Chapter 1

Introduction

Abstract

This introductory chapter gives the general aspects of polymer blends its classification, compatibilization of polymer blends, and the role of nanoparticles as compatibilizers, by incorporating the recent works done in this field. A brief report of the research works in the polymer blend nanocomposites, pointing mainly to the compatibilizing action of nanoparticle in immiscible polymer blends is included. This chapter also describes the different characterisation techniques like morphology, rheological behaviour, mechanical and dynamic mechanical properties etc. used in analysing the properties of polymer blend nanocomposites. The last portion of this chapter discusses the motivation for this research work and objectives of the present study.¹

¹ The review presented in this chapter has been communicated to Progress in Polymer Science.
1. **General introduction**

1.1 **Why do we blend polymers**

During the first part of the twentieth century, with the advent of polymer materials such as nylon and Kevlar a big boom in polymer chemistry occurred. Today, most work with polymers focus on improving and fine-tuning existing technologies. Polymer Chemistry is product-oriented and involves many scientific disciplines. It is very important in fields that develop products such as plastics and synthetic fibres, agricultural products, paints, adhesives, biomedical applications, automobiles etc. To some extent during their careers it is assumed that as many as 50% of all chemists will work in polymer science field. Chemists try to develop new polymers, by manipulating the large complex molecules and find the relations between their molecular structure and their properties, to make them more useful. They can thus be used to make ingredients for products, with unique physical and chemical properties. There are many more opportunities, still ahead, for polymer chemists. As James Shepherd, a research associate in Polymer Chemistry at Hoechst Celanese has stated, “We may not discover a new polyethylene, but we may find materials of smaller-volume which are potentially more cost-effective”.

When existing polymer plastics are not suited for a particular application, blending and compounding different materials are done to come up with the right combination of properties. "Compounding is both an art and a science" says Jim Mason, a senior chemist in the polymers division of Bayer Corporation. By altering the composition and the nature of polymers that are mixed, the properties of polymer blends can be tuned, based on the requirements. Blending and compounding existing polymers is one of the key areas of research in a polymer chemist's work. Polymer blending thus has been recognized as the most versatile and economic method to produce new
materials needed to satisfy various requirements. The annual growth rate of the polymer blending industry is approximately 10% and it is estimated that 60-80% of all polymers are sold as polymer blends\(^1\). Blending of polymers assumes a major role when we take into account the economical and technical uncertainties associated with synthesizing new polymeric materials. Thus, the development of polymer mixtures to attain a desired combination of properties has obvious attractions. Schematic illustration given in Figure.1.1 shows two situations where blending and/or compounding are especially attractive from a commercial point of view.\(^1\)

![Figure 1.1 Schematic illustration of two situations where blending and/or compounding are especially attractive from a commercial viewpoint](image)

The thick vertical line represents the minimum acceptable performance required to qualify a material for a certain application. The ellipses represent regions on the "price-performance plane". \(P_a\) is an expensive engineering polymer that far exceeds the performance requirements of the application. \(CP_a\) is a cheaper composite of \(P_a\) with less expensive ingredients, but which still
exceeds the minimum performance requirements. Pₚ is a commodity polymer that does not meet the performance requirements of the application. CPₚ is a composite of Pₚ that exceeds the minimum performance requirements but has to be sold at a substantially higher price. BPₚₐₚ, a blend of Pₚ and Pₐ, exceeds the minimum performance and can be considered as more economical.

Blending can be used to accomplish various economic and material advantages like

- Development of new materials with required properties.
- Reduction in cost of production, with or without little sacrifice in properties.
- Improvement in the processability of materials.
- Developing a material with improved material property/ies like oil resistance, impact strength, improved modulus and hardness, improved barrier property and flame retardant property, improved impact and environmental stress cracking resistance, etc.
- Possibility to tune the final morphology so as to suit the expected property by simple variation in blend composition, method of mixing, processing conditions etc.
- Economic as there is the possibility of developing a material with better properties.

In short, through blending, specific materials with better processability and or performance can be generated.

Due to their high molar mass, the entropy of mixing of polymers is relatively low and consequently, specific interactions are needed to obtain blends, which are miscible or homogeneous on a molecular scale. Therefore, when two or
more polymers are mixed, the phase structure of the resulting material can be either miscible or immiscible. In the case of immiscible systems, the overall physico-mechanical behaviour depends critically on two demanding structural parameters. First, the interfacial tension should be low so that the phase size is small enough to allow the material to be considered as macroscopically homogeneous. Secondly, the interphase adhesion should be strong enough to assimilate stresses and strains without destroying the established morphology.

1.2 Thermodynamics of binary polymer systems

A polymer blend is a mixture of at least two polymers which have been mixed together while melted. Such blends may be miscible or immiscible. Miscible polymer blends are homogeneous at the molecular level. The rules governing miscible behaviour of polymer blends are understood in a thermodynamic sense through the Gibbs free energy of mixing, $\Delta G_m$. The free energy of mixing can be described in terms of enthalpic and entropic contributions as

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{(1.1)}$$

Where, $\Delta G_m$ is the free energy of mixing per unit volume and $\Delta H_m$ and $\Delta S_m$ are enthalpy and entropy of mixing respectively. $\Delta H_m$ is independent of molecular weight and is a measure of energy change associated with intermolecular interactions. The entropy for long chain macromolecules is usually low because of the restricted number of possible molecular configurations and so entropic contributions cannot overcome the positive enthalpy of mixing. Thus, most polymer pairs are immiscible and their melt blending usually leads to the formation of systems in which the minor component is dispersed in the matrix phase. Therefore, the free energy...
depends on the change in enthalpy. So, for the Gibbs free energy to be negative, there should be good inter-molecular interactions.

For miscibility, in addition to a negative value of $\Delta G_m$, the following inequality must also hold

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_{T,p} > 0 \quad \text{..................(1.2)}$$

Where $\phi_i$ is the volume fraction of component. $\Delta G_m$ for a binary mixture can vary with composition. (Fig. 1.2)

![Figure 1.2 Gibbs free energy of mixing of binary blends](image)

In immiscible polymer blends, Gibbs free energy of mixing is positive. The above criteria are met by curve B (Fig 1.2) for all compositions. Blends described by curve A violate Eq. (1.1) and are completely immiscible. A system described by curve C is partially miscible, in which a single amorphous phase can be formed at compositions to the left and right of the minima of curve C. In miscible polymer blends, molecular level mixing of the components is obtained and is characterized by single phase morphology. Immiscible blends do not satisfy the conditions proposed in Eq. (1.1) and show
a two-phase morphology. In the case of partially miscible blends, the second criterion is not satisfied and will show either two phase or single-phase morphology. However, the manifestation of superior properties depends on the miscibility behaviour of homopolymers.

1.3 Classification of polymer blends

Polymer blends may be classified according to whether they consist of separated or single phases. Another classification of polymer blends may be based on the miscibility of the polymer components or on the thermodynamics of the system. There can be mixtures of structurally different homopolymers, co-polymers, terpolymers and they can be of random, alternating, graft or block type compatibilizers. So there can be several criteria that we can take while classifying the polymer blends.

1.3.1 General

In general, polymer blends can be considered as a mixture of homopolymers and copolymers. The following definitions for 9 classes of polymer blends can be conceived:

1. Homologous polymer blends:- polymer blends of chemically identical polymers differing in molar mass.
2. Polymer alloys (PA):- polymer blends of polymer mixtures with stabilized morphologies.
3. Miscible polymer blends:- polymer blends which exhibit single phase behaviour.
4. Immiscible polymer blends:- polymer blends that exhibit two or more phases at all compositions and temperature, and the properties of which are inferior to that of the individual polymers.
5. Partially miscible polymer blends: - polymer blends including those blends that exhibit miscibility only at certain concentrations and temperature.

6. Interpenetrating polymer network (IPN): - mixtures of two polymers where both components form continuous phases and at least one is synthesised, or crosslinked in the presence of the other.

1.3.2 Based on the method of preparation.

Polymer blends can be arranged into the following chart based on the method of preparation (Scheme 1.1). The structurally different polyblends like homopolymers, copolymers, terpolymers wherein the copolymers, terpolymers etc., are in random, alternating, graft or block type can be prepared by

- **Mechanical mixing** - means either on an open roll mill, in an extruder or in a suitable internal mixer. The processing temperature must be well above the glass transition temperature of each constituent for mixtures of amorphous polymers and above the melting temperature ($T_m$) of mixtures containing semicrystalline polymers, whichever, is higher.

- **Mechanochemical blending** - Depending on the state of the thermal stability of the polymers being mixed, the high processing shear could initiate degradation, resulting in free radicals. If the free radicals react with the other structurally different polymers present, resulting in true chemical graft or block copolymer and the mixture is referred to as a mechanochemical blend.

- **In situ polymerisation** - A chemical polymer blend can be made through this method which gives an interpenetrating crosslinked polymer network of structurally different polymers.

- **Solution cast polymer blends** – by dissolving the constituent polymers in a common solvent in such a way that the solutions have about the same
viscosity. The resulting solution can be film cast to form the solution cast polymer blend.

- **Latex blending** - When the individual components can be obtained in latex form, they may be conveniently combined by blending the latices. The polymer is then recovered by coagulation or spray drying.

