional layered nanoclays as well as nanoparticles into polymer matrices. In contrast to the traditional fillers, nano-fillers are found to be effective even at as low as 5-wt% loading. Nano-sized clays have dramatically higher surface area compared to their macro-size counterparts like
china clay or talc. This allows them to interact effectively with the polymer matrix even at lower concentrations. As a result, polymer nanoclay composites show significantly higher modulus, thermal stability and barrier properties without much increase in the specific gravity and sometimes retaining the optical clarity to a great extent. As a result the composites made by mixing layered nanoclays in polymer matrices are attracting increasing attention commercially. Thus, the understanding of the links between the microstructure, the flow properties of the melt and the solid-state properties is critical for the successful development of polymer nanoclay composite products.

1.5 Types of nano fillers

Fillers with average particle size in the range 1 to 100 nanometer may be defined as nano filler. Unlike traditional non-active fillers, mainly used for cost reduction, nano fillers are performance-enhancing. They can be used in relatively small amounts (5 - 10%) in order to provide substantial improvements in physical and other properties. Nano sized particles can form a very fine and homogenous distributed network in the polymer matrix. As compared to micron size filler particles the nano size filler particles are able to occupy substantially greater number of sites in the polymer matrix. The significant increase in specific surface area of filler particles contributes to the enhanced physical property of the polymer matrix. Nano sized fillers increase the barrier properties by creating a maze or “tortuous path” that slows the progress of gas molecules through the polymer matrix thereby substantially improving the gas / air permeability of the polymer. In addition they improve surface properties like gloss, surface finish, grip (friction) etc of the matrix in which they are incorporated. Composite materials are the most advanced and adaptable engineering materials known to man. A composite is a heterogeneous material created by the synthetic assembly of two or more components constituting selected fillers or reinforcing fiber and a compatible matrix, in order to obtain specific characteristics and properties. Nanocomposites are a new class of composites, which are particle filled polymers for which at least
one dimension of the dispersed phase, is in the nanometer range. One can distinguish three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range. When the three dimensions are in the order of nanometers, we are dealing with iso dimensional nanoparticles like silica obtained by in situ sol gel methods. When two dimensions are in the order of nanometers and the third is larger, we are dealing with carbon nanotubes or cellulose whiskers. The third type of nanocomposites is characterized by only one dimension in the nanometer range and this family is known as layered silicate nanocomposites.

1.5.1 Three dimensional fillers

A relatively new type of nanocomposite involves the synthesis of “ultrastructure” materials, that is, materials in which structure can be controlled at the level of around 10 nm. An example of such a synthesis is the “sol-gel” hydrolysis of alkoxy silanes (organosilicates) to give silica, SiO₂. Silica has been used as an important reinforcing agent in rubber compounds together with carbon black [12-14]. Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds [15, 16]. In that case, a chemical linkage between the silica and the rubber matrix is needed to achieve the desired reinforcement. This chemical coupling is provided by a coupling agent which is usually a bifunctional silane [17,18]. In general, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the silica dispersion and to prevent adsorption of curatives on the silica surface [19-21]. A typical general structure is (RO)₃SiCH₂CH₂CH₂-X, where RO is a hydrolyzable group, such as methoxy, ethoxy, or acetoxy, and X is an organo functional group, such as amino, methacryloxy, epoxy, etc. Silane coupling agents have the unique chemical and physical properties not only to enhance bond strength but also, more importantly, to prevent de-bonding at the interface during composite ageing and use. The coupling agent provides a stable bond between two otherwise poorly bonding surfaces. In addition to silica various
nano particles like titanium dioxide, zinc oxide, calcium carbonate, ceramic oxides etc are also used to reinforce various polymer matrices.

1.5.2 Two dimensional fillers

There are numerous examples where animals or plants synthesize extra cellular high performance skeletal biocomposites consisting of a matrix reinforced by fibrous biopolymers. The physical properties of natural fibers are mainly determined by the chemical and physical composition, such as the structure of fibers, cellulose content, angle of fibrils, cross-section, and by the degree of polymerization. Compared to inorganic fillers the main advantage of lignocellulosics is their renewable nature and easy availability, low cost, low density, high specific strength and modulus. The reinforcement of rubber with fibers combine the elastic behavior of rubber with the strength and stiffness of reinforcing phases. Carbon fiber reinforced composites due to their high specific strength and specific stiffness have become attractive structural materials not only in weight sensitive aerospace industry, but also in marine, armor, automobile, railways, civil engineering structures, sport goods etc. Nanofibers in particular, have been used for a wide range of applications such as tissue engineering [22], filter media [23], reinforcement in composites [24] and micro/nano-electro-mechanical systems (MEMS/NEMS) [25]. Such fibers can be made from various materials such as polymers, carbon and semiconductors into the form of continuous nanofibers, nanofibrous networks or short nanowires. Depending on the source, they offer a wide variety of aspect ratios ($l/d$, $l$ being the length and $d$ the diameter), from almost particulate fillers ($l/d \approx 1$ to about 100. Another type of two dimensional filler in this nano-era that has received tremendous attention is the carbon nanotubes. Ideal CNTs are hexagonal network of carbon atoms rolled up in a seamless graphite sheet. There are two types, i) single-wall carbon nanotubes (SWNTs), which are one-atom thick sheets of graphite rolled up in cylinders and ii) multi-wall carbon nanotubes (MWNTs), which are made of coaxial cylinders.
This interest in CNTs is due to their large aspect ratio (>1000), and their mechanical, electronic and conductive properties. They are among the strongest and stiffest materials known, in terms of tensile strength (63 GPa for MWNTs, compared to 1.2 GPa for steel). CNTs have also very high elastic modulus, in the order of 1 TPa. They can be either metallic or semiconducting (in theory, metallic CNTs have an electrical current density more than 1000 times greater than metals such as silver or copper) and they have been shown to have a thermal conductivity at least twice that of diamond, which was previously believed to be the best thermal conductor. The extremely small size makes it suitable to be embedded into any type of light weight and soft materials as reinforcements to form strong and light nanocomposites [22]. Although there has been a large amount of work in synthesizing CNTs, the existing methods still produce a material that contains bundles of nanotubes, together with amorphous carbon and residual metal catalysts. Before CNTs can be used in different applications, impurities must be removed and most importantly, the bundles must be separated into individual tubes [26]. CNTs are held together as bundles due to strong van der Waals forces. In order to manipulate and process CNTs, it is desirable to functionalize the sidewall of CNTs, thereby generating CNT-derivatives that are compatible with solvents as well as organic matrix materials. Both chemical functionalization techniques and non-covalent wrapping methods have been reported. It is preferable to use a non-covalent method to functionalize CNTs, since covalent functionalization of CNTs was shown to dramatically decrease the mechanical and electronic properties compared to pristine CNTs. Non-covalent methods involve the use of surfactants, oligomers, biomolecules and polymers to “wrap” CNTs to enhance their solubility. The advantage of this method is that the integrity of the CNT structure is not disrupted and the properties of the CNTs are therefore retained. A number of macromolecules, like poly (styrene sulfonate), arabic gum, amylose, or more commonly small molar mass surfactants have been successfully used to modify the CNT surface chemistry. Attractive classes of surfactants that have been successfully used to disperse CNTs in water are amphiphilic block copolymers [27-30].
1.5.3 One dimensional fillers

In the case of layered silicates the filler is present in the form of sheets of one to a few nanometer thick to hundreds to thousands nanometers long. In recent years polymer/layered silicate (PLS) nanocomposites have attracted great interest, because they often exhibit remarkable improvement in material properties when compared with virgin polymer or conventional micro and macro-composites. These improvements can include high moduli [31-36], increased strength and heat resistance [27], decreased gas permeability [38-42], flammability and increased biodegradability of biodegradable polymers [43-48]. The major finding that stimulated the revival of interest in these materials was the report from the Toyota research group of a Nylon-6 (N6)/montmorillonite (MMT) nanocomposite[31], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties. Aluminosilicate condensates in 2:1 ratio of tetrahedral Si sheets with an octahedral Al sheet are called as 2,1 phyllosilicates. Coupling of only one Si sheet to one Al sheet gives rise to 1,1 phyllosilicates called as kaolinite. In many phyllosilicates either Al or Si ions are isomorphically substituted partially by lower valency metal cations of similar sizes like Mg and Fe. The type of the cation occupying the tetrahedral and octahedral sites is dependent on the ionic size and coordination rather than the valency. Phyllosilicates are categorized broadly depending on the type and location of these substituted lower valency cations as 1) Trioctahedral, in which all Al in the octahedral sites are substituted by lower valency cations, e.g., three Mg cations replace two Al, and 2) Dioctahedral, in which two-thirds of the Al ions are substituted by the lower valence cations. Various groups of naturally occurring phyllosilicates are listed in Table 1.1.
Table 1.1 Naturally occurring phyllosilicates

<table>
<thead>
<tr>
<th>Mineral Group (Type)</th>
<th>Structural formula</th>
<th>Formula unit charge</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite (1:1)</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>0</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Serpentinite (1:1)</td>
<td>Mg₅Si₃O₁₀(OH)₄</td>
<td>0</td>
<td>Tricatedral</td>
</tr>
<tr>
<td>Pyrophyllite (2:1)</td>
<td>Al₃Si₆O₁₀(OH)₄</td>
<td>0</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₆Si₆O₂₀(OH)₄</td>
<td>0</td>
<td>Tricatedral</td>
</tr>
</tbody>
</table>

Smectite (2:1)

| Montmorillonite      | Na₀.₂Ca₀.₄Al₀.₃Si₄O₁₀ (OH)₂ (H₂O)₆ | ~0.25-0.6 | Dioctahedral |
| Saponite             | Ca₀.₄Al₀.₄Mg₀.₃Fe²⁺₀.₀₂₅Si₄O₁₀ (OH)₂·4(H₂O) | ~0.25-0.6 | Tricatedral |
| Vermicullite         | Mg₁.₆Fe²⁺₀.₆Al₄.₃Si₄O₁₀ (OH)₂·4(H₂O) | ~0.6-0.9  | Dioctahedral |
| Illite               | K₀.₆₃(Al₃O₂)₀.₄₃Mg₀.₃Fe²⁺₀.₁Si₃.₃O₁₀(OH)₂ (H₂O) | ~0.9     | Dioctahedral |
| Mica (2:1)           | Muscovite           | KAl₃Si₃O₁₀(OH)₂  | ~1.0    | Dioctahedral |
|                      | Phlogopite          | KMg₃AlSi₃O₁₀(OH)₂ | ~1.0    | Tricatedral |

The deficiency of positive charge on the layers of smectites is intermediate between the end member mica and the starting pyrophyllite groups of phyllosilicates. The externally sorbed mobile hydrated cations, which balance the positive charge deficiency, can be replaced with other cations by simple ion exchange methods. [49,11] The ability to exchange cations, usually referred to as the Cation Exchange Capacity (CEC), distinguishes smectites from other phyllosilicates, which do not have any ion exchange ability. These cations can be exchanged with suitable organic cations to make silicate surface more organophilic. [50,51]. The structure of phyllosilicates is represented in figure 1.2.
Fig 1.2. The chemical general structures are respectively for, 2,1 phyllosilicates (top) and LDH (bottom) [49].

