# I. Introduction
and
Literature Survey

The general term "polyurethanes" is used to describe a broad class of polymers prepared by polyaddition polymerization between a di- or poly-isocyanate with compounds containing two or more acidic-hydrogen such as hydroxyl or amino groups [1-3]. The urethane group [-NHCO-O-] formed in these polyaddition reactions is a characteristic feature common to all polyurethanes. Other polymers such as poly(urethane-urea) are also referred to as polyurethanes because they contain some amount of urethane-groups. Polyurethane is a versatile polymeric material which can be tailored to meet the diversified demands of modern technologies such as coatings, plastics, fibers, artificial heart and blood vessels, foams, textiles, paints, rubber, elastomers and composites [4-7].

Isocyanates are very reactive and can be easily conversed into urethanes and urea [1, 3]. The high reactivity of isocyanates also leads to unwanted reactions with water or with urethane or urea groups to form allophonates and biurets respectively. Hence, moisture and stoichiometry of the reactants must be carefully controlled to prevent byproduct formation. For the sake of clarity, segmented polyurethane elastomers as depicted in **Figure 1** can be divided into two groups. The first group is characterized by the presence of urethane linkages in the hard segment, and the other is characterized by the presence of urea linkages in the soft segment. Segmented polyurethane elastomers with urea linkages in the hard segments are called segmented poly(urethane-urea) (SPUU). It has been shown that SPUU elastomers have superior mechanical properties compared to segmented polyurethanes. This is because the incorporation of urea linkages in the hard segments leads to stronger hydrogen bonds in the hard domains and enhanced phase separation [8 -12].
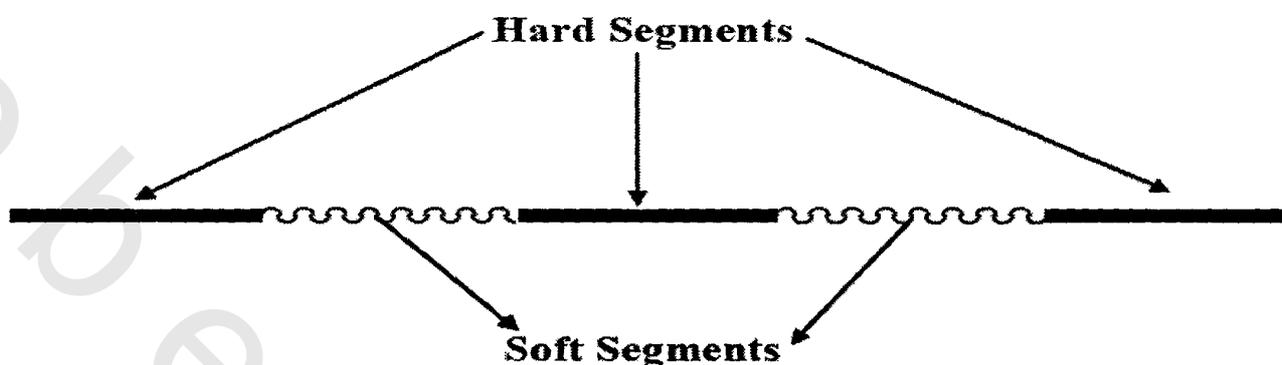
Figure 1: Schematic representation of segmented polyurethane.

1. Polyurethane Elastomer Chemistry

A list of representative polyaddition reactions in polyurethane formation is shown in **scheme 1** for synthesis of thermoplastic polyurethane elastomers, where crosslinking occurs by physical phase-separation of hard and soft domains, reactions **(1.1)** and **(1.2)** are desirable. The reaction path and hence the final product (urethane or urea) depends on whether a hydroxyl or amine curative is reacted with the isocyanate. Water's ubiquitous nature makes it difficult to suppress reaction **(1.4)**, and a small amount of water is usually present in commercially available solvents. The formation of allophonates and biurets at high temperatures (100 °C – 150 °C) and also at low temperatures in the presence of excess diisocyanate [1, 3], leads to chemical crosslinking in polyurethanes. Chemical crosslinks in the polyurethane network tend to prevent hard segment crystallization, increasing phase mixing and form a more homogenous network. These changes in the two-phase morphology of segmented polyurethanes lead to an increase in the soft segment glass transition temperature and a broadening of the glass transition region [12-16].
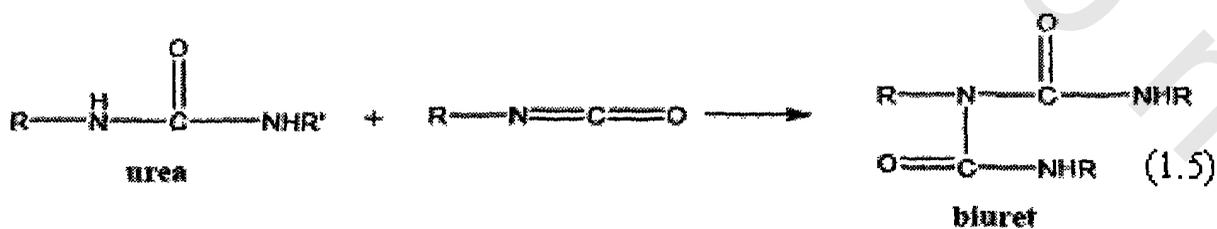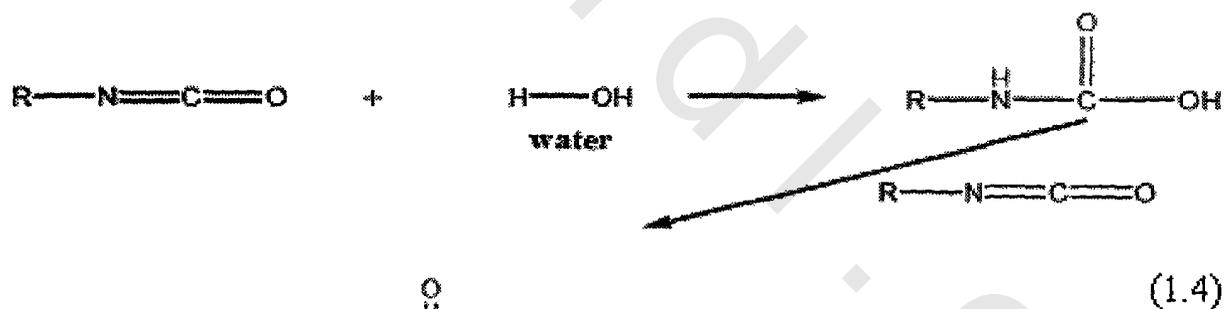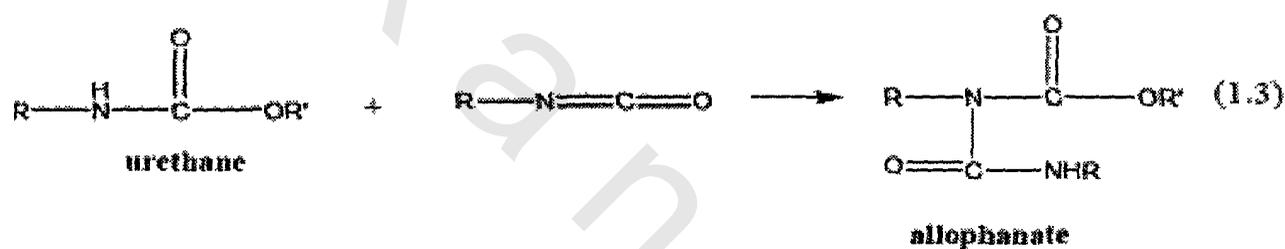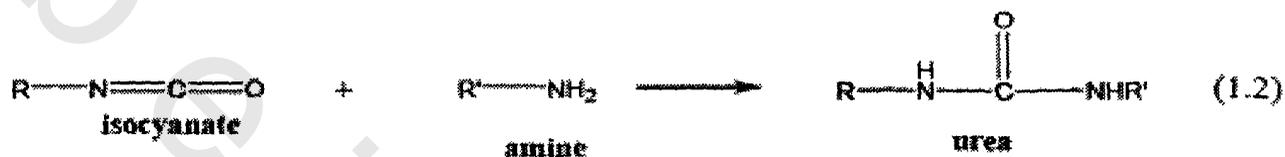
Scheme 1: polyaddition reactions in polyurethane formation