**Scheme 1.1** Classification of polymer blends based on methods of preparation

**1.3.3 Based on the miscibility:** On the basis of miscibility there are three different types of blends.

**1.3.3.1 Completely miscible blends:** On nanometer level or molecular level, homogeneity can be observed. This type of blends exhibits only one glass transition temperature ($T_g$) and it will be between the glass transition temperatures of the blend components and also $\Delta H_m < 0$

Eg. PS/PPO, which is miscible over a very wide temperature range and in all compositions

**1.3.3.2 Partially miscible blends:** If one of the blend component is dissolved partially in the other polymer and exhibits a fine phase morphology and satisfactory properties, they can be considered to be compatible.
Both blend phases have their own $T_g$ and are shifted from the values for the pure blend components towards the $T_g$ of the blend component. They have wide interface and a good interfacial adhesion. An example is the PC/ABS blends. In these blends, PC and the SAN phase of ABS partially dissolve in one another.

1.3.3.3 Immiscible and incompatibile blends:- The term immiscible means that the Gibb’s free energy of mixing, $\Delta G_m$ is positive, whereas “incompatible” is defined with respect to properties and means that the properties of the blend are inferior to those of pure polymers. Components which resist phase segregation and which shows desirable blend properties are considered to have good compatibility even though they are immiscible in a thermodynamic sense. But most pairs of high molecular weight polymers are immiscible or incompatible. The immiscible polymer blend exhibits coarse morphology, sharp interface and poor adhesion between the blend phases. So these blends are of no use without compatibilisation. These blends will exhibit different $T_g$s corresponding to the $T_g$ of the component polymers. Examples of fully immiscible blends are PA/ABS, PA/PPO, PA/EPDM and PA/PP. As given by the laws of thermodynamics, majority of polymers are immiscible at molecular level. Eventually, the internal disorder of the polymer mixture will result in phase separation on a macroscopic scale. The relative miscibility of polymers control their phase behaviour, which is of crucial importance for final properties. Polymer-polymer miscibility depends on a variety of independent variables, viz., composition, molecular weight, temperature, pressure etc.
1.4 Types of immiscible blends

Properties of immiscible blends are more difficult to predict. The property depends on additional factors such as shape and orientation of the dispersed phase, nature of the interface etc. These blends can be divided into three categories:

1.4.1 Polymers differing primarily in polarity

Polarity in the polymers is due to the presence and absence of functional groups. Blend components having different polarities lead to immiscible blends. Example is blend of natural rubber (NR) with nitrile rubber (NBR). Here the difference in polarity of the two polymers causes a variation in the distribution of curatives and vulcanization intermediates. Although NBR may appear to have a substantially lower level of unsaturation relative to NR, the higher density of NBR and lower molecular weight of the butadiene lead to a molar concentration of unsaturation of about $11 \times 10^3$ mol/m$^3$ for high acrylonitrile NBR, in comparison with about $13 \times 10^3$ mol/m$^3$ for NR. Selection of curatives should thus be taken into consideration while compounding mixing.

1.4.2 Polymers differing primarily in degree of unsaturation

Rubbers are also immiscible due to the difference in degree of unsaturation - Eg. Natural Rubber (NR) & ethylene propylene diene monomer(EPDM) Here also there will be a tendency of curatives to partition in favour of the NR phase. But proper use of di-thiophosphate accelerators, which have high solubility in both NR and EPDM, has been found to lead to improved blend properties. Several other attempts have also been made as this is a commercially important blend.

1.4.3 Polymers differing little, in either polarity or degree of unsaturation

Usually blends of the general purpose rubbers – NR, BR (butadiene rubber) and SBR (styrene butadiene rubber) come under this group. Among these,
blends of NR or IR and BR have received most importance. Although it appears that there is little difference between the two in unsaturation or polarity, and an even distribution of crosslinks is anticipated, in practice, there are significant differences. The difference can be observed from analytical techniques that shows difference in curing rate of one of the elastomers, which can or may attenuate the property of one elastomer

1.5 **Compatibilizer - A way for property enhancement in immiscible polymer blends**
Most of the incompatible blends are characterized by a two-phase morphology, narrow interphase, poor physical and chemical interactions across the phase boundaries, and poor mechanical properties\(^1\). Converting these immiscible blends into useful polymeric products is a highly investigated topic and is an industrially important field. The addition of a third component called a compatibilizer into an incompatible polymer blend, can enhance the degree of compatibility between the constituent components\(^2\). The compatibilizing action of this compatibilizer differs with the nature of the polymers and the compatibilizer. The role of compatibilizer is similar to that of emulsifiers in classical emulsion technology.

1.5.1 **Theory of compatibilization**
A good compatibilizer should migrate to the interface and reduce the interfacial tension coefficient, decreasing the dispersed phase dimensions, thereby stabilizing the blend morphology and enhancing the adhesion between phases in the solid state\(^3\). Compatibilizing agents often provide additional morphology stabilization by acting as a surfactant and decreasing the interfacial surface tension. In general, the added compatibilizers, if compatible with both phases, segregate preferentially at the interface and ensure strong interfacial adhesion.
**Figure 1.3** Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence\(^{17}\).

A successfully compatibilized blend of moderate composition (up to 30 wt% minority component) exhibits spherical dispersed phases with consistent diameters, averaging on the micron and submicron scale. Such consistent morphologies can be achieved when the compatibilizing agent provides a steric hindrance to the dispersed phase coalescence. Compatibilizers which provide steric hindrances act as anchors for minority phase droplets in the matrix, (Fig 1.3) and also serve as repulsive “springs” when two droplets are in proximity.
1.5.2 Types of compatibilizers

There are three major classes of compatibilizers and they can be distinguished from each other in terms of the primary mechanism by which they reduce the interfacial tension between incompatible polymers. They are

a) **Block or graft copolymers or block copolymers** (Figure 1.4a): Here the copolymer will act as compatibilizer by migrating to the interface thereby reducing the interfacial tension. One part will be compatible to one polymer and the other end with the second polymer. This will render lower interfacial tension, better interfacial adhesion and better dispersion. In Fig (1.4a) Red blocks are compatible with Polymer A (matrix) and Blue blocks are compatible with Polymer B (dispersed phase).

b) **Nonreactive polymers containing polar groups** (Fig. 1.4b): Compatibilization using nonreactive polymer containing polar groups creates non-bonded interactions. Here the compatibilizer must be compatible with one phase (generally with the nonpolar phase) and must create specific interactions with the other phase.

c) **Reactive functional polymers** (Fig.1.4c): Reaction at the interface between functional groups on the different polymers creates, "in-situ", a grafted block copolymer. The functionalized copolymer is miscible with the matrix and will react with functional groups of the dispersed phase.

d) **Polymers with polar functional groups or reactive groups** (Fig 1.4d) Certain polymers containing polar functional groups and/or reactive groups can function effectively as coupling agents between polymers and inorganic fillers, in composites (Fig. 1.4d) and/or as adhesion promoters between incompatible polymers in a laminate, or between polymers and a substrate such as glass or a metal.
Figure 1.4  a) Block or graft copolymers  b) Nonreactive polymers containing polar groups  c) Reactive functional polymers  d) A polymeric coupling agent attaches an inorganic filler to the polymer matrix and thus compatibilizes the filler with the polymer by non-bonded (physical) interactions and/or chemical bonds. It must be compatible with the polymer (ideally, it should have the same chemistry as the polymer), as well as being able to interact with, react with, or even better “glue” to the filler.
1.5.3 Other compatibilization techniques

While these are established and effective methods, there are some disadvantages: These can

- be difficult and / or expensive to produce.
- be of lower molecular weight than the two matrix polymers, and can result in a loss of mechanical properties.
- degrade at the processing temperatures near the melting temperature of the matrix polymers, thus creating a narrow processing window.
- degrade upon exposure to multiple heat histories, which is common during recycling\textsuperscript{18}.

To overcome these, other compatibilization techniques like solid-state polymer processing or addition of other materials which are advantageous over the conventional compatibilizers are done and has some benefits.

1.5.3.1 Solid-state polymer processing\textsuperscript{19}

All of the previous blend compatibilization techniques introduced additional species, or created block copolymers while the blend was in a melted or dissolved state. Though successfully demonstrated in the academic setting, these processing methods have major limitations, preventing commercial application. Solid-state polymer processing can be considered as an alternative, in situ reactive technique, ie using mechanochemical blending in the solid state. This eliminates many of the problems found in the melt and solvated states.

a) **Mechanochemistry of solids** - Mechanochemistry of polymers in the solid state is a simple and effective method of compatibilizing
immiscible polymer blends. Here the chemical reactions can be initiated by mechanical forces.

b) **Solid-state batch milling method** - Various mechanical procedures have been explored to compatibilize immiscible polymer blends via free radical formation and in situ block copolymer formation.

- Pan milling followed by a twin-screw extrusion
- Ball milling followed by powder pressing, dry ice, or cryogenics such as liquid nitrogen.

c) **Solid-state shear pulverization**-Solid-state shear pulverization (SSSP) is a continuous and industrially-scalable process, utilizing a modified twin-screw extruder to exert high shear force and pressure while mixing polymer blend, but maintaining the solid state through continuous cooling.

### 1.5.4 Janus Particles

A recent trend in compatibilization is by using Janus particles in analogy to colloid science. This is a novel concept of compatibilizing polymer blends by controlling the locations of the particles within the blend structure have reported. Janus particles are compartmentalized colloidal particles, which show segregation into two hemispheres. These particles uniquely combine the so-called Pickering effect with amphiphilicity and are thus known as surfactant particles. It has been calculated and experimentally shown for liquid-liquid interfaces that these particles adsorb strongly at interfaces, in particular stronger than standard surfactants or homogeneous particles. Prompted by these stimulating results, a lot of works have been done by using Janus particles, having for the blend compatibilization. In immiscible blend system the unwanted coalescence of domains of the dispersed phase is expected to be diminished using these highly surface-active particles. In general,
Janus particles can be divided into several classes according to their architecture and dimensionality. Most commonly, spherical Janus particles can be imagined. In addition, two types of Janus cylinders (1D) and two types of disc-like particles (2D) are conceivable. Walther, et al. have used Janus particle in PS/PMMA blend and found that the size of the dispersed domain was decrease as the percentage of Janus particles are increased. This was proposed to be taking place as a result of the adsorption of Janus particle at the interface and secondly by the structural order. The efficiency of Janus particle in compatibilizing an immiscible blend was found to be higher compared to that of block or graft copolymer.

**Scheme 1.2** Possible Janus Architectures with Phase-Segregated shells. Janus particles of different architectures, (1) spherical Janus micelles, (2 and 3) two types of Janus cylinders, and (4) Janus discs.

If these compatibilizers or compatibilizing techniques enable certain polymers to blend better, or certain fillers to be incorporated more effectively into
polymers, and enhance its properties, it will be more acceptable commercially. But it will be more advantageous and economic if we can use a compatibilizer which can be used in low amount so as to take advantage of its lower mass. Then it can provide better properties due to its larger surface area, providing larger matrix/filler interface and hence more mutual interactions. As a result, large reinforcing effect may be reached at much lower filler content. The reduction of particle size obtained in such materials increases the specific surface area of the filler and reduces the cost in many ways, like decreasing the weight of the product, ease of mixing etc.

1.6 Nanoparticles in immiscible polymer blends

Use of nanofillers is one of the recent techniques that is commonly used in science and technology. Nano is a world where there are still unknown ways to explore. Smaller than the world of cells, bacteria, viruses and even visible light waves, yet bigger than the world of atoms, this new world of nano has made a huge revolution in the research field as well as in mainstream industries. Materials at the nanoscale behave differently than they do in our day to day world. Nanofillers lead to an improvement in properties such as material reinforcement, due to their larger surface area. In general, a smaller filler particle size will have a greater impact on the material properties, when the particles are properly dispersed. Compared to traditional fillers, these nano-scale reinforcements have the following advantages:

1. Low-percolation threshold (~0.1–2 vol.%).
2. Large number density of particles per particle volume ($10^6$–$10^8$ particles/$\mu$m$^3$).
3. Extensive interfacial area per volume of particles ($10^3$–$10^4$ m$^2$/ml).
4. Short distances between particles ($10$–$50$nm at $\sim$1–8 vol.%$)^{25}$. 
Therefore, nanofillers may provide a better route towards future material innovations paving way for producing a more economic and beneficial technology. Fig. 1.5 a-c shows different filler particle sizes. The specific surface area increases to 100-fold when going from 10µm to 100nm.

![Figure 1.5 Different filler particle sizes at the same filling level\textsuperscript{26-27}.](image)

Depending upon the geometry of the nano fillers, they can be classified into three categories as shown in Fig 1.6:

1. Zero-dimensional (0D) e.g., polyhedral oligomeric silsesquioxane (POSS)
2. One-dimensional (1D) e.g., carbon nanotubes.
3. Two-dimensional (2D) e.g., silicate clays, layered double hydroxide.
4. Three-dimensional (3D), e.g., silica, metal nanoparticles.
As already discussed, the major challenging difficulty of immiscible blends is overcoming the inherent immiscibility of polymers, to allow nanometer-sized domains in the matrix phase. Adding solid particles in immiscible polymer blends is a traditional technique in rubber and thermoplastic processing. The typical size of classical particles (calcium carbonate, talc, silica) was of the same order of magnitude or greater than the size of the dispersed polymer phase morphologies, to arrest the domain coarsening. Control of the blend morphology involves not only the shape and size of the dispersed polymer domains, but also the state of dispersion and the distribution of the particles. The use of nanofillers can have a large impact on the morphology of the immiscible polymer blends. Originally, the purpose of adding particles in polymer blends was obviously for applicative purposes like, obtaining high electrical conductivity or improving the mechanical properties\textsuperscript{28}. But the recently researchers have done quite a lot of work on the property enhancement aspect as well, by using higher surface area nanoparticles\textsuperscript{29-32}.

**Figure 1.6** The different types of nanofillers based on the nanodimensions\textsuperscript{27}
Among these different dimensional nanofillers used in polymer blends, many are used as reinforcing fillers and compatibilizers\textsuperscript{33}. It also offers electrical and thermal conductivity properties. Graphene, carbon nanotube, POSS, silica particles, nanoclay etc are some of the nanofillers which have gained wide interest in polymer research and technology.

**a) Polyhedral oligomeric silsesquioxane (POSS)**

Polyhedral oligomeric silsesquioxane (POSS) molecules represent a comparatively new approach as building blocks for new nanocomposite materials. The biggest advantage of using a molecular approach can be found in a true dispersion at the nanometre level. POSS molecules can be used as reinforcing filler in plastics to increase the mechanical strength. They are also relevant as abrasion protector in paints and coatings and as fire retardant material in polymers\textsuperscript{26,34}.

**b) Nano silica**

Fumed or pyrogenic silica is a form of non-crystalline silicon dioxide. Primary particle sizes are between 5 – 30 nm which aggregate into larger agglomerates while maintaining a fairly large specific surface area of 10 – 600 m\textsuperscript{2}/g. It is widely used as anti-caking additive and thickening agent with thixotropic property (becomes liquid when stirred or shaken but returns to original state when at rest)\textsuperscript{35}.

**c) Precipitated silica**

Precipitated silica consists of porous particles with a primary particle size of about 5 – 100 nm which form large agglomerates of several micrometres. The specific surface area can be as high as 200m\textsuperscript{2}/g. Precipitated silica is mainly
used as reinforcing filler in the rubber industry and also as filler in plastics and sealants (silicone rubber) and adhesives (epoxy).

d) Titanium dioxide (TiO₂)

Titanium dioxide (TiO₂) is naturally occurring in three different forms - rutile, anatase, and brookite. Rutile is mainly used as white pigment in paints and coatings while the anatase modification is widely used in photocatalytic applications. TiO₂ is also used as filler in silicone rubber and thermoplastics such as PVC.

e) Carbon nanotubes

Carbon nanotubes (CNT) have been researched intensively for their unique mechanical and electrical properties. A key application of multiwalled carbon nanotubes (MWNT) is seen as functional fillers in plastic composites and paints. They have also been studied as reinforcing fillers in concrete and have been proven to prevent crack propagation.

f) Carbon black

Carbon black (CB) is a nano particulate amorphous form of carbon, mainly used as a filler in rubber and as pigments. It is also used as a filler in plastic and paints to induce electrical conductivity. Additionally, it has been proven as a UV - stabilizer in plastics improving their weatherability. However, the market for non - rubber applications is comparatively small.

g) Graphene

Graphene, considered as a single sheet of graphite also serves as filler for conductive and reinforcing applications.
h) Nanoclays

Nanoclays are nanoparticles of layered silicates with plate-like morphology. Clay minerals are divided into numerous classes such as bentonites or hectorites. Bentonites mainly consist of the so-called montmorillonites, which is one of the most widely used nanoclay in material applications. Montmorillonites are built up of stacked nanoscopic aluminosilicate plates, each around 1 nm in height and 1 µm in diameter. Organically modified montmorillonites, the so-called organoclays, are used for making materials with a variety of applications like, increase in the flame retardancy of polymers (especially used in cables), barrier properties and is also widely used as a reinforcing agent.

1.6.1 Compatibilization effect of nanoparticles - theory of nanofillers as compatibilizing agents

The first reported nanoparticles used as a compatibilizer, is carbon black dispersed in elastomers. Studies have also been carried out using silica particles and layered silicates acting as compatibilizing agents in immiscible polymer blends. Compatibilizing effect can be taken to the maximum when the particles are present at the interface between two polymer phases. Numerous experimental works confirm the compatibilizing effect of nanoparticles on binary polymer blends, and several interpretations have been proposed. The different possibilities of compatibilizing action by the nanoparticles are given by Fenouillot et al.

i) a reduction of the interfacial energy when localizing the nanoparticles at the interface.

ii) the restriction of coalescence by the presence of nanoparticles which acts as a solid barrier around the minor polymer drops.
iii) the alteration in viscosity ratio due to a preferential distribution of the fillers\textsuperscript{39}.

iv) the immobilization of the dispersed drops (or of the matrix) due to the formation of a physical network of nanoparticles when the concentration of solid is above a certain threshold value.

v) the steric hindrance caused by the strong interaction of polymer chains onto the solid particles\textsuperscript{40}.

So the main mechanisms that take place, can be due to either thermodynamic effect, kinetic effect, particle localization, or transfer of particles, and is influenced profoundly by the magnitude of each effect. Also the modification of the viscosity ratio of the phases, in relation to the local filler concentration and state of dispersion or exfoliation, is very complex. The stability of the morphology is another important aspect in the development of new materials. Gubbels et al.\textsuperscript{41} studied the 45/55 PE/PS co-continuous blends and found that the morphology coarsening was found to be reduced when the amount of carbon black was above 2 wt%.

1.6.2 Localization of nanoparticles in polymer blends

The localization of nanoparticles in the polymer blend system plays an important role in the compatibilizing action of the immiscible blend system. The various factors like polarity, viscosity ratio and several other parameters like the interactions between nanoparticles and polymers, compounding procedures etc can cause the nanoparticles to distribute unequally between the polymer phases. Any physical interaction between nanoparticles and the polymer components also localize the nanoparticle in a particular phase. Another parameter which influences the localization of nanoparticles is wetting parameter $\omega_{12}$ which is calculated using (Eq. 1.3)\textsuperscript{42}. 

where $\gamma_{S-1}$ and $\gamma_{S-2}$ is the interfacial tension between the nanoparticle and polymer 1 & polymer 2 respectively, $\gamma_{12}$ is the interfacial tension between two polymers.

If $\omega_{12} > 1$, the particles are only present in polymer 1, while $\omega_{12} < -1$, they are only found in polymer 2.

If $-1 < \omega_{12} < 1$, the particles are concentrated at the interface between two polymers. The last case corresponds to $|\gamma_{S-2} - \gamma_{S-1}| < \gamma_{12}$ which is more probable to occur in polymer blends when the differences in the filler/polymer interactions are very small and the polymers are of high degree of incompatibility. In addition to the physical interactions i.e. thermodynamic effects, the final equilibrium of the distribution of nanoparticles is influenced by the mixing process, viscosity ratio, shear rate, filler loading, modification of the filler and presence of additional compatibilizing agents etc.

Another significant criterion that can influence the final property of the blend nanocomposite is the order of addition of the components. This is because of the strong influence of this on the kinetics of mixing, as there is direct influence of the medium with which the particles will be in contact during the course of its incorporation. One of the most reported and usually effective method reported in literature is adding the components simultaneously into a mixer in the molten state. The mixing of nanoparticles and polymers, evolution of morphology of the polymer blend together with the dispersion and migration of the nanoparticles inside the molten material, occur concurrently. Preparation of a master batch i.e. to incorporate the nanoparticles into the first polymer and then introducing the second polymer is also done
Introduction

occasionally to tune the morphology. In all cases, there is the possibility of the nanoparticles to migrate from one phase to the other to reach its equilibrium distribution depending on affinity. One effective way to confirm the existence of particle mobility inside a blend is to incorporate the nanoparticles into the polymer which has a lower affinity with the nanoparticles, and then to add the other polymer. Vo et al.\textsuperscript{43} studied the migration of nanoclay when a master batch was prepared with PVDF and then blended with nylon-6(N6). It was found that the nanoclay particles migrated from PVDF to N6 and to the interface due to the better affinity it had with N6, while a master batch with N6 couldn’t improve the property to that extent.

The migration of silica nanoparticles in the polypropylene/polystyrene (PP/PS) blend using a different compounding order was studied by Elias et al.\textsuperscript{44}. Pötschke and coworkers\textsuperscript{45} incorporated multiwall carbon nanotubes (MWNTs) into poly(carbonate) (PC)/SAN blends, and found that MWNTs preferred to be in the PC phase, independent of the blending procedures. It was found that all the hydrophilic silica transferred from the PP phase with which it has lower affinity, to the PS phase. Chung et al.\textsuperscript{46} presented a systematic study of partitioning of silica nanoparticles into the PMMA-rich phase during phase separation of a PMMA/SAN blend. Li et al.\textsuperscript{47} tried to prepare co-continuous microstructured blends of polymers and nanoparticles, by forming a percolating network of particles within one phase of a polymer mixture undergoing spinodal decomposition. Beyond a critical loading of nanoparticles, phase separation is arrested due to the aggregation of particles into a network (or colloidal gel) within the poly(vinyl methyl ether) phase, yielding a co-continuous spinodal-like structure with a characteristic length scale of several micrometers. A series of studies were carried out by Wu et al.\textsuperscript{48} and they introduced carbon black
in polystyrene/polyethylene (PS/PE) blend to obtain electrical conductivity. It was observed that if mixing was stopped at certain time when the solid particles were transformed from one phase to the other, the particles would remain at the interface upon cooling the blend.

Yet another criterion that affects the localization of nanoparticle in polymer blend is the viscosity of the two polymers. The viscosity ratio of two polymers is reported to play a dominant role in the localization of the nanoparticles in polymer blends. Vo et al.\textsuperscript{43} studied the effect of viscosity ratio in N6/PVDF/cloisite 30A nanocomposites and reported that the effect of viscosity ratio played a predominant role when the influence of interaction parameter was less. Bitinis et al.\textsuperscript{49} prepared a novel, toughened poly lactic acid (PLA) bionanocomposite with tunable properties by melt mixing PLA with natural rubber and several montmorillonites (MMTs). The organoclays were preferentially located at the interface, acting as compatibilisers between both polymer phases. This location resulted in a marked improvement of the physical and mechanical properties of the system. Moreover, these properties can be considered as a function of the nanofiller nature. Feng et al.\textsuperscript{50} studied the effects of viscosity ratio based on PP/PMMA/carbonblack blends, in which PMMA is the minority phase. On adding these three components at the same time in the mixer, with PMMA of three different molar masses and PP of the constant molar mass, the confinement of carbon black in the PMMA phase was only attained in the system where the viscosity ratio of PP and PMMA was close to 1, while from the calculated $\omega_{12}$, the carbon particles should be dispersed in the PMMA phase. Persson et al.\textsuperscript{51} hypothesized that the viscous ratio effect was weak and dominated only when the difference of interactions between polymer1/filler and polymer 2/filler was small.
The effect of modification of the nanoparticle can also influence the final properties to a large extent. In their work on PVDF/N6/nanocomposites, it was reported by Vo et al.\textsuperscript{43} that the nanoclay migrated to interphase when 20A was used as the nanofiller for simultaneous mixing, but when 30A was used for simultaneous mixing, the nanoclay migrated to N6 phase and the interface. Zhao, et al.\textsuperscript{52} have studied the influence of selective localization of silicon carbide (SiC) and polystyrene (PS)-coated SiC (p-SiC) nanoparticles on the thermal conductivity and flame retardancy of immiscible PS/poly(vinylidene-fluoride) (PVDF) blends. The selective localization of SiC in the PVDF phase of the PS/PVDF 70/30 blends produced a slightly higher thermal conductivity than that of p-SiC in the PS phase of the PS/PVDF 30/70 blends. The composites with selective localization of p-SiC exhibited excellent properties of thermal conductivity and flame retardancy. Martin et al.\textsuperscript{53} have done a detailed, chemically sensitive study of the morphology of nanocomposites prepared by melt blending of polypropylene (PP) reinforced with an organically modified nanoclay (montmorillonite 20A) and toughened with poly(styrene-b-ethylenebutylene-b-styrene) (SEBS). With the addition of polar functionalities, the nanoclay locates at the PP-SEBS interface rather than interacting just with the SEBS elastomer. Depending on the nature, content, and distribution of the polar groups in the material, the 20A locates selectively in the phase with which it has more affinity.

Ray et al.\textsuperscript{54} have reported that the effect of nanoparticle loading also can induce the final morphology and the resultant property significantly, in their study on polylactide/poly[(butylene-succinate)-co-adipate (PLA/PBSA) organo clay composites. On varying the weight fraction of the organoclay from 0 to 9% for 70:30 PLA-PBSA composition the small angle X-ray
scattering patterns showed a tendency of the silicate layers to delaminate in PBSA at low clay content. Thermal analysis revealed that crystallinity was dependent on the clay content as well as its localization within the composite. Tensile properties showed dependence on clay content and localization. Composite with 2 wt % clay content showed slight improvement in elongation at break. The optimum property was found for a composite with 2 wt % of the organoclay and the study thus demonstrated the significance of the clay content and localization on the properties of the PLA/PBSA blends.

1.7 Nanoclay as a filler and compatibilizer

Clay belongs to a wider group of minerals. However, in chemistry, all clay minerals may simply be described as hydrous silicates. The structure of clay minerals can be described in terms of arrangement of tetrahedral and octahedral sheets. The tetrahedral sheet is composed of silicon-oxygen tetrahedra, linked to neighbouring tetrahedra by sharing three corners, resulting in a hexagonal network. The remaining fourth corner of each tetrahedron forms a part of the adjacent octahedral sheet. The octahedral sheet is usually composed of aluminum or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The two sheets together form a layer, and several layers may be joined in a clay crystallite by interlayer cations, vander Waals force, electrostatic force, or by hydrogen. One of the important and widely used nanoclay raw material is montmorillonite, a 2:1 sheet-layered smectite clay mineral with platey structure. Chemically, it can be described as hydrated sodium calcium aluminium magnesium silicate hydroxide, \((\text{NaCa})_{0.33} (\text{AlMg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}\). A structure of montmorillonite (MMT), is shown in Fig. 1.7
Montmorillonite clay is one of the widely used reinforcing agent. This nanoclay is also used as “compatibilizers” for immiscible polymers. It is one of the useful and effective methods used nowadays, as it is a good reinforcing agent also. The compatibilizing action of nanoclay differs from the earlier mentioned compatibilizers. First, while the usual compatibilizers are well-defined organic molecules, nanoclays are not molecules. Secondly, while an organic compatibilizer reduces interfacial tension between the polymers, the presence of nanoclays cannot be expected to reduce the interfacial tension in the usual way, as they are not molecules. And finally the mechanism by which the property is enhanced or the blend is compatibilized by an organic molecule is very well defined, while that of nanoclay is not. Several factors like blend ratio, viscosity ratio, polarity, nature of polymer and nanoclay modification influences the compatibilizing action. On adding nanoclay to immiscible polymer blends, there occurs some compatibilization, and a decrease in the dispersed domain size was also observed. This sparked the interest of the researchers to expand investigation into the potential role of nanoclay as blend
compatibilizers. These organoclays are uniquely qualified as “inorganic” compatibilizers due to the fact that

- The high surface area of the modified organoclays, makes it possible to absorb in-situ grafts by absorbing many matrix polymer chains of both polymers and thus helps in lowering the interfacial tension between the immiscible polymers.