The replacement of inorganic exchange cations by organic onium ions on the gallery surfaces of smectite clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries. This facilitates the penetration of the gallery space intercalation by either the polymer precursors or preformed polymer [50]. Depending on the charge density of clay and the onium ion surfactant, different arrangements of the onium ions are possible. In general, the longer the surfactant chain length, and the higher the charge density of the clay, further apart the clay layers will be forced. This is expected since both of these parameters contribute to increasing the volume occupied by the intragallery surfactant. Depending on the charge density of the clay, the onium ions may lie parallel to the clay surface as a monolayer, a lateral bilayer, a pseudo-trimolecular layer, or an inclined paraffin structure as illustrated in Fig. 1.3. [51]
Fig 1.3. Orientations of alkyl ammonium ions in the galleries of layered silicates with different layer charge densities [51].

Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of PLS nanocomposites are thermodynamically achievable.

1.6 Morphology of polymer layered silicate nanocomposites

In general, the microstructures of polymer-layered silicate nanocomposites are classified in two idealized morphologies viz., intercalated and exfoliated. In an immiscible composite or an unmixed system the polymer does not penetrate inside the galleries between the clay layers and hence the pristine gallery distance is maintained in the composite. In intercalated structures however, polymer chains penetrate inside the galleries and effectively expand the silicate layers. Such structures consist of ordered, alternating polymer–silicate layers with repeat distance of a few nanometers. The equilibrium gallery height is determined by entropic and energetic factors. When the gallery distance (h), is less than the radius of gyration, ($R_g$), of the polymer chains, the configurational entropic penalty of polymer chain confinement may be compensated by increased conformational freedom of the tethered surfactant chain. When $h > R_g$, the entropy change is almost zero. [51, 52]
An ideal exfoliated state refers to a structure, where the polymer extensively penetrates in the silicate galleries so as to completely delaminate the layered structure. In the exfoliated state the average gallery height is determined by clay loading. This class of microstructure can be further classified based on the relative change in the separation between platelets with silicate volume fraction. Low silicate loadings result in disordered exfoliated nanocomposites in which single clay platelets are randomly suspended in the polymer matrix and are typically separated by an average distance of > 10 nm. Above a critical clay loading, the platelets start arranging in an ordered fashion and this is called the ordered exfoliated nanocomposites, as shown in Figure 1.4. However, real nanoclay composites exhibit morphologies, which are combinations of these idealized morphologies. The state of dispersion of clay in polymer is in general dictated by the polymer-silicate interactions, aspect ratio of silicate, method of manufacturing (melt, solution, in-situ polymerization) and possible orientation of layers during processing.

1.6.1 Intercalated nanocomposites

In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer.
1.6.2 Flocculated nanocomposites

Conceptually this is same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge–edge interaction of the silicate layers.

1.6.3 Exfoliated nanocomposites

In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading.

![Fig 1.4. Schematic illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites.](image)

1.7. Manufacturing techniques

The preparative methods of rubber nanocomposites are divided into four main groups depending on the starting materials and processing techniques,

1.7.1. Intercalation of polymer or prepolymer from solution
This is based on a solvent system in which the polymer or prepolymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent like chloroform, toluene or cyclohexane. When the polymer and the layered silicate are mixed the polymer chains intercalate and displace the solvent within the interlayer of the silicate. The solvent is evaporated and the intercalated structure remains. For the overall process, in which polymer is exchanged with the previously intercalated solvent in the gallery, a negative variation in Gibbs free energy is required. The driving force for polymer intercalation into layered silicate from solution is the entropy gained by desorption of solvent molecules, which compensates for the decreased entropy of the intercalated chains. This method is good for the intercalation of polymers with little or no polarity into layered structures, and facilitates production of thin films with polymer-oriented clay intercalated layers. The major disadvantage of this technique is the non-availability of compatible polymer-clay systems. Moreover this method involves the copious use of organic solvents which is environmentally unfriendly and economically prohibitive.

Biomedical polyurethane urea (PUU)/MMT (MMT modified with (dimethyl ditallow ammonium cation) nanocomposites were prepared by adding OMLS (organically modified layered silicate) suspended in toluene drop wise to the solution of PUU in N,N dimethyl acetamide(DMAC). The mixture was then stirred overnight at room temperature, the solution degassed and the films were cast on round glass Petri dishes. The films were air dried for 24 h, and subsequently dried under vacuum at 50°C for 24 h. WAXD analysis indicated the formation of intercalated nanocomposites. [53]. The effects of heat and pressure on microstructures of isobutylene-isoprene rubber/clay nanocomposites prepared by solution intercalation (S-IIRCNs) were investigated [54]. A comparison of the WAXD patterns of untreated S-IIRCN and nanocomposites prepared by melt intercalation(M-IIRCN) reveals that the basal spacing of the intercalated structures in untreated M-IIRCN (i.e.,5.87 nm) is much larger than that in S-IIRCN (i.e.,3.50 nm), which is likely a result of the different methods of preparation.
1.7.2. In situ intercalative polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution and so the formation cannot occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step. Yao et al. [55] reported the preparation of a novel kind of PU/MMT nanocomposite using a mixture of modified 4,40-di-phenylmethane diisocyanate (MMDI) modified polyether polyl (MPP) and Na-MMT. In a typical synthetic route, a known amount of Na-MMT was first mixed with 100 ml of MPP and then stirred at 50 °C for 72 h. Then, the mixture of MPP and Na-MMT was blended with a known amount of M-MDI and stirred for 30 s at 20 °C, and finally cured at 78 °C for 168 h. Wang and Pinnavaia [56] reported the preparation of polyurethane-MMT nanocomposites using this technique. It can be seen, that the extent of gallery expansion is mainly determined by the chain length of the gallery onium ions and is independent of the functionality or molecular weight of the polyls and the charge density of the clay. These nanocomposites exhibit an improvement in elasticity, as well as in modulus. In another study, Lan and Pinnavaia [57] reported the preparation of nanocomposites with a rubber/epoxy matrix obtained from DGEBA derivatives cured with a diamine so as to reach sub ambient glass transition temperatures. It has been shown that depending on the alkyl chains length of modified MMT, an intercalated and partially exfoliated or a totally exfoliated nanocomposite can be obtained.

1.7.3. Melt intercalation

Recently melt intercalation technique has become the standard for the preparation of polymer nanocomposites. During polymer intercalation from solution a relatively large number of solvent molecules have to be desorbed from the host to accommodate the incoming polymer chains. The desorbed solvent molecules gain one translational degree of freedom, and the resulting entropic gain compensates for the decrease in conformational entropy of the confined polymer chains. There are many advantages
to direct melt intercalation over solution intercalation. Direct melt intercalation is highly specific for the polymer, leading to new hybrids that were previously inaccessible. In addition the absence of solvent makes the process economically favorable method for industries from a waste perspective. On the other hand during this process only a slow penetration (transport) of polymer takes place within the confined gallery. Very recently, EPDM/clay nanocomposites were prepared by mixing EPDM with OMLS via a vulcanization process [58]. WAXD analysis and TEM observation revealed that the clay layers were exfoliated and almost dispersed as monolayers. Polyamide 66/SEBS-g-M alloys and their nanocomposites were prepared by melt compounding using a twin screw extruder. Morphological investigations with different methods show pseudo-one-phase type morphology for these prepared alloys at all percentage of rubber. Impact and tensile test results showed that rubber toughened samples exhibit significantly more impact strength and elongation at break comparing to virgin polyamide. Samples with 20% of rubber show impact strength about 15 times and elongation at yield several times more than those of virgin polyamide. So, these rubber modified polyamide can be considered as super toughened rubber. A general type organoclay at 4% and 8% has been used with rubber toughened samples to tolerate their modulus and tensile strength. Obtained results show that nanoclay could significantly increase modulus and tensile strength of rubber modified Polyamide 66 without considerable effects on impact strength. WAXD and SEM results show that the Polyamide 66 nanocomposites are better exfoliated in presence of SEBS-g-MA. The reduced modulus and strength of alloys with functional rubber addition was counteracted by incorporation of organoclay without significant negative effects on the impact strength. Comparison of mechanical properties of this rubber toughened polyamides with virgin polyamides shows an increase about 1200% and 240% for impact strength and elongation at break, respectively, which is a very interesting result and show excellent toughening of polyamide 66 with SEBS-g-MA rubber. [59].