2.   Phase-Separation   and   Hydrogen   Bonding   in   Segmented   Polyurethanes.

As stated before, segmented polyurethanes are a two-phase system with alternating hard and soft phases. **Figure 2a** shows an ideally phase-separated polyurethane network. However, the network of most synthesized polyurethane materials is far from ideal. As shown in **Figure 2b**, polyurethane networks are marked by some degree of phase mixing, where in hard segments are found within soft segment domains and soft segments within hard segments domains. Hard segment lengths and distribution of lengths also vary within the polyurethane network. The mechanical properties of polyurethanes are strongly dependent on the kind and strength of hydrogen bonding within the hard segment, which influences the degree of phase mixing in polyurethanes. The perfection and degree of phase separation, which is reflected in the size and perfection of the domains has been studied
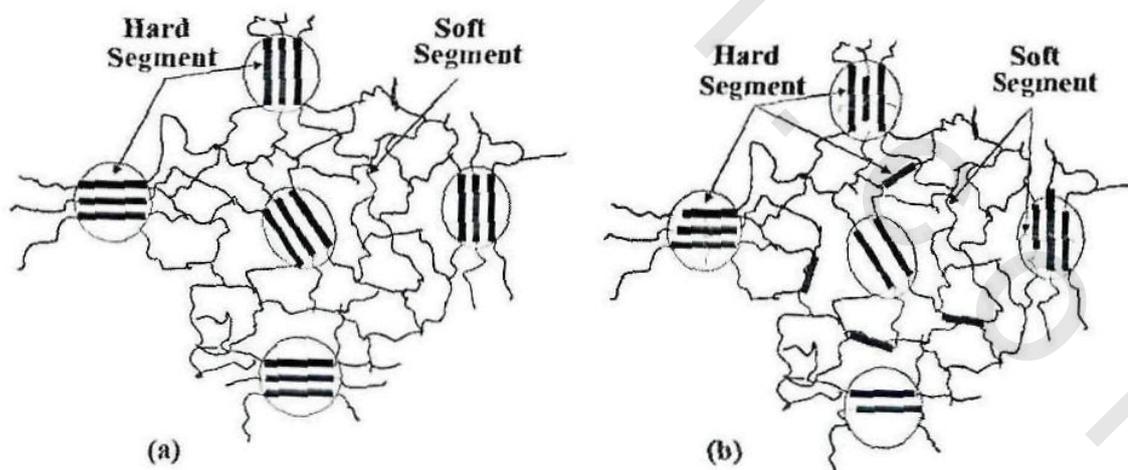
Figure 2: Schematic representation of the morphology of segmented polyurethane network: (a) ideally phase separated network, (b) mixed phase network.

successfully using FTIR, because of the existence of bands sensitive to mixed and phase separated states [1]. Polyurethanes and poly(urethane-urea) are capable of forming different kind of hydrogen-bonds. Invariably, the hydrogen bond donor is the hydrogen atom on the N-H group in the urethane or urea linkage. Potential hydrogen bond acceptors are: (1) the carbonyl oxygen in urethane or urea linkages, (2) adjacent ether oxygen or nitrogen in the urethane or urea linkages respectively, (3) carbonyl and adjacent oxygen atom when a polyester soft segment is used, and (4) ether oxygen when a polyether soft segment is used. Hydrogen-bonding in polyurethanes (**Figure 3**) and poly(urethane–urea) is manifested by shifts in the N-H and C=O stretching frequencies to lower values compared to non-hydrogen bonding N-H and C=O groups [11, 17]. The stretching frequency range for the N-H and C=O groups in polyurethanes and poly(urethane-urea) are ($3200 - 3500 \, cm^{-1}$ and $1600 - 1740 \, cm^{-1}$) respectively.

Figure 3: A representation of hydrogen bond formation in polyurethanes [1].

Quantitative analysis of the degree of H-bonding is usually conducted using peaks in the carbonyl region. This is because the carbonyl stretching vibration is sensitive to long-range order in the phases, and the peaks ('free' non-hydrogen bonded, ordered and disordered H-bonded) in this region can be differentiated easily [17].

3. Elastomers and Rubber Elasticity.

Polymeric elastomers exhibit rubber elastic properties and undergo reversible deformations provided the applied stress is less than the breaking stress. The rubber-elastic behavior of elastomers stems from the storage of elastic strain energy as chains are extended. The ultimate strength is related to the ability to dissipate energy via viscoelasticity, chain rupture, H-bonding, etc. Such behavior requires highly flexible, low glass transition (Tg) chains, i.e. low degree of intermolecular interactions, connected by physical or chemical crosslinks that prevent plastic flow by hindering sliding of chains against their neighbors [1, 18]. Segmented polyurethane and poly(urethane-urea) elastomers have crosslinked network in both physical and chemical properties, and can be explored to first order using the theory of rubber elasticity. Unlike natural rubber, segmented polyurethanes have hard domains that are not point crosslinks. The hard domains act as filler within the network and are also deformable, which complicate interpretation of experimental results.

4. Fracture of Elastomers.

Fracture can be defined as the mechanical rupture of a material under stress into two or more pieces. In a typical fracture process, only few molecules that cross the fracture plane are broken successively as the fracture

propagates across the specimen at a finite speed [19]. Fracture occurs because every solid body contains flaws and region of weakness, characterized by cuts, dirt particles or scratches, where the applied stress is greatly magnified and the flaw begins to grow as a crack.

Elastomers are viscoelastic and have the ability to store strain energy in the form of decreased chain conformational entropy and dissipate energy via local viscoelastic chain motion, chain alignment, chain rupture, strain-induced crystallization, H- bonding, and cavitation of hard fillers. The design of optimally strengthened elastomers involves increasing energy dissipation and prolonging chain rupture. During crack propagation, new surface area is created at the crack location, which increases the surface free energy of the system.

5. Nanocomposite Materials.

Polymer composites are widely used in a variety of applications involving construction, transportation, electronics, and consumer products. The properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the dispersed phase. In recent years, polymer-clay nanocomposites have drawn great interest form both the industry and academic views because they often exhibit remarkable improvements in materials properties at very low clay loading (up to 10 wt. %) when compared to pristine polymer or composites with macro-dispersed phase [20-23]. Nanocomposites constitute a new class of material having nano-scale dispersion, typically 1-100 nm, of the dispersed phase in a given matrix [24, 25]. The outstanding reinforcement of nanocomposites is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase (e.g. 750 m^2/g). The nanolayers have much higher aspect

ratio than typical microscopic aggregates [26-28]. Mineral clays that can be dispersed as silicate nanolayers of high aspect ratio are attractive for polymer reinforcements.

Polymer-clay nanocomposites have shown drastically enhancements in mechanical properties (modulus and strength) [29-32], thermal properties (heat resistance and flammability) [25, 33], barrier properties [34-40], and biodegradability [41, 42] of the pure polymer. The colloidal state and the surface chemistry of the silicate layers in the polymer matrix play important roles in the synthesis of polymer-clay nanocomposites.

Electrostatic forces maintain the clay layers together forming face-to-face stacks in agglomerate tactoids which complicate their dispersion in polymers [43]. Also, the incompatibility between the hydrophilic clay and the hydrophobic polymer hinders nanoscale dispersion of the clay. In order to achieve a high degree of dispersion, the silicate layers can be functionalized by attaching of organic molecules such as surfactants to diminish the surface forces contributing to layer-stacking. Intercalation of organic molecules modifies the hydrophilic surface of the clay layers into hydrophobic, raising the level of compatibility between the clay and the polymer. Intercalation can be achieved in the clay interlayers by ion exchange of cations loosely held by the negatively charged layers. Polar organic molecules replace these cations rendering the clay organophilic.

The fast growing of research in polymer-clay nanocomposites has already developed some products that are being used commercially for certain applications such as automotive with nylon nanocomposites (the most utilized system) in timing belt cover for automobiles [44], and in packaging film [45].

5.1. Clay Structure and Cation Exchange with Surfactants

Clay minerals consist of a group of hydrous layered magnesium- and aluminosilicates (phyllosilicates). Each phyllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designated O and T, respectively [27-28, 43, 46]. In the tetrahedron, Si^{+4} is surrounded by four O^{-2} in the corners; three of the four oxygens are simultaneously attached to adjacent tetrahedrons. These connecting oxygen atoms are arranged in-plane so as to create a net of surfaces with six tetrahedrons arranged in rings. The tetrahedral layers are interlinked at their vertices by metal ions such as Al^{3+} and Mg^{2+}. The connecting cations are arranged in octahedral coordination, with free valences saturated by O^{-2} and/or OH^- ions. The tetrahedral and octahedral sheets can be stacked on top of each other to form two basic types of clay structure: TO or TOT. Kaolinite is the most common mineral of the non-expanding TO type group. In the kaolinite clay layer, oxygens located at the apices of the silicate tetrahedra of the tetrahedral sheet and hydroxyls of one of the two OH planes of the octahedral sheet are condensed, forming a single plane common to both sheets. In the other basic clay structure, TOT, four main groups can be distinguished: talc-pyrophyllite, smectite (montmorillonite), vermiculite, and illite. Only smectite and vermiculites are expanding type clays.

The most commonly used layered silicates for the preparation of polymer-clay nanocomposites belong to the TOT family, in particular montmorillonite (MMT), are shown in **Figure 4.** The layer thickness is around 1 nm, and the lateral dimensions of these layers can vary from 100 nm to several microns. Stacking of the layers leads to a regular van der Waals gap between the layers called interlayer or gallery. The isomorphic substitution within the layers (i.e. Al^{3+} in the aluminate sheet with Mg^{2+})

generates negatively charged layers, which are then balanced by alkali and alkaline earth cations (Na^+, K^+, Ca^{2+}) to maintain charge neutrality [27]. These cations are arranged in between the parallel-superimposed layers. One particular characteristic of these silicate layers is a moderate surface charge known as cation exchange capacity (CEC), generally expressed as mEq/100 g. This charge is not locally constant; it varies from layer to layer, and must be considered as an average value over the whole crystal [23].
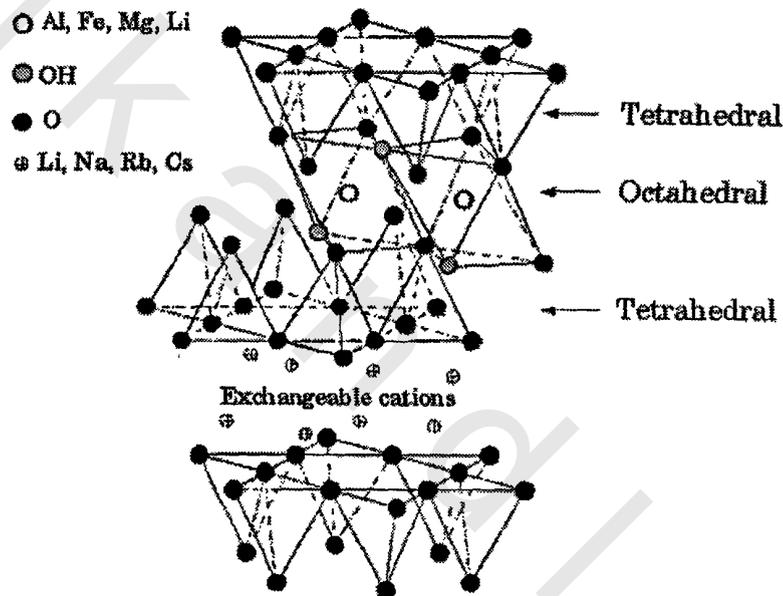
Figure 4: Structure of 2:1phyllosilicates

Montmorillonite is originally hydrophilic and must be converted to hydrophobic or organophilic nature in order to make it compatible with polymer matrices. Normally, this can be done via ion exchange of the inorganic cations for organic ones such as from surfactants and polyelectrolytes. Ion exchange reactions depend on the CEC of the clay. The organic cations lower the surface energy, and improve the wetting and intercalation of the polymer matrix, resulting in a larger interlayer spacing. Additionally, the organic cations may provide functional groups that can

react with monomer or polymer to enhance interfacial adhesion between the clay nanolayers and polymer matrix [22, 47].
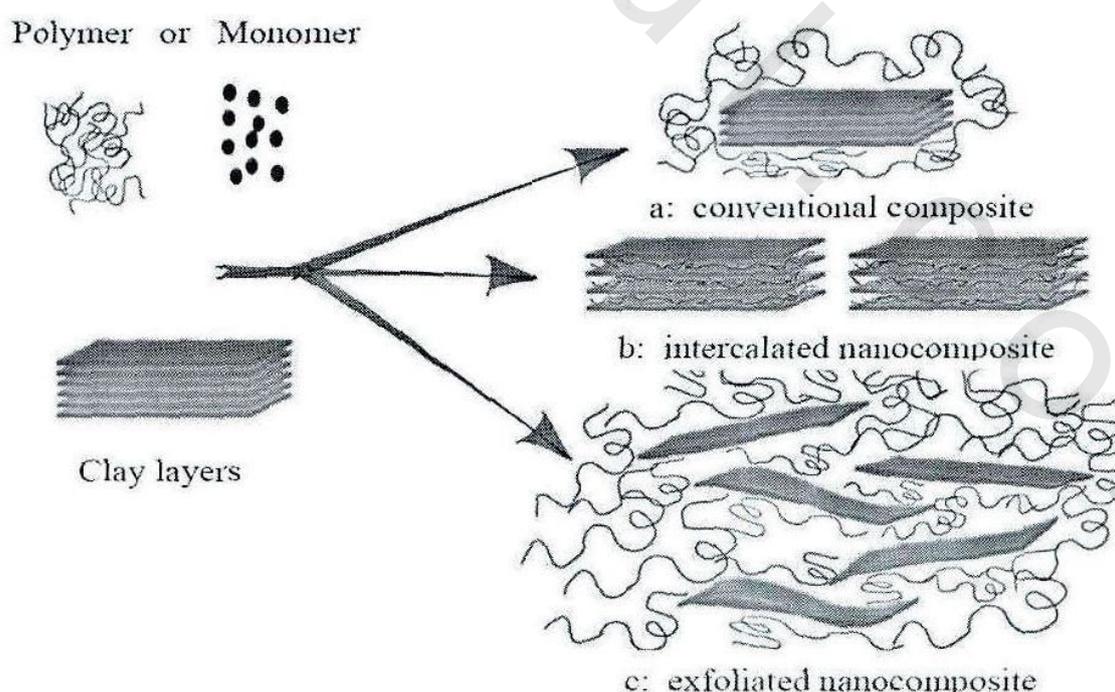
Extensive research has been devoted to the understanding of ion exchange and adsorption of surfactant molecules into the clay surface and gallery since organoclays are used in many industrial applications (i.e. thickeners in paints, oil-based glue, grease and cosmetic products) [27, 48]. The negatively charged clay layers attract the organic cations primarily by electrostatic forces. In addition, van der Waals forces act between the flat oxygen planes and the organic species located in the interlayers. With increasing the size of the adsorbed organic cation, there is an increase in the sorption energy as the van der Waals contribution to the adsorption process becomes more significant [27]. Due to the increase in the van der Waals interactions, montmorillonites have high affinity towards long chain organic cations. Many surfactants including primary, secondary, tertiary and quaternary alkylammonium cations are water soluble, and most cation exchange reactions are performed in aqueous suspensions. Another point about the surfactant adsorption onto the clay layers is that it is not controlled by the critical micelle concentration (CMC) of the surfactant solution [49].

Several characterization techniques such as adsorption isotherm and precise calorimetry can be used to determine the type of adsorption and quantify the interactions between cationic surfactants and clay [50]. In addition, x-ray diffraction determines the increase of the gallery spacing in the clay due to surfactant intercalation, which has prompted speculations about the orientation and arrangement of surfactant in the interlayer. The type of clay and alkyl chain length of the surfactant affect the amount and the enthalpy of adsorption (exothermic) as well as the surfactant arrangement

inside the gallery: either parallel or tilted, as monolayer, bi-layer, or triple layer.

5.2. Polymer-Clay Nanocomposites Structure.

This new class of material involves nano-scale dispersion of dispersed phase in a polymer matrix, which leads to improved properties over regular composites. The complete dispersion or exfoliation of the clay layers in the monomer or polymer may comprise up to three steps similar to dispersion of powders in liquid, described by Parfitt [51]. The first step is wetting the surface of clay tactoids by monomer or polymer molecules. Secondly, intercalation or infiltration of the monomer or polymer takes place, followed by the third step, exfoliation of the clay layers. Thermodynamics controls the first and second steps, while mechanical and reaction driving forces determine the extent of the third step.

Polymer or Monomer

a: conventional composite

b: intercalated nanocomposite

Clay layers

c: exfoliated nanocomposite

Figure 5. Schematic illustration of three types of polymer nanocomposites [22]

Depending on the strength of interfacial interactions between the polymer matrix and the silicate layers, three types of polymer composites may be formed as shown in **Figure 5.** In conventional composites, the clay tactoids exist in their original aggregated state with nanolayers stacked face to face and without any polymer intercalation, which results in poor mechanical properties. In the case of intercalated polymer-clay nanocomposite few molecular layers of polymer penetrate the clay host galleries increasing the d-spacing. Finally, exfoliated polymer-clay nanocomposites contain individual nanolayers separated in a continuous polymer matrix by an average distance which depends on the clay loading. Usually, the clay content of an exfoliated nanocomposite is lower than that of an intercalated nanocomposite. Exfoliation is more appealing for enhancement of certain properties of the material because of the high degree of dispersion and maximum interfacial area between polymer and clay [52].