- The diffusion or intercalation of polymer layers in between the clay platelets retards the polymer chain mobility and thereby prevents the phase growth by coalescence.\(^{18}\)

### 1.7.1 Polymer- clay nanocomposites

This is one of the comparatively cheapest and nontoxic nanomaterial. This organically modified layered silicate was already found to be an effective filler in polymer nanocomposite materials. The rich intercalation chemistry, high strength and stiffness, high aspect ratio of individual layers, abundance in the nature and low cost are some important characteristics of clays that make it relevant in polymer nanocomposites. The research of intercalation of organic molecules into the interlayer space of clay minerals started in the 1920s, after the introduction of X-ray diffraction. Jordan first developed a research group on those organophilic clays\(^ {59}\) and published papers on their properties\(^ {60}\). Studies of interactions between clay minerals and organic compounds have been reported.\(^ {61-64}\)

Due to its hydrophilic nature the nanoclay does not spontaneously form a nanocomposite. Poor physical interaction between the organic and inorganic components eventually leads to agglomeration of clays and hence poor mechanical and thermal properties. To make the two compatible, the clay’s polarity must be modified to be more “organic”, to interact successfully with
Introduction

Hauser (1950) in his patent (US 2,531,427) described procedures for obtaining organoclays that swell and disperse forming gels in organic liquids in the same way as sodium smectites usually swell in water. Modification of clay, by exchanging organic ammonium cations for inorganic cations from the clay’s surface will lead to the dispersion of silicates at nanometer scales and to improved mechanical and thermal properties. Generally this is done through various types of organic treatment such as exchanging the interlayer inorganic cations (Na\(^+\), K\(^+\), Ca\(^+\), etc.) with organic ammonium cations. Another method is to swell the interlayer space and reduce the layer-layer attraction. These treatments make the clays more hydrophobic and hence they become more compatible with the polymers.

This was revolutionized by the Toyota research group in the early 1990s, when they reported the successful synthesis and characterization of a nylon 6 polymer–clay nanocomposite (Nylon-6-PCN) for the first time. The incorporation of the nanoclays into various polymers has been shown to result in the increase of tensile properties (elastic modulus, tensile strength), decreased thermal expansion coefficients and improved thermal stability, increased barrier properties and improved flammability properties.

Interest in the area of PCNs has increased significantly from both the academic and industrial perspectives as can be seen by the numerous journal articles, patents and commercialized products. The presence of well dispersed clay nanoplatelets within the nanocomposite, and understanding and controlling the clay surface, plays an important role in the optimization of these material systems. A nominal sized nanoclay particle of 8 microns contains over 1,000,000 platelets (Fig1.8f). The ability to control the dispersion of these nanofillers in a polymeric phase is the key issue that affects the performances of the final material. The improved properties of nanocomposites depend on
the high aspect ratio and surface area of the individual platelets of montmorillonite (MMT). The final morphology of the nanocomposite depends on how well these clay layers are dispersed. When a polymer enters the galleries of the clay, pushing platelets apart, it results in intercalated nanoclay in stacks of about 100-150nm. This results in an exfoliated morphology, once these platelets are eventually allowed to peel off the intercalated clay stacks. But for this highly acceptable morphology to occur, there are several aspects that should be taken care of. Poor compatibility between the polymer and the clays can create tactoids that are dispersed in the polymer matrix to yield a microcomposite. Good compatibility between the clay and the polymer matrix, results in faster delamination. Dispersion, method of mixing, processing conditions, temperature, presence of other ingredients or nanoparticles also plays a major role in the delamination of the clay platelets. However, these clay nanoplatelets are remarkable as an element of composite material.
1.7.1.1 Methods of preparation of polymer clay nanocomposites

For most applications, the main aim for the successful development of polymer clay nanocomposites is dispersion of the MMT aggregates into tactoids and ultimately into fully delaminated (exfoliated) platelets in the polymer matrix. Therefore, preparation method clearly plays a vital role in achieving this. There are three common techniques used to prepare polymer
nanocomposites; namely, in situ intercalative polymerisation, polymer solution mixing and polymer melt mixing.

a) **In situ intercalative polymerisation**

In this method, a layered silicate is swollen in a liquid monomer or monomer solution and, then inducing polymerisation using heat or radiation or by adding a suitable initiator or catalyst into the interlayer region. Polymer chains are formed between the intercalated silicate layers as illustrated in Fig. 1.9.\(^{74}\)

![Sodium MMT](image)

Figure 1.9 In-situ polymerized Nylon-6 clay nanocomposites\(^{75}\)

b) **Polymer solution intercalation**

In this method, a polymer and nanoclay are swollen in an appropriate solvent. The solvent can be used both to dissolve the polymer and swell the layered silicate. The polymer penetrates into the galleries by displacing the solvent in the galleries (or interlayers) of the layered silicate and finally, after proper mixing it is casted and the solvent is removed\(^{76}\)(Fig1.10). This method is
suitable for polymers that have little or no polarity. However, polymer solution intercalation has some disadvantages; such as the choice of polymer-solvent pairs and the limitation in industrial applications, due to problems associated with the use of large amounts of solvent, which is not environmentally suited.

![Figure 1.10](image)

**Figure 1.10** Representation of the process of solution casting

**c) Polymer melting mixing.**

The nanocomposite is prepared when a layered silicate and a molten polymer are mixed under shear. The increase in mobility of polymer chains at their melt temperatures, paves way for the polymer chains to diffuse into the galleries of the clay. Depending on the processing conditions (such as the level of shear and residence time) and on the degree of polymer-clay interaction, intercalated and/or exfoliated structures can be obtained (Fig 1.11). Melt intercalation is a widely accepted method and has good industrial applications as it is more environment friendly, and requires no solvent. However, this method has the disadvantage in that, the risk of polymer degradation and organic modifier decomposition at high temperatures during melt processing needs to be taken care of.
Figure 1.11  Different morphology of polymer clay nanocomposites through melt blending.\textsuperscript{80}

However, based on the method of preparation, nature of components, the thermodynamic driving forces and the interfacial interactions between polymer matrix and nano-clays, three main different structures can be distinguished\textsuperscript{81} as shown in Fig. 1.12.
As represented in the Fig.(1.12) first case, polymer chains are not able to enter into the interlayer space of the clays, which preserve their agglomerated stacked structure, due to low affinity of the organic and inorganic phases and poor interface properties. In this case properties are similar to those of conventional filled composites and the polymer and clay can be said to be immiscible. In the second case polymer chains enter into the silicate interlayers and wet the clays with few polymer layers, thereby increasing the basal distance but with the ordered stacked structure still maintained. The resulting structure is known as intercalated nanocomposites. In a third case, which is the most acceptable method, the single nanoclays are completely and randomly dispersed into a continuous polymer matrix, making it possible for each of the nanoclay layers to interact with the polymer matrix, thereby reinforcing the system.
Chapter 1

1.8 Rubber compounding

The necessary physical and chemical properties for a finished product can be combined by selecting and combining elastomers and additives to obtain an intimate mixing for them. The objectives of rubber compounding are:

1. To secure certain properties in the finished product to satisfy service requirements.
2. To attain processing characteristics necessary for efficient utilization of available equipment.
3. To achieve the desirable properties and processability at lowest possible cost.

1.8.1 Vulcanization

Vulcanizing agents - Once the elastomers and the filler needed for the property enhancement is decided we need to decide proper formulation. Usually the remaining compounding ingredients other than filler and the polymer are included.

i. Vulcanizing Agents (Curatives)- are used to cause chemical reaction resulting in crosslinking of elastomer molecules. Sulphur is by far the most widely used vulcanizing agent. Others include organic peroxides, metallic oxides, organic amines phenolic resins etc.

ii. Accelerators- are used to reduce vulcanization time, or cure time by increasing the speed of vulcanization. Most of these are organic substances containing both nitrogen and sulphur and they include aldehyde-amine, amines, guanidines, thioureas, thiazoles thiurams (tmtd), sulfenamides(cbs), dithiocarbamates, xanthates.
iii. Activators - are used to activate the accelerator and improve its effectiveness and attain good crosslink efficiency (ZnO, stearic acid, litharge, magnesia, and amine)

iv. Retarders - are used to reduce the scorchness (phthalic anhydride, salicylic acid and sodium acetate) to retard the deterioration of rubber compounds initiated by oxygen, ozone heat, light, metal catalyst and mechanical flexing.

v. Processing Aids - peptizers, lubricants, release agents.

During vulcanization, the rubber mixture is turned from a viscoelastic material into an incompressible elastic one. In vulcanization, permanent crosslinks are created between elastomer chains and a three–dimensional network is formed. Crosslinks can be sulphur chains, single sulphur atoms, or direct carbon–carbon linkages. The shorter the linkages are, the more rigid they become and better mechanical properties are achieved.

