Chapter 1

Introduction, Literature Review and Objective of the Research Work

1.1 Introduction

Homopolymers may not always satisfy all the requirements for various practical applications. Thus, initially the trend was to develop new polymers from a wide variety of monomers. For tailoring or modifying the properties of polymers, copolymerization has been used as an effective technique. However, due to the economic and technical uncertainties associated with synthesizing new polymers, recently efforts were focused on multiphase polymeric systems to obtain materials with improved physical and chemical properties and such considerations were the basis of polymer blends [1-7].

Mixing two or more polymers together to produce blends is economically a more attractive way than the copolymerization process to develop new polymeric materials with improved performance properties. From the standpoint of commercial applications and developments, polymer blending represents one of the growing segments of polymer technology due to the realization that new materials with improved properties can be obtained to meet the specific end use requirements. Thus, the market for polymer blends has increased continuously during the past two decades, and is expected to increase in the coming decade. The major application areas of polymer blends are in automotive industries, electrical and electronic devices, packaging industries and building and household materials.

1.2 Problem Definition and Research Issues

The manifestation of superior properties of polymer blends depends upon the compatibility or miscibility of the constituent polymers at the molecular scale. However, because of unfavorable enthalpy of mixing associated with their inherent thermodynamic incompatibility, most polymer pairs are immiscible and, thus, form phase-separated morphology in the blends [8, 9]. The properties of multiphase polymeric materials are determined by the properties of the component polymers and the microstructure in the blend. Therefore, controlling the microstructure becomes a key factor in determining the performance of polymer blends. Traditionally, the most effective way to attain satisfactory performance in incompatible polymer blends is to minimize the interfacial tension and increase the interfacial adhesion between the blending components. Use of block or graft copolymer as compatibilizer during processing plays an important role by making entanglement or bridging different polymer chains near the interface. The compatibilizer improves the miscibility of the component polymers in immiscible polymer blends and hence, reduces the average domain sizes of the disperse phase in the matrix phase of the blend [10-13]. However, synthesis of various blocks or graft co-polymers depending on the blend components limits the use of polymeric compatibilizer in various immiscible polymer blends.

In recent years, several research groups [14-20] have shown that organically modified nanoclay could play the role of a compatibilizer in immiscible polymer blends. Reports on various immiscible polymer blends in presence of clay indicated a reduction in dispersed domain sizes through selective localization of clays in the matrix phase. The reduction in domain sizes in several immiscible polymer blends by the addition of clay has been explained through various assumptions. There are several viewpoints: (i) selective localization of organoclays in the matrix (major) phase of the blend increased the viscosity of the matrix phase and thus, lowered the viscosity ratio of dispersed/matrix phases (η_d/η_m) in the blends. Thus, decrease in domains sizes of the disperse phase in the blends has been explained on the basis of decrease in (η_d/η_m) value in presence of clay; (ii) the organoclay could act as physical barrier that prevented the agglomeration of dispersed phases during mixing [16, 17]; (iii) the formation of *in-situ* grafts (polymer) during mixing [18, 19], which were unstable in either of the phases and thus located at the interface of the blends. These grafts could act the similar way as block copolymer in decreasing the interfacial tension and thus, reduced the domain sizes of the dispersed phase; and (iv) co-intercalation of both the polymers in the same clay gallery which can act as block copolymer has also been reported [20].

Thus, the actual mechanism behind the compatibilization effect of nanoclay in immiscible polymer blends is not clear. Now one can raise an important question: is it possible to reduce the domain sizes of disperse phase in immiscible polymer blends by using nanoclay where viscosity increment of the matrix polymer by the clay is almost negligible? Again, stability of the matrix-droplet morphology of an immiscible polymer blend in presence of nanoclay against thermal annealing has rarely been reported.

This provides the scope for further investigation on the morphology of immiscible polymer blends in presence of nanoclay and to explore the proper mechanism behind the compatibilization effect of nanoclay in the blend. This investigation deals with the morphology of various immiscible, binary polymer blends of asymmetric compositions, without and with the nanoclay and (or) polymeric compatibilizers (block and graft copolymers) at different loading, prepared by the conventional melt-mixing method. The change in dispersed domain sizes in the blends in presence of clay, as affected by the location of clay in the phases, has been investigated and compared with the domain sizes of the blends with various amount of block or graft copolymer as compatibilizer. On the basis of morphological study and rheological analysis of the pure blends and the blends with clay, efforts have been made to elucidate the most suitable mechanism behind the compatibilization effect of clay in immiscible polymer blends.

1.3 Types of Polymer Blends

Polymer blends may be defined as intimate mixture of two or more polymers resulting from the common processing steps, e.g. mixing of polymers in the molten state, casting from common solvents etc., with no covalent bonds between them.

Polymer blends are either homogeneous (miscibile) or heterogeneous (immiscible). In homogeneous blends, both blend components lose part of their identity and the final properties usually are the average of both blend components. In heterogeneous blends, the properties of all blend components are present. Weaknesses of one polymer can, to a certain extent, be camouflaged by strengths of the other.

Polymer blends can be broadly divided into three categories:

(i) Miscible
(ii) Partially miscible, and
(iii) Immiscible

A miscible polymer blend is a polymer blend which is homogeneous down to the molecular level, is associated with a negative value of the free energy of mixing and the domain size is comparable to the dimensions of the macromolecular statistical segment. For example, poly(phenylene oxide) (PPO), is a very heat resistant polymer, however very hard to process. With a T_g of 210 ^oC, heating PPO is enough to make it soft, but expensive. However T_g drops down considerably when polystyrene (T_g of 100 ^oC) has been blended with PPO which make the blend much more processable than straight PPO.

In partially miscible blends both interacting phases (one being rich in polymer 1, the other phase being rich in polymer 2) are homogeneous. An example is the polycarbonate (PC)/acrylonitrile butadiene styrene (ABS) blends. In these blends, PC and the styrene acrylonitrile (SAN) phase of ABS partially dissolve in one another. In this case, the interphase is wide and the interfacial adhesion is reasonable.

However, immiscible polymer blends exhibit phase separation between the interacting polymers resulting in poor bonding but one of the immiscible materials, upon blending, have turned out to be nifty and useful. Polybutadiene and polystyrene are immiscible in each other; however upon blending they tend to show a different phenomenon. Polystyrene is a rather brittle material, but polybutadienes are rubbery in nature and can absorb energy under stress. Blending of polystyrene with polybutadiene keeps polystyrene from breaking.