5.3. Synthesis of Polymer-Clay Nanocomposites.

Polymer-clay nanocomposites can be synthesized via four approaches depending on the starting materials and the synthesis techniques [22]. The first approach is via *in situ* polymerization which consists of swelling the organophilic clay layers in the presence of liquid monomer followed by polymerization. It can be initiated by either heat or radiation, by diffusion of an appropriate initiator, or by a catalyst attached inside the clay via ion exchange. The ability of the small monomer molecules to intercalate in the nanolayers for polymer formation to occur makes this technique very successful in achieving fully exfoliated layers. The disadvantage is the limitation of polymers/monomers that can intercalate directly into the clay gallery.

Emulsion polymerization is another method where the layered silicate is dispersed in an aqueous phase in the presence of a surfactant. The surfactant is not necessarily cationic; it can be anionic or zwitterionic. The monomer is added to the solution and adsorbs onto the clay layers. The advantage is the fact that the clay is modified in the same solution where polymerization occurs rather than functionalizing the clay in a separate stage as done for in-situ polymerization. The third type of synthesis involves dissolving a polymer in a solvent, mixing with organoclay-solvent dispersion where the polymer will displace the solvent and intercalate within the interlayer. The solvent is finally removed, yielding the nanocomposite. The fourth technique, melt intercalation, is more industrially favorable due to its ease of implementation and production, but results in a loss of control over the molecular weight of the final polymer [53]. This method consists of annealing, statically or under shear, a mixture of polymer and treated clay at a temperature above the glass transition or melting temperature of the polymer. A majority of nanocomposites can be synthesized with this approach.

6. Examples of Polymer Clay Nanocomposites.

Nanocomposite technology has reached a variety of polymers systems that can be mixed with layered silicates. This section will focus on the different synthesis and properties of certain nanocomposites such as Nylon 6, polystyrene (PS), epoxy, polypropylene (PP), polyimide, and poly(methyl methacrylate) (PMMA).

6.1. Nylon 6-Clay Nanocomposites

Toyota research group was the pioneer in polymer nanocomposites by synthesizing nylon-6-clay nanocomposite via *in-situ* polymerization of

ε-caprolactam in the clay interlayers [20, 29, 54]. Montmorillonite was modified with ω-amino acids [$H_3N^+(CH_2)_{n-1}COO^-$] and it was demonstrated that the surfactant chain length affected the final morphology of the nanocomposite. The protonated alkylammonium cations catalyzed the intragallery ring-opening polymerization of caprolactam, providing a driving force for exfoliation of the nanolayers. For the system using 12-aminolauric acid, transmission electron microscopy (TEM) and x-ray diffraction (XRD) revealed complete delamination of individual clay layers homogenously dispersed in the matrix. Mechanical properties showed significant improvements with the addition of only 4.2 wt. % of modified MMT. These exfoliated nanocomposites demonstrated also significant increase in dimensional stability and barrier property [55].

The enhancement in properties of nanocomposites led to further researcher from other groups in the polymerization of caprolactam or different techniques to make nylon-6-clay. Messermith and Giannelis [36] polymerized ε-caprolactam inside clay gallery modified by protonated aminolauric acid at high temperature. The exfoliated nanocomposite containing 4.8% silicate by volume showed a reduction in water vapor permeability of almost an order of magnitude over pure poly(ε-caprolactam) [36]. Cho and Paul [56,57] prepared nylon- 6-clay nanocomposites via direct melt compounding using a twin screw extruder. The mechanical properties and morphology of these nanocomposites were similar to the ones prepared by *in situ* polymerization.

6.2. Polystyrene-Clay Nanocomposites

Polystyrene (PS) is one of the most researched nanocomposite systems, being synthesized via *in-situ* and emulsion polymerization, and by

melt intercalation. There are several literature papers on polystyrene nanocomposites from different research groups. Akelah and Moet [58] synthesized intercalated nanocomposites by using MMT modified via cation exchange with a polymerizable surfactant, vinylbenzyl-trimethyl ammonium chloride. Styrene was *in-situ* polymerized in the presence of a solvent to facilitate intercalation. Do and Cho [59] also synthesized intercalated PS nanocomposite but without the use of solvent. By functionalizing MMT with different surfactants that contained tetraalkylammonium cations, the modified clay was directly dispersed in styrene followed by polymerization. These intercalated polystyrene nanocomposites exhibited enhanced thermal properties than pure polystyrene. Similar results were also reported by Weimer et al. [60].

Exfoliated PS-clay nanocomposite was synthesized by Fu and Qutubuddin via *in situ* polymerization of styrene with a reactive organoclay [30, 52]. MMT was functionalized with a polymerizable cationic surfactant vinylbenzyldimethyldodecylamonium hydrochloride (VDAC). The storage modulus of the nanocomposite was higher depending on the clay loading when compared to pure PS. In addition, both intercalated and exfoliated structures were observed for PS-clay nanocomposite synthesized via melt intercalation [24, 61-63], while emulsion polymerization produced only intercalated hybrid [64].

6.3. Epoxy Resin-Clay Nanocomposites

Several research groups have also studied the use of clay with epoxy resin. The studies revealed clay intercalation as well as exfoliation, and were focused on the use of diglycidylether of bisphenol A [EPON-828] as epoxy resin. The composites were synthesized via *in-situ* technique. Kelly et al

[65, 66] has synthesized epoxy resin cured in the presence of organophilic montmorillonite (OMMT) and intercalation was observed due to high interlayer spacing verified by both XRD and TEM. Several OMMTs were prepared from different surfactants, such as tyramine hydrochloride, aminolauric acid, and a polyamide curing agent. XRD data indicated that generally the intercalated d-spacing was around 1.3-1.4 nm, and an extreme case had a 4.2 nm increase in the basal spacing. MMT modified with tyramine provided the best performance with the epoxy. Also, the addition of epoxyphilic polyamide-MMT reduced residual stress the most, approximately 50-60%. Dynamic scanning calorimeter (DSC) measurements showed that the Tg were higher than for the pure resin. It was clearly illustrated that the functional group used to modify clay significantly influences the behavior of the nanocomposite.

Exfoliated nanocomposites were also synthesized using modified clay layers in the epoxy matrix. Pinnavaia's research group synthesized composites using EPON-828 with H^+, NH_4^+, H_3^+N $(CH_2)_{n-1}CH_3$, $H_3^+N(CH_2)_{n-1}COOH$, $H_3^+N(CH2)_nNH_2$, and $H_3^+N(CH_2)_n^+NH_3$ exchanged forms of MMT, where n = 6 and 12 [21,67,68]. XRD and TEM confirmed the delamination of the clay layers in the polymerized epoxy resin. A 5 wt. % of MMT-$O^-H_3N^+$ (CH_2) $_{n-1}COOH$ -polyether nanocomposite revealed that the interlayer spacing ranged up to 200 nm.

Longer linear alkyl chain lengths benefited gallery accessibility and facilitated the formation of nanocomposite. The mechanism of exfoliation was dependant on the accessibility of the epoxy and its curing agent to the clay galleries and on the relative rates of intra- and extra gallery network formation. In the $CH_3(CH_2)_{17}N^+H_3$-MMT /EPON-828 system, more than a 10-fold increase in tensile strength (8 MPa) and tensile modulus (25 MPa)

was obtained by addition of only 15 wt.% of organophilic MMT. This was due to the fact that the rubbery epoxy allows the silicate particles to align to best resist the applied stress. Messersmith and Giannelis [25] maximized the interfacial adhesion between the epoxy and the silicate layers leading to exfoliated nanocomposites with enhanced mechanical properties.

6.4. Polypropylene-Clay Nanocomposites

One of the most used polyolefins in the industry is polypropylene. One obstacle for synthesizing nanocomposites in this system is the thermodynamic incompatibility between PP and organoclay since PP does not contain any polar groups in its backbone [69-71]. However, Toyota research group developed PP-clay hybrid by using simple melt mixing of three components: PP, maleic anhydride modified propylene oligomers (PPMA), and clay intercalated with stearylammonium cation. XRD and TEM indicated that both intercalated and exfoliated composites were produced, depending on the type of maleic anhydride groups used: intercalated for PP-MA (acid value = 52 mmol of KOH/g) and exfoliated for PP-MA (acid value = 26 mmol of KOH/g). It was concluded that two factors influence the exfoliation and homogenous dispersion of the layers in the hybrid: (i) the intercalation capability of the oligomers in the layers, and (ii) the miscibility of the oligomers with PP. In terms of improved properties, PP-clay hybrids exhibited higher storage moduli compared to that of PP especially in the temperature range from Tg, which is 13°C, to 90°C.

6.5. Polyimide-Clay Nanocomposites

Polyimide-clay nanocomposites have demonstrated a great improvement in barrier properties with very small clay content. The

nanocomposites were synthesized from polymer solution: 4,4'-diaminodiphenyl ether and pyromellitic dianhydride were polymerized in dimethylacetamide (DMAC) solvent, followed by mixing of the poly(amic acid) solution with organoclay dispersed in DMAC [34, 38]. Clays with different aspect ratios were used (hectorite 46, saponite 165, montmorillonite 218 and synthetic mica 1230 [38]. XRD and TEM indicated primarily exfoliated nanocomposites with mica and MMT, while monolayer intercalation was observed with hectorite and saponite. The permeability of several small gases such as O_2, H_2O, and He, decreased tremendously with clay content. For instance, with 2.0 wt. % of mica, the water vapor permeability decreased to less than one tenth of that of unfilled polyimide. Lan et al. [35] used a similar procedure to prepare polyimide nanocomposite MMT modified with octadecylamine but obtained only intercalated hybrid. Still, the CO_2 permeability decreased significantly by 80% with 7% volume fraction of clay. Such a decrease was justified by a staircase alignment of the flakes, which can provide high tortuosity for the diffusing gas.

6.6. Poly(methyl methacrylate)-Clay Nanocomposites

The synthesis of PMMA-clay nanocomposite has been reported recently using a variety of surfactants, dispersion techniques and polymerization conditions [72-79]. Lee and Jang [72] were the first to report synthesis of PMMA nanocomposite via emulsion polymerization, which was carried out at 70°C for 12 hours. Their results, using an anionic surfactant, sodium dodecyl sulfate (SDS), indicated an intercalated hybrid. Bandyopadhyay et al. [75, 76] synthesized PMMA nanocomposite via emulsion polymerization at 80°C with SDS as the emulsifier and 5 wt. % of MMT. The nanocomposites were well dispersed and showed enhanced

thermal stability, an increase in Tg by 6°C, and slightly higher molecular weight than pure PMMA.

Akelah and Doh [58, 59] developed PMMA nanocomposite using 5 wt. % of MMT and a polymerizable surfactant, [2-(methacryloyloxy)ethyl] trimethylammonium chloride, via emulsion polymerization at 80°C for 12 hours. The morphology appeared to be exfoliated by XRD but no TEM evidence was presented. Thermal degradation for 20 wt.% loss was enhanced significantly up to 341°C, Tg increased by 15°C over the pure polymer, and molecular weight increased to 565,000 for the nanocomposite.

Meneghetti and Qutubuddin [80, 81] synthesized PMMA-clay nanocomposites via both *in situ* and emulsion polymerization techniques with MMT and a zwitterionic surfactant, octadecyl dimethyl betaine (C18DMB). Partial exfoliation was achieved with significant improvement in Tg by 18°C for the emulsion product over pure PMMA [81]. Intercalated nanocomposite from *in situ* polymerization had a Tg 10 °C lower than the emulsion product. The storage modulus of partially exfoliated nanocomposite was superior to the intercalated structure at higher temperatures and to the pure polymer. The rubbery plateau modulus was over 30 times higher for the emulsion product versus pure PMMA. Emulsion technique produced nanocomposites of highest molecular weight (930,000) with bimodal distribution reported in the literature.

6.7. Rubber Clay Nanocomposites [82-89].

The field of nanocomposites has extended to elastomeric matrices, particularly, for potential applications where enhanced barrier properties are desired. Styrenebutadiene rubber (SBR) is a commodity elastomer due to its high volume production and its low market price. SBR-clay nanocomposites

have synthesized, in most cases, by mixing the organoclay in an industrial mixer (2-roll mill and/or Brabender mixer) followed by vulcanization. Mousa and Karger-Kocsis [82] reported an increase in tensile strength by 5 times with 10 phr (parts per hundred rubber) of clay content. Ganter et al. [85,86] prepared intercalated and partially exfoliated SBR-clay nanocomposites with 30 phr organoclay as verified by TEM. The authors also prepared samples using solvent, where the organoclay is dispersrsed in toluene, and mixed with a toluene-rubber solution for 24 hours followed by solvent removal. Solvent mixed systems demonstrated higher clay dispersion. The results of SBR-clay nanocomposites [85] showed the tensile strength and strain and also for precipitated silica (3370) filled systems; organoclay system demonstrated higher strength than silica.

6.8. Polyurethane Clay Nanocomposites

Since early 90's, Toyota researchers demonstrated the enhancement of mechanical and thermal properties of Nylon 6 by dispersing nanometer size clay particles in the polymer matrix [90-93], many polymer/silicate nanocomposite systems [94, 95] have been investigated, including polyurethane [96-98] and poly(urethane-urea) [99] nanocomposite systems.

The improvement of polyurethane properties can be achieved by; varying its microstructure, mixing with another polymer or inorganic reinforcement.

Poly(ε-caprolactone)-based nanocomposite synthesis has been recently applied by Chen et al. [100] to produce novel segmented polyurethane/clay nanocomposites articulated on diphenylmethane diisocyanate, butanediol and preformed poly(caprolactone diol). Even if the mechanism proposed for the chemical link between the nanofiller surface and

the polymer does not appear appropriate (ammonium salts are not known to induce ε-caprolactone ring-opening polymerization), they succeeded in producing a material where the nanoclay acts as a multifunctional chain extender inducing the formation of star-shaped segmented polyurethane.

A common an approach for PUI phenolic resin composites is to use the reaction between the NCO group in the PU prepolymer and the OH group in the phenolic resin, forming a crosslinked polymer or interpenetrating network [101, 102]. However, traditional phenolic resins are also associated with some short comings, such as the use of phenols and the strong acids as catalysts, and the release of formaldehyde and ammonia during the curing process, which creates serious threats to environment and human health. To overcome the disadvantages of traditional phenolic resins, polybenzoxazines were used with their unique advantages like near-zero shrinkage upon polymerization, no need of using a strong acid catalyst. The combination of good thermal stability and high mechanical properties were used for forming a blend with PU by blending the PU prepolymer with benzoxazine monomer [103].

Also the synthesis and properties studies of caster oil based PU/PMMA interpenetrating polymer networks (IPNs) with ratio/fiber nanocomposites were studies by Cunha, F et al [104]. A series of castor oil PU/PMMA (IPNs) cured at room temperature were synthesized by simultaneous method. Component analysis and viewing results of morphology and miscibility among the multi phases of materials obtained by TEM indicate that systems belong to graft mode IPNs and domains between two phases are controlled in the nanometer scale rang.

Acrylate-modified polyurethane (PU) resin was used and then interpenetrated with unsaturated polyester resin (UPR), to form

interpenetrating polymer networks (IPNs) and gradient IPNs cured at room temperature. Results of the morphology and miscibility of the multi-phase materials, obtained by TEM, indicate that the domains in these systems were constricted to the nanometer range. Mechanical properties showed that the IPNs obtained exhibit different types of characteristics varying from elastomer to brittle plastics [105].

Solarski, S, et al. [106] studied nanocomposites in textile applications, and in particular of polyurethane (PU) coatings reinforced by various additives [clay and polyhedral oligomeric silsesquioxane (POSS)]. For cloisite 30B (a montmorillonite organo-modified by an alkyl ammonium cation bearing two primary hydroxyl functions): the thermal behavior and the reaction to fire were improved, but the structure (microcomposite, exfoliated, intercalated) was not really determined. The TEM observations revealed an intercalated structure. The TG results showed an improvement in the thermal stability, particularly at the start of the degradation (an increase of 35°C was observed), in spite of the small amount of Cloisite 30B used (5 wt %).

Sreedhar et al. [107] investigate PU nanocomposites: Organophilic montmorillonite co-treated by cetyl trimethyl ammonium bromide (CTAB) was synthesized and used to prepare PUU/ montmorillonite nanocomposites coatings. PUUs were prepared from poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), trimethylol propane (TMP), and 4,4'-diphenylmethane diisocyanate (MDI) by reacting excess diisocyanate with polyether glycols. The excess isocyanate of the prepolymers was cured with atmospheric moisture. The thermal stability of the PUU nanocomposites was higher relative to the mother PU-urea films. DSC results showed a slight enhancement in the soft segment glass transition temperature after 3 wt % clay loading. The surface properties showed an

enrichment of the soft segment toward the surface. An enhancement in the hard segment composition in the nanocomposite coatings has resulted in enhancing the phase mixing process.

A novel elastomeric polyurethane (EPU)/organic montmorillonite (OMMT) nanocomposite has been synthesized [108]. 18- Alkane-3 methyl-ammonium chloride and dihydroxethyl-12-alkane-3-methyl-ammonium chloride were used as intercalation agents to treat sodium-montmorillonite and for forming two kinds of OMMTs. Three types of EPU/OMMT nanocomposites were synthesized by in situ polymerization of EPU, with different amounts of OMMT. A combination of FTIR, WAXRD, and transmission electronic microscopy (TEM) studies showed that EPU/ OMMT composites were on the nanometer scale and the segmented structure of EPU was hindered by the presence of the OMMT, due to the reaction between toluene diisocyanate (TDI) and the intercalation agents. Results showed that the EPU/3% OMMT had the best physical and mechanical properties because of its uniform dispersion of the organic silicate layers.

Silicon dioxide nanocomposites of polyurethane and epoxy resin interpenetrating network were prepared by adding nanosilica to interpenetrating polymer networks (IPN)s of polyurethane and epoxy resin (PU/EP). The nanocomposites were studied and the results showed that adding nanosize silicon dioxide could improve the properties of compatibility, damping, and phase structure of IPN matrices [109-113]. Polyurethane/clay and polyurethane/polyhedral oligomeric silsesquioxanes (POSS) were prepared and used in coating of cotton and polyester fabrics which showed a good fire retardant [114, 115]. Novel polyether polyurethane/clay nanocomposites were synthesized with organic-modified montmorillonite (OMMT) as chain extenders where Na^+O-MMT was treated

with 1,6-hexamethylenediamine as swelling agent to replace a part of the extender to form PU/clay, nanocomposites. Mechanical analysis indicated that, the strength and strain at break of the polymer were enhanced with increased content of O-MMT in the matrix [116-119].

Silicon dioxide/polyurethane nanocomposites by sol gel process were studied by Yang - Zhu and Duo - Xian –Sun [120]. Aqueous emulsions of cationic polyurethane ionomers, based on ploy(ε-caprolactone glycol) as soft segment, isophorone diisocyanate as hard segment, 3-dimethylamino-1,2-propanediol as chain extender and potential ionic center, and hydrochloric acid as neutralizer, were mixed with tetraethoxysilane to prepare silicon dioxide polyurethane (SiO_2/PU) nanocomposites by sol-gel process during which the inorganic mineral was deposited in-situ in the organic polymer matrix.