1.9 Characterization - Assessment of compatibilization in elastomer binary systems

After compounding the rubber blends with the filler and the suitable rubber compounding ingredients, the compatibilizing effect of the nanofiller can be assessed by using various characterization techniques. Table 1.1 gives the common characterization techniques for clay based polymer nanocomposites and the purpose for doing the characterizations.
Table 1.1. Common characterization techniques for clay based polymer nanocomposites

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Characteristics and properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD (WAXD)</td>
<td>Degree of swelling and interlayer distance of clays</td>
</tr>
<tr>
<td></td>
<td>Dispersion degree of clay platelets</td>
</tr>
<tr>
<td></td>
<td>Morphology (intercalated or exfoliated) and its development</td>
</tr>
<tr>
<td></td>
<td>Kinetics of intercalation process</td>
</tr>
<tr>
<td>SAXS</td>
<td>Phase behavior and structure evolution</td>
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<tr>
<td></td>
<td>Lamellar texture and thickness</td>
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<tr>
<td></td>
<td>Dispersion of clay platelets</td>
</tr>
<tr>
<td></td>
<td>Morphology (intercalated or exfoliated)</td>
</tr>
<tr>
<td>SEM</td>
<td>Surface roughness and morphology</td>
</tr>
<tr>
<td></td>
<td>Dispersion degree of platelets</td>
</tr>
<tr>
<td>TEM, TEM/HR</td>
<td>Morphology and its development Microstructure</td>
</tr>
<tr>
<td></td>
<td>Spatial distribution of clay platelets</td>
</tr>
<tr>
<td></td>
<td>Structural heterogeneities</td>
</tr>
<tr>
<td></td>
<td>Defect structure and atomic arrangement</td>
</tr>
<tr>
<td>AFM</td>
<td>Crystallization behavior of polymer</td>
</tr>
<tr>
<td></td>
<td>Surface roughness</td>
</tr>
<tr>
<td></td>
<td>Particle size and distribution</td>
</tr>
<tr>
<td></td>
<td>Morphology and microstructure (exfoliated or intercalated)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Component identification and analysis</td>
</tr>
<tr>
<td></td>
<td>Interfacial interactions</td>
</tr>
<tr>
<td></td>
<td>Crystallization and orientation of polymer</td>
</tr>
<tr>
<td>NMR</td>
<td>Local dynamics of polymer chains</td>
</tr>
<tr>
<td></td>
<td>Morphology and dispersion of clay platelets</td>
</tr>
<tr>
<td></td>
<td>Surface chemistry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Stability</td>
</tr>
<tr>
<td>DSC</td>
<td>Melting and crystallization behavior</td>
</tr>
<tr>
<td></td>
<td>Local dynamics of polymer chains</td>
</tr>
<tr>
<td>Cone calorimetry</td>
<td>Flame retardancy (heat release and carbon monoxide yield</td>
</tr>
<tr>
<td></td>
<td>Thermal stability</td>
</tr>
<tr>
<td>Rheometry</td>
<td>Nano rheology</td>
</tr>
<tr>
<td>Mechanical test</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td></td>
<td>Tensile strength</td>
</tr>
<tr>
<td></td>
<td>Elongation at break</td>
</tr>
<tr>
<td></td>
<td>Viscoelastic properties</td>
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1.9.1 X-ray diffraction pattern

1.9.1.1 Wide angle X-ray diffraction

X-ray diffraction is related to constructive interference of an X-ray beam and a lattice crystal. When an incident beam of X-ray hits an atom, the beam is scattered in all directions. As the atomic planes in a crystal are arranged in a regular pattern, the scattered X-ray can undergo constructive interference and generate a diffraction peak. The distance between a given set of planes is called ‘d-spacing’, which is determined by the Bragg equation.(Eq. 1.4)

\[ n\lambda = 2d \sin \theta \]  

Where \( n \) is an integer, \( \lambda \) is wavelength of the incident radiation and \( \theta \) is the angle of incidence of the beam to the atomic planes as shown in Fig. 1.13.

Using WAXD to measure the \( d_{001} \) spacing (resulting from the gallery spacing between silicate lamellae), it is possible to gain information on polymer clay nanocomposite structure, intercalated or exfoliated, as each structure produces different X-ray diffractograms. Fig. 1.14 summarises the x-ray spectra of various types of polymer-clay nanocomposites. In the case of an exfoliated
structure, in which the layered silicate is completely delaminated into individual platelets, total disappearance of the $d_{001}$ peaks is observed due to the large spacing between the platelets and the randomisation of their positions\textsuperscript{85-87}. A shift of the scattering peak towards lower angles, due to the increased gallery height, indicates the formation of an intercalated structure\textsuperscript{88-92}. Moreover, the intensity of basal reflection can provide information about layer stacking. An increase in the degree of order in the layer stacking results in a sharp intensity, whilst more disordered system causes peak broadening and intensity loss. In the case of immiscible polymer-clay mixtures, the basal reflection of the original clay does not change.

![Figure 1.14](image)

**Figure 1.14** Schematic of X-ray diffraction for various types of nanocomposites\textsuperscript{93}

The WAXD analysis of the nanocomposites can give details regarding degree of swelling and interlayer distance of clays, ‘dispersion degree’ of clay platelets, morphology (intercalated or exfoliated) and its development,
kinetics of intercalation process etc. Krishnamoorti et al.\textsuperscript{94} have observed that the kinetics of intercalation even under quiescent conditions (absence of external shear) are quite rapid. Using in-situ XRD they studied the intercalation kinetics of model polymers (mono-disperse polystyrene) in organically modified fluorohectorite.

Using XRD, Reyes et al.\textsuperscript{95} have studied, the degree of exfoliation of clay platelets encapsulated within the polymer particles dispersed in the water, in their study on waterborne PVA clay nanocomposites. Liu and Berglund \textsuperscript{96} studied the effect of positively charged chitosan on the clay nanopaper composite based on MMT and cellulose nanofibers, and found that in the WAXD patterns all silicates shift to lower angle with increased chitosan content. Wang et al.\textsuperscript{97} have studied the state of dispersion of nanoclay, in the study on MMT/PVA nanocomposites prepared by evaporation induced assembly. Roth et al.\textsuperscript{98} have reported the effect of applied pressure on X-ray diffraction patterns of the Na montmorillonite and could depict the relation between the swelling pressure and interlayer distances\textsuperscript{99}

1.9.1.2 Small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering (SAXS) is a valuable tool for molecular structural analysis due to it’s ability to provide information about non-crystalline samples, macromolecular systems and heterogeneous solutions. The ability to non-destructively analyze larger molecular systems in solutions make it particularly useful to scientists in fields concerned. When the effects of small-angle scattering are taken into account, it becomes possible to study non-repeating structures. The smaller angle causes the scattering vector’s modulus to become dependent on the reflected angle in the form $2\pi\theta/\lambda$. Since amplitude is defined as $2\pi/q$, the amplitude is equal to $\lambda/\theta^{100}$. X-rays interact with the
electrons surrounding the atoms, and the inhomogeneities in the electron density will affect the scattering pattern\textsuperscript{100-102}. At a larger angular range, these effects are diminished due to the large number of contributing particles, while at small angles (<10 degrees) these effects can be observed and will provide information about the size and shape of macromolecules in the sample\textsuperscript{103}.

Vianna\textsuperscript{104} and co workers have reported the SAXS pattern of neat PET and MMT nanocomposites. The in situ SAXS experiment assessed the evolution of craze like structures and void sizes. The changes of structural and morphological variables such as the scattering, crystallization etc were studied by SAXS analysis in their study on morphological and structural development in PE and PC. Xing \textit{et al.}\textsuperscript{105} in their SAXS study on ionic liquid modified PVDF showed the insertion of molecules in the gallery of PVDF lamella. Bandyopadhyay\textsuperscript{106} studied the effect of frequency and temperature on the structural modification of clay platelets using SAXS studies and found out that an isotropy attained the maximum value when the dispersed clay layers arranged themselves in a flocculated structure.

1.9.2 Microscopy

1.9.2.1 Optical microscopy

Phase contrast optical microscopy is used to differentiate components in gum and also lightly coloured blends. To improve the contrast between different phases a variety of methods including swelling, etching and freezing are used. portion gives a necessary contrast. Another method of improving the phase contrast is by staining with Osmium tetroxide which stains the unsaturated rubber portions. Hemmati \textit{et al.}\textsuperscript{107} have studied the demixing temperature of the polyethylene (PE)/ethylene vinyl acetate copolymer (EVA) blends
nanocomposites with unmodified nanoclay (natural montmorillonite) samples by optical microscopy.

### 1.9.2.2 Scanning electron microscopy (SEM)

SEM's are one of the most versatile and widely used tools of modern science as they allow the study of both morphology and composition of materials. Scanning electron microscopes or SEM's are microscopes that use a focused beam of high-energy electrons to generate a variety of signals, at the surface of solid specimens. This analyzes the surface of materials, measures and evaluates surface pitting, failure, characterization of dust, deposits, contaminants, particles & filter residues, and other applications.

### 1.9.2.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a technique regularly used to characterize the dispersion of nanofillers. TEM allows a qualitative evaluation of the internal structure and spatial distribution of the nanofillers and its various phases, through direct visualization of blends which are incompatible polymers or block copolymers, and have a definite domain type and size in the processed material. (Fig 1.15). In multicomponent systems, it is also desirable to know which polymers constitute the phases. Often, staining and beam interaction techniques will give an identification of the phases. A variety of compatibilizing agents and processing conditions are also tried. After blending, the bulk polymer specimens are sectioned, stained and examined. The micrographs recorded give the researcher, information about the efficacy of the compatibilizing agent for blend of incompatible polymers [such as polyethylene, polystyrene, and poly (methyl methacrylate)], based on domain type and size, which may be measured from the micrograph.
In preparing a polymer latex, a variety of reaction conditions are tried, to produce uniform particles. The various conditions result in different particle sizes and distributions. Dilute suspensions of the particles are sprayed on carbon coated specimen grids. The grids may then be shadowed at an angle with a heavy metal, or used directly. TEM images of the particles provide the researcher with measurements of particle sizes and information about the range and distribution of sizes in the specimen. The researcher is then able to correlate reaction conditions with product characteristics.

![Figure 1.15](Image)

Figure 1.15 TEM images of CNT/acrylonitrile–butadiene–styrene nanocomposites fabricated by melt mixing the selective and good level of dispersion of CNT in the styrene-acrylonitrile (SAN) section of the ABS polymer is observed (b) TEM micrograph taken from compatibilized PA6/PP/organoclay nanocomposite containing 5 phr of EPRgMA (PA6/PP/5E/4TC).

1.9.2.4. **Atomic force microscopy (AFM)**

Atomic force microscopy (AFM) is a powerful characterization tool for polymer science, capable of revealing surface structures with superior spatial resolution (Fig 1.16). It is capable of non-destructively imaging cells and molecules with a resolution comparable with that of an electron microscope,
and providing structural, mechanical and functional information under physiological conditions. The local surface molecular composition and mechanical properties of a broad range of polymer materials, including block copolymers, bulk polymers, thin-film polymers, polymer composites, and polymer blends can be analysed. Deeper understanding of these forces is important for proper imaging because the atomic force microscope relies on the forces between the tip and sample.

1.9.2.5 Scanning transmission X-ray microscopy (STXM)

Chemical differentiation and observation of all details of organic materials (e.g., polymer blends), are difficult with conventional characterization techniques due to the inability of many of these methods to analyse without damage, staining or preferential solvent washing. One of the recent characterization techniques, advantageous to the study of polymer films, is Near Edge X-ray Absorption Fine Structure (NEXAFS) Microscopy in a Scanning Transmission X-ray Microscope (STXM). STXM combines microscopic and spectroscopic information at

Figure 1.16 FIB-AFM images of the PS/PLLA/PS-b-PLLA sheath structure at the EPDM/PCL interface in the EPDM/PCL/PS/PLLA/PS-b-PLLA blend after (a) 15 min and (b) 60 min of quiescent annealing.
the nanoscale, to enable the identification and chemical composition at the nanocomposite interfaces. NEXAFS microscopy can be used to quantitate the sample composition\(^{115}\) at relatively low damage\(^{116}\), and with a spatial resolution of about 50 nanometers\(^{115}\).

Compositional mapping of polymeric samples with STXM is a three step process

1) Acquire good reference spectra
2) Acquire a series of STXM micrographs from the same sample area
3) Align the images and perform singular value decomposition on the data.

Fig. 1.17 gives this compositional mapping technique on a symmetric blend of polystyrene (PS) and poly(methyl)methacrylate (PMMA) which was spun cast onto silicon surfaces and annealed at 180\(^\circ\)C for 1 week.

Figure 1.17 STXM composition maps of a)PP/20A/SEBS/PP-g-MA-5 b)PP/20A/SEBS/PP-g-MA-15c) PP/20A/SEBS/PP*-5 d) PP/20A/SEBS/PP*-5 \(^{117}\)
1.9.3 Thermal Stability

1.9.3.1 Dynamic mechanical analysis (DMA)

By applying controlled oscillatory stress the resulting strain can easily be measured. An elastic material will have stress and strain in phase, while a viscous-elastic material will have strain lagging stress. This behaviour of the polymeric material is very important in many applications during quality control and R&D. For example, polymer coatings, like that found on solar panels and medical devices need to be studied by DMA to understand the transition between viscous and elastic properties. The behaviour of polymers is greatly affected by time and temperature, which can greatly affect the long term longevity of a device once the properties are not well understood. The glass transition temperature, storage modulus, loss modulus and damping behaviour have profound influence on the physical properties of the polymer. These results will be used for a better understanding of the life cycle of the polymer coating among others. The investigation of dynamic modulus and damping behaviour over a range of temperatures and frequencies was reported to be very useful in giving information regarding the structure, crystallinity, extent of crosslinking etc. This in turn helps in understanding the structural features of polymer blends ie the phase morphology of multiphase polymer systems and the variation of properties with respect to end use applications 118-124.
Quite a lot of work have been done by the researchers \(^{126-132}\) to investigate the effects of blend ratio and compatibilisation on the dynamic mechanical properties. Figure 1.18 gives the changes in storage modulus with temperature and transitions for polymers. The effect of compatibilizers on the dynamic mechanical properties of PS/polybutadiene blends was studied by Joseph\(^{133}\) and he reported that the storage modulus, loss modulus and tan delta values underwent dramatic change in the presence of compatibilizers.

Kumar \textit{et al.}\(^{134}\) have studied the dynamic mechanical properties of EPDM-g-VOS/LLDPE blends with special reference to the effect of blend ratio. and found that increasing the proportion of LLDPE decreases the \(T_g\) value of blend and there was increase in \(E'\) and \(E''\) due to increase in crystallinity. The morphology and dynamic mechanical properties of EPDM/PP blends and PP block polymers was investigated by Karger-Kocsis and Kiss\(^{135}\). Recently Li \textit{et al.}\(^{136}\) studied the dynamic mechanical properties of poly(L-lactic acid)/poly(oxymethylene) (PLLA/POM) blends prepared by simple melt blending.
The phase diagram, miscibility, glass transition temperatures, and physical properties have been investigated systematically. Two distinct glass transition temperatures are observed for the all blends when quenched from the homogeneous state. More surprisingly, both POM and PLLA exhibit the apparent glass transition temperature ($T_g$) depression in the blends, compared with $T_g$s of the neat polymers. The behaviours are totally different from other reported miscible or partially miscible polymer blends, in which $T_g$s shift to each other or merge into one glass transition temperature (Fig 1.19). The investigation indicates that the crystallization of POM in the blend induces the phase separation of PLLA/POM blends and forms novel morphologies with the inter-penetrated (co-continuous) PLLA and POM phases. The double glass transition temperature depression of both PLLA and POM in the blends originates from the mismatch thermal shrinkage during cooling down from the high temperature.

Figure 1.19. Dynamic loss for the PLLA/POM blends as a function of temperature: (a) neat POM, (b) PLLA/POM = 20/80, (c) PLLA/ POM = 40/60, (d) PLLA/POM = 50/50, (e) PLLA/POM = 60/40, (f) PLLA/POM = 80/20, and (g) neat PLLA.\textsuperscript{130}
1.9.3.2 Differential scanning calorimetry (DSC)

DSC is a method of thermal analysis that is widely used to study thermal transitions, i.e., solid-solid transitions as well as solid-liquid and various other transitions and reactions. Using thermal analysis, it is possible to understand what is happening in a material, even if there is no visual evidence that a change has occurred. A solid-solid phase transition would be there if the material had its structure altered, but not gained enough energy to become a liquid. The technique is widely used for determination of the glass transition temperature ($T_g$), crystalline melting temperature ($T_m$), crystallisation temperature ($T_c$) and heat of fusion of polymers. DSC measurements provide both qualitative and quantitative data on endothermic (heat absorbing) and exothermic (heat evolving) processes. Several studies are done on polymer blends and their nanocomposites through differential scanning calorimetry. Marsh et al.\textsuperscript{137} have used this technique to characterize a number of blends of commercial importance. It was found in many cases that the DSC patterns for a given elastomer are retained in the blend, thus providing a basis for identifying the polymers in the blend. Zhao et al.\textsuperscript{138} have studied the $T_g$s in miscible blends of polyisoprene/poly(4-tert-butylstyrene). Conventional and temperature-modulated differential scanning calorimetry (DSC) experiments have been carried out on miscible blends of polyisoprene (PI) and poly(4-tert-butylstyrene) (P4tBS) over a broad composition range. This system is characterized by an extraordinarily large $T_g$ difference ($\sim 215$ K) between the two homopolymers. Polymer blends are miscible if their components form a single homogeneous phase at the molecular scale, or immiscible if they exhibit several distinct phases. Yamada and Funayawa\textsuperscript{139} reported that by measuring the glass transition temperature ($T_g$), the miscibility of the blends of IR and vinyl functionalized BR (V-BR) with various percentage of vinyl contents...
Sircar and Lamond\textsuperscript{140} used DSC to distinguish between SBR, BR or blends from NR. (Figure 1.20). The $T_g$ of NR is visible in blends containing 20\% or more NR. The $T_g$ for SBR is observed at concentrations as low as 10\% SBR, although the transition is not very sharp. The composition dependence of $T_g$ is shown in Figure 1.21\textsuperscript{141} which emphasizes their very small deviation from the corresponding values for pure NR and BR. For SBR/BR blends of various compositions, unlike the previous NR/SBR and NR/BR blend systems, a single $T_g$ between $T_g$s of SBR and BR was observed, regardless of blend compositions. The explanation given for the behaviour of this blend is that, due to covulcanization, a new "phase" is formed that behaves differently from SBR or BR. It was also reported that for certain composition of the blends, a single $T_g$, of one of the components, is observed. It should, therefore, be possible to determine the composition of the blends from the DSC data.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{DSC_curves.png}
\caption{DSC curves of NR, SBR and BR\textsuperscript{135}.}
\end{figure}
1.9.4 Fourier transform infra-red spectroscopy (FTIR)

The analysis of polymers and polymer blends by DSC is often accompanied by analysis techniques based on infrared (IR) spectroscopy\textsuperscript{142-146}. This non-destructive technique is commonly used for identifying polymers and is also useful in determining various structural parameters of polymers and polymer blends. In polymer analysis the investigation of structures\textsuperscript{147}, composition, density and crystallinity degree of oxidative degradation, degree of functionalization and blend compatibility are common applications of IR spectroscopy. FTIR has been extensively used to study hydrogen bonding in polymer blends\textsuperscript{148}. These interactions not only affect the OH absorption region but also the CO stretching (1737 cm\textsuperscript{-1}), the CH\textsubscript{2} symmetric stretching (2886 cm\textsuperscript{-1}) as well as the fingerprinting frequency region (1300 to 650 cm\textsuperscript{-1}). The density of PE can be monitored using IR spectroscopy by observing the absorbance band at 730 cm\textsuperscript{-1} that increases in intensity with increasing crystallinity. Furthermore, the crystallinity of PE can be calculated using the IR absorbance bands at 722 cm\textsuperscript{-1}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig1-21.png}
\caption{The glass transition temperatures of (a) NR/SBR blends as a function of the weight fraction of SBR, (b) NR/BR blends as a function of the weight fraction of BR, (c) SBR/BR blends as a function of the weight fraction of SBR.\textsuperscript{141}}
\end{figure}
and 730 cm\(^{-1}\). The extent of crystallinity can also be estimated using the absorbance band at 1894 cm\(^{-1}\). The position of the methyl deformation band usually centred at 1378 cm\(^{-1}\) can be used to identify branches in LDPE. Different types of LDPE can be distinguished by taking the ratio of the Fourier-transform infrared (FT-IR) absorbance bands at 1368 cm\(^{-1}\) and 1378 cm\(^{-1}\) to give an estimate of the length of branching in the structure.

### 1.9.5 Rheometry - nano rheology

Rheology is the science that studies the deformation and flow of materials in liquid, melt, or solid form in terms of the material's elasticity and viscosity. This is accomplished by applying a precisely measured strain to the sample to deform it, and accurately measuring the resulting stress developed in the sample. The developed stresses are related to material properties through Hooke’s and Newton’s laws. The material is characterized in terms of its modulus, elasticity, viscosity, damping behaviour, and glass transition temperature, and the resulting changes of these with strain, strain rate, temperature, and oscillatory frequency. Rheological properties of a two-phase system depend not only on the rheological behaviour of the components, but also the size, size distribution and the shape of discrete phase and droplets dispersed in a continuous matrix phase. The morphology, which depends on the thermodynamic interactions between the constituent polymers and flow history also influence the rheological property. Therefore, rheological properties are essential in order to relate the morphology of the phase-separated state to the processing of multiphase systems\(^{149}\). Recently it was reported that diffusion processes can also be investigated and quantified by a rheological tool\(^{150}\). The mutual diffusion process and interphase development taking place at an asymmetrical polymer–polymer interface between two compatible model polymers, (poly(methyl methacrylate) (PMMA) with varying molecular weights and poly(vinylidene fluoride) (PVDF) in the molten state),
were investigated by small-amplitude oscillatory shear measurements. Determination of percolation threshold using rheological data is also widely used. The percolation threshold is closely related to the geometry of the dispersed particles, because it also depends on the relative strength of filler-filler and polymer–filler interactions. The presence of changes in frequency dependence of storage ($G'$) and loss ($G''$) moduli, complex viscosity ($\eta^*$), and/or loss tangent (tan $\delta$) indicates the formation of percolation nanoparticles.

1.9.6 Dielectric properties

The term dielectric means insulating behaviour of a materials. In general, most polymers come under insulators unless the polymer possess highly electronic groups like aniline. The dielectric properties of polymers are largely predictable from the chemical structure of the polymer. The chemical structure determines the polar or non-polar nature of the final polymer and this in turn determines the behaviour of the polymer under different conditions. The dielectric property of an insulating material is the ability of the insulator to store electrical energy under the influence of an electric field. It can be said to be the voltage which when applied to an insulating material will result in the destruction of its insulating properties, i.e. if the operating voltage is increased gradually, at some value of voltage, the breakdown of the insulating materials will occur. The property which attributes to such type of breakdown is called the dielectric strength. For example, when you say the dielectric strength of mica is 80kV/mm, it means, if the voltage applied across 1mm thick sheet of mica becomes 80kV, mica will lose its insulating properties and current will start passing through mica sheet. Dielectric strength is affected by temperature, absorption of the moisture, frequency etc. It reduces as the temperature of the insulating material is increased. Ageing also reduces the dielectric strength of the insulators. On increasing the frequency of the applied
voltage the dielectric strength of the insulating material also increases. In equation it can be considered as the ratio of the capacity of storing the electric charge by an insulating material to that of air. It is called dielectric constant of the material. Every insulating material has the property of storing electric charge ‘Q’, when a voltage V is applied across it. The charge is proportional to the voltage applied (Eq 1.5).

\[ Q \alpha V \text{ and we get } Q = CV \]

\[ \ldots \ldots \ldots \ldots (1.5) \]

Where C is the capacitance of the capacitor, which was formed by placing the material between the conductors across which voltage is applied. Dielectric strength of an insulating material is therefore the maximum potential gradient that the material can withstand without rupture. Electrical appliances/apparatus is designed to operate within a defined range of voltage. Since polymers and polymer blends find wide applications as insulating materials in electrical appliances, due to their low dielectric loss; dielectric analysis of polymers and their blends might provide useful information. Figure. 1.22, represents the dependence of the dielectric constant (\( \varepsilon \)) of PS/CB and PVDF/CB nanocomposites, on the volume fraction of CB nanoparticles (vCB) at room temperature of 25 °C and 1 kHz. It can be seen that the ‘\( \varepsilon \)’ increases with increasing vCB up to 10.3 vol %. A further increase of vCB to 12.1 vol % causes the decrease rather than the increase of ‘\( \varepsilon \)’ because of the formation of conductive network of CB nanoparticles in the polymer matrix.
1.9.7 Mechanical test

The extent to which addition of organoclay to a polymer blend matrix affects the mechanical properties provides another way to measure the degree of organoclay dispersion in the polymer matrix. The increase in modulus, which is a function of the level of organoclay exfoliation, is measured by tensile testing of the samples at room temperature according to ASTM D4. The stress-
Introduction

strain diagram is generally accepted as the plotted results of a tensile test completed under carefully controlled conditions on a specimen. It establishes the physical properties of the material under test including the yield strength, the ultimate strength, the elongation at fracture, the elastic limit etc. The stress-strain diagram differs for various materials. The stress strain curve of a polymer and the important points is given in Fig1.23. The graph shows how to relate to these different graphs and the important data mentioned above which can be extracted from these graphs.

**Figure 1.23** The stress-strain curve of a polymer and the important parameters that can be elucidated from it.

1.10 Project motivation

The purpose behind doing this research was to find the potential use of polymer blends in the industrial field. Blending the widely available natural rubber with good abrasion resistance, mechanical properties etc, and nitrile rubber having good oil and solvent resistance, was not just aimed to create an elastomer blend with acceptable properties. Rather, the work aimed at
improving the properties of this immiscible and incompatible NR/NBR blend by using nanofillers, and to study its compatibilizing effect. Although the presence of nanofillers improve the various properties, as it has been reported in many studies, the role of nanofiller in compatibilizing these immiscible system and thereby improvement in its properties have been focused in this study. The use of nanofiller was tried primarily due to the ease of availability, processing and its nontoxic nature. The wide number of research works done using nanoclay and the new publications coming based on it, shows the potential scope of this nanofiller which can be explored further. The higher aspect ratio of this filler compared to other potential fillers makes nanoclay unique, especially with its nontoxic nature.

The processing method used was mainly traditional - two roll mill melt mixing method, giving regard to its industrial viability. However, to know the beneficial effect of other preparation methods in the dispersion of nanoclay, solution mixing technique also was tried. To know the effect of clay modification two types of clay modifications which differ in their polarity were chosen. The study was focussed mainly to know the effect of nanoclay alone in compatibilizing the immiscible NR/NBR system. The study was conducted based on the localization and the dispersion of the nanoclay. Various characterization techniques were used to observe the compatibilizing effect and the effect of blend composition ad filler loading was also studied.

1.10.1 Scope and objective of the work

Research work in elastomer blends remains still to be explored further, since the first reported research work on it started few decades back only. Scientists still haven’t explored completely the benefits of polymer blends to its maximum because of the various thermodynamic and kinetic phenomenon involved. So,
any research work can add to the knowledge in this field and cannot be considered as astray. Although blends of NR/NBR have already been reported and scientists have successfully produced their blend nanocomposites with other nanofillers\textsuperscript{154-156} no work has been reported till date focusing on the compatibilizing action of nanoclay in this particular blend.

1.10.2 Objectives

- To prepare NR/NBR blend nanocomposites by varying the filler loading and blend composition.
- To compare the properties of blend nanocomposites prepared using different preparation methods.
- To investigate the morphological analysis of the prepared blends.
- To analyse the mechanical property of NR/NBR blend.
- To evaluate the time dependent properties of the prepared composites like stress relaxation.
- To examine the barrier properties of the prepared blend nanocomposites.
- To study the non linear viscoelastic nature of the prepared nanocomposite.
- To explore the effect of clay in improving the thermo mechanical properties.
- To optimize the blend composition and filler loading for further studies.
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Chapter 1


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