1.7.4. Sol gel method
Sol-gel chemistry offers a unique advantage in the creation of novel organic–inorganic hybrids. The sol-gel process requires a combination of metal alkoxide precursors \([M(OR)n]\) and water, where \(M\) is a network forming inorganic element and \(R\) is typically an alkyl group. Hydrolysis and condensation of the metal alkoxide are the two fundamental steps to produce inorganic network within the polymer matrix in presence of an acid or base catalyst. Silicon alkoxide (e.g. tetraethoxysilane, TEOS) is the most commonly used metal alkoxide due to its mild reaction condition [60,61]. Tang and Mark [62] have reported mechanical properties of sol-gel hybrids prepared. The reaction parameters that influence the sol-gel chemistry are the pH of the solution, the mole ratio of Si to \(H_2O\), catalysts, solvents and reaction temperature. Also, pH plays a key role in determining the nature of the hybrids when all other parameters are kept constant. A typical application area for hybrid materials are optical systems that require homogeneous and transparent materials which cannot be obtained from mixtures that are already macroscopically phase separated. This is often the case if hydrophobic polymers are mixed with sol–gel solutions. Therefore, organic polymers with functional groups that have specific interactions with compounds created in the sol–gel process, e.g. hydrogen bonding to residual silanol groups on the formed silica, have to be chosen. If the time of the sol–gel network formation is fast enough, a macroscopic phase separation is avoided. This was proved applying the very fast non-aqueous sol–gel process where formic acid is used together with silicon alkoxides. In this process water is necessary for the condensation of the silicate, kaolin or carbon black. Species is produced by an esterification reaction of the alcohols released by the silica precursor and formic acid. Bandyopadhyay and coworkers [63,64] conducted a detailed study on the structure–property relationship of the rubber/silica hybrid nanocomposites (ACM and ENR based) by varying the reaction parameters like solvents, Si to \(H_2O\) mole ratio and temperature. Polysiloxane elastomers have been reported to be reinforced by precipitated silica particles which are nanosized and highly dispersed through a sol–gel technique. Although theoretically this method has the potential of promoting the dispersion of the silicate layers in a one-step process, without needing the presence of the onium ion, it
presents serious disadvantages. First of all, the synthesis of clay minerals generally requires high temperatures, which decompose the polymers. An exception is the synthesis of hectorite-type clay minerals which can be performed under relatively mild conditions [65].
1.8 Elastomers

Elastomers (Rubbers) are macromolecular substances characterized by a unique combination of useful properties such as elasticity, flexibility, toughness and impermeability. The American Society for Testing and Materials (ASTM) uses the following criteria to define the term “elastomer”

1. It must not break when stretched approximately 100%
2. After being held for five minutes @ 100 stretch, it must retract to within 10% of its original length with in 5 minutes of release.

Generally elastomers are classified as commodity or general purpose elastomers such as NR & SBR, high volume speciality elastomers, such as EPDM, CR and NBR etc. and low-volume speciality elastomers such as polyurethanes, Silicones, Flurocarbons, Polyacrylates, Epichlorohydrin and CSM elastomers etc. Table 1.2 shows the most important types of rubbers, their groupings and ASTM D 1418 abbreviations based on the nature of their back bone and table1.3 shows the structural formulas of most commonly used elastomers.

1.8.1 Natural Rubber (NR)

Natural rubber (NR) is produced from the latex of Hevea Brasiliensis tree. Before coagulation the latex is stabilized with preservatives (ammonia, formaldehyde, sodium sulphite) and hydroxyl amine may be added to produce technically specified, constant viscosity grades of NR. The Tg of NR is -70°C and its structure is thought to be completely cis-1,4-polyisoprene except for the chain ends. NR contains small amounts of fatty acids and proteinaceous residues that promote sulphur vulcanization. NR macromolecules are configured identically and so they spontaneously pack together as crystallites on standing at low temperature, with a maximum rate at temperatures around -25°C. NR also crystallizes upon straining. In fact strain induced crystallization imparts outstanding green strength and tack and gives vulcanizates with high resistance to cut growth at severe deformations. NR macromolecules are susceptible to fracture on tearing. High shearing stress and
oxygen promotes the rate of molecular scission. Several modified natural rubbers are available commercially. Some examples are

1. Deproteinized, to reduce water absorption, i.e. in electrical appliances where maximum resistivity is required.
2. Skim rubber, a high protein, fast curing product used in cellular foams and pressure sensitive adhesives.
3. Superior processing in which ordinary and vulcanized lattices are blended in about 80:20 ratio before coagulation. Unfilled or lightly filled compounds made with superior processing NR give smoother and less swollen extrudates compared to those prepared from regular NR.
4. Isomerized, prepared by milling NR with butadiene sulfone, resulting in cis/trans isomerization which inhibits crystallization.
5. Epoxidised, an oil resistant rubber, which retains the ability to strain crystallize.

1.8.2 Synthetic rubber

The extensive development of the synthetic rubber industry originated with the World War II emergency, but continued expansion has been the result of the superiority of the various synthetic rubbers in certain properties and applications. Synthetic rubbers are widely classified into general purpose and special purpose rubbers.
1.8.2.1 General purpose rubber

General purpose rubbers are hydrocarbon polymers. They include styrene-butadiene rubber (SBR), butadiene rubber (BR), and polyisoprene rubber. These “deine” rubbers contain substantial chemical unsaturation in their backbones causing them to be rather susceptible to attack by oxygen, and especially by ozone. Additionally they are readily swollen by hydrocarbon fluids. The primary application of these elastomers is in automobile and truck tyres.

Styrene-Butadiene rubber (SBR)

SBR denotes a copolymer of styrene and butadiene, typically containing about 23% styrene, with a $T_g$ value of approximately -55°C. It is the most widely used synthetic elastomer with the largest volume production. It is synthesized via free radical polymerization emulsion in water, or anionically in solution. In emulsion polymerization, the emulsifier is usually a fatty acid or a rosin acid. The former gives a faster curing rubber with less tack and less staining. The molecular weight is controlled by mercaptan chain transfer agents. Solution SBR is purer than emulsion SBR because of the absence of emulsion residues. But when compared at similar molecular weights emulsion SBRs are more extensible in the uncured state than anionic SBRs.

Polyisoprene (IR)

IR is produced both anionically and by Zeigler-Natta polymerization. The former material has up to 95% cis microstructure, while the latter has 98% stereoregularity. Both types of IR have less green strength and tack than NR. IR compounds have low modulus and higher breaking elongation than similarly formulated NR compositions. This is due, at least in part, to less strain induced crystallization with IR especially at high rates of deformation.

Polybutadiene (BR)

Like isoprene, BR can be synthesized anionically or via Zeigler-Natta polymerization. Cold emulsion BR is also available. Anionic BR prepared in
hydrocarbon solvent, contains about 90% 1,4 structure and 10% 1,2 structure (vinyl). The vinyl content can be increased by adding an amine or ether as cosolvent during polymerization. The 1,4 structure is an equal mixture of cis and trans forms. Because it consists of mixed isomers, anionically prepared BR does not crystallize. Emulsion BR has a mostly trans microstructure and also does not crystallize. On the other hand the Zeigler Natta product has very high cis content and can crystallize [26]. The Tg of low-vinyl BR is about -100°C, among the lowest of all rubbers, while that of high vinyl BRs can reach to 0°C. Low vinyl BRs are highly resilient and are often blended with SBR, NR and IR to make tire treads with good abrasion resistance. Unlike NR, BR is resistant to chain scission during mastication.

1.8.2.2 Special Purpose rubber

In many applications general purpose rubbers are unsuitable due to their insufficient resistance to swelling, ageing, and elevated temperatures. Speciality elastomers have been developed to meet these needs.

Polychloroprene (CR)

Polychloroprene is an emulsion polymer of 2-chlorobutadiene and has a Tg of about -50 °C. The electron withdrawing chlorine atom deactivates the double bond towards attack by oxygen and ozone and imparts polarity to the rubber making it resistant to swelling by hydrocarbons. Compared to general purpose elastomers, CR has superior weatherability, heat resistance, flame resistance and adhesion to polar substrates, such as metals. In addition CR has a low permeability to air and water vapour. The microstructure of CR is mostly trans-1,4 and homopolymer grades crystallize upon standing or straining, even though they are not as stereoregular as NR. Apparently C-Cl dipoles enhance inter chain interaction and prompt crystallization. Copolymer grades of CR crystallize less or not at all. Applications include wire, cable, hose and some mechanical goods.

Acrylonitrile-Butadiene rubber (NBR)
NBR also termed as nitrile rubber, is an emulsion copolymer of acrylonitrile and butadiene. Acrylonitrile content varies from 18-50%. Unlike CR, polarity in NBR is introduced by copolymerization with the polar monomer, acrylonitrile, which imparts excellent fuel and oil resistance. With increased acrylonitrile content, there is an increase in Tg, reduction in resilience, lower die swell, decreased gas permeability, increased heat resistance and increased strength. Because of unsaturation in the butadiene portion, NBR is still rather susceptible to attack by oxygen and ozone. Ageing behavior can be improved by blending with small amounts of PVC. Nitrile rubber is widely used for seals and fuel and oil hoses.

**Hydrogenated Nitrile rubber (HNBR)**

Nitrile rubber can be hydrogenated to eliminate most of the unsaturation and hence greatly improve ageing and heat resistance. Fuel resistance is also maintained. HNBR is used especially in oil field applications, where resistance to hydrocarbons at elevated temperature is required.

**Butyl rubber (IIR)**

Butyl rubber is a copolymer of isobutylene with a small percentage of isoprene to provide sites for curing. IIR has unusually low resilience for an elastomer with such a low Tg (-70°C). Because IIR is greatly saturated, it has excellent ageing and extremely low permeability to gases. Thus it is widely used in inner tubes and inner liners. Brominated (BIIR) and Chlorinated (CIIR) modifications of IIR are also available. They have enhanced cure compatibility with general purpose diene rubbers.

**Ethylene Propylene rubber (EPR, EPDM)**

The commercial rubbers with the lowest density are ethylene propylene copolymers made by Zeigler-Natta and metallocene polymerization. To introduce unsaturated cure sites, a non-conjugated diene termonomer, such as 1,4 hexadiene, ethylidene norbornene, or dicyclopentadiene is employed. EPDM (Etylene- Propylene Diene Monomer) has a small number of double bonds external to the backbone,
introduced in this way. The ratio of ethylene to propylene in commercial grades
varies from 50/50 to 75/25 and a typical Tg is -60°C. EPRs and EPDMs have
excellent resistance to weathering and good heat stability. They can be made
partially crystalline to give high green strength, but they possess poor building tack.
Applications include roofing, seals, gaskets and hose.

*Silicon rubber*

Unlike the previously discussed elastomers which have carbon back bones, silicon
rubbers contain very flexible siloxane back bones and have very low glass transition
temperatures. The most common silicon elastomer is polydimethylsiloxane with a
Tg of -123°C. Silicon rubbers have both excellent high temperature resistance and
low temperature flexibility. In addition, they possess good biocompatibility and thus
are used in implants and prostheses. Other uses include gaskets, seals and O-rings.