Depending on the blending composition and viscoelastic properties of each blend component, immiscible polymer blends prepared by melt-blending show, generally, two types of morphology: dispersed domain structure in the matrix phase, and co-continuous structure [21, 22]. Asymmetric blend compositions show the former-type morphology, namely, the minor component forms the dispersed phase in the continuous phase of the major component. The co-continuous structure is anticipated for immiscible polymer blends when the following condition is met [23, 24]:

$$\phi_A/\eta_A \sim \phi_B/\eta_B \qquad (1)$$

in which ϕ_i and η_i (i =A and B) are the volume fraction and the viscosity of the component i. An immiscible polymer blend with $\eta_B/\eta_A >> 1$ (or $\phi_A/\phi_B >>1$) the component B forms the dispersed domains in the matrix of A. On the other hand, immiscible polymer blends with $\eta_B/\eta_A \sim 1$, show the co-continuous morphology for nearly symmetric compositions or blend compositions where the weight fraction of a minor component is not smaller than ~ 35 wt %.

1.4 Thermodynamics of Polymer Blends

Whether a particular polymer blend will be homogeneous or phase separated will depend upon many factors, such as the kinetics of the mixing process, the processing temperature, and the presence of solvent or other additives; however, consideration for determining miscibility of two polymer is a thermodynamic issue which is governed by Gibbs free energy parameter. The relation between the change in energy, ΔG_m, the enthalpy ΔH_m and entropy of mixing ΔS_m at temperature T, respectively, is given as:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (2)$$

If ΔG_m is positive over entire composition range at a given temperature, the two polymers in the blend will separate into phases that are pure in either component, providing that a state of thermodynamic equilibrium has been reached.

For complete miscibility, two conditions are required: ΔG_m must be negative and the second derivative of ΔG_m with respect to the composition (φ) in a binary mixture must be greater than zero over the composition range.

$$\left(\delta^2 \Delta G_m / \delta\varphi^2\right)_{T,P} > 0 \qquad (3)$$

ΔG_m can be described in polymers by the Flory-Huggins equation

$$\Delta G_m = RTV_C\left[\left(\varphi_A / N_A\right)\ln\varphi_A + \left(\varphi_B / N_B\right)\ln\varphi_B + \chi_{AB}\varphi_A\varphi_B\right] \quad (4)$$

where *R* is the gas constant, *T* is the temperature in K, *V*c is the molar volume of each segment φ_A, φ_B are the volume fractions of polymers A and B in the mixture, N_A, N_B are the number of segments in the polymers A and B and χ_{AB} is the Flory-Huggins interaction parameter describing the interactions between A and B segments. The parameters mainly determining miscibility are the volume fractions φ_A, φ_B in the mixture (composition), the molar volumes of the polymers A (V_A) and B (V_B), representing the size of the segments on their places, the interaction parameter χ_{AB}, reflecting indirectly the chemical structure of the polymers.

1.5 Factors affecting miscibility and immiscibility of polymer blend

1.5.1 Polarity: Polymers that are similar in structure or more generally similar in polarity are less likely to repel each other and more likely to form miscible blends [25, 26].

1.5.2 Specific group interaction: Polymers that are drawn to each other by hydrogen bonding, acid-base, charge transfer, ion-dipole, and donor-acceptor adducts or transition metal complexes are less common, but when such attractions occur they are very likely to produce miscibility [27-29].

1.5.3 Molecular weight: Lower molecular weight permits greater randomization on mixing and therefore greater gain of entropy, which favors miscibility [30]. More surprisingly, polymers of similar molecular weights are more miscible, while polymers of very different molecular weights may be immiscible, even if they both have the same composition.

1.5.4 Crystallinity: When a polymer crystallizes, it forms a two phase system. Thus in a polymer blend when a polymer crystallizes, this adds another phase to the system. If both polymers in a blend crystallize, they will usually form two separate crystalline phases; it is quite rare for the two polymers to co crystallize in a single crystalline phase [31].

1.5.5 Blend Ratio: Even though two polymers appear immiscible at a fairly equal ratio, it is quite possible that a small amount of one polymer may be soluble in a large amount of the other polymer and vice versa, as understood in conventional phase rule.

1.6 Blend morphology

Heterogeneous blends appear in a variety of morphologies (Figure 1.1). The best known and most frequently observed morphologies are: (i) a dispersion of one polymer in the matrix of the other polymer; and (ii) a co-continuous two-phase morphology.

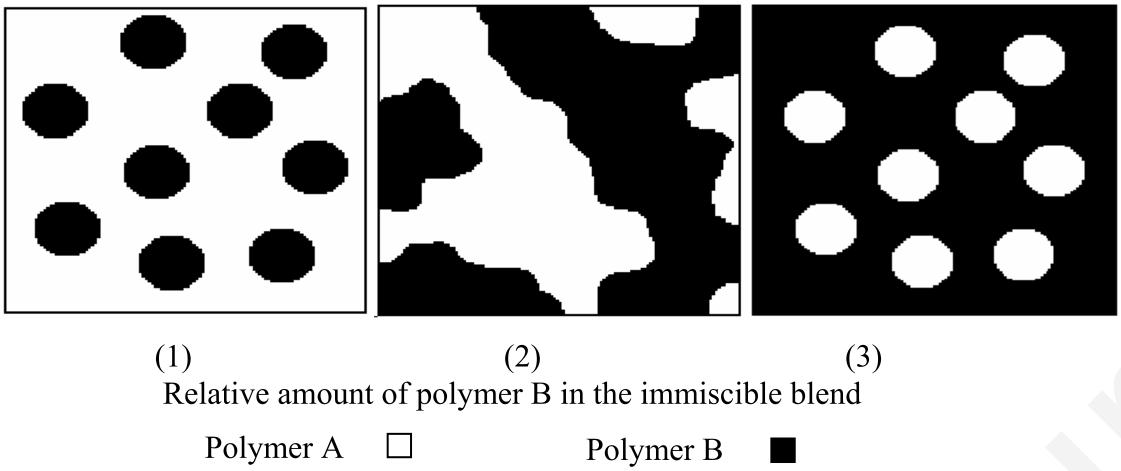


Figure 1.1: Different types of blend morphology of two polymers blend system. (1) and (2) are dispersed spherical domain-matrix structure; (3) co-continuous blend morphology.

The morphology (shape, size and spatial distribution of the phases) results from a complex interplay between viscosity (and elasticity) of the phases, interfacial properties, blend composition and processing conditions. Thus control of the phase morphology during blend processing is a key issue for the production of new materials with improved properties compared with the constitutive immiscible polymers.

1.7 Compatibilization

As it follows from thermodynamics, the blends of immiscible polymers obtained by simple mixing show a strong separation tendency, leading to a coarse structure and low interfacial adhesion. The final material then shows poor mechanical properties. On the other hand, the immiscibility or limited miscibility of polymers enables formation of wide range structures, some of which, if stabilized, can impart excellent end-use properties to the final material. To obtain such a stabilized structure, it is necessary to ensure proper phase dispersion by decreasing interfacial tension to suppress phase separation and improve adhesion. This can be achieved by modification of the interface by the formation of bonds (physical or chemical) between the polymers. This procedure is known as compatibilization, and the active component creating the bonding is termed as the compatibilizer [32-34].

Two general methods are used for compatibilization of immiscible polymers:

(i) Incorporation of suitable block or graft copolymers,

(ii) Reactive compatibilization.

