



Journal of Applied Sciences

ISSN 1812-5654

science
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Review of Polymer-Organoclay Nanocomposites

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Abstract: This study focuses on polymer nanocomposites and their syntheses, properties and future applications, several of these applications will be successful in the near future. Polymer-Layered Silicate Nanocomposites (PLSN's) have been widely studied as property enhancers for thermoplastic materials due to their ability to improve mechanical, thermal, flame resistance and barrier properties of thermoplastics. Due to this property enhancement at low filler content (2-6 wt. %), PLSN systems have drawn tremendous attention. In the present review, a brief overview of history and some commercial applications of nanocomposites, importance of polyolefin's and the development of polyolefin-nanocomposites, techniques used for the synthesis of nanocomposites, techniques used for the characterization of nanocomposites, factors affecting the dispersion of clay and the effects of dispersion on the properties of the nanocomposites, importance for considering orientation along with the dispersion of clay and relation between rheology and the orientation of clay platelets in the polymer matrix of the nanocomposites, is discussed.

Key words: Nanocomposite, organoclay, rheology, platelets, orientation

INTRODUCTION

Organically modified layered silicates have been widely studied for the past decade as property enhancers for polymeric materials. Various studies report improvement in mechanical (Hambir *et al.*, 2001; Fornes *et al.*, 2001; Oya *et al.*, 2000; Ke and Stroeve, 2005), thermal (Beyer and Eupen, 2001; Gilman, 1999), flame resistance (Beyer and Eupen, 2001; Gilman, 1999) and barrier (Kojima *et al.*, 1993b; Messerlith and Giannelis, 1995) properties of thermoplastics by addition of organically modified layered silicates (Esfandiari *et al.*, 2007; Saito *et al.*, 2006) to polymer matrices. These modified thermoplastic systems are called Polymer-Layered Silicate Nanocomposites (PLSN). Due to this property (Okamoto, 2006) enhancement at low filler content (2-6 wt. %), PLSN systems have drawn tremendous attention. In general these PLSN systems possess several advantages including; they are lighter in weight compared to conventionally filled (Ton-That *et al.*, 2006) polymers due to property enhancement even at small clay loadings; they have enhanced flame retardance and thermal stability and they exhibit outstanding barrier properties without requiring a multi-layered design, allowing for recycling.

A few of those are explained as follow:

- Bayer AG, Germany developed nylon 6 nanocomposites for transparent barrier film packaging. Bayer is marketing two grades of nanocomposites, Durethan LPDU 601-1 and LPDU 601-2, which in comparison to neat nylon offers decrease in the Oxygen Transmission Rate (OTR) by 50%. The nanocomposites are made in the reactor using nano-clay from Nanocor.
- Montell North America, General Motors R and D in Warren, Mich. and Southern Clay have jointly developed Thermoplastic polyolefin (TPO) based nanocomposites for use in the molding of body-side claddings and step assist for the GMC Safari and Astro vans in 2002 (Fig. 1a).
- Unitika Co. of Japan developed Nylon 6 nanocomposite (Nylon M2350) using synthetic clay as reinforcement during polymerization. Nylon M2350 has been used by Mitsubishi Motors for an engine cover on its GDI models, where the nanocomposite is said to offer a 20% weight reduction and excellent surface finish.
- Japan's Ube Industries developed a commercial nanocomposite of nylon 6 and nylon 6/66 copolymer

(NCH) for film and structural applications. Commercial applications of NCH include nylon 6 barrier films for food packaging. NCH has also been used by Toyota Motor Company for manufacturing the timing-belt cover on the Toyota Camry (Fig. 1b).

Most of the commercial applications of polymer-clay nanocomposites use a polar polymer like (Nylon, EVA etc.) and the applications using non-polar polymers like PE and PP are limited. The main reason for this is the poor compatibility between a non-polar polymer and the organo-clay. Polyolefins like PE and PP cover almost 70% of the thermoplastic market with major applications in the automotive and packaging industry. These are the applications where further improvement in stiffness, impact, thermal and barrier properties without a significant increase in weight is always pleasing and wanted. Reports on enhancement of barrier, mechanical and thermal properties on addition of clay to a polymer have thus opened new fields of research, involving improving compatibility between the polymer and the organo-clay, in the polyolefin industry (Table 1).

Polyethylene (PE) counts for approximately 60% of the polyolefin market and is thus one of the most researched thermoplastic and is also the focus of the present research. A description of polyolefin, organo-clays and the interaction between the two is described as:

Polyethylene: Polyethylene (PE) is one of the most widely used commercial thermoplastics in the world today. PE counts for nearly 40% of the total thermoplastic production in the United States (Equistar Chemical Corporation Technical Bulletin). The low cost (~49 cents Lb⁻¹) of PE, plus versatility of attainable properties with modifications in its molecular weight and chain architecture has generated a plethora of commercial applications for PE.