*Polysulphide rubber*

Polysulphide Rubbers contain substantial proportion of sulphur in their structure.
For example the polysulphide rubber made by reacting dichloroethane with sodium
tetrasulphide contains about 80% sulphur by weight. This results in high density
(1.34g/cm³) and outstanding resistance to ketones, esters and most solvents. Major
uses of polysulphide rubbers include permanent putties for fuel tank sealants, fuel
hose liners and gaskets

*Chlorosulphonated polyethylene (CSM)*

When polyethylene is chlorosulphonated its crystallinity is disrupted and chemically
stable elastomer results. Commercial grades contain 25 to 45% chlorine and 1 to
1.4% sulphur. These elastomers have excellent weatherability and good flame
resistance. Oil resistance increases with increase in chlorine content, while low
temperature flexibility and heat aging resistance are improved when the chlorine
content is low.

*Chlorinated polyethylene(CM)*
Another modification of polyethylene to produce an elastomer is simple chlorination (25 to 42%, typically about 36%). CMs are less expensive than CSMs and provide vulcanizates with lower compression set. Increased chlorine content improves oil, fuel and flame resistance but results in poorer heat resistance. CM has excellent weatherability and heat resistance (150⁰C to 175⁰C), even when immersed in many types of oil. Hose, wire and cable coverings are typical applications.

*Ethylene-methyl acrylate rubber (AEM)*

This elastomer is a terpolymer of ethylene, methyl acrylate and small amount of carboxylic monomer as a cure site. Amines and peroxides are used as curatives. AEM has a heat resistance between that of CSM and MQ elastomers. It is resistant to aliphatics, but has poor resistance to strong acids and other hydrolyzing agents. Weathering and heat ageing resistance are good up to 150⁰C. Applications are power steering hose, spark plug boots, and transmission seals.

*Acrylic rubber (ACM)*

ACMs are copolymers of a dominant acrylate monomer (Ethyl or Butyl) and a cure site monomer, such as 2 chloroethyl vinyl ether. Butyl acrylate results in a lower Tg but poorer oil resistance compared to ethyl acrylate. Copolymerization with acrylonitrile improves oil resistance. Although acrylate rubbers have good heat resistance, they have poor resistance to alkali and acids. Applications include gaskets O-rings, oil hose and transmission seals.

*Fluorocarbon rubbers*

Fluorocarbon rubbers are made in emulsion and are among the most inert and expensive elastomers. A typical one is made by copolymerizing the fluorinated analogs of ethylene and propylene. This rubber has a density of 1.85 g/cc and has a service temperature exceeding 250⁰C. It is little affected by immersion in acids, bases, or aromatic solvents; however, ketones and acetates attack the material. There are many aircraft applications for fluoro rubbers including O rings, seals and gaskets.
Epichlorohydrin rubber (CO, ECO)

Two common types are polyepichlorohydrin (CO) and copolymers with ethylene oxide (ECO), which have lower Tg. Epichlorohydrin rubbers are quite resistant to aliphatic and aromatic fluids, and have good building tack. Other notable properties include good ozone resistance, low gas permeability (about one third that of butyl rubber), and heat resistance up to 150°C. Applications include wire and cable jackets, hoses, belting and packing.

Urethane rubber

Polyester type and polyether type urethane rubbers are available. The latter have better hydrolytic stability, but somewhat worse mechanical properties. Urethane rubbers can be cured with sulphur or peroxide, and the vulcanizates have excellent resistance to weathering, abrasion and swelling by oil. Some applications are industrial rolls, castor wheels, gaskets, shoe soles and conveyor belts.

Table 1.2 The Most Important Types of Rubber, Their Groupings and Abbreviations

<table>
<thead>
<tr>
<th>ELASTOMER CHEMICAL NAME</th>
<th>ASTM-D1418 ABBREVIATIONS</th>
<th>ELASTOMER GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>Isoprene Rubber</td>
<td>IR</td>
<td>&quot;All these rubbers have an unsaturated Carbon – Hydrogen backbone”</td>
</tr>
<tr>
<td>Polybutadiene Rubber</td>
<td>BR</td>
<td></td>
</tr>
<tr>
<td>Isobutylene-Isoprene Rubber</td>
<td>IIR</td>
<td></td>
</tr>
<tr>
<td>Bromobutyl Rubber</td>
<td>BIIR</td>
<td></td>
</tr>
<tr>
<td>Chlorobutyl Rubber</td>
<td>CIIR</td>
<td></td>
</tr>
<tr>
<td>Chloroprene Rubber</td>
<td>CR</td>
<td></td>
</tr>
<tr>
<td>Nitrile Butadiene Rubber</td>
<td>NBR</td>
<td></td>
</tr>
<tr>
<td>Hydrogenated Nitrile</td>
<td>HNBR</td>
<td></td>
</tr>
<tr>
<td>Carboxylated Nitrile</td>
<td>XNBR</td>
<td></td>
</tr>
<tr>
<td>Rubber Type</td>
<td>Abbreviation</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Styrene Butadiene Rubber</td>
<td>SBR</td>
<td></td>
</tr>
<tr>
<td>Carboxylated SBR</td>
<td>XSBR</td>
<td></td>
</tr>
<tr>
<td>Ethylene Propylene Diene Rubber</td>
<td>EPDM</td>
<td></td>
</tr>
<tr>
<td>Ethylene Propylene Rubber</td>
<td>EPM</td>
<td></td>
</tr>
<tr>
<td>Chlorosulphonated Polyethylene Rubber</td>
<td>CSM</td>
<td></td>
</tr>
<tr>
<td>Fluorocarbon Rubber</td>
<td>FKM</td>
<td></td>
</tr>
<tr>
<td>Tetrafluoro ethylene Propylene Rubber</td>
<td>FEPM</td>
<td></td>
</tr>
<tr>
<td>Perfluorinated Elastomer</td>
<td>FFKM</td>
<td></td>
</tr>
<tr>
<td>Polyacrylate Rubber</td>
<td>ACM</td>
<td></td>
</tr>
<tr>
<td>Methyl Silicone Rubber</td>
<td>MQ</td>
<td></td>
</tr>
<tr>
<td>Methyl Phenyl Silicone Rubber</td>
<td>PMQ</td>
<td></td>
</tr>
<tr>
<td>Methyl Phenyl Vinyl Silicone Rubber</td>
<td>PVMQ</td>
<td></td>
</tr>
<tr>
<td>Methyl vinyl Silicone Rubber</td>
<td>MVQ</td>
<td></td>
</tr>
<tr>
<td>Fluoro Silicone Rubber</td>
<td>FVMQ</td>
<td></td>
</tr>
<tr>
<td>Epichlorohydrin Rubber</td>
<td>CO</td>
<td></td>
</tr>
<tr>
<td>Epichlorohydrin - Ethylene oxide Copolymer Rubber</td>
<td>ECO</td>
<td></td>
</tr>
</tbody>
</table>

**M**

“All these rubbers have a saturated Carbon - Hydrogen backbone”

**Q**

“All these rubbers have a silicon in their backbone”

**O**

These rubbers have an oxygen atom in its main back bone chain
<table>
<thead>
<tr>
<th>Polyester Urethane Rubber</th>
<th>AU</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Urethane Rubber</td>
<td>EU</td>
<td></td>
</tr>
</tbody>
</table>

These rubbers have carbon, hydrogen and nitrogen in the main backbone chain.
Table 1.3 Structural formulas of most commonly used elastomers

<table>
<thead>
<tr>
<th>ASTM-D1418 ABBREVIATION</th>
<th>STRUCTURAL FORMULAS</th>
</tr>
</thead>
</table>
| NR/IR                    | \[
| \text{CH}_3 \]
| \[
| \text{CH}_2\text{C}≡\text{CH}\text{-CH}_2\]_n |
| IIR                      | \[
| \text{CH}_3 \]
| \[
| \text{CH}_2\text{C}≡\text{CH}\text{-CH}_2\]_y
| \[
| \text{CH}_3 \]
| \[
| \text{CH}_2\text{C}≡\text{CH}\text{-CH}_2\]_x
| \[
| \text{CH}_3 \]
| \[
| \text{CH}_2\text{C}≡\text{CH}\text{-CH}_2\]_n |
| BIIR                     | \[
| \text{CH}_2 \]
| \[
| \sim \text{CH}_2\text{-C}≡\text{CH}\text{-CH}_2\sim \]
| \[
| \text{Br} \] |
| CR                       | \[
| \text{Cl} \]
| \[
| \text{CH}_2\text{C}≡\text{CH}\text{-CH}_2\]_n |
| NBR                      | \[
| \text{CH}_2\text{-CH}≡\text{CH}\text{-CH}_2\]_x
| \[
| \text{CH}_2\text{-CH}≡\text{CH}\text{-CH}_2\]_y
| \[
| \text{CH}_2\text{-CH}≡\text{CH}\text{-CH}_2\]_n |
| BR                       | \[
<p>| \text{CH}_2\text{-CH}≡\text{CH}\text{-CH}_2]_n |</p>
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formula</th>
</tr>
</thead>
</table>
| CSM     | \[
\left(\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\right)_n\text{Cl} \]
|        | \[
\text{SO}_2\text{Cl} \] |
| EPDM    | \[
\left(\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\right)_n\text{CH}_3 \]
|        | \[
\text{(diene)}_{0.2} \] |
| FKM     | \[
\left(\text{CH}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\right)_n \]
| MQ      | \[
\left(\text{CH}_3\text{-Si}\text{-O}\text{-CH}_3\right)_n \]
| ECO     | \[
\left(\text{CH}_2\text{-CH-O}\text{-CH}_2\text{-CH-O}\right)_n \]
| ACM     | \[
\left(\text{H-C-H}_2\text{Cl}\text{-C}_2\text{H}_4\text{-Cl}\text{-H-C-H}_2\text{-H-C-H}_2\text{-H-C-H}_2\right)_n \]
| AU      |
Elastomers that exhibit high resistance to ozone and weather are characterized by a saturated backbone. Hence M group elastomers are weather resistant. R group elastomers with highly unsaturated backbone like NR and polybutadiene are not ozone and oxygen resistant. Therefore antiozonant and protective waxes are added during compounding to improve their weather resistant properties. CR though highly unsaturated like NR show fair ozone resistance due to the presence of chlorine atom which reduces the reactivity of double bonds to oxidizing agents including ozone and oxygen. Elastomers having polar groups in the polymer chain shows resistance to mineral oils. Halogen containing rubbers like FKM, CR, CSM, ECO are inherently flame resistant. Halogen free elastomers are not flame resistant unless they contain a high concentration of flame retardants.