Also polyurethane-clay nanocomposites via bulk polymerization methods were studied [121-123]. In this study, polyurethane/nanocomposites of organically modified clay were synthesized by bulk polymerization methods. The polymerization methods took into account the possibility of the formation of clay tethered polymeric chains via reactions between isocyanate groups in the chains of prepolymer and chain extended polymers with the hydroxyl groups on organic modifier of clay. The thermal and mechanical properties of the resultant materials were evaluated as function of the method of nanocomposites preparation. As high as 110% increase in modulus and 170% increase in tensile strength were observed with only 5 wt % organically treated clay particles. The method based on chain-extended polymers performed better than the method based on prepolymer. Also polyurethane adhesive nanocomposites as gas permeation barrier were investigated by Osman et al and Jin et al [124, 125]. Adhesive

nanocomposites of organically modified montmorillonite (OMMT) and polyurethane have been synthesized and their permeability to oxygen and water vapor has been measured. The gas permeability through the composites was correlated to the volume fraction of the impermeable inorganic part of the OMMT. The incorporation of small volume fractions of the plate like nanoparticles in the polymer matrix decreased the gas transmission rate, when the interface between the two heterogenous phases was properly designed. Polyurethane/benzoxazine blend PU/Pa was modified with organophilic montmorillonite (OMMT) to enhance the mechanical properties such as tensile modulus and strength, also thermal stability were enhanced and exhibited excellent resistance to the solvent [126]. Thermal and mechanical properties of polyurethane/montmorillonite nanocomposites based on a novel reactive modifier were prepared by Xiong. J. et al [127], in which polyurethane/ montmorillonite (PU/MMT) nanocomposites based on thermally stable, aromatic amine modifier containing active groups (methylene bisorthochloroanilline, MOCA) were synthesized by intercalative polymerization. The cured hybrid exhibited higher thermal stability and better mechanical strength than pure polyurethane or polyurethane/cetyltrimethylammonium bromide (CTAB)-modified MMT. Song- M et al [128] prepared high performance nanocomposites comprising a polyurethane elastomer (PUE) and an organically modified layered silicate. These nanocomposites are based on poly(propylene glycol), 4, 4-methylene bis(cyclohexyl isocyanate), 1,4-butandiol, and organically modified montmorillonite. The tensile strength and strain at break for these novel PUE nanocomposites increased more than 150% but the hardness remains on unchanged effect of organophilic montmorillonite.

Polyurethane/montmorillonite nanocomposites were investigated by Han-Bing and et al [129]. Different kinds of organophilic montmorillonite treated with cetyltrimethylammonium bromide (CTAB) and aminoundecanoic acid were synthesized and used to obtain polyurethane/montmorillonite nanocomposites via solution intercalation. The tensile properties of montmorillonite polyurethane (PU) nanocomposites were enhanced relative to PU matrix.

Thermal properties of rectorite/thermoplastic polyurethane nanocomposities were studied by Ma-Xiaoyan et al [130] organophilic rectorite clay (OREC)/ therermoplastic polyurethane (TPU) nanocomposites were prepared via melt blending. OREC was prepared with natural rectorite dodecanic quaternary ammonium salt through ion exchange. The nanoscale dispersibility of the OREC layers in the TPU matrix was revealed by using transmission electron microscopy (TEM). The thermodynamic mechanical analysis (DMA), thermo gravimetric analysis (TGA), oil-resistant and hot air a gang of nanocomposites were also measured. The results showed that the largest storage modulus is 7 times more than that of pure TPUs. A study on intercalation and exfoliation of layered silicate nanoparticles in thermoplastic polyurethane was investigated by Pattanayak et al [131], in which the unreacted isocyanate groups in the chains of prepolymer and chain extended polyurethane were used to tether layered silicate nanoclay particles. The clay galleries are easily intercalated by low molecular weight diisocyanates, polyols and butandiol prior to polymerization. The tensile strength increased by up to 216% and the elongation at break by 87%, for polyurethanes, containing with 1-2 % organically treated clay particles. Also PU/Metal nanocompisites were prepared where PU contains 0.043% gold nanoparticles (similar to 5 nm) by mixing the waterborne PU with gold suspension. The

gold nanoparticles were found to be well dispersed in PU and a significant increase in the pyrolysis temperature and the glass transition temperature was demonstrated in the nanocomposite films [132, 133]. New biomedical poly(urethane urea) layered silicate nanocomposites were studied by XU-Rujan et al [134]. Experiments on polymer / inorganic hybrids based on a generic poly(urethane urea) and an alkylammonium-modified montmorillonite were investigated. A novel nanocomposite approach for PUU that results in the reduction in gas permeability is described. An improvement in mechanical properties is also observed.

Tien-YI et al [135] studied the thermal transitions of montmorillonite/ polyurethane nanocomposites. The hard segment phase thermal transitions and heat resistance of benzidine modified-montmorillonite (BZD-MMT)/ polyurethane nanocomposites of different hard segment contents were found to be affected by a small a mount of BZD-MMT. In particular, the presence of less than 5 wt % layered silicates from BZD -MMT can result in hard segments not only having a more thermally stable long range order and a higher melting temperature, but also showing a loss of crystallinity of the hard segment in polyurethane.

Also, Morphology and properties of thermoplastic polyurethane nanocomposites incorporating hydrophilic layered silicates were studied by Finnigan-B et al [136] in which hydrophilic layered silicate/PU nanocomposites were prepared via twin screw extrusion and solvent casting. Good dispersion and delamination was achieved regardless of processing route, suggesting that the need for optimized processing conditions diminishes when there is a strong driving force for intercalation between the polymer and organosilicate. Evidence for altered polyurethane microphase morphology in the nanocomposites was provided by DMA and DSC.

WAXRD results suggested that the appearance of an additional high temperature melting endotherme in some melt-compounded nanocomposites was not due to the formation of a second crystal polymorph, but rather due to more well-ordered hard micro domains. Solvent casting was found to be the preferred processing route due to the avoidance of polyurethane and surfactant degradation associated with melt processing. While tensile strength and elongation were not improved on organosilicate addition, large increases in stiffness were observed.

7. Aim of the Work

The aim of this thesis is to study different organoclay which can be used to obtain PU-layered silicate nanocomposites with improved mechanical and thermal properties of PU. PU nanocomposites were prepared via in situ polymerization technique to maximize organoclay/matrix interaction. In addition, a series of PU nanocomposites with different organoclay content were prepared via pre-polymer technique and the PU end capped with vinyl group was mixed with organoclay functionalized with vinyl group to interact with polymer matrix through free radical polymerization. All the nanocomposites were characterized by; IR, XRD, SEM, TGA, swelling test, calcinations measurements, and mechanical measurements (tensile strength and elongation at break).