1.8 Incorporation of Copolymers (Nonreactive Compatibilization)

Block or graft copolymers with segments that are miscible with their respective polymer components show a tendency to be localized at the interface between immiscible blend phases. The copolymers anchor their segments in the relevant polymer, reducing interfacial tension and stabilizing the dispersion against coalescence [35-55] being used as compatibilizer by reducing interfacial tension, but their ability to stabilize the phase structure is limited [56]. Creton and co-workers [57] have reviewed the molecular criteria for copolymers linking two immiscible homopolymers that must be fulfilled to achieve a good stress-transfer ability of the interface.

This process, however, inherently bears two practical limitations. Blending of an immiscible polymer pair requires a specific block or graft copolymer. Consequently, a specific synthetic procedure is necessary to obtain the desired copolymer. This can be costly, and sometimes there is no feasible technology at a manufacturer's disposal. Moreover, the amount of the copolymer to be added is often significantly higher than that for saturation of the interface. A part of the copolymer may be trapped in the bulk phase during blending and never reach the interface. This fact can negatively affect the blend morphology and may lead to higher compatibilizer consumption.

During more than three decades, much information on nonreactive compatibilization has been obtained and successfully applied in the development of new multiphase materials. Moreover, the proven efficiency of block or graft copolymers in the controlling of the phase structure development has led to new, more effective approaches to producing these copolymers directly during the blending. This process is known as reactive compatibilization.

1.9 Reactive Compatibilization:

Reactive compatibilization is the process that allows generating graft or block copolymers acting as compatibilizers *in-situ* during melt blending [58, 59]. These copolymers are formed by reactions at the interfaces between suitably functionalized polymers, and they link the immiscible phases by covalent or ionic bonds. In this process, the copolymers are formed directly at the interfaces, where they act like preformed copolymers, i.e., they reduce the size of the dispersed phase and improve adhesion. For this reason, the problem with transport of the compatibilizer to interface is not relevant and structure control is easier than in the case of adding preformed copolymers.

In addition to these two types of compatibilization processes, sometimes filler and fibers are also used for compatibilization of immiscible polymer blends. When polymers in a blend are immiscible, repel each other, and form weak interfaces of poor mechanical properties, it has occasionally been reported that the addition of reinforcing fibers can successfully bridge across the weak interfaces, connect the strong individual polymer phases with each other, and thus enhance mechanical properties and practical compatibility.

However, most of the organic hydrocarbon based compatibilizers have low thermal oxidative stability, and resistance to fire and light. On the other hand inorganic materials possess high thermal and oxidative stability, high solvent resistance, excellent mechanical strength and biocompatibility [60].

1.10 Thermodynamic Consideration of Immiscible Polymer Blends in Presence of Compatibilizer

The compatibilization effect of two immiscible polymers by adding the third component can be described from the framework of the Flory-Huggins theory. The change in the free energy of mixing three components (per unit volume) is expressed as:

$$\frac{\Delta G_{mix}}{V} = RT\left[\left(\frac{\varphi_A \ln \varphi_A}{V_A} + \frac{\varphi_B \ln \varphi_B}{V_B} + \frac{\varphi_C \ln \varphi_C}{V_C}\right) + \chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C\right] \quad (5)$$

Where V is the mixture volume and χ_{ij} is the interaction parameter between components i and j; which determines the sign and value of the heat of mixing. Φ_i is the volume fraction of component i. For polymer mixtures the combinational entropy contributions may be neglected as their miscibility is driven by enthalpic force. Therefore supposing that the parameters χ_{ij} do not depend upon the composition, equation (5) may be presented as:

$$\Delta G_{mix} = RTV\left(\chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C\right) \quad (6)$$

The terms in brackets may be expressed through the thermodynamic interaction parameter for the ternary blend

$$\chi_{A+B+C} \cong \chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C \quad (7)$$

A positive value of the parameter χ_{A+B+C} corresponds to an immiscible system whereas a negative value is indicative of miscibility. Generally in the presence of filler compatibilizers, the immiscible polymeric components got adsorbed onto the surface of the compatibilizer and therefore the interaction parameters of a polymer A and B become negative in magnitude. The introduction of a compatibilizer that strongly interacts with polymer A and B will decrease the value of χ_{A+B+C} and therefore bring about the thermodynamic stability of the system [61, 62].

1.11 Thermoplastic Composites

A composite is defined as a material consisting of two or more distinct phases with an interface between them. This definition is basically used for materials containing reinforcement fillers characterized by a high aspect ratio, as in the case for fibers, platelets and flakes. The incorporation of these materials into thermoplastics matrices results in improved, but possibly anisotropic, mechanical and thermal properties. The role of the matrix, reinforcing filler and interface in composites are well defined. The matrix is responsible for transferring the load from the matrix to the reinforcing filler. Meanwhile, the task of the reinforcing filler is to carry the load and give higher stiffness and strength compared with that matrix. The interface (for two dimensions) or the interphase (for three dimensions) is a negligible or finite thin layer with its own properties, and its role is stress transfer from the matrix to the reinforcement [63]. The mechanical performance of reinforced thermoplastic blends is affected by several factors, including blend composition and morphology, type and amount of the reinforcing filler, interface and interphase between matrix and reinforcement, processing methods and testing conditions.

1.12 Polymer Nanocomposites

Polymer nanocomposites are a new class of composite, being particle filled polymers for which at least one dimension of the dispersed particles 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 three dimensional nanoparticles, such as spherical silica nanoparticles obtained by *in-situ* sol gel methods. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or whiskers as, for example, carbon nanotubes or cellulose whiskers which have been extensively studied as reinforcing nanofillers yielding materials with exceptional properties. The third type of nanocomposites is characterized by only one dimension in the nanometer range.

In this case the filler is present in the form of sheets of one to a few nanometer thick by hundreds to thousands nanometers wide. Most of this family of composites can be gathered under the name of polymer-layered silicate nanocomposites. These materials are almost exclusively obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layer silicates. Among all the potential nanocomposite precursors, those based on clay and layered silicates have been most widely investigated, probably because the starting clay materials are easily available and of their potential intercalation ability.

1.13 Polymer-Clay Nanocomposites

In recent years polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties at very low clay content (3-6 wt%), when compared with virgin polymer or conventional micro and macro-composites. These are composites with high aspect-ratio inorganic reinforcements with lateral dimensions in the range of 1 to 100 nm. Some of the attractive properties of nanocomposites include improved electrical and mechanical properties (e.g, increased strength and modulus without sacrificing impact properties), reduced gas and water permeability for barrier applications (e.g packaging and fuel containment), increased thermal stability, flame resistance, and resistance to wear, elevated heat distortion temperature, recyclability, enhanced ionic conductivity, and improved processability (extrusion and molding). Other advantages include increased dimensional stability at elevated temperatures, better surface gloss, increased tear resistance of elastomers, optical transparency, accelerated cure of elastomers, and reduced shrinkage.