PE can be classified into three main categories according to the architecture of its main chain. The three principal types of PE, which are used extensively in commercial film processing, are, high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). Some

Table 1: Partial listing of nanocomposite suppliers

Supplier (Trade name)	Base resin	Reinforcement	Commercial applications
Bayer AG, Germany (Durethan LLDPU)	Nylon 6	Organo-clay	Barrier films
Clariant technologies	Polypropylene (PP)	Organo-clay	Packaging
GM R and D, basell polyolefins and southern clay Prod.	Thermoplastic polyolefin (TPO)	Organo-clay	Auto body-side claddings, Step assist for 2002 GM Safari and Astro vans
Ube Industries, Japan	Nylon 6 and nylon 6/66 copolymer	Organo-clay	Barrier films, Timing belt cover for Toyota Motors
Honeywell (Aegis)	Nylon 6	Organo-clay	Bottles and film
Mitsubishi Motors	Nylon	Organo-clay	Engine cover on its GDI models
Kabelwerk Eupen of Belgium	Ethylene vinyl acetate copolymer	Organo-clay	Wire and cable
Nanocor (imperm) imperm	Nylon 6	Organo-clay	Molding, PET beer bottles
RTP	Nylon 6	Organo-clay	Multi-purpose

Source: Bins and Associates, Sheyboygan, Wis., <http://www.plasticstechnology.com/articles/199906fa4.html>, http://zeus.plmnc.psu.edu/~manias/news/plastics_tech_oct_2001.pdf

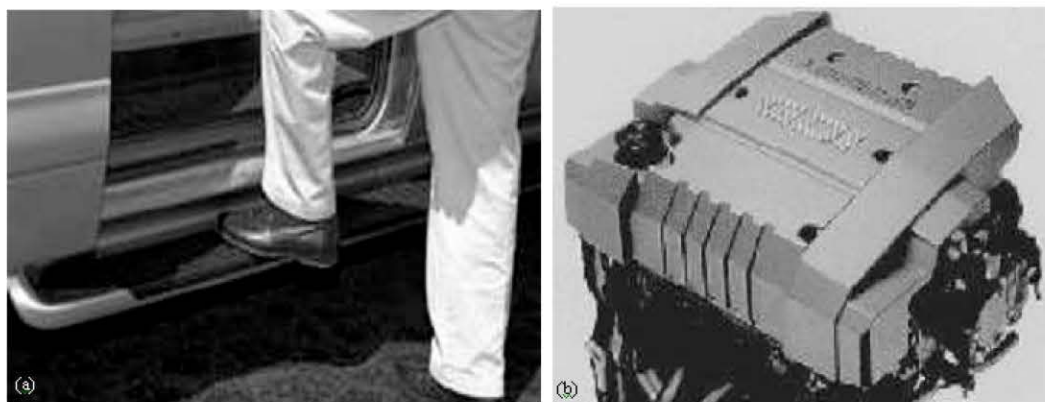


Fig. 1: Step assists on the GMC Safari developed by GM. a and b) Timing belt cover

typical applications for PE are, LDPE- bags, textile products, moisture barriers, greenhouses, cable insulation; HDPE- bottles, pails, tubes, caps, uses where injection molding of complex shapes is required but low load is required, film, sheet, wire and cable insulation, pipes and drums (Equistar Chemical Corporation Technical Bulletin). A large portion of the polyolefin produced is consumed as film. Due to its low cost, high-density polyethylene finds acceptance as a wrapping material for food products. HDPE is known to have poor barrier properties for gases, organic solvents and hydrocarbons (Gonzales-Nunez *et al.*, 2001; Yen *et al.*, 1997). Reports on enhancement of barrier, mechanical and thermal properties on addition of clay to a polymer have opened new fields of research in the polyolefin industry. Polyolefin's, being non-polar, show poor compatibility with modified clays. Various authors Hambir *et al.* (2001), Wang *et al.* (2001), Kodgire *et al.* (2001) and Hasegawa *et al.* (1998) reported on the dispersion of clay platelets in polyolefin's by addition of a compatibilizer such as maleated polypropylene or maleated polyethylene.

Clay: PLSN systems are usually made of two components; the base resin and a modified layered silicate (clay). A potential third component is a compatibilizer. Modified layered silicates are composed of silicate layers that can intercalate organic polymer chains if appropriate ionic or hydrogen bonding groups are present on the polymer. For example, montmorillonite is a 2:1 type layered silicate and is the most commonly used filler in PLSN systems (Brindley and Brown, 1980). 2:1 layered silicates are composed of an octahedral alumina or magnesia sheet sandwiched between two tetrahedral sheets of silica. The silica sheets have Na⁺, Ca²⁺, or K⁺ ions on their surfaces. The combined thickness of the two silica and one alumina or magnesia sheet is about 0.95 nm (Brindley and Brown, 1980).

In its pristine form the clay is present as a crystal which is made up of stack of silica sheets (platelets) along the (002) plane of the crystal. The presence of positive ions on the surface of the silica sheets increases the d-spacing in the (002) direction of the clay crystal which generally varies from 1.0-1.3 nm. The presence of positive ions on the surface also makes the clay crystal (002) planes hydrophilic and thus incompatible with many polymers. The organophilicity of the clay crystal (002) planes can be increased by exchange of these ions with organic cations (alkyl ammonium ions) (Alexander and Dubios, 2000). Ion exchange and surfactant treatment are not absolutely effective in commercially modified clay. Generally, two clay species result: unmodified clay

(Bafna *et al.*, 2003) with small layer spacing on the order of 1 nm and onium (alkyl ammonium) modified clay with a layer spacing on the order of 1-5 nm (Brindley and Brown, 1980) depending on the number of carbon atoms in the chain of the onium ion. The onium modified clay is thought to retain planar 0.95 nm thick trilayers of layered silicates. The main evidence for this comes from the existence of a stacking period after intercalation. Two diffraction peaks are generally observed from these trilayer structures; a long-period like layer spacing, (002), oriented normal to the layer face and a weaker (110)/(020) combined orthogonal reflection at about 0.44 nm. The 0.44 nm reflection should always orient orthogonal to the layer spacing peak for planar alumino silicate tri-layers (Takahashi *et al.*, 2002).

Benefits of clay over other nano-sized conventional filler:

It is of interest to know the advantages of clay over other nano-sized filler like nano-fibers. The most important characteristic of filler that possibly plays an important role in deciding its reinforcing ability is its surface area to volume ratio (A/V). In order to determine the ratio for these fillers let us consider nano-fibers (Diameter = D and length = L) and clay layers (thickness = D, length and width = L) as shown in Fig. 2.

Surface area of each fiber,

$$A \text{ nano-fiber} = \pi D^2/2 + \pi DL \tag{1}$$

Volume of each fiber,

$$V \text{ nano-fiber} = \pi D^2 L/4 \tag{2}$$

Therefore from Eq. 1 and 2,

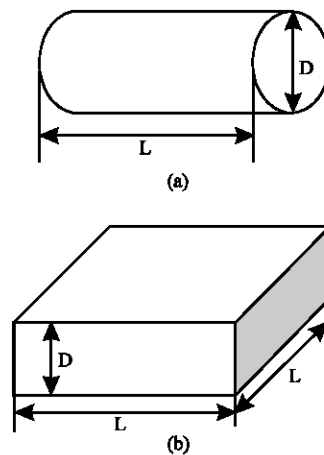


Fig. 2: Schematic of (a) nano-fiber and (b) clay layer

$$\begin{aligned} A \text{ nano-fiber}/V \text{ nano-fiber} &= 2/L + 4/D \\ &\sim 4/D \text{ (since } L \gg \gg \gg D) \end{aligned} \quad (3)$$

Surface area of each clay layer,

$$A \text{ clay} = 4DL + 2L^2 \quad (4)$$

Volume of each clay layer,

$$V \text{ clay} = DL^2 \quad (5)$$

Therefore from Eq. 3 and 4,

$$A \text{ clay}/V \text{ clay} = 4/L + 2/D \sim 2/D \text{ (since } L \gg \gg \gg D) \quad (6)$$

Comparing A/V value of a nano fiber (Eq. 3) and a clay layer (Eq. 6), it is clear that the ratio for nano-fiber is two times higher than that for clay. This means that for a fixed volume fraction of filler, the nano-fibers would have higher surface area of the filler exposed to the polymer matrix and thus would have higher reinforcing ability than the clay layers. Higher reinforcing ability of the nano-fibers gives them an advantage over clay layers. On the other hand, when oriented strongly in a particular direction in the composite, the ability of clay layers to reinforce the composite bi-axially gives them an advantage over nano-fiber which just reinforces the composite uni-axially (Fig. 3).

Thus applications where biaxial reinforcement is required would surely prefer clay as filler. Also properties like barrier, flame retardancy etc. in which hindrance to the transport of gases or fluids along a particular composite direction is required, requires large amount of filler surface area to be normal to that direction of the composite. For highly oriented filler, this area would be significantly larger in a clay composite than in a nano-fiber composite. Therefore even though the nano-fibers have higher A/V ratio, factors like biaxial reinforcing ability and higher ability to prevent the transport of gases and fluids, makes clay highly preferable filler than nano-fibers. For exactly the same reasons, clay was used as reinforcement in our studies.

Polymer-clay interaction: For the greatest property enhancement in PLSN systems it is generally believed that the clay layers should disperse as single platelets throughout the polymer matrix. This is termed exfoliation. Applying tensile or compressive load to a polymer nanocomposite would produce different values of stress, in the polymer matrix and in the clay layers, due to a significant difference in their modulus. Dispersion of clay

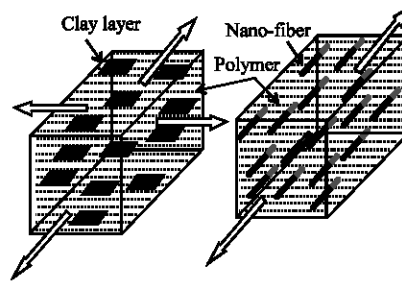


Fig. 3: Ability of (a) clay layers and (b) nano-fibers to reinforce a composite biaxially and uni-axially respectively. Arrows indicate the direction of reinforcement

as single nm sized layers in the polymer matrix prevents stress concentration. To attain such dispersion of clay platelets the polymer should first penetrate between the clay platelets. This intercalation is possible if both the polymer and the clay layers have polar groups that have favorable interaction. Depending on the interaction between the clay and the polymer and the clay loading (Giannelis *et al.*, 1999; Fong *et al.*, 2002) different regimes of dispersion are expected (Fig. 4). If the polymer and clay are incompatible, the clay platelets remain as large stacks (chunks) without any polymer chains entering the region between the clay platelets (clay gallery) (Fig. 4a). Here the clay persists as chunks of face to face stacked layers throughout the polymer matrix. This incomplete and non-uniform dispersion of clay layers creates large regions of pure polymer in the nanocomposite leading to poor properties. If the polymer enters the clay gallery but the platelets still remain as a stack, the system is said to be intercalated (Fig. 4b). Intercalation generally increases the d-spacing of the clay platelets by around 0.5-1.5 nm which is evident from the shifting of the clay stacking peak to smaller angles in an x-ray diffraction pattern. Such intercalated systems have regions of very high and very low reinforcement concentration limiting stress transfer throughout the composite, as explained earlier, giving comparatively less than optimal reinforcement (Fornes *et al.*, 2001; Varlot *et al.*, 2002; Kojimae *et al.*, 1993a). Exfoliated systems (Fig. 4c) are formed when the polymer enters between the clay platelets and force them apart so they no longer directly interact with each other.

Evidence of exfoliation comes from the weakening or absence of the clay stacking peak, (002), in the x-ray diffraction pattern. The highest degree of property enhancement is obtained only when the clay layers are completely and uniformly dispersed or exfoliated in the polymer matrix (Fornes *et al.*, 2001; Varlot *et al.*, 2002).

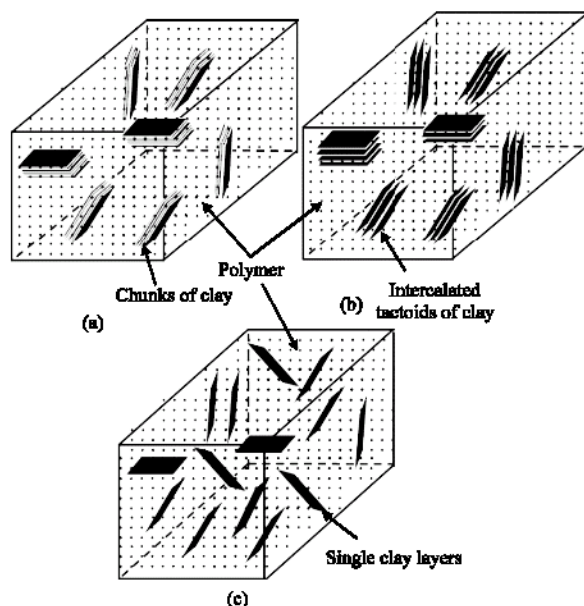


Fig. 4: Different nanocomposite systems obtained depending on the dispersion of the clay platelets in the polymer matrix. (a) Incompatible system (chunks of clay platelets), (b) Intercalated system (tactoids of clay platelets) and (c) Exfoliated system (single clay platelets)

(Brune and Bicerano, 2002) have proposed that exfoliated platelets could have a high degree of flexibility based on their ability to produce large bending moments due to high aspect ratio.

Microscopic study made by Schon *et al.* (2002) evidenced the bending of clay layers in TEM micrographs. However, the presence of the (110) reflection in careful studies on single clay layers (Takahashi *et al.*, 2002) seems to contradict the TEM micrographs of Schon *et al.* (2002) since it would be impossible to obtain long-range 3-d ordering in the plane of the exfoliated platelets if they were bent. Additionally, the reason for a continuous curvature of the clay platelet proposed by Brune and Bicerano (2002) rather than a folded or crumpled structure remains vague. The curvature observed in TEM may reflect the sample preparation technique where thin slices normal to the clay platelets are used. Such thin slices might display continuous curvature in response to residual stress from the sample preparation procedure. No direct evidence of curved platelets in their native 3-d state exists in the literature. The mechanical property of isolated platelets of this type is an open question. If isolated, exfoliated clay platelets truly display compressive flexibility, then there may be some advantage to intercalated clay where such flexural rigidity is retained.

In the case of polar polymers like nylon and EVA (ethylene vinyl acetate copolymer) the organophilic surfaces of clay have sufficient interactions with the polar groups of the polymer to easily produce exfoliated nanocomposites. On the other hand, the case of non-polar polymers is completely different. In the case of non-polar polymers like polyethylene (PE), polypropylene (PP) there is very little or no interaction between the polar modified clay layers and the non-polar polymer. In such situations one of the following processing routes are used:

- Adding small amount of a polymer, which is compatible with both clay and the polymer in which it is dispersed. The polar polymer enters the gallery first, pushes the clay layers apart and therefore increases the gallery height. This facilitates the non-polar polymer to enter the gallery. For example, maleic anhydride grafted PP was used as a compatibilizer in PP/clay nanocomposite (Svoboda *et al.*, 2002). Since it is only the polar polymer, which interacts with the organo-clay, it is generally preferred to make a master-batch of the polar polymer and clay so as to attain maximum interactions between the clay and the polar polymer (Mehta *et al.*, 2004). This master-batch is then let down into the non-polar polymer making this route a two step process.
- Polar groups may be added to the backbone of the non-polar polymer thus increasing the interaction between the polymer and the clay. This route involves mixing the polymer directly with the organo-clay, making it a one-step process and thus preferable than the method (a) described earlier. The explanation of the routes for the synthesis of a polymer-clay nanocomposite is given further.

SYNTHESIS OF POLYMER-CLAY NANOCOMPOSITES

***In situ* polymerization:** Toyota Motor Company (Japan) filed the first US patent (#4739007) for the development of nylon-clay nanocomposites by *in situ* polymerization route (Okada *et al.*, 1987). This route involves intercalation of monomers between the clay galleries and then polymerizing it *in situ*. To facilitate the polymerization reaction and intercalation, catalysts are supported on the clay surfaces. The solution containing catalyst supported on the clay is then introduced into a high-pressure polymerization reactor along with the monomer. Reaction is carried out at high temperature and pressure to obtain a polymer nanocomposite. Various polymer-clay nanocomposites, using polymers like

polystyrene (Okamoto *et al.*, 2001), epoxy (Beker *et al.*, 2002), poly (ethylene terephthalate) (Sekelik *et al.*, 1999), polyethylene (Gopakumar *et al.*, 2002; Jin *et al.*, 2002), poly (methyl methacrylate) (PMMA) (Okamoto *et al.*, 2000) etc., have been synthesized by this route.

Although nanocomposites prepared by this route have promisingly showed improved properties, the batch size achieved by this route in a laboratory is limited due to very small reactors. From an industrial point of view, presence of additives in the system lead to complicated reaction conditions making the production of these materials very complicated in the large reactors used in an industry (Feng and Nelson, 2002). These are some of the reasons that have made the bulk production of the nanocomposites by this route very unlikely in the industry.

Melt blending: polymer-clay nanocomposites could be developed by melt blending the polymer and an organophilic clay in a twin-screw extruder. In this route both polymer and clay are either simultaneously fed, or separately premixed and then fed, to the twin-screw extruder (Giannelis, 1993). The heat and shear generated by the screw in the barrel of the extruder facilitates the intercalation/exfoliation of clay in the polymer matrix. Various polymer-clay nanocomposites, using polymers like nylons (Fornes *et al.*, 2001), PET (Davