

1. Introduction

A composite may be defined as a material made up of multiple phases within a single matrix differing in their physical and chemical properties leading to a material with properties different from those of the individual constituents. In a composite, one of the phases is usually continuous and is called the matrix phase, while the other phase (or phases) is usually a reinforcing material and is called the dispersed phase. The materials embedded inside the matrix in a composite normally overcome the deficiencies of the matrix material. The term composite was coined in the year 1937 when salesmen from the Owens Corning Fiberglass Company began to sell fiberglass. In a broader sense, composites may be divided into three classes depending upon their matrix material composition, such as; polymeric, metallic or ceramic matrices. Polymers are the most abundantly used matrix material in preparing the composites, because of their excellent processibility, lower cost, low specific gravity and easy formability. However, the stiffness and strength of the polymers are quite low as compared to those of the metals and ceramics. Thus, reinforcement achieved by preparing polymer composites is highly beneficial for ultimate product performance as compared to other matrix composites. Moreover, polymer composites can be processed at lower temperatures as compared to metallic and ceramic counterparts. Thus, the problems associated with the processing as well as degradation in reinforcement during preparation are the least in polymer matrices as compared to other matrices.

In most of the conventional composite materials, the structural units (dispersed phases) are either in the macro or in the micrometer length scale. However, the first discovery of polymer clay nanocomposite by Toyota research group [Kojima et al. (1993); Usuki et al. (1993)] has brought a significant change in the research on

polymer composites. It has been observed that about 87 °C improvement in heat distortion temperature (HDT) of the Nylon-6 montmorillonite clay nanocomposite can be achieved, as compared to the neat Nylon-6 along with significant improvement in mechanical properties. It has been assumed that the improvement in the physicochemical properties of the nanocomposites may be due to the large interfacial area per unit volume of interaction which is far less in case of conventional composites.

Layered silicates, metal oxides, layered titanate, inorganic nanotubes and polymeric nanomaterials like expandable graphite, cellulose nano-whiskers, polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes, and many others are among the popular choice of nanofillers used today. Nanoclay is still the most preferred and popularly used nanomaterial to prepare the nanocomposites because of its easy availability, unique layered structure (absent in other nanomaterials) and lower cost as compared to other nanomaterials [Alexandre and Dubois (2000)].

Some of the technologically important classes of clay minerals used in making polymer-clay nanocomposites are listed in Table 1.1. Layered silicates are divided into three main types based on the relative ratio of two unit crystal sheets, like:

- 1:1 type: one silica tetrahedron following one alumina octahedron present in unit lamellar crystal
- 2:1 type: two silica tetrahedron with one alumina octahedron sandwiched in unit lamellar crystal
- 2:2 type: four crystal sheets in which silica tetrahedron and alumina or magnesium octahedron are alternately arranged.

Table 1.1: Important clay minerals used to prepare polymer clay nanocomposites

Type	Name of Clay*	General Formula
1:1	Kaolinite ^{b,N}	$Al_2Si_2F_5(OH)_4$
	Halloysite ^{b,N}	$Al_2Si_2F_5(OH)_4 \cdot n H_2O$
2:1	Montmorillonite ^{a,N}	$M_x(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2 \cdot n(H_2O)$
	Hectorite ^{a,N}	$M_x(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2 \cdot n(H_2O)$
	Saponite ^{a,N}	$M_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_2 \cdot n(H_2O)$
	Laponite ^{a,S}	$M_x(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2 \cdot n(H_2O)$
	Fluorohectorite ^{a,S}	$M_x(Mg_{3-x}Li_x)Si_4O_{10}F_2 \cdot n(H_2O)$
	Fluoromica ^{a,S}	$NaMg_{2.5}Si_4O_{10}F_2$
	2:2	Sapiolite ^S
Attapulgite ^S		$Mg_5Si_8O_{20}(HO)_2(OH_2)_4 \cdot 4H_2O$

*“a” represents clays with negative surface charges; “b” represents clays with positive charge; N-Natural; S-synthetic

Amongst these nanoclays, the most abundantly explored and used variety of nanoclay is Montmorillonite (MMT), popularly known as ‘Cloisite[®]’ and is available commercially in various grades depending on the types of modifiers used (almost exclusively marketed by Southern Clay Limited, USA). However, other varieties of nanoclays lag behind in bulk production and application as compared to the Cloisite[®]. MMT is a natural hectorite clay whereas, Laponite is a synthetic variety of hectorite clay. The diameters of individual diskettes (or platelets) of MMT vary from 150 to 250 nm whereas, diameter of the platelets of Laponite vary from 25 to 30 nm. Laponite platelets possess well controlled dimension, smaller in size and is chemically pure as compared to MMT. In case of MMT interstitial charge deficiency is created by the replacement of Al^{3+} with Mg^{2+} or Fe^{2+} but in case of Laponite the same is possible by the replacement of Mg^{2+} with Li^{1+} .

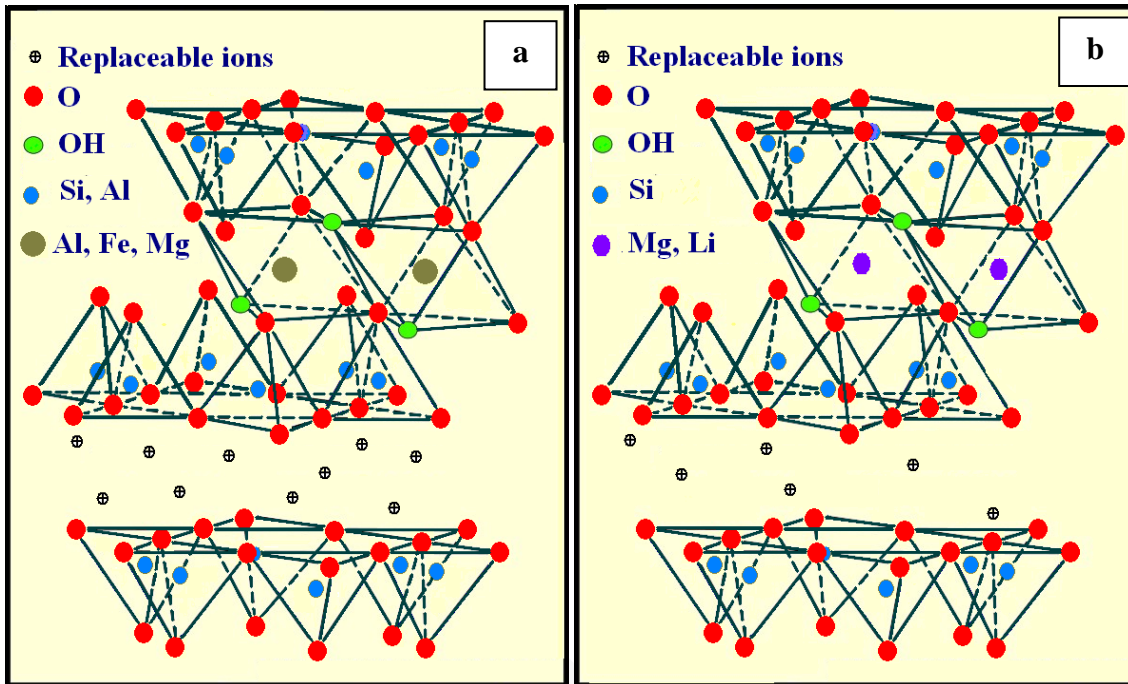


Figure 1.1: Structure of platelets of (a) Montmorillonite and (b) Laponite

These negative charge deficiencies are counterbalanced by the alkali or alkaline earth metal cations. These alkali or alkaline earth metal cations generally present in between the lamellar spacing of the clay galleries (since clay possesses layered structure, Fig. 1.1a and b). These alkali or alkaline earth metal cations can be ion exchanged with alkyl ammonium halides (known as modifier or surfactant in the literature) [Herrera et al. (2006); Ni et al. (2004, 2006); Tien and Wei (2001a, 2002)]. The $-OH$ groups present at the edge of lamellae, provides site for covalent modification of the nanoclay by using alkoxy silanes [Herrera et al. (2004, 2005); Park et al. (2004); Wheeler et al. (2005, 2006)]. Modification of the interlayer space and/or surface of the platelets renders the clay surface hydrophobic. The modification also increases the gallery spacing of the clay. The clay becomes more compatible with the polymer as a whole, due to such modifications.

1.1 Polymer-clay Nanocomposite

In the last few decades polymer clay nanocomposite has come to the forefront and has been recognized as one of the frontier areas of research in the field of polymer science and technology. This is possible only because of the many fold increase in property spectrum of the nanocomposite as compared to those of the neat polymers and conventional macro- and micro- composites. Nanoclay is the most popular nanomaterial because of its unique layered structure. The state of dispersion of the nanoclay in the polymer matrix is classified into three categories, e.g., intercalated, exfoliated and aggregated/agglomerated. Successful thermal and mechanical property enhancement of polymer matrices through nanoclay reinforcement is expected because of complete exfoliation of the clay platelets [William et al. (2005)]. Complete exfoliation is often very difficult because of the hydrophilic-hydrophobic repulsion between clay and polymer matrices. Large viscosity barrier for both polymer melts and solutions makes the situation even more unfavorable. Generally, the unmodified clay surface is hydrophilic, but most of the polymers are hydrophobic in nature. Several attempts have been made to render the clay surface organophilic [Blumstein et al. (1974); Solomon (1968); Theng (1974, 1979)] for achieving better dispersion of clays into the polymer matrices.

1.2 Polyurethanes

Polyurethanes find plenty of applications in a wide range of engineering works including in the biomedical field. Polyurethane is a class of polymer containing organic segments joined to each other by urethane linkages. Otto Bayer and co-workers have invented this polymer at the I.G. Farbenindustrie, Germany in 1937, but production in the industrial scale started only in 1940 when DuPont and ICI recognized its extraordinary elastic properties.

The key components required for the synthesis of polyurethanes are:

- a. Diisocyanate (aliphatic or aromatic)
- b. Polyol (polyester or polyether)
- c. Chain extender (low molecular weight diol or diamine).

The most commonly used diisocyanates are 4,4'-methylene bis(phenyl isocyanate) (MDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), isophoron diisocyanate (IPDI), etc.

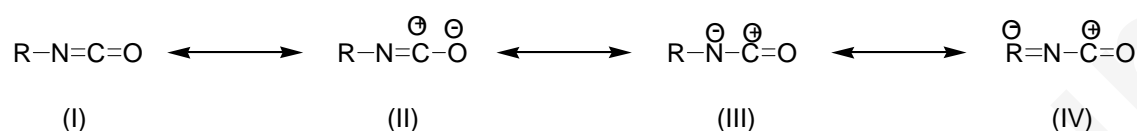
Although isocyanates play a vital role in the polyurethane synthesis (due to the differences in their reactivity depending on the presence of aromatic and aliphatic moieties) but the final property of the polyurethane is mostly determined by the type of polyol used. Functionality of the polyols may vary from 2 to 8 with an average molecular weight of 400 to 6000 gms per gm mole (\bar{M}_n). In practice, polyol with molecular weight 1000 and 2000 gms per gm mole are most widely used [Petrovic and Ferguson (1991)]. Polyether polyol based polyurethanes are more resistant to hydrolysis, whereas, the polyester polyol based counterparts are thermally more stable. Polytetramethylene glycol (PTMEG) based polyurethane possess excellent hydrolytic stability and microbial resistance, outstanding dynamic properties including resilience and low temperature flexibility.

The third most important component is the chain extender. The most widely used chain extender in preparing polyurethanes is 1,4-butane diol but methylene bis (o-chloro aniline) is normally used for the preparation of polyurethane urea [Hepburn (1982)].

Catalysts play an important role in the synthesis of polyurethanes. Tertiary amines are mostly used in the synthesis of polyurethane foams (as it also promotes the reaction of the isocyanate with water). However, organometallic compounds

especially dibutyl tin dilaurate is most widely used catalyst for the synthesis of thermoplastic polyurethanes (TPUs) [Hepburn (1982)].

In the synthesis of polyurethanes, chemistry of diisocyanate plays a vital role. The isocyanate group contains a highly electrophilic carbon atom, which possess the resonating structures as shown in Scheme 1.1.



If R= Aromatic

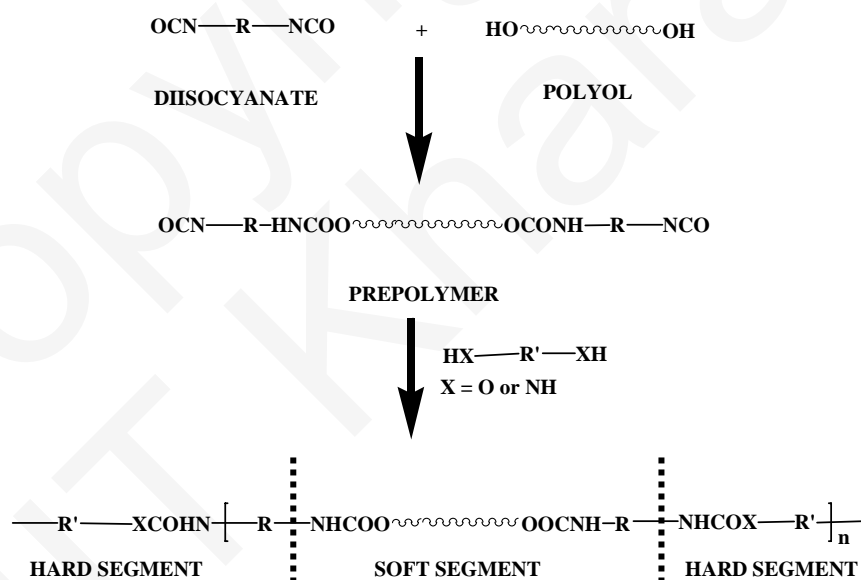
Scheme 1.1: Resonating structures of isocyanate

This electrophilic carbon present in the $-\text{NCO}$ group plays a pivotal role in polyurethane chemistry. Three resonating structures (II, III and IV), out of the four, contain carbon atom having positive charge on it with the delocalization of negative charge on oxygen, nitrogen and R group (provided 'R' is aromatic). This is the only reason for the high reactivity of isocyanates towards nucleophiles and higher reactivity of aromatic isocyanates over aliphatic isocyanates. It is also found that the reactivity of aromatic isocyanate containing electron withdrawing group on the aromatic ring increases when present in ortho- and para- positions. Similarly, the reactivity diminishes significantly when the aromatic ring(s) contains electron donating substituents.

The methods of synthesis of polyurethanes can be differentiated according to the medium of preparation (bulk, solution, aqueous) and the addition sequence of the reactants (one shot process, two step prepolymer process). Bulk polymerization (either one shot or two step prepolymer process) is generally preferred in industries as the process is cost effective and environment friendly because of solvent-free

synthesis, whereas, solution polymerization is being used for laboratory synthesis [Hepburn (1982); Woods (1990)]. However, reaction in aqueous media via miniemulsion polymerization technique is mostly limited to the preparation of certain coatings and adhesives [Dieterich (1994)].

In one shot process, all the ingredients (polyol, diisocyanate, chain extender and catalyst) are mixed together. However, in the prepolymer process, polyol is first reacted with the diisocyanate to prepare the prepolymer, followed by chain extension reaction. In case of one shot process, high degree of shear is required to render homogeneous mixing. Prepolymer process is most widely used method as one can precisely control the morphology of the final product by this method. Scheme 1.2 depicts the schematic representation of synthesis of polyurethanes by the prepolymer route.



Scheme 1.2: Preparation of polyurethane by prepolymer method

Polyurethanes can be classified into various categories depending on their properties and applications, e.g.,

- a. Thermoplastic Polyurethane (Segmented polyurethane) – ranging from thermoplastic to thermoplastic elastomer
- b. Castable Polyurethane
- c. Millable Polyurethane
- d. Polyurethane foams (Rigid and Soft)
- e. Coatings
- f. Adhesives.

1.3 Thermoplastic Polyurethane (TPU)

Amongst all the grades of polyurethanes, TPU is the most widely used material. This is because of its higher mechanical strength, excellent abrasion resistance, ease in processing and bio-compatibility. TPU is a block copolymer composed of hard segments and soft segments arranged in a (A-B-A)_n fashion. The soft segment is prepared by the reaction between the polyol and the diisocyanate, but hard segment is formed by the reaction between the diisocyanate and the chain extender. Phase separation (segregation) between the hard and soft segments occurs due to the difference in secondary forces (van der Waals, dipole-dipole, H-bonding interactions, etc. [Hepburn (1982)]). Thus, the degree of segregation between the hard and soft segments depend on the extent of interaction of the hard segments with each other and also with the soft segments [Senich and Macknight (1980); Seymour et al. (1970); Sheneider and Paiksung (1977); Srichatrapimuk and Cooper (1978)]. The phase segregation is less pronounced in polyester polyurethane than in polyether polyurethane and is most pronounced in polybutadiene based (e.g., HTPB) polyurethane. Also a drastic development in phase segregation and domain organization can be encountered due to the incorporation of urea moiety in the hard segment [Bonart et al. (1974); Sung et al. (1980a)], which causes improved

mechanical strength such as higher mechanical properties, lower hysteresis, greater toughness and slower rate of stress relaxation [Sung et al. (1980b)]. Phase separation increases with increasing chain length of soft segment or with the increasing polarity leading to lesser hard-soft segment interactions. Bonart (1968) and Clough et al. (1968) reported the first direct evidence of the occurrence of two-phase morphology from small angle X-ray scattering (SAXS) study.

Despite several advantages, TPU suffers from lower thermal stability and flame retardancy as compared to other engineering thermoplastics (polyether imides, polyether esters etc.) for similar applications [Holden et al. (2004); Troughton (2008)].

1.4 TPU-clay Nanocomposites

The aforesaid limitations of TPU may be overcome by three different ways:

- a. Changing the three basic building blocks i.e. polyester/polyether polyol, diisocyanates and chain extender
- b. Blending with a suitable polymer
- c. Incorporation of inorganic fillers especially the nanofillers into the polyurethane matrix.

Amongst these three techniques, incorporation of inorganic nanofillers is found to be most effective commercially and technically viable process. This is because, nanofillers have the advantage of improving barrier property along with improvement in mechanical properties and thermal stability (which is difficult to achieve in other cases) and cost effectiveness. Segmented polyurethane (TPU)-clay nanocomposite was first introduced by Wang and Pinnavaia (1998). It has been observed that montmorillonite clay modified with long chain onium ions (carbon number ≥ 12) exhibited very good compatibility with several polyols commonly used

for polyurethane synthesis. Also an increase in the chain length of alkyl groups in the long chain onium ions results in the increased interlayer distance between the clay platelets in the nanocomposites.

TPU- clay nanocomposites (TPUCNs) may be prepared by three distinct methods, e.g.,

- a. Melt blending
- b. Solution mixing and
- c. *In-situ* synthesis.

In case of melt blending technique, nanoclay is mixed with the molten TPU in an internal mixer or extruder. Solution mixing involves the intermixing of solution of TPU and the solvated nanoclay utilizing mechanical stirring and/or ultrasonic vibration, followed by the evaporation of solvent. Whereas, in case of *in-situ* synthesis technique, clay is dispersed either with the polyol or with the prepolymer followed by further course of polymerization.

Several factors responsible for the dispersion of nanoclays [Takeichi et al. (2002)] in the polymer matrix which can be listed below, as:

- a. method of preparation
- b. mixing temperature and thermal history
- c. mixing time
- d. shear rate and extent of deformation
- e. solvent used (especially in solution mixing and *in-situ* preparation method)
- f. concentration of polymer solution (for solution mixing and *in-situ* preparation)
- g. Molecular weight of the monomer (for *in-situ* preparation method) or polymer
- h. Types of modifier used for modification of nanoclay
- i. Extent of modification of the nanoclay.

1.5 Literature Review on TPU-clay Nanocomposites

1.5.1 Structure and Morphology

First successful dispersion of nanoclays in polyurethane matrix by Wang and Pinnavaia (1998), have attracted tremendous interest among the scientific community. It has been observed that morphology of clay platelets play a vital role in improving the properties of the TPU-clay nanocomposites (as discussed earlier). Several techniques have been utilized to visualize the surface and bulk morphology of the nanocomposites like SEM, FESEM, AFM, XRD and TEM.

The effect of hard segment content and the amount of clay on the morphology has been reported by Hu et al. (2001). Increased hard segment content has been observed to increase the basal spacing of the clay platelets at lower clay content but reverse phenomenon has been observed at higher clay contents.

Two varieties of modified MMT have been dispersed in TPU matrix by Chen et al. (2000) (clay modified with 12 aminolauric acid and benzidine) to study the effect of modifier on the morphology and property of the resulting nanocomposites. Complete exfoliation has been observed upto 5% and 3% of clay modified with 12 aminolauric acid and benzidine, respectively.

An intercalated to exfoliated morphology has been observed with the incorporation of clay modified with dilauryldimethyl ammonium bromide and 4,4'-diaminodiphenylmethane, respectively [Chen-Yang et al. (2004)].

Intercalated structures have been predominantly observed when the clay was used as a pseudo chain extender [Rehab and Salahuddin (2005)]. However, Xia and Song (2006) have observed preponderance of intercalated morphology with nontethered clay (physically mixed clay), and exfoliated morphology with the tethered clay (clay having active functional group) for the nanocomposite prepared by

in-situ synthesis technique. It has been observed that nanoclay possessing active functional groups can form H-bonding if physically mixed and if it can act as a pseudo chain extender by *in-situ* method.

The surface –OH group of the nanoclays has been reacted with the isocyanate and dispersed in polyurethane matrix. Highly exfoliated morphology has been observed by *in-situ* synthesis technique [Seo et al. (2006)] while intercalated morphology has been pronounced by solution mixing technique [Cheng et al. (2006)]. Both solution mixing and twin screw extrusion have been observed to give higher degree of delamination and slight intercalation of Cloisite[®] 30B with two varieties of polyurethanes differing from each other by the content of hard segment [Finnigan et al. (2004)]. These have been explained on the basis of the formation of H-bonding (acting as a driving force) for the intercalation of the modified clay in the TPU matrix. A comparative study between four varieties of clay (unmodified MMT, Cloisite[®] 15A, Cloisite[®] 25A and Cloisite[®] 30B) in two types of TPU (polyether and polyester based TPU) has been reported by Dan et al. (2006). A very poor dispersion has been observed with natural clay (unmodified clay) in both types of TPU. Partially intercalated morphology has been obtained with both Cloisite[®] 15A and Cloisite[®] 25A. Cloisite[®] 25A has been found to give better dispersion as compared to Cloisite[®] 15A. However, presence of –OH groups (tethered) on the modifier has been observed to render mostly exfoliated morphology in case of Cloisite[®] 30B. Similarly, dominant intercalated and exfoliated morphology has been obtained by *in-situ* polymerization of Cloisite[®] 20A (non-tethered) and Cloisite[®] 30B (tethered), respectively [Xia et al. (2005)]. It has been reported by several other researchers also that tethering of the clay leads to exfoliation of the clay platelets [Gorrasi et al. (2005); Kuan et al. (2005b); Pattanayak and Jana (2005a); Ni et al. (2004)]. Interestingly, occurrence of

highly exfoliated morphology upto 40 wt% of nanoclay has been reported by Ni et al. (2004, 2006) by using clay as a pseudo chain extender.

Intercalated morphology has been predominantly obtained by using Cloisite[®] 30B as pseudo chain extender by bulk polymerization method due to high viscosity barrier for exfoliation of clay [Pattanayak and Jana (2005c)].

The effect of changing the number of end tethered –OH functional groups on the tail of the modifier (for the modification of Montmorillonite) have been studied (from 1 to 3) by Tien and Wei (2001b). The morphology of clay has changed from intercalated to exfoliated, with the increase in number of –OH groups in the modifier. Moon et al. (2004) have modified Montmorillonite with tris(hydroxymethyl) aminomethane to prepare a tethered clay having three –OH groups and it has been used as a pseudo chain extender. Intercalated to exfoliated morphology has been observed for all the nanocomposites but increased aggregation tendency has also been reported at higher clay contents.

Interestingly, a contrasting result has been reported by Pattanayak and Jana (2005b). High mechanical shearing (not the tethering of the clay) has been found to be the main reason for the complete exfoliation of the nanoclay. Similar observations have also been reported by Meng et al. (2008). The degree of exfoliation has been found to increase with increase in time of mixing.

Choi et al. (2005) modified the clay with in-house synthesized organifier (modifier) and subsequently dispersed such modified clays into the TPU matrix. It has been observed that 60 minutes of sonication provided better dispersion of modified nanoclays as compared to the nanocomposite prepared without sonication.

Song et al. (2005) have found that hard domain of TPU can self organize to form spherical aggregates. Size of these aggregates has been found to decrease from 800 nm to 500 nm with the incorporation of Cloisite[®] 20A.

1.5.2 Mechanical Properties:

Mechanical properties of TPU are of great importance due to their usefulness in many engineering applications, where strength properties play a vital role. It is observed that addition of nanoclay into the polyurethane matrix improves the tensile properties significantly. Addition of conventional fillers into the polyurethane matrix has been reported to improve the modulus by sacrificing the long range elastic properties [Torro-palau et al. (1997)]. However, addition of 10% of modified clay has been reported to increase the tensile strength, modulus and strain at break by more than 100% [Wang and Pinnavaia (1998)]. More than 100% increase in tensile strength and elongation at break have also been reported by several other researchers [Ni et al. (2004); Pattanayak and Jana (2005a,b,d)]. Xiong et al. (2004) have used Cetyl trimethyl ammonium bromide (CTAB) and methylene bisortho-chloro aniline to prepare C16-MMT and MOMMT, respectively (modified MMT). Addition of 5% of modified clay has been found to increase the mechanical properties by 600% and 450% for MOMMT and C16-MMT, respectively. Dia et al. (2004) have prepared TPU clay nanocomposites by *in-situ* polymerization technique from MDI, PTMEG and 1,3-propylenediamine in DMF solvent. It has been observed that 1700% increase in elongation at break along with the increase in tensile strength and Young's modulus occur with only 2% CTAB modified montmorillinite.

Addition of modified clays has been found to increase the tensile strength by 2 fold as compared to the neat TPU [Chen et al. (2000); Ni et al. (2004, 2006); Song et al. (2003a)]. Young's modulus of the TPUCN has been found to increase with the

addition of modified nanoclays [Choi et al.(2005); Finnigan et al. (2004); Tien et al. (2001); Zheng et al. (2006)]. However, improved Young's modulus with reduced tensile strength and elongation at break upon the addition of clay has also been reported in the literature [Choi et al. (2006)].

Chen et al. (1999) have prepared polycaprolactam based TPU modified clay nanocomposite by *in-situ* preparation technique. An increase in elongation at break at lower clay content following a reverse effect at higher clay content has been observed. Decrease in H-bonding in the hard segment of TPU with the incorporation of modified nanoclays (nontethered) has been reported by Tien and Wei (2001a). However, it has been found to enhance the strength and modulus values compared to the neat TPU. Destruction of H-bonding in the hard segment of TPU due to the incorporation of tethered nanoclays has also been reported by Pattanayak and Jana (2005b). The destruction in H-bonding stems from the H-bond formation between the carbonyl group of the TPU and the –OH group present on the tail of the modifier to the clay. However, modulus and tensile strength has been found to be increased by 110 and 160%, respectively for the nanocomposite containing 5 wt% of Cloisite[®] 30B.

Reaction of the surface –OH group of the MMT with the isocyanate during *in-situ* synthesis, leading to an improvement in tensile strength and elongation at break has been reported by Zhang et al. (2003).

A comparison between the Cloisite[®] 30B, 25A, 15A and Na⁺MMT has been reported by Dan et al. (2006) with both ether and ester type of TPU. It has been observed that nanocomposites with Cloisite[®] 30B provided greater tensile properties as compared to those of the other types of clay. Higher degree of increase in tensile properties has been reported to be with ester type TPU as compared to the ether type

of TPUCN due to the higher degree of compatibility between the polymer and the modified nanoclay.

Tensile strength and elongation at break of the TPU remaining constant, an increase in the Young's modulus of TPUCN by 3.2 fold by the addition of 7% clay has been reported by Finnigan et al. (2004).

Effect of the modifier on the improvement in property of the TPU has been studied by Tien and Wei (2001b) by using three types of modifiers. Greater extent of improvement in tensile properties has been reported with the clay modified by trihydroxy ammonium ions as compared to those of clay modified with dihydroxy and monohydroxy ammonium ions.

The effect of modifier on the property of TPUCNs has also been studied by Cheng et al. (2006). Montmorillonite has been modified with CTAB to prepare OMMT. This OMMT has been further modified with MDI to prepare MOMMT. Improvement in tensile strength and tear strength has been reported in case of MOMMT as compared to OMMT with the addition of same amount of clay. However, elongation at break has been found to be decreased.

Pattnayak and Jana (2005c) have found an increase in tensile strength and elongation at break by 61% and 47%, respectively over the neat TPU by using Cloisite[®] 30B as a pseudo chain extender in the preparation of TPUCN derived from MDI, polypropylene glycol and 1,4-butanediol.

With the increase in the degree of exfoliation, the tensile strength and elongation at break has been found to increase. However, increasing the mixing time (to achieve greater exfoliation) for prolonged time is found to cause the degradation of TPU matrix [Meng et al. (2008)].

From the review of the above literature, it is observed that better properties are obtained when the degree of exfoliation of the clay platelets are higher. This is due to an increase in the mass to volume interaction between the clay and polymer in the exfoliated state of clay in polymer matrix which in turn is highly dependent on the type of modifier used.

1.5.3 Thermal Properties

Thermal stability of TPU is very important as its degradation commences at around 250-300 °C. TPU also possess two Tg's (one for the soft segment and another for the hard segment) due to its two-phase morphology. However, in most of the cases hard segment Tg is not observed due to the dominance of the soft segment and ordered hard domains. Thermal properties generally include the glass transition temperature, melting temperature, dynamic moduli and thermal stability. Overall, composition, molecular weight, hydrogen bonding and thermal history play vital roles towards the thermal properties of the TPUCNs.

Hard segment content remaining same, neat TPU and TPUCN have been found to register nearly similar glass transition temperatures (Tg) [Tien and Wei (2000)]. Tg of the TPU has not been changed with the modified clay acting as a pseudo chain extender [Moon et al. (2004)]. However, addition of small amount of tethered clay has been reported to increase the Tg of the hard segment by 44 °C [Tien and Wei (2002)]. Similarly, a 13 °C rise in Tg value of the soft segment with the addition of Cloisite[®] 20A has been reported by Zheng et al. (2006). Several researchers have reported an increase in Tg of TPUCNs with the increase in the amount of clay [Chen et al. (2000); Choi et al. (2005); Dia et al. (2004); Finnigan et al. (2004); Kim et al. (2005); Ni et al. (2004, 2006)]. Extent of sonication during the preparation of the TPUCN has been found not to have any influence on the Tg of the

nanocomposites [Choi et al. (2005)]. In contrast, a decrease in T_g and the heat capacity at glass transition temperature (ΔC_p) of the nanocomposites with the increase in the clay content has been reported by Seo et al. (2006). It has been reported that this decrease in ΔC_p is due to the increase in steric hindrance by the exfoliated clay layers. Decrease in ΔC_p with the increase in clay content has also been reported by Yao et al. (2000) and Barick and Tripathy (2010b). Lower T_g of the nanocomposite as compared to the neat TPU has been reported by Pattanayak and Jana (2005b) and Xiong et al. (2004).

TPU have been found to exhibit two stages of degradations during decomposition. The 1st stage of degradation corresponds to the degradation of the hard segment and the 2nd stage of degradation corresponds to the degradation of the soft segment [Petrovic et al. (1994); Shieh et al. (1999)].

TPUs generally have been found to commence degradation at a temperature of 250 °C. However, the major weight loss starts around 300 °C. But presence of the modifier in the interlayer gallery spacing has been observed to start degrading from 275 °C upto 325 °C [Chen et al. (1999); Gorrasi et al. (2005); Ma et al. (2001)]. Song et al. (2005a) have reported that hexadecyl trimethyl ammonium starts degrading at 200 °C and proceeds through the Hoffmann degradation mechanism leaving behind an acidic proton on the surface of clay which catalyses the initial degradation of the organic material within the clay. To avoid the confusion between the degradation of TPU and the modifier, generally 5% weight loss is taken into account as the onset of degradation. The same is reflected by an increase in thermal stability of TPUCN after the complete decomposition of the modifier as compared to that of the neat TPU [Chen et al. (1999); Chen-Yang et al. (2004); Gorrasi et al. (2005); Ma et al. (2001)]. Increase in the amount of clay from 1 to 5% has been reported to increase the thermal

stability of TPU by 12 to 34 °C, respectively by Tien and Wei (2000). The increase in thermal stability with an increase in the amount of modified MMT in the TPU matrix has also been reported by several researchers [Barick and Tripathy (2010a, b); Chang and An (2002); Chen et al. (2000); Finnigan et al. (2004); Kim et al. (2005); Ni et al. (2004, 2006)]. The improvement in thermal stability of the TPUCN has been found to be directly related to the degree of dispersion of the nanoclay in the TPU matrix [Choi et al. (2005)]. Enhancement of the thermal stability as well as flame retardant property of the TPUCN has been reported by Chen-Yang et al. (2004) and Song et al. (2003a). The thermal stability has been found to be enhanced by 25 °C with 5% clay content. The heat release rate (HRR) has also been found to decrease by 63% with the addition of 6% clay as compared to that of the neat TPU. However, HRR has been found to be decreased with further increase in the clay content.

1.5.4 Rheological Characteristics

Rheology plays a vital role to monitor the flow behavior under different conditions, e.g., shear rate, temperature, pressure, time etc. The rheological (rheometry - the measuring arm of rheology) and viscoelastic measurements on TPU are important at least for two reasons. Firstly, rheological techniques can be used as a noninvasive experimental tool (though indirect) for the investigation of the rich phase transition/relaxation behavior of this class of nanocomposites. Secondly, rheology could be useful to investigate the effect of phase transitions or relaxations on the processibility of the TPUCNs.

In most of the published work, viscoelastic property measurements of TPUs at higher temperatures have employed temperature-sweep mode in dynamic mechanical analysis (DMA) [Borgart et al. (1983); Kajiyama et al. (1969)]. But the limitation involved in this experiment is that it ends when the sample begins to flow.

Investigations on the rheological properties in the heating and cooling processes is important for polymer processing operations because TPU is mostly processed under high temperature followed by slow cooling to shape the final product. A direct consequence of the incorporation of nanoclay in molten TPUs is the significant change in their viscoelastic properties. Since, the linear dynamic rheological behavior of nanocomposites are sensitive to the structure, particle size, shape and surface characteristics of the silicate phase, the rheological tool is intensively used to assess the state of dispersion of nanoparticles in the molten state.

Addition of Cloisite[®] 30B to the TPU matrix [Meng et al. (2008)] has been found to increase both storage modulus and complex viscosity, especially in the terminal region. Storage modulus has been found to increase as a strong function of the degree of exfoliation of the nanoclays.

Viscosity of the TPUCN has been found to increase with the increase in clay content in the TPU matrix [Rhoney et al. (2004)]. This has been postulated to be due to the increased polymer-clay interaction. At low shear rate region, a yield stress with a shear thinning behavior has been observed. At high shear region, nanocomposites possess a rapid shear thinning behavior as compared to the neat TPU. Shear thinning behavior of the nanocomposites with modified nanoclays (Cloisite[®] 30B, 25A and 15A) have also been reported by Dan et al. (2006). However, Newtonian behavior has been observed with the neat TPU (both ether and ester based) and their nanocomposites with unmodified clay (within a frequency range of 0.1 to 100 rad/s).

The effect of three varieties of clay (unmodified MMT, Cloisite[®] 30B (tethered) and modified MMT (non-tethered)) on the dynamic rheological behavior of TPU matrix have been studied by Pattanayak and Jana (2005a). An increase in the storage modulus values has been observed with the addition of tethered and non-

tethered clays. However, lower storage modulus value with the unmodified clay has been ascribed to the presence of aggregates of clay in micron size scale and owing to poor clay-polymer interaction. The highest value of storage modulus has been found in case of the nanocomposite containing tethered clay. This has also been argued to be due to the greater interaction between the polymer and clay because of tethering.

1.6 TPU-Laponite clay Nanocomposites

Most of the studies on TPUCNs have been focused on MMT based clays whereas, such studies with Laponite based clays have not been frequently encountered in literature. This is because, clays having high aspect ratio (namely MMT and Cloisite[®]) possess the capability in enhancing the stiffness of the matrix even at small mass fractions due to their high surface area to volume ratios. However, owing to higher aspect ratio, probability of the particle to shield the matrix from straining is greater, which negatively influence the load transfer [Sheng et al. (2004)]. Consequently, this is detrimental to the elastic properties. This can be avoided by using clay with smaller aspect ratio. It has also been reported that reinforcement capabilities of the clay depend primarily on the finer dispersion of the clay in the matrix. In this regard, the type of clay used has little significance [Kuan et al. (2005a); Varghese et al. (2004); Zilg et al. (1999)].

The effect of particle size on the mechanical properties of the TPUs has been studied by Finnigan et al. (2005 and 2007). Clay has been found not to possess any observable effect on the microphase separation process of the TPU during both solution casting and annealing. It has also been found not to affect the morphological response of TPU to deformation regardless of the platelet size [Finnigan et al. (2005)]. Clay particles have been observed to increase the stiffness of TPU, especially at low strains, through mechanical restraintment and hydrodynamic effects. These effects

have been found to increase with the increased diameter of the clay particles. At intermediate strains microphase structure dominates and contribution due to clay is minimum at this stage. However, at high strain regions, clay particles can be well aligned to interact with individual segments. Hence, at higher strain clay can significantly influence the tensile properties of the nanocomposites. A lower platelet size has been found to impart better tensile properties as compared to the clay having higher diameter. This has been found to be due to the prominence in void formation with clay having larger diameter during alignment of clay particles [Finnigan et al. (2005)].

It has been observed that the stiffening effect is relatively less with the clay having smallest particle size (30nm) [Finnigan et al. (2007)]. This has been postulated to be due to reduced long range intercalation and molecular confinement along with ineffective stress transfer from matrix to filler. The permanent set and hysteresis value has also been found to be reduced with the clay of particle size ~30nm.

Thus, the aspect ratio of the clay, interaction between the TPU macromolecules and clay particles in combination with the state of dispersion of the clay are some of the important factors those can be ascertained to influence the properties. Based on this approach, TPU-Laponite clay nanocomposites have been prepared by Korley et al. (2006) and Liff et al. (2007) by using their unique solvent exchange approach. Unmodified Laponite RD is very difficult to disperse in common solvents like tetrahydrofuran (THF), dimethylformamide (DMF) and dimethyl acetamide (DMAc), in which, TPU is highly soluble. But Laponite in the unmodified stage can be easily dispersed in water. 1.5% solution has been prepared by mixing unmodified Laponite RD dispersed in water and subsequently the TPU solution in DMAc has also been prepared. Both were mixed together and sonicated for 1 hr,

before solution casting in an oven at 60 °C, with $\sim 0.02 \text{ m}^3\text{hr}^{-1}$ N_2 flow rate. By this process, complete exfoliation of the unmodified Laponite RD has been observed in the TPU matrix. An increase in initial modulus by 23 fold, 1.5 fold increase in ultimate strength (tensile strength) and 4 fold increase in toughness with 20% clay loading have been reported. Consequently, improvement in heat distortion temperature has also been claimed. This process has been found to lead unmodified Laponite RD to get preferentially associated with the more polar hard domains because of the higher surface energy of the unmodified clay.

However, few demerits like, decrease in onset of degradation temperature of the resultant TPUCNs, use of huge quantities of solvents during preparation, etc., limits this process. A very precise and controlled evaporation of solvent for the preparation of the nanocomposites is often difficult to achieve, which ultimately makes the process technically nonviable.

Later on, Polyurethane urea (PUU) clay nanocomposites have been prepared by Sormana et al. (2008) by *in-situ* synthesis technique using Laponite RD modified with monoamine and diamine based modifiers. The modification has been done by following the standard ion exchange process. A 3 fold increase in tensile strength and 1.4 fold improvement in elongation at break of the nanocomposites have been observed as compared to that of the neat PUU. Laponite with reactive functional groups (Laponite modified by diamine) have been found to impart better tensile strength to the PUU matrix as compared to that of the nontethered clay.

1.7 Summary of the Literature Review

Literature survey on TPU-clay nanocomposites reveals that most of the work carried out till date, encompasses the use of Montmorillonite (MMT) clay as the nanofiller (unmodified or modified). The key features for the improvement in

technical properties of the TPU lie on the dispersion of clay into the TPU matrix. In this regard, modifiers to the clay and the method of preparation of the nanocomposites play vital roles. Tethering of the clay and *in-situ* synthesis technique have been found to impart improved technical properties of the TPU. It has been observed that the dispersion of the nanoclay, rather than the size of the nanoclay, matters more for the improvement in technical properties of the TPU. It has also been reported that the matrix stiffening effect due to the use of clay possessing large aspect ratio can be greatly reduced by using clay with lower aspect ratios. This opens up a new area of research on the use of the nanoclay with smaller dimension like Laponite. Laponite has a well controlled dimension of 25-30 nm as against the 150-300 nm in diameter for MMT. Laponite is also chemically pure and free from impurities as compared to its naturally occurring MMT counterpart. The first attempt towards the use of Laponite RD (unmodified and modified) in the TPU and PUU matrix, respectively has paved the path for further exploration in this area.

1.8 Scope and Objectives

The detailed investigation on the structure-property relationship of the TPU-modified Laponite RD has not yet been fully explored till date. Thus, there is a wide scope for detail investigation in this area. Use of Laponite RDS (possessing larger number of sites for ionic modification) in TPU matrix has also remained an unexplored area. Use of dual modified Laponite RD has been established in other polymer matrices, but its consequence in the TPU matrix has remained untouched. Tethering of Laponite RD (with active functional groups) to make it more useful as a nanofiller in the preparation of TPUCNs by *ex-situ* method and to use it as a pseudo chain extender during the synthesis of TPUCNs by *in-situ* technique, have not been fully explored.

The thesis aims to explore the structure-property relationship between the TPU and the TPU-modified Laponite clay nanocomposites prepared following *ex-situ* and *in-situ* techniques by using various modified clays. The objectives of the thesis are manifold and are presented precisely below:

- To compare the effect of particle size, degree of dispersion and modifier type on the structure-property relationship of TPU-clay nanocomposites prepared by solution mixing technique. For this study, Cloisite 20A, Laponite RD modified by standard ion exchange process utilizing dodecylammonium ion (d) and cetyltrimethyl ammonium ion (c) are used.
- To study the effect of increased extent of ionic modification and effect of modifiers on the degree of dispersion and technical properties of the nanocomposites. For this study, Laponite RDS is modified with 'd' and 'c', respectively and then the modified clays are dispersed in TPU matrix by solution mixing technique.
- To establish the structure-property relationship between the covalently modified and dual modified Laponite RD (modified by ionic and covalent modification technique in two different routes) dispersed in the TPU matrix by solution mixing technique.
- To study the effect of tethering on the morphology and technical properties of the TPU-clay nanocomposites prepared by *ex-situ* and *in-situ* techniques.

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