The initial findings in the field of polymer clay nanocomposite were developed by the Toyota team for nylon6/MMT (montmorillonite) nanocomposite for which very small amounts of layered silicate loading resulted in pronounced improvement of thermal and mechanical properties.

1.14 Structure and properties of layered silicates

The commonly used layered silicates for the preparation of PLS nanocomposites belong to the same general family of 2:1 layered or phyllosilicates. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Figure 1.2). The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{+}) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal.

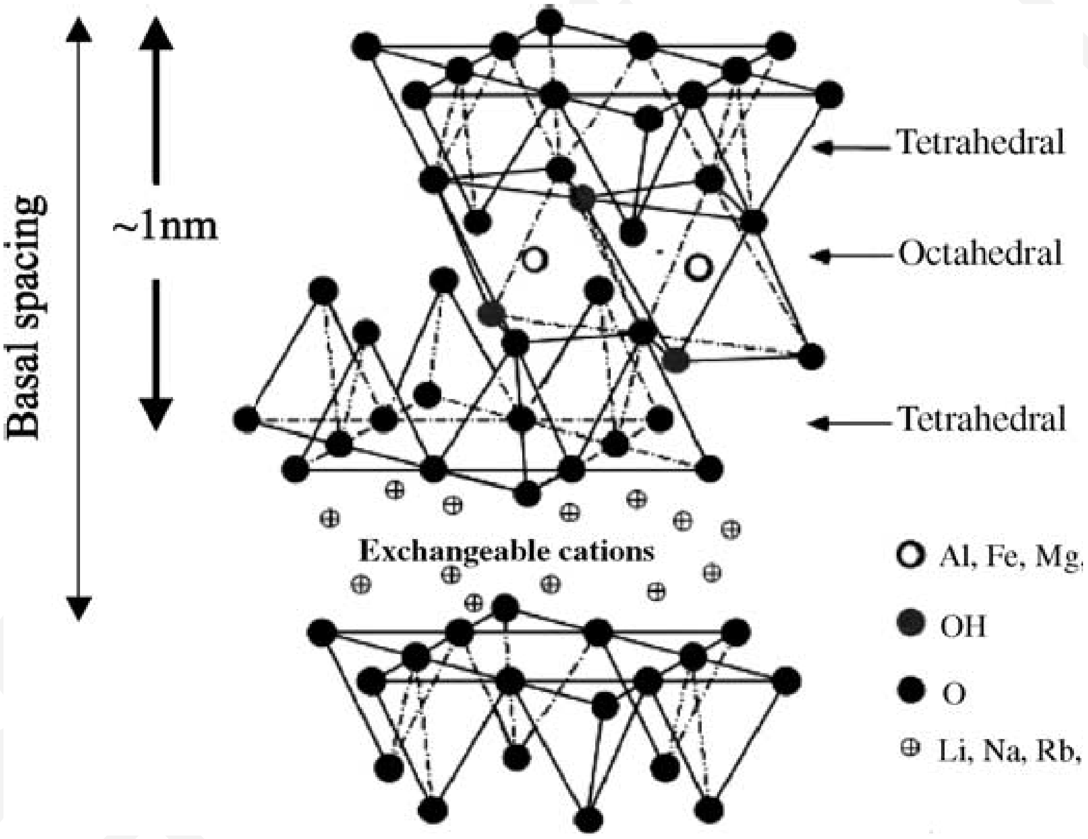


Figure 1.2: Structure of Montmorillonite clay

Montmorillonite (MMT), hectorite, and saponite are the most commonly used layered silicates. Layered silicates have two types of structure: tetrahedral-substituted and octahedral substituted. In the case of tetrahedrally substituted layered silicates the negative charge is located on the surface of silicate layers, and, hence, the polymer matrices can interact more readily with these than with octahedrally-substituted material. Two particular characteristics of layered silicates are generally considered for PLS nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation.

1.15 Structure and properties of organically modified layered silicate (OMLS)

In nanocomposites, the interfacial effect between the silicate layers and matrix polymers is a key factor leading to high stiffness, high modulus and heat resistant composites which can be by far superior to conventional filler, provided that the silicate layers are completely delaminated and thoroughly homogenized into the polymer matrix. Pristine layered silicates usually contain hydrated Na^+ or K^+ ions [64]. So pristine layered silicates are hydrophilic in nature and thus, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly(ethylene oxide) (PEO) [65], or poly(vinyl alcohol) (PVA) [66].

To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [67, 68].

Generally, there are two objectives for clay modification before melt compounding. The first is to weaken the polar interaction between adjacent MMT layers and increase the distances between MMT layers, which are a prerequisite for polymer macromolecules to intercalate into the MMT galleries. The second is to enhance the affinity/compatibility between polymer and MMT, which provides a driving force for polymers to migrate into the MMT galleries.

The formation of nanocomposites by means of melt compounding is strongly influenced by several vital factors such as type of alkylammonium additive present during clay modification, processing temperature, shear rates, type and content of compatibilizer, and polymer viscosity. Wang et al. [69] reported that the exfoliation and intercalation behaviors depended on the chain length of organic modifier in the clay and the hydrophilicity of polyethyelene grafted with maleic anhydride. According to Fornes et al. [70], a larger initial interlayer spacing may lead to easier exfoliation since platelet-platelet attraction is reduced. It is implied that diffusion of polymer chains inside clay galleries is less hindered due to increased spacing and this leads to improved exfoliation and performance.

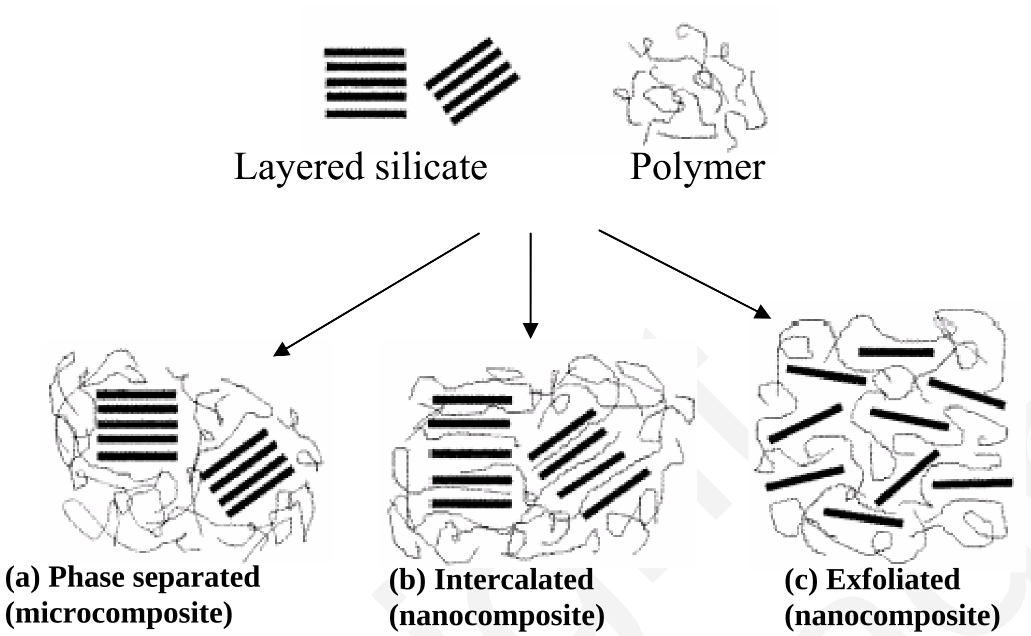
1.16 Types of polymer-clay nanocomposites

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 (see Figure 1.3):

a. **Phase separated nanocomposites**: A phase separated nanocomposite is a conventional polymer- clay composite where the nanoclay layers are aggregated in polymer matrix.

b. **Intercalated nanocomposites:** In intercalated nanocomposites, the insertion of a polymer chains into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. The interlayers in intercalated nanocomposites are normally interlayer by a few molecular layers of polymer.

c. **Exfoliated nanocomposites:** In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.