1.9 Butyl Rubbers

Butyl rubber is derived from the monomer of another rubber called polyisobutylene. Although polyisobutylene is a rubber it had minimal use as rubber, because being unsaturated it could not be cured with sulphur and attempt to cured with peroxide simply leads to degradation of the polymeric materials. In addition to this, polyisobutylene is having very high cold flow and creep. This problem of polyisobutylene was overcome in 1939 through copolymerization of isobutylene with small amount of a diene monomer called isoprene.

Butyl rubber is a random co polymer of isobutylene and a small amount of isoprene. It is also known as isobutylene-isoprene rubber, abbreviated as IIR according to ASTM D 1418. The amount of isobutylene part in the butyl rubber ranges from 97 to 99 mol % and that of isoprene part is from 0.8 to 2.5 mol %. The
term “mole percent unsaturation” refers to the number of isoprene molecules in 100 monomer molecules in the polymer. Thus, a one – mole percent unsaturated butyl would contain one molecule of isoprene and ninety nine molecules of isobutylene. In a single butyl macromolecule made up of thousands of monomer units, the isoprene units are randomly distributed. Figure 1.5 shows the repeating unit of a butyl elastomer.

Efficient intermolecular packing of polyisobutylene leads to lower fraction free volumes and low permeabilities. Moreover the sp³ hybridisation affording tetrahedral arrangement of carbon atoms leads to effective close packing due to geminal dimethyl atoms. Butyl rubber has the smallest coil dimension among elastomers. As a result of its molecular structure, IIR possesses superior air impermeability due to the sluggish movement of its methyl groups. The exceptional air impermeability of butyl rubber has made it the elastomer of choice for the inner tubes and liners of tires. While this market consumes the majority of its annual worldwide production, butyl rubber is also used in mechanical damping applications due to its high loss modulus, extended fatigue life and oxidative stability. Butyl
rubbers are available in different types and grades. Fig 1.6 shows various types of butyl rubbers.

![Fig 1.6 Different types of Butyl rubbers.](image)

1.10 Chemistry of the Manufacturing process of chlorobutyl rubber.

Butyl rubber (IIR) is prepared from high purity isobutylene and isoprene. The mechanism of polymerization consists of complex cationic reactions. The catalyst system is a Lewis acid co-initiator with an initiator. Typical Lewis acids co-initiators include aluminum trichloride, alkyl aluminum dichloride, boron trifluoride, tin tetrachloride, and titanium tetrachloride. Bronsted acids such as water, hydrochloric acid, organic acids, or alkyl halides are used as initiators. The mechanism follows initiation, propagation and termination.

Initiation step: In this step the isobutylene monomers reacts with the catalyst-co-catalyst system to produce a carbocation. As shown in fig1.7
Propagation step: Monomer units continue to be added in the propagation step (fig 1.8) until chain transfer or termination reactions occur. Temperature, solvent polarity, and the presence of counter ions can affect the propagation of this exothermic reaction.

Termination step: In the chain transfer step that terminates propagation of the macromolecule, the carbonium ion of the polymer chain reacts with the isobutylene or isoprene monomers, or with other species such as solvents or counter ions, to halt the growth of this macromolecule and form a new propagating polymer chain (Figure 1.9). Lowering the polymerization temperature retards this chain transfer and leads to higher molecular weight butyl polymers. Isoprene is co-polymerized mainly by trans-1,4-addition. Termination of polymerization results from the irreversible destruction of the propagating carbonium ion either by the collapse of the ion pair, by hydrogen abstraction from the co-monomer, by formation of stable allylic carbenium ions, or by reaction with nucleophilic species such as alcohols or amines.
The termination point is determined so as to control the molecular weight of the butyl rubber.

In addition, two minor processes can occur as follows:

In the most widely used butyl rubber manufacturing process, slurry of fine particles of butyl rubber dispersed in methyl chloride is formed in the reactor after Lewis acid initiation. The reaction is highly exothermic, and a high molecular weight can be achieved by controlling the polymerization temperature, typically from -100°C to -90°C. The most commonly used polymerization process uses methyl chloride as the reaction diluent and boiling liquid ethylene to remove the heat of reaction and maintain the required low temperature. The final molecular weight of the butyl rubber is determined primarily by controlling the initiation and chain transfer reaction rates. Water and oxygenated organic compounds that can terminate the propagation step are minimized by purifying the feed systems. The methyl chloride and unreacted monomers are flashed off with steam and hot water, dried and purified, and then recycled back to the reactor. Stabilizers (calcium stearate) and an antioxidant (BHT) are introduced to the hot water/polymer slurry to stabilize the polymer and prevent agglomeration. For regular butyl rubber production, the polymer is then removed from the hot water slurry using screens and
dried in a series of extrusion, dewatering, and drying steps. Fluidized bed conveyors or airvey systems are used to cool the product to a suitable packaging temperature. The dried product is in the form of small crumbs, which are subsequently weighed and compressed into 75lb bales for wrapping in PE film and packaging.

1.11 Literature review on nanocomposites

The effects of the coating amount of surfactant and the particle concentration on the impact strength of polypropylene (PP)/CaCO₃ nanocomposites were investigated [66]. The morphological features and the free volume properties of an acrylic resin/laponite nanocomposite are investigated using X-ray diffraction and Positron Annihilation Lifetime Spectroscopy [67]. Structure and rheological properties of hybrids with polymer matrix and layered silicates as filler were studied. The peculiarity of this study is that the matrix depending on temperature can form different phase states including liquid-crystalline (LC). So, a possibility of coexistence and superposition of different ordered structures can be realized at different temperatures. Three different fillers were used, natural Na-montmorillonite (MMT) and organoclays obtained by treating MMT with surfactants varying in polarity of their molecules. Depending on the type of clay, materials with different morphology can be obtained. X-ray data showed that PEG intercalates all types of clay used whereas penetration of HPC macromolecules into clay galleries during mixing does not occur. Clay modified with more polar surfactant should be treated as the most convenient material to be intercalated by PEG [68]. With the incorporation of less than 9 wt. % nanoclay, the dynamic storage modulus above the glass transition region of such a blend increases from 2 MPa to 54 MPa. This tremendous reinforcing as well as the compatibilization effect of the nanoclay was understood by thermodynamically driven preferential framework-like accumulation of exfoliated nanoclay platelets in the phase border of CR and EPDM, as observed i.e. from transmission electron microscopy [69]. Modified method for interconnecting multi-walled carbon nanotubes (MWCNTs) was put forward. And interconnected MWCNTs by reaction of acyl chloride and
amino groups were obtained. Scanning electron microscopy shows that hetero-
junctions of MWCNTs with different morphologies were formed. Then specimens
of pristine MWCNTs, chemically functionalized MWCNTs and interconnected
MWCNTs reinforced epoxy resin composites were fabricated by cast moulding.
Tensile properties and fracture surfaces of the specimens were investigated [70].
A model to simulate the conductivity of carbon nanotube/polymer nanocomposites is
presented. The proposed model is based on hopping between the fillers. A
parameter related to the influence of the matrix in the overall composite
conductivity is defined. It is demonstrated that increasing the aspect ratio of the
fillers will increase the conductivity. Finally, it is demonstrated that the alignment
of the filler rods parallel to the measurement direction results in higher
conductivity values, in agreement with results from recent experimental work [71].
Polybutadiene (PB)/Allylisobutyl Polyhedral Oligomeric Silsesquioxane (A-POSS)
nanocomposites have been prepared by using A-POSS and butadiene (Bd) as
comonomers, n-BuLi as initiator, cyclohexane as solvent, ethyltetrahydrofurfuryl
ether as structure modifier through the anionic polymerization technique. The
reaction conditions, the kind and content of the modifier and POSS, etc. affecting the
copolymerization process and the microstructure of the nanocomposites were also
investigated. The results showed that POSS incorporation obviously decreased the
rate of polymerization and the molecular weight of the copolymers and increased
polydispersity index of the copolymers. The reaction conditions (the reaction time
and reaction temperature) had little effect on copolymerization [72].

Some important rubber engineering products containing high pressure air, for
example tire inner-tubes, air springs and cure bladders, etc. demand a high barrier to
gas permeation. Several rubber/clay nanocomposites, such as natural rubber
(NR)/clay, nitrile rubber (NBR)/clay, ethylene–propylene–diene rubber
(EPDM)/clay and styrene butadiene rubber (SBR)/clay, have been successfully
prepared [73-77]. Several studies have been made to modify the properties of halo
butyl rubber [78-88]. Hendriske and coworkers [78] studied the vulcanization of
chboro butyl rubber and determined the crosslink densities. Dadvand et. al.[79] evaluated the thermal stability characteristics of Neoprene/chlorobutyl rubber composites before and after ageing. Takashi et al [88] synthesized butyl rubber/vermiculite nanocomposites and studied the gas barrier properties of these nanocomposite coatings on a PPO coated ceramic disc. It was found that gas permeability of the nano composites decreased remarkably by the presence of high loadings of vermiculite. Capps [89] and coworkers compared the viscoelastic and dielectric relaxations in butyl and chloro butyl rubber as a function of carbon black loading. Sridhar and coworkers studied the relaxation behavior of chloro butyl nano clay composites [90].