(a) Phase separated (microcomposite)

(b) Intercalated (nanocomposite)

(c) Exfoliated (nanocomposite)

Figure 1.3: Different Types of Polymer-clay Nanocomposites

1.17 Literature Survey on Polymer blend-clay nanocomposite

In today's competitive global scenario improvement of compatibility in immiscible polymer blends is most important research field and for this block or graft copolymers or *in-situ* reactive compatibilizers, have been employed that reduce the dispersed domain sizes by increasing the interfacial adhesion and lowering the interfacial tension in blends [71-75]. One recent method of controlling and tailoring morphology of polymer blends is the addition of nanoparticles as a compatibilizer into immiscible blends. The potential use of nanoadditives, such as organoclay or silica nanoparticles in tailoring the morphology of various polymer blends can have a wide range of advantages, such as enhancing material properties, ease of processing and, especially, lower cost in comparison to copolymer compatibilizers. It should be noted that because of their physical nature, copolymer compatibilizers could plasticize the matrix and soften the interface, thus compromising physical and mechanical properties of the matrix, while on the contrary, nanoparticles, such as organoclay, have been shown to enhance the mechanical and thermal properties of polymers and stabilize different crystalline phases.

In this context, researchers have proposed several approaches for achieving requisite improvement in thermal, mechanical, and morphological properties of polymer blends aided by organoclay as compatibilizers. This chapter briefly describes these approaches and aims at identifying the mechanism behind the compatibilization action of organoclay in an immisible blend.

Lipatov et al. [76] considered the thermodynamics of mixing of two miscible or immiscible polymers with a solid. It was shown theoretically that the introduction of a specific filler in binary polymer mixtures increased the thermodynamic stability of the ternary system. The compatibilizing effect of the filler depends on the change in free energy of mixing between the two polymers, the effect being more pronounced for immiscible systems.

The interaction of organically modified montmorillonite (OMMT) in the polymer blend of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) was demonstrated by Lim et al. using dicholomethane as a cosolvent at room temperature [77]. By evaluating the Flory-Huggins interaction parameter between polymers and silicates layers in a PEO/PMMA/OMMT system they showed that OMMT interacted with PMMA better than with PEO.

Voulgaris et al. [78] prepared blends of two immiscible polymers, (25/75 w/w) polystyrene (PS) and poly (ethyl methacrylate), in tetrahydrofuran solution, with modified hectorite and observed reduced domain size of the PS-phase. They explained it in terms of emulsification effects of the excessive surfactants in the organoclay.

Morphological observations of (80/20 w/w) HDPE/polyamide 6 (PA6) blend with different (5 and 10 wt%) amounts of modified clay was done by Kamal et al. [79]. They showed that the addition of 5 wt% clay to (80/20 w/w) HDPE/PA6 blend caused a reduction in the size of the PA6 domains and the morphology was changed from spherical to laminar. They suggested the phenomenon was caused by suppression of coalescence of the domains by clay layers. According to them incorporation of maleated polyethylene caused further reduction of the domain size and corresponding increment in the adhesion between two phases.

Gelfer et al. [80] studied a (50/50 w/w) blend of polystyrene (PS) and poly (methyl methacrylate) (PMMA) and found that the presence of clay had little influence on the dispersed phase size, except when the clay particles contained excess surfactant; in the latter case, clay particles were found in an intercalated state and a reduction in dispersed phase domain size was observed. They also reported that preferential location of nanoclay in the PMMA phase increased the viscosity of PMMA in the PS/PMMA blends that lowered the dispersed PS domain sizes.

In support of the above, Wang et al. [81] showed similar results in (30/70 w/w) polystyrene (PS)/poly(propylene) PP blends. They reported decreased domain size in (30/70 w/w) PS/PP blend by the addition of organoclays which was attributed to the fact that two immiscible polymer chains can exist together between the intercalated clay platelets; thus these two polymer chains played the role of a block copolymer.

Similar result was observed by Khatua et al. [82] in nylon6/EPR/organoclay blends. They explained the reduction of domain sizes in terms of preventing the coalescence of the dispersed domains by the exfoliated clay platelets. Li and Shimizu [83] reported a significantly decreased domain size in the poly (phenylene oxide) PPO/polyamide 6 blend by adding 2% clay, and a co-continuous morphology by adding 5% clay. They attributed it to the change of the viscosity ratio at higher clay content. They reported that the selective localization of exfoliated clay platelets in the PA 6 phase not only increased the viscosity of PA 6 and the PPO phase, but also impeded the coalescence of the PPO phase.

Lee et al. [84] in their study of polymer blend nanocomposites showed that the dispersion of the nanoclay in a polymer blend depends upon different addition sequences in the blending process.

Kamal et al. [85] showed that compatibility of the clay modifier with the polymer matrix plays an important role in exfoliation. Clay acted as a nucleating agent for which the crystallization temperature increased marginally and reduced the crystallite site. Thus, clay in the PA-66/HDPE blend nanocomposite act as a compatibilizer.

Mehta et al. [86] showed that the EPR morphology in TPO/clay nanocomposites undergoes progressive particle breakup and a reduction in the particle size as the clay loading increases from 0.6 to 5.6 wt%. This was ascribed to two potential mechanisms: (i) the melt viscosity of the TPO phase increases as the clay loading increases, and this may play a role in the control of the particle size through shear-mixing coalescence and breakup, and (ii) the clay preferentially segregates to the rubber particle/matrix interface, and it was suspected that the progressive breakup of the EPR particles was due to the action of the clay, associated chemical modifiers, and the compatibilizer on the clay as interfacial agents.

Sinha Ray et al. [87] also showed that the presence of organoclay in PS/PP and PS/PP-g-MA blends decreased the interfacial tension and domain sizes. They also reported that the compatibilization action was more efficient in the presence of PP-g-MA due to better interaction of clay with PP-g-MA.

Lee et al. [88] in their study of nylon 6/LLDPE blends and organoclay showed that LLDPE domain sizes in the blends decreased with addition of organoclay and this organoclay was mainly located in nylon 6 matrix due to their high affinity towards nylon6 . Sinha Ray et al. [89] showed the compatibilization efficiency of clay in an immiscible (40/60 w/w) PC/PMMA blend.

Li et al. [90] studied novel morphology of (40/60 w/w) polyamide 6 (PA6)/ acrlonitrile-butadiene-styrene (ABS) nanocomposite, prepared by the melt mixing of PA6, ABS and organoclay. The blend nanocomposites had a co-continuous structure, in which both PA6 and styrene-acrlonitrile (SAN) were continuous phases. It was found that the toughening rubber particles were only located in the SAN phase and the strengthening clay platelets were selectively dispersed in the PA6 phase. The co-continuous nanocomposites showed greatly improve mechanical properties over the whole temperature range when compared with the same blend sample without clay.

Jana et al. [91] investigated the role of layered silicate clay on the morphology development in chaotic mixing of two immiscible polymers, polypropylene (PP) and polyamide 6 (PA6). They showed that clay particles helped to produce droplets of much smaller size and with narrower size distribution due to their direct influence on the break up of PP domains. The clay particles were seen to reduce the interfacial tension between PP and PA6 phases. This, in turn, led to generation of thinner fibrils and smaller droplets. The clay particles later migrated to the PA 6 phase and became intercalated by PA6 chains. The absence of PP chains in the galleries of clay particles, which already migrated to PA6 phase indicated that clay particles did not participate in compatibilization of the phases. Therefore the reduced droplet size observed can be attributed primarily to generation of thinner fibrils and subsequent break up into smaller droplets.

Kocsis et al. [92] observed the phase structure and clay dispersion in (70/30/4 w/w) polyamide 6 (PA6)/polypropylene (PP)/organoclay systems with and without an additional 5 parts of maleated polypropylene (MAH-g-PP) as a compatibilizer. They showed that in the absence of the MAH-g-PP compatibilizer, the organoclay located in the PA6 phase and PP was coarsely dispersed in PA6 and the adhesion between PA6 and PP was poor. The addition of MAH-g-PP resulted in a markedly finer PP dispersion and good interfacial bonding between PA6 and PP. In this system organoclay was likely dispersed in the PA6-grafted PP phase.

Narkis et al. [93] in their studies with Nylon-6/EVOH blend showed that a chemical reaction occurred during melt-mixing, affecting thermal, morphological and mechanical properties of the ternary systems containing clay. The addition of clay seemed to interrupt the chemical reaction between the host polymers at certain compositions, leading to lower blending torque levels when clay was added. The ternary systems had combined intercalated and delaminated morphology or complete exfoliated morphology depending on blend composition and clay content. The thermal properties of the polymers were found to be affected by the occurrence of a chemical reaction, the level of intercalation and exfoliation and plasticizing effect of the low molecular weight onium ions treating the clay.

Paul et al. [94], in their study, balanced between stiffness and toughness of nylon 6/MMT/EPR-g-MA by altering the ratio of polymers and clay in the blend. They also showed that the morphology of the blend depend on the sequence of blending and location of clay in the blend, which actually the main reason of different blend properties.

Si et al. [95] studied the morphology of blends of PS/PMMA, PC/SAN24, and PMMA/EVA and compared the morphologies with and without Cloisite 20A or Cloisite 6A clays. In each case they found a large reduction in domains size and the localization of the clay platelets along the interfaces of the components. In addition, the modulus of all the systems increased significantly. A model was proposed in which *in-situ* grafts were forming on the clay surfaces during blending and the grafts then had to be localized at the interfaces.

Hong et al. [96] showed a decrease in the domain sizes in poly(butelene terephthalate)/high density polyethylene (PBT/HDPE) blend as long as the clays were dispersed in the PBT matrix. The presence of clay changed the viscosity ratio of the polymers and suppressed the coalescence of dispersed domains in the blend.

Bernreitner et al. [97] studied the rheological and morphological interactions in polypropylene/polyamide-6 nanocomposites. They showed that in all cases the inorganic filler enriched in the PA phase, resulting in a phase coarsening of the PP/PA nanocomposite as compared to the non-filled PP/PA blend. The reason behind it was the higher affinity of the polar-layered silicates (even after organophilic modification) to the more polar PA phase than to the PP phase.

Kim et al. [98] studied the morphology of (70/30 w/w) ABS/PP blend clay nanocomposites and showed that the size of the PP droplet was decreased with increased amount of clay in ABS matrix. The structure of PP changed from droplet to mixed droplet/elongated with the increase of the clay which can be explained by decreased viscosity ratio of the dispersed PP and continuous (ABS/clay) because of location of clay in ABS matrix.

Kelnar et al. [99] showed that presence of 5 wt% nanoclay in (90/10 w/w) PA6/PS blends resulted in a finer distribution of PS particles and better interfacial adhesion between the polymers.

Fang et al. [100] investigated the location of nanoclay in (80/20 w/w) and (20/80 w/w) poly(϶-caprolactone), (PCL)/poly(ethylene oxide), (PEO) blend and its effect on the compatibility of the components. They reported that when the blend based nanocomposites were prepared via a two-step process in which silicates were first premixed with PEO component or with PCL component, the silicate layers migrated from the PEO phase or PCL phase to the interface. A monotonic decrease of the PEO domain size in the (80/20) PCL/PEO blend was observed as a function of the organophilic clay content. Therefore a clear emulsifying effect was induced by the organophilic layered silicates in the immiscible PCL/PEO blend.

Tsai et al. [101] conducted an investigation over blending, rheological and tensile properties of poly(vinyl alcohol) (PVA) and nylon6-clay nanocomposite blends. They suggested that the presence of PVA in nylon6-clay can interfere, break the hydrogen bonded carbonyl groups originally present in nylon6-clay resins and even form new interactions between the carbonyl and hydroxyl groups as the weight ratio of nylon6/clay to PVA was increased.

Haponiuk et al. [102] studied the properties of polyamide 6 (PA6) and thermoplastic polyurethane (TPU) blends containing two type of modified montmorillonites, one was aromatically modified and the other was aliphatically modified. They showed that the addition of clay in a PA6/TPU blend caused exfoliated or intercalated structure depending upon the clay modifiers. In both cases improvement in thermal and tensile properties was estimated. The strengthening of the amorphous phase was represented by the increase of the dynamic storage modulus above the glass transition.

Naderi et al. [103] studied the morphological and rheological properties of thermoplastic elastomer nanocomposites using different viscosities of polypropylene (PP) and ethylene propylene diene monomer (EPDM) rubber content (20, 40, 60 wt%). The distribution state of the clay between the two phases (PP and EPDM) was found to depend on the viscosity ratio of PP to EPDM. In the nanocomposite based on low viscosity PP and EPDM, the clay was mostly dispersed into the PP phase and the size of the dispersed rubber particles decreased in comparison with unfilled blend. However, the dispersed elastomer droplet size in the high viscosity PP blends containing 40 and 60% EPDM increased with introduction of the clay.