1.12 Characterization of polymer nanocomposites

Generally, the structure of nanocomposites has typically been established using WAXD analysis and transmission electron micrographic (TEM) observation. Due to its easiness and availability WAXD is most commonly used to probe the nanocomposite structure [91-95] and occasionally to study the kinetics of the polymer melt intercalation [96]. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. For example, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1–4 nm), little can be said about the spatial distribution of the silicate layers or any structural non-homogeneities in nanocomposites. Additionally, some layered silicates initially do not exhibit well-defined basal reflections. Thus, peak broadening and intensity
decreases are very difficult to study systematically. Therefore, conclusions concerning the mechanism of nanocomposites formation and their structure based solely on WAXD patterns are only tentative. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. However, special care must be exercised to guarantee a representative cross-section of the sample. Both TEM and WAXD are essential tools [97] for evaluating nanocomposite structure. However, TEM is time-intensive, and only gives qualitative information on the sample as a whole, while low-angle peaks in WAXD allow quantification of changes in layer spacing. Typically, when layer spacing exceed 6–7 nm in intercalated nanocomposites or when the layers become relatively disordered in exfoliated nanocomposites, associated WAXD features weaken to the point of not being useful. However, recent studies of Sinha Ray on simultaneous small angle X-ray scattering (SAXS) and WAXD yielded quantitative characterization of nanostructure and crystallite structure in N6 based nanocomposites [98].

1.12.1 XRD

X-ray diffraction (XRD) has long been successfully used to study various aspects of the structures in semicrystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers. With the availability of intense X-ray sources, high-speed detectors and faster methods of analyzing the data, it is now possible to examine the structure at higher spatial resolution and smaller time scales. Organo-montmorillonite (OMMT)/fluoroelastomer (FKM) nanocomposites were prepared by melt intercalation and characterized by XRD. The figure 1.10 shows that the reflection of OMMT in the nanocomposites was not seen when the OMMT content was below 6 wt%. This may indicate an exfoliation of OMMT in FKM. As the OMMT content was 12 wt %, the reflection of OMMT appeared at 2θ=1.96°, corresponding to a basal spacing of 4.50 nm, which indicated that the FKM chains were intercalated into the OMMT [99].
It was discovered by means of SAXS that disordered exfoliation of clay could be easily formed in HTPB/clay nanocomposite [100]. Kader et al. [101] performed diffraction studies of 001 plane in montmorillonite (Na-MMT), DCA treated Na-MMT, NBR and NBR/Na-MMT nanocomposites with various Na-MMT loadings. Figure 1.11 shows that the interlayer spacing of Na-MMT was observed at 2θ = 7.37° (d spacing calculated from Bragg’s law = 1.20 nm) whereas DCA treated Na-MMT showed the peak at 2θ = 6.27° (d001 = 1.41 nm). For NBR/Na-MMT samples, the peak appeared at 2θ value of 6.35° (d001 = 1.39 nm) with a decrease in peak intensity compared to pristine Na-MMT as given in figure 1.11. This indicates a small gallery expansion of about 0.2 nm in the layered clay in Na-MMT/DCA and NBR/Na-MMT samples. However, in addition to the presence of a peak, there was an increase in breadth of the peak which extends towards lower 2θ values for nanocomposites. Such broadening of the diffraction peak suggests that the occurrence of partial exfoliation as the crystal size decrease.
1.12.2 SEM

This technique gives qualitative information about the morphology of rubber nanocomposites. SEM micrographs of NR containing 10 wt % of M2 and M3 [dimethyl dihydrogenated-tallow ammonium montmorillonite (M2), and dimethyl hydrogenated tallow (2-ethylhexyl) ammonium montmorillonite (M3)] are shown in the Figure 1.12. The clay particles are dispersed in the elastomeric matrix without much agglomeration of particles and the platelet dimensions calculated from these figures were 1 µm [102].

Fig 1.12. SEM micrographs of NR filled with 10% wt of organoclay (a) M2 (b) M3 [102].
The morphology of Chloroprene rubber clay nanocomposites have been investigated with the help of SEM by Amit Das et al.[103]. Figure 1.13 reveals that on the contrary with the gum, the fractured surface of CR–OMMT is very rough with frequent ridgelines indicating the direction of crack propagation. These ridgelines often propagate through the particle polymer interface and these ridgelines of reinforcement indicate the good compatibility of OMMT and polar CR matrix. On the other hand, the MMT particles are found to homogeneously disperse throughout the fractured surface (Fig. 1.13 c) and no crack initiation can be observed at the interface. The higher magnification images of CR–MMT vulcanizates (Fig. 1.13 d) reveal that the MMT particles are simply pulled out of the matrix.

Fig 1.13. SEM micrographs of the tensile fractured surface of chloroprene rubber vulcanizates of (a) gum; without any filler, (b) filled with OMMT, (c) filled with MMT and (d) filled with MMT (in higher magnification). The arrows indicate the particles which have been pulled out from the CR matrix[103].
1.12.3 TEM

Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1–4 nm), little can be said about the spatial distribution of the silicate layers or any structural non-homogeneities in nanocomposites. Additionally, some layered silicates initially do not exhibit well-defined basal reflections. Thus, peak broadening and intensity reduction are very difficult to study systematically. Therefore, conclusions concerning the mechanism of nanocomposites formation and their structure based solely on WAXD patterns are only tentative. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. TEM allows a qualitative evaluation of the internal structure and spatial distribution of the various phases through direct visualization [109]. The above technique can also prove, besides the occurrence of intercalated and exfoliated nanocomposites, the formation of flocculated structures [104-106]. Although TEM represents a powerful tool for the characterization of nanocomposites, problems concerning tedious sample preparation and modification of the latter have to be considered. In this respect, even though the possible structural changes of clay minerals, caused by TEM analysis, are well documented in mineralogy [107-110], as far as nanocomposite study is concerned the above drawback has not been analyzed in detail. However, special care must be exercised to guarantee a representative cross-section of the sample. Nanocomposites of natural rubber latex and layered silicates were prepared by Valadares et al.[111] by a mild dispersion shear blending process. The results of X-ray diffraction (XRD) and transmission electron microscopy (TEM) show that clay particles are well dispersed in the dry latex and the platelets have a preferential orientation, forming translucent nanocomposites. TEM micrographs of thin cuts of dry nanocomposites are given in figure1.14. The dark lines are the cross-sections of single or multiple silicate platelets. Figure1.15 shows a rubber particle, approximately spherical, in the
center of the image. There are some clay particles without contact with the rubber lying in the image plane and these produce low contrast in the bright field image because they are very thin. Many other clay particles are in contact with the rubber and these are oriented normal to the image plane. These particles produce high contrast due to their alignment that produces strong interaction with the electron beam. The superimposition of clay and rubber domains (as opposed to mutual exclusion) and the deformation of rubber and clay particles is a strong evidence in favour of clay–rubber compatibility, that is all but unexpected due to the great differences between the properties of the two phases. In the 30 phr sample, TEM images show mainly tactoids but it is also possible to observe exfoliated structures with single 1 nm thick platelets. Most important, void formation in the polymer–filler interface is never observed, providing a strong evidence for good adhesion between the clay lamellae and the rubber. Similar results using TEM were obtained by Cho and Paul [112].
Fig 1.14. TEM micrographs of 5 phr (a top) and 30 phr (bottom) NaMMT–NR composite. The thin cuts were made normal to the nanocomposite film plane [111].
The role of the aspect ratio of the layered silicate platelets on the mechanical and oxygen permeation properties of hydrogenated nitrile rubber (HNBR)/organophilic layered silicate nanocomposites was investigated. Montmorillonite (MMT) and fluorohectorite (FHT) bearing the same type of intercalant (i.e., octadecylamine; ODA), however, showing different aspect ratio was involved in this study. Figure 1.16 shows the dispersion of the layered silicates assessed by transmission electron microscopy (TEM) [113].
Fig 1.16 TEM images of (a) HNBR/MMT-ODA and (b) HNBR/FHT-ODA nano composite (10 phr filler) [113].

1.12.4 AFM

Besides the capability of measuring lateral sizes and height features, AFM has the potential to investigate numerous additional material properties, such as friction forces and adhesion between tip and sample surface, stiffness, hardness and functional properties of the sample, such as conductivity and magnetic properties. AFM does not require a conductive coating or staining. Besides, this multifunctional technique is suitable to understand the nanofiller dispersion in the matrix along with surface topography. In addition to the normal topographical imaging, AFM can also measure fundamental properties of sample surfaces, e.g., local adhesive or elastic properties on a nanometric scale. Hence, AFM analysis of the nanocomposites can be a good alternative to electron microscopy, without any limitations regarding contrast and resolution. Moreover, AFM can be used as an automated characterization method. Interestingly, in the literature there have been only a few reports on the morphology of rubber clay nanocomposites by atomic force microscopy (AFM) [114-118]. Topographic and phase imaging in tapping mode atomic force microscopy was performed to investigate the size of clay platelets, the polymer filler interface, pull-off and contact forces between the sample and the tip, power spectral density, fractal dimension and spatial distribution of the nanoclays in a fluoroelastomer by Maiti and Bhowmick[119]. Figure 1.17 shows the AFM images of HNBR sepiolite nanocomposite samples prepared using different solvent combinations by Anasuya et
al.[120]. From the figure it is evident that in Ch/ MEK system, nanoclays are dispersed uniformly, while in Ch/Et solvent combination, there is poor dispersion of the nanoclays in the rubber matrix, an example of homogenous and heterogeneous dispersion respectively. These photographs further reveal that average thickness of clay particles is 10–15 nm in Ch/MEK solvent combination while clays form agglomeration in the case of Ch/Et solvent system having an average thickness of about 60–120 nm.

**Fig 1.17**  Phase image and 3D image of HNBR–sepiolite nanocomposite for chloroform/MEK solvent combination (left) and chloroform/ethanol solvent combination (right) [120].
1.12.5 Other methods

The rubber nanocomposites have been characterized by several other methods like FTIR, NMR, Small angle neutron scattering etc. Julian Oberdisse and coworkers [121] reported on the synthesis of a model soft hard nanocomposite material formed from nanolatex and nanosilica spheres. The physicochemical parameters relevant for the synthesis have been varied systematically, and for each sample a structural analysis by means of small-angle neutron scattering has been performed. The system has a high contrast for small-angle neutron scattering (SANS) experiments. Because of important structural changes, the observed SANS spectra are very heterogeneous, and no simple description in terms of some generic fitting function seems feasible. However, it has been possible to identify the main features of the scattering function, and this has lead us to a coherent description of the scattered intensity of all samples. As an important result, the evolution of the average number of aggregation could be followed and the close correlation between the parameters of the synthesis of the material and its structure could be confirmed. Although, there are several techniques to understand dynamics in polymer nanocomposites, dielectric spectroscopy is a well established tool for materials characterization [122,123]. Broad band Dielectric Spectroscopy (BDS) was employed in order to investigate relaxation phenomena occurring in natural rubber (NR), polyurethane rubber (PUR) and PUR/NR blend based nanocomposites [124]. The glass transitions of acrylonitrile butadiene rubber (NBR)/organoclay nanocomposites with various silicate contents were investigated using positron annihilation lifetime spectroscopy (PALS). The glass transition temperature of NBR was determined using differential scanning calorimetry (DSC). However, it seemed to be very difficult to clearly resolve the very small differences in Tgs caused from various loading of nanosized silicate in NBR/OC30B nanocomposites. The Tg, PALS values were found to increase with increasing organoclay content in the samples. These observations are consistent with PALS having a higher sensitivity in the detection of very small changes in free volume properties [125].
1.13 Nanocomposite properties

Nanocomposites consisting of a rubber and nanofiller frequently exhibit remarkably improved mechanical and material properties when compared to those of composites with macro sized fillers. Improvements include a higher modulus, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers. The main reason for these improved properties in nanocomposites is the stronger interfacial interaction between the matrix and filler, compared with conventional filler-reinforced systems.

1.13.1 Mechanical properties

One of the important characteristics that make rubber nanocomposites promising for industrial applications is their improved mechanical properties. The mechanical properties of Natural rubber sodium montmorillonite nanocomposites were studied by Abdollahi et al.[126] After introduction of Na-MMT, the modulus of NR within the strain before tensile crystallization is significantly improved because of mark reinforcement of nanodispersed Na-MMT. The magnitude of improvement rises with increasing Na- MMT content as shown in figure 1.18.

![Stress-strain curves for pure NR and NR/Na-MMT nanocomposites](image)

**Fig 1.18** Stress-strain curves for pure NR and NR/Na-MMT nanocomposites [126]
Silicone based elastomers have been mixed with single-wall carbon nanotubes or larger carbon nanofibrils by [127]. Tensile tests as shown in figure 1.19 show a dramatic enhancement of the initial modulus of the resulting specimens as a function of filler load, accompanied by a reduction of the ultimate properties. The modulus enhancement of the composites initially increases as a function of applied strain, and then at around 10–20% strain the enhancement effect is lost in all of the samples. This “pseudo-yield” in elastomeric (or rubber) composites is generally believed to be due to trapping and release of rubber within filler clusters. The mechanical properties like tensile strength, elongation etc. of butadiene rubber was found to be enhanced when nano calcium carbonate was uniformly dispersed at very low filler loadings (10 Wt%) [128].
1.13.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) measures the response of a given material to an oscillatory deformation as a function of temperature. DMA results are composed
of three parameters: (1) storage modulus ($G'$), (2) loss modulus ($G''$), (3) $\tan \delta$. The ratio ($G''/G'$), useful for determining the occurrence of molecular mobility transitions, such as glass transition temperature ($T_g$). The effect of the CNTs (Ball milled as well as Purified) on the dynamic mechanical property of NR material was analyzed by Sui et al. [129]. The high specific surface areas and essential modulus of CNTs enhanced the stiffness of the NR, which resulted in an increment of storage modulus of the CNT/NR nanocomposite as shown in figure 1.20. The storage modulus of B-CNT/NR nanocomposites is the highest among all specimens due to the improved dispersion of CNTs in the NR matrix and good interfacial bonding between them. It can be seen from the figure that the peak of $\tan \delta$ of the CNT/NR nanocomposite slightly shifts to a higher temperature compared to that of the neat NR. This implies that the mobilization of rubber macromolecules was restricted due to the addition of CNTs. The $\tan \delta$ value of NR composites comes from the contribution of both NR and filler materials. The adding of CNTs reduces the volume percentage of the NR in composites, which lowers hysteresis loss of rubber composites under a dynamic condition. This can be beneficial for the actual application of some rubber products, such as tires etc.

**Fig 1.20** Dynamical mechanical spectra CNT/NR nanocomposites [129].

The reinforcement effects of organoclay in XNBR have been investigated by Fritzsche et al. [130] using dynamic-mechanical analysis. The glass transition process is detectable at $-10^\circ$C and the $\tan \delta$ maximum decreases slightly with
increasing filler content. An additional relaxation process at high temperatures is also confirmed in dynamic mechanical investigations as shown in figure 1.21 but the difference between different amounts of organoclay are not very significant. The concentrations of sulfur and accelerator were varied in the nanocomposites of carbon black (CB) - filled styrene-butadiene rubber (SBR) matrix to introduce the gradation of the crosslink density and the static and dynamic mechanical characterizations of these rubber nanocomposites were carried out by Ahankari and Kar [131].

![Figure 1.21](image)

**Fig1.21**  Representation of tanδ vs. temperature of organoclay in XNBR nanocomposite [130].

### 1.13.3 Barrier properties

The primary advantage of polymer/clay nanocomposites, especially with exfoliated morphology, is dramatic improvement in gas barrier properties. Some important rubber engineering products containing high pressure air, for example tire inner-tubes, air springs and cure bladders, etc. need a high barrier to gas permeation. Indeed, the literature contains numerous reports on decreased gas permeability [132-135] caused by addition of layered silicates to various polymer matrices. The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be
substantial. Clays are believed to increase the barrier properties by creating a maze or ‘tortuous path’ (Figure 1.22) that retards the progress of the gas molecules through the matrix resin. In particular, aspect ratio is shown to have a major effect, with high ratios (and hence tendencies towards filler incorporation at the nano-level) quite dramatically enhancing gaseous barrier properties. Such excellent barrier characteristics have resulted in considerable interest in nanoclay composites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite formulations would be expected to enhance considerably the shelf life of many types of food.

![Figure 1.22 Schematic representation of gas permeation through conventional layered silicate nanocomposite (left) and microcomposite (right)](image)

Permeability of a membrane is given by the following equation

\[ P = \frac{1 \times J}{l \times \Delta P} \]

where \( J \) is the gas volumetric flow rate per unit area of the membrane, \( l \) the thickness of membrane, \( \Delta P \) pressure difference across the membrane and \( P \) is the permeability. Much of the literature is devoted to nanocomposites made by addition of organoclays, formed from montmorillonite, using various techniques. It is clear that the property benefits of adding plate-like fillers to polymers will increase as
both the volume fraction, $f$, and the aspect ratio, $a$, of the platelets increase, there are
natural limits on both $f$ and $a$ inherent to this approach imposed by the effect such
particles have on melt rheology [136-138]. Goldberg and co-workers have recently
described a water-based approach for forming elastomeric nanocomposite coatings
with high loadings of high-aspect ratio platelets specifically designed for gas barrier
applications [139-141]. Gas permeation properties of nanocomposites based on
butyl rubber with high loadings of vermiculite, viz. 20 and 30 wt%, were
investigated in a study [140,141]. Figure 1.23 shows that the gas permeability is
reduced by 20–30-fold by the vermiculite. The role of the aspect ratio of the layered
silicate platelets on the mechanical and oxygen permeation properties of
hydrogenated nitrile rubber (HNBR)/organophilic layered silicate nanocomposites
was investigated [142]. Montmorillonite (MMT) and fluorohectorite (FHT) bearing
the same type of intercalant (i.e., octadecylamine; ODA), however, showing
different aspect ratio was involved in this study. Increasing aspect ratio (MMT <
FHT) resulted in higher stiffness under uniaxial tensile loading. The dispersion state
(“secondary structure”) of the organophilic layered silicates reduced dramatically
the oxygen permeability of the rubber matrix based on the labyrinth principle. The
lowest oxygen permeability was measured for the HNBR/FHT–ODA films in which
the layered silicates had the highest aspect ratio. The effect of the different aspect
ratio of the related organoclays was best reflected in the oxygen permeation
measurements. The organo-fluorohectorite created a more extended tortuous path
against gas penetration compared to organo-montmorillonite, thus, lowering
permeation values. The same scene was maintained when test were performed in
humid environments.
Fire hazards result primarily from the combination of a number of different factors. These include ignitability, ease of extinction, flammability of the generated volatiles, amount of the heat released on burning; rate of heat release, flame spread, smoke obscuration, and smoke toxicity. Nanocomposites avoid the disadvantages of these traditional flame retardant systems. Nanocomposite usually exhibits increased thermal stability and improved flame retardancy, which are important characteristics for high-temperature applications [143-150]. Blumstein [151] was the first to report the improved thermal stability of a polymer–clay nanocomposite. For many polymers, preparing polymer–clay nanocomposites is a good way to, not only reduce the flammability of a polymer, but also to improve its mechanical properties. Flammability studies of montmorillonite (MMT)/ SBR nanocomposites, performed on the cone calorimeter, showed that the maximum heat release rate (HRR) of SBR decreased from 1987 to 1442 kW/m² with the introduction of nanoclay (20 phr) as shown in table 1.4 [152]. The measuring principle is the oxygen-consumption principle. The principle states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released. In many case, the
ignition of a material can be expected to occur due to thermal radiation from nearby flames, not from the direct impingement of a small flame onto the material. The cone calorimeter has the capability of radiant ignition of materials in laboratory. The heat flux of ignition is selected from 25, 50, and 100 kW/m$^2$. Therefore, the cone calorimeter is one of the most effective bench scale methods for studying the flammability properties of materials. Heat release rate (HRR), in particular peak value of HRR, has been found to be the most important parameter to evaluate fire safety. Figure 1.24 indicate the heat release rate of SBR nanocomposites.

Table 1.4  Cone calorimeter data for pure SBR and its composites [152].

<table>
<thead>
<tr>
<th></th>
<th>$t_{\text{ignition}}$</th>
<th>PHRR [KW/m$^2$]</th>
<th>$t_{\text{PHRR}}$</th>
<th>Mean HRR [KW/m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SBR</td>
<td>18</td>
<td>1987</td>
<td>76</td>
<td>393</td>
</tr>
<tr>
<td>Nanocomposite</td>
<td>44</td>
<td>1442(27)</td>
<td>117</td>
<td>234</td>
</tr>
<tr>
<td>Microcomposite</td>
<td>31</td>
<td>1693(13)</td>
<td>85</td>
<td>371</td>
</tr>
</tbody>
</table>

Fig 1.24. Comparison of the heat release rate for SBR nanocomposites at 50kW/m2 heat flux [152]

1.13.5 Rheological properties
The measurement of viscoelastic properties of polymers are most commonly done on dilute solutions or molten polymers, and are critical for determining molecular architecture (molecular weight, molecular weight distribution, and degree of branching), processing behavior and end product performance. Polymers are complex rheological materials in that they exhibit both viscous and elastic (viscoelastic) properties under varying conditions of stress, strain and temperature. Understanding the rheological properties of polymer nanocomposites is crucial to gain a fundamental understanding of the processability and structure property relations for these materials. In addition, it is well-known that the clay nanostructure and the polymer-clay interaction can strongly influence the linear and nonlinear rheological responses of polymer/clay nanocomposites. Because of the widespread use of fillers in polymeric products, the influence of the filler particles on the viscoelastic properties of polymer based composite materials has been of significant technological interest. At the same time, rheological properties are essential to determine the structure-property relationships of these materials. The ability of large amplitude oscillatory shear to orient mesostructured materials such as liquid crystalline materials and block copolymers is well documented. Nanocomposites exhibit similar ability to orient due to the application of an external shear field and this is reflected in the linear viscoelastic measurements after alignment. For nanocomposites with silicate loadings well above the percolation threshold, the viscosity at low shear rates diverge and the viscoelastic behavior is consistent with the presence of a finite apparent yield stress. On the other hand, at high shear rates the silicate loading has only a relatively small influence on the steady shear viscosity. In the temperature range from 26 to 136 °C, it is observed that the HTPB/organo-clay nanocomposites as shown in figure 1.25 exhibit novel rheological properties [153]. This is the first rheological observation of the in-situ exfoliation process and orientation disorientation transition of clays arising from the polymer-clay interaction, the shear field, and temperature in polymer/clay nanocomposites. It is also suggested that the HTPB/clay nanocomposite gels could be an ideal model system because it can provide detailed information about the
effect of the polymer-clay interaction on the exfoliation of the clays and unique rheological behavior in polymer/nanocomposites over a wide range of temperatures.

**Fig 1.25.** Temperature dependence of the steady shear viscosity for HTPB4200/C18-clay (5 wt %) and HTPB2200/C18-clay (5 wt %) [153].

The tentative model as given in figure 1.26 suggested that by mixing HTPB/C18-clay sample at room temperature, the clay is partially exfoliated. When heated with or without shear, complete exfoliation can be achieved at temperatures greater than the transition temperature. The exfoliated silicate layers can be oriented by cooling with shear. Shear-induced disorientation can be observed at temperatures greater than the transition temperature. The orientation of silicate layers can be maintained at a wide range of temperatures without shear. Both the temperature-sensitive polymer-clay interaction and the shear field are critical factors controlling the disorientation process of oriented clay layers.
Stephen and coworkers studied the change in viscosity of nanocomposites of NR and carboxylated SBR lattices [154]. Ana et al. [13] studied the viscosity changes with shear rate of polyurethane containing different silicas. It was found that the addition of silica modifies the rheological, mechanical and adhesion properties of PU composites.

1.13.6 Thermal properties

Rubber nanocomposite preparation involves high temperatures irrespective of the fabrication route and also most polymeric materials require prolonged service in air at high temperatures. In the case of layered silicate reinforced rubber nanocomposites if the processing temperature is higher than the thermal stability of the organic component used for montmorillonite (MMT) modification, decomposition will take place, leading to variations in organically modified MMT (OMMT) structure as the material degrades. Thus, determination of the onset temperature of degradation, resultant products of degradation and the stability of the
polymer in the presence of layered silicates as well as understanding the relationship between the molecular structure and the thermal stability (decomposition temperature, rate, and the degradation products) of the organic modifier in the galleries of layered silicate is critical. The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. It has been reported that some nanocomposites combining MMT and polymer matrix exhibited improved thermal stability [155,156]. When the heating occurs under an inert gas flow, a non oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples. Generally the incorporation of nano clay into the matrix was found to enhance the thermal stability by acting as a superior insulator and mass transport barrier. The role of thermal stability of organic modifier during preparation of nanocomposites was also pointed by Acharya et al. in a work on ethylene–propylene–diene terpolymer (EPDM) nanocomposites [157]. The thermal degradation of polyurethanes (PU) usually occurs in two stages, the first stage is mainly governed by the degradation of the hard segments and the second stage correlates well with the degradation of the soft segments. The nanocomposites with improved dispersion of organoclay showed the onset temperature of degradation ($T_{onset}$), the temperature of maximum decomposition rate for the first stage ($T_{max1}$) and that for the second stage ($T_{max2}$) about 10°C higher than pristine PU. The highest thermal stability was observed for the OMMT content of 5 wt % and its $T_{onset}$, $T_{max1}$ and $T_{max2}$ were about 30, 35 and 65°C higher than those of pure PU. Moreover, Choi et al. [158] showed that the effect of clay as thermal insulator and mass-transport barrier on thermal stability can be increased with improving the dispersibility of organoclay in polyurethane matrix. In the case of PU-layered silicate nanocomposites based on polyether, toluene diisocyanate, diglycol (as a chain extender) and glycine (as a cross-linking agent), a decrease in onset temperature of decomposition was ascribed to catalytic effect of OMMT by Song et al. [159]. Takeichi and Guo [160] reported that the improvement in thermal stability of poly (urethane-benzoxazine) (PU-Pa) nanocomposites with OMMT was based on two effects, first, part of the thermally decomposed volatiles
was captured by OMMT; second, the efficient cure of benzoxazine monomer (Pa), from the catalytic effect of OMMT on the ring-opening polymerization, resulted in higher cross-link density of PU-Pa. The TGA and DSC curves of PU and PU/organic-MMT (3 wt %) nanocomposites are presented in Fig. 1.27. The results show that the degradation rates of the nanocomposites become slightly slower compared to that of PU, indicating an improvement of thermal stability of PU because the inorganic material can prevent the heat to expand quickly and limit the further degradation. The effect of different organic-MMT on the glass transition temperature (Tg) of PU was studied by DSC. The DSC curves of PU and PU/organic-MMT (3 wt %) nanocomposites are shown in figure 1.27. The PU has an endotherm at 12.5°C, slightly higher than that of the PU/organic-MMT nanocomposites, -13.9°C for the PU/MO-MMT and -17.1°C for the PU/C16-MMT. This may be attributed to thin polymer confined between layers tending to lower the Tg and enhancing the segmental dynamics of the polymer chains. In Figure 1.27, the Tg of the PU/C16-MMT shifts to lower temperature than that of the PU/MO-MMT because the interaction between polymer and organic-MMT for the PU/MO-MMT is stronger than that for the PU/C16-MMT.

![DSC and TGA curves](image)

Fig 1.27 DSC curves (left) and TGA curves (right) of (a) PU (b) PU/3 wt% C16-MMT and (c) PU/3 wt% [139].
High temperature degradation of a fluoroe lastomer and its nanocomposites was carried out from room temperature to 700 °C using thermogravimetric analysis (TGA) in nitrogen and oxygen atmospheres by Madhuchhanda Maiti et al. [161]. On the basis of observed changes in degradation routes of polymers it was found that the ‘labyrinth effect’ of dispersed MMT is responsible for restricted diffusion of oxygen into polymer matrix and causes pyrolytic like conditions inside nanostructured composite material[162].

1.14 Motivation of the work

The major intention of the project was the development of impermeable membranes from halobutyl rubber nanocomposites. We have successfully synthesized calcium phosphate nanoparticles and characterized them to ensure that the particles are within the nano regime. The preparation of nanocomposites of chlorobutyl rubber was done by incorporating fillers like titanium dioxide, calcium phosphate and various organically modified nanoclays. The traditional two roll mixing was followed in the case of nano calcium phosphate and titanium dioxide fillers. In the case of layered silicates the two roll mixing gave rise to inferior properties and so it paved the way for the development of a novel technique for the processing of the layered silicate reinforced nanocomposites. The novel technique so adopted was a hybrid of two roll mixing and solution mixing. The choice of the solvent was done after a series of experiments using various solvents like cyclohexane, toluene, xylene, THF, chloroform etc which vary in their cohesive energy density. The properties obtained with different solvents were correlated with the solubility parameters of the nanocomposites and the ideal solvent for the process was selected. Thus nanocomposites using different clays with varying d spacing and surfactants/modifier concentrations were prepared and the properties were analysed. The mechanical, barrier, thermal, dynamic mechanical and dielectric properties of the aforementioned nanocomposites were analysed.

1.15 Scope and objectives of the work
Eventhough research on CIIR based nanocomposites has been reported, careful and systematic survey of the research done till now in this field revealed that no systematic study has been done to analyse the effect of different types of fillers and the resulting changes in the properties of the nanocomposites. Since fillers such as layered silicate, calcium phosphate and titanium dioxide have entirely different chemical as well as physical properties, it is worthwhile investigating the extent of interaction of these fillers with the chlorobutyl rubber and analyzing the resulting property changes. Therefore our primary aim is to investigate the missing aspects in this field. Besides we think that there is a great industrial and commercial future for Chlorobutyl rubber based Nanocomposites.
The specific objectives of the present work are

- Optimization of processing parameters for the processing of chlorobutyl rubber nanocomposites.
- Evaluation of the effect of various organic solvents in the preparation of organically modified layered silicate chlorobutyl rubber nanocomposites using solution mixing technique.
- Preparation of chlorobutyl rubber composites with different filler morphology.
- Effect of surfactant type and modifier concentration and d spacing of the layered silicates on the properties of nanocomposites.
- Evaluation of the thermal, morphological, mechanical, dielectric and barrier properties of the chlorobutyl rubber nanocomposites.
References


120. Anusuya Choudhury, Anil K. Bhowmick, Christopher Ong, Polymer, 50, 201, 2009.


142. Z. Mogri, D. R. Paul, Polymer, 42, 2531, 2001


153. Xiaoliang Wang, Yun Gao, Kanmi Mao, Gi Xue, Tiechong Chen, Jianjun Zhu, Baohui Li, Pingchuan Sun, Qinghua Jin, Datong Ding, Macromolecules, 39, 6653, 2006.