Katti et al. [104] investigated the mechanism behind the enhancement of the physical properties of polymer-clay nanocomposites (PCN) in comparison to pure polymer. Their study revealed that the interactions between polymer, organic modifiers and intercalated clay are critical factors in controlling the crystallinity and the enhancement of nanomechanical properties of PCN. They showed that attractive interaction between functional groups of the polymer and modifier and simultaneous repulsive interactions between modifier and backbone of the polymer resulted in conformational changes in the polymer, which causes disruption of periodicity of polymer manifesting in changes in crystallinity of polymer in PCN. The higher the level of these disruptive interactions, the lower the crystallinity of the polymer in the PCN and the higher the nanomechanical properties.

Ozkoc et al. [105] studied the effects of microcompounding process parameters on the properties of (80/20 w/w) and (20/80 w/w) ABS/polyamide 6 blends based nanocomposites. They showed that the microcompounding conditions had a great influence on blend morphology. In the case of dispersed phase morphologies, the average size of the dispersed phase was smaller in nanocomposites processed with co-rotation rather than counter-rotation. For the nanocomposite based on (50/50/5 w/w) ABS/polyamide 6/clay, the co-continuous morphology in co-rotation mode was disturbed in counter-rotation yielding a mixture of nonspherical dispersed particles in co-continuous ABS/PA6.

Rodriguez et al. [106] showed that the number of tallow groups in the organic modifier influences nanoclay integration in PP-EP/EVA/nanoclay nanocomposites. Two hydrogenated tallows are better than one in promoting nanoclay exfoliation. Thermal degradation of the organic modifier during melt blending of the mixture was discarded as a potential cause of exfoliation. The introduction of the organoclay in the PP-EP/EVA system, under compatibility conditions, preserved the original domains type morphology. It was also determined that the silicate layers were hosted by the EVA domains.

Fang et al. [107] studied (80/20 w/w) PP/PS/clay composites and found that the clay plates located in the PS phase with the PS chains intercalated into clay layers. After introducing polar maleic anhydride group to PP chains, all the clays migrated from the PS phase to the modified PP phase.

Filippone et al. [108] studied the effect of organoclay on the morphology and properties of extruded (75/25 w/w) HDPE/PA6 blend and found that the filler exclusively located in the more hydrophilic polyamide phase during melt mixing. As a consequence a complex microstructure was formed with organoclay rich PA6 separated and elongated domains. Co-continuous morphology was achieved when the extrudate was re-melted.

Calcagno et al. [109] found the increment in the domain diameter of PET in the presence of clay in (70/30 w/w) PP/PET blend as the clay platelets are mostly intercalated in PET domain. They also reported that presence of PP-MA compatibilizer reduced the PET domain in the blend compared to that of uncompatibilized blend. They explained that the presence of compatibilizer molecules at the surface of the small domains prevents the coalescence of the domain during melt mixing. The morphology in presence of both clay and compatibilizer was more homogeneous, indicating a good interaction between the PP and PET phases promoted by the presence of PP-MA.

Kusmono et al. [110] investigated the compatibilizing effect of SEBS-g-MA on the mechanical properties of different types of organoclay filled (70/30 w/w) PA 6/ PP nanocomposites. They reported that the incorporation of SEBS-g-MA into PA6/PP/organoclay produced a more fine, uniform and stable phase morphology. They explained it by a strong interaction and adhesion between PA6, PP, and organoclay in the presence of compatibilizer. This may be attributed to the interfacial chemical reaction between the maleic anhydride groups of SEBS-g-MA and the amine terminal groups of PA6, leading to the formation of a SEBS-g-PA6 copolymer which contributes to decrease the interfacial tension and to enhance PP phase dispersion and interfacial adhesion between PA6 and PP.

Kelnar et al. [111] showed that on changing the composition of PA6/PS blend with different amount of clay content the morphology of the blend changed from particulate to co-continuous structure and the changed morphology also depended on the nature of modified clay.

The morphology and rheology of (60/40w/w) poly(phenylene sulfide) (PPS)/poly(butylenes terethalate), (PBT) blend nanocomposites were studied by Wu et al. [112]. Though the wt% of PBT was less, due to its lower viscosity, PBT was the continuous phase and the intercalated clay tactoids were selectively located in the continuous PBT phase due to high affinity. According to them, addition of a small amount of clay increased the discrete PPS domain size. With increasing clay loading, the PPS phase transformed to a fibrous structure, and finally to the partial lameller structure at the high clay loading, in which a large scale phase separation was visualized. The presence of clay, however, did not impede the coalescence of the PPS phase because phase size increased with increasing clay content.

Nataranjan et al. [113] examined the effect of clay on thermal and mechanical properties of the miscible poly(phenylene oxide)/polystyrene blend. Better dispersion of clay in the blend matrix was observed at a low level of clay content. The nanocomposites showed improved tensile modulus in comparison to the blend, whereas the tensile strength and elongation decreased in the presence of higher clay loading.

Gcwabaza et al. [114] showed that intercalation of both the PP and PBS chains into the same silicate layers at the interface and change in viscosity ratio of the polymers resulted in a homogeneous dispersion of PBS domains in (70/30 w/w) PP/poly(butylene succinate) (PBS) blends with various amount of clay (0.5-5 wt%).

Yu et al. [115] studied the effect of morphology and mechanical properties of PVC/ABS blends in presence of organoclay. They showed that the clay was preferentially located in the PVC phase and across the interface of PVC/ABS. The size of the ABS particles was decreased with an increase in clay content in the PVC/ABS/clay nanocomposites and the ABS particles were more uniformly dispersed in the PVC matrix.

Martins et al. [116] reported that in (60/40/5 w/w) of PP/EVA/organoclay blend, the particles of EVA phase were lamellar shape when the organoclay was dispersed in the EVA phase, and the impact strength was considerably higher than the neat blend. On the other hand, for the nanocomposite where the clay platelets were not well dispersed in the EVA phase, the impact strength was decreased relative to the neat blend.

Filippi et al. [117] studied the morphology of (75/25 w/w) LDPE/PA6 blends with and without SEBS-g-MA compatibilizer in the presence of organoclay. They reported that by optimization of compounding procedure and the use of an appropriate proportion of SEBS-g-MA and organoclay allow the preparation of composites with excellent morphology and a satisfactory balance of stiffness and toughness.

Kelnar et al. [118] proposed that addition of clay to (90/5/5 w/w) PA6/PS/elastomer (EPR or EMA) blend led to a decrease in domain size of the blend and the compatibilization action of clay enhanced the mechanical properties of the blend except the toughness, which was decreased with addition of clay.

As mentioned by Baghaei et al. [119], a reduction in the size of the elastomer phase occurred in (75/25 w/w) LDPE/POE blend in presence of clay. They explained the compatibilization action of the clay by two competing effects during melt processing. One is the viscosity effect due to an increase in clay content and the other is the barrier effect of the clay on the rubber particle coalescence. In the presence of both clay and PE-g-MA, which acted as an effective compatibilizer for clay dispersion, the clay layers were located both in the POE and LDPE phase and more exfoliation of clay in the blend lead to increment of mechanical properties compared to the LDPE/POE/clay nanocomposites.

Gallego et al. [120] studied the effect of montmorillonite (MMT) and compatibilizer quantities on stiffness and toughness of polyamide nanoblends. The main influence on the mechanical properties was achieved by controlling micro-structure of polymer blend. Addition of greater amounts of compatibilizer led to greater impact strength, because of the enhancement of the interaction between PA6 and EPDM-g-MA rubber. On the other hand, higher amounts of MMT, if a high exfoliation was achieved, promoted an improvement of all the properties related to the stiffness.

Joseph et al. [121] studied nanoclay filled ester-TPU/PP blends where maleic anhydride-g-PP was used as the compatibilizer. They showed that with substantial increment in modulus, tensile strength and other properties, organoclay functions as a surface modifier for TPU hard segments which improved the dispersion in the blend. They indicated that ester-TPU-organoclay/PP/MA-g-PP exhibited better dispersion than other blend systems.

Fillipone et al. [122] investigated the effect of small amounts of organically modified clay on the morphology and mechanical properties of blends of low density polyethylene and polyamide 11 at different compositions. They showed that most of the filler was located in the more hydrophilic PA 11 phase than the LDPE matrix phase. This strongly affected the micron-scale arrangement of the polymer phases, causing a drastic refinement of the micro structure and an enhancement of the interfacial adhesion. In addition to the expected reinforcing action of the filler, the resulting fine micro structure played an important role in improving the mechanical properties of the blends.

Yu et al. [123] investigated the effect of organoclay (OMMT) on the compatibility and properties of PA 66/PP blend. They showed that OMMT could play the role of compatibilizer in nylon66/PP blend prepared by melt compounding using nylon6/OMMT master batch as the source of OMMT. The size of the dispersed phase was dramatically reduced with only 3-5 wt% of OMMT, which was dispersed mostly (60 wt%) at the interface and in nylon phase. The compatibilization action of OMMT was explained by hydrogen bonding between OMMT and nylon66, nylon-g-PP and maleated polypropylene (MAPP). The increased compatibility in the presence of OMMT was also reflected by a significant increase in stiffness without sacrifice to toughness.

Somwangthanaroj et al. [124] studied the morphology and mechanical properties of polypropylene/nylon6/clay nanocomposites by varying the loading of PP-g-MA compatibilizer and organoclay (OMMT). The compatibilizer PP-MA was used to improve the adhesion between the phases of polymers and the dispersion of OMMT in the polymer matrix. The viscosity of the nanocomposites was increased with increasing OMMT loading due to the interaction between the clay platelets and polymer chains. The SEM and TEM study revealed that the clay platelets were located at the interface between PP and PA6.

The effect of organoclay on the morphology and properties of two HDPE/PA6 blends at opposite composition was investigated with varying the filler content by Filippone et al. [125]. Depending on whether PA6 represents the major or the minor blend constituent they noticed different effects of clay on the microstructure of the blends as the filler preferentially located in the more hydrophilic polyamide phase. When PA6 was the major phase, an abrupt reduction of the average size of the dispersed polyethylene phase was noticed even for low filler loadings. This finding was mainly ascribed to the inhibition of coalescence ensured by the platelet-like structure of the organoclay stacks, which acted as physical barriers that hindered the merging of colliding droplets during the melt mixing. When the filler was confined inside the minor constituent of the blend, two situations were observed:1) at low filler contents, the organoclay caused a gradual refinement of the morphology, which, however, remained globular; 2) for filler loading higher than a critical threshold, the filled polyamide assembled into a highly continuous structure finely interpenetrated with the major polyethylene phase. The filler content at which such a morphological transition occurred corresponded to that at which a rheological transition from a liquid-to gel-like behavior took place in the filled polyamide.

1.18 Objective of the Research Work

The objective of the present research was to study the role of nanoclay on the morphology and properties of various immiscible binary polymer blends and to determine the most suitable mechanism behind the compatibilization action of nanoclay in immiscible polymer blends. Thus, in the present investigation, efforts have been put forward to investigate the following major issues in polymer blend-clay system:

- Change in blend morphology depending on the location of the nanoclay at different phases in various immiscible polymer blends. The role of nanoclay on the morphology of a blend when the clay layers are selectively located in the matrix phase, dispersed phase and in both the phases of the blend.
- The effect of melt viscosity increment of the matrix polymer, in the presence of clay, on the morphology of the blends.
- The morphology of a blend that contains high viscosity polymer as the matrix phase and to compare the stability of the developed morphology against thermal annealing, both in absence and presence of nanoclay in the blend.
- Synergistic effect of nanoclay and polymeric compatibilizer on the morphology and properties of immiscible polymer blends.
- Mechanism behind the compatibilization effect of the nanoclay in immiscible polymer blends.

1.19 Structure of the Thesis

The thesis is organized into 9 chapters to report the whole research work with the objectives as outlined above.

Chapter 1 of the present thesis gives a general introduction of different types of polymer blends and different polymer clay nanocomposites systems. The thermodynamic of mixing in polymer blends and different factors affecting the miscibility of polymers in the blend with compatibilization action were discussed. An in-depth analysis on the effect of organoclay in the blend systems to improve the properties of the blend with change in the morphology of the blends has been reported. Finally the objective and plan of work of the present investigation have been mentioned.

Chapter 2 illustrates the materials details, experimental procedures for the preparation of different types of polymer blends and various characterisation methods for the analysis of different polymer blends and blend-clay nanocomposites systems.

Chapter 3 deals with the synergistic effect of nanoclay and EPR-g-MA on the properties of (70/30 w/w) nylon 6/EPR blend.

Chapter 4 discussed the effect of nanoclay on morphology and mechanical property of PMMA/HDPE blends**.**

Chapter 5 deals with the effects of nanoclay and SEBS-g-MA on the morphology and properties of (70/30 w/w) immiscible PMMA/polystyrene (PS) blends. Thermal, mechanical and thermo mechanical properties of the corresponding blend nanocomposite systems were also reported in this chapter.

Chapter 6 deals with the morphology and properties of nylon 6/HDPE blends without and with nanoclay or PE-g-MA.

Chapter 7 reports the synergistic effect of nanoclay and PE-g-MA on the morphology and properties of (80/20 w/w) nylon 6/HDPE, blend. The morphology of the blends containing organoclay with and without compatibilizer (PE-g-MA) was examined with SEM and XRD analysis.

Chapter 8 illustrates the effect of nanoclay on the morphology and properties of (70/30 w/w) nylon 6/PMMA blend. Mechanical properties and thermal stability of the blends were also investigated in presence of clay.

Chapter 9 gives the summary of the results and conclusion from the investigation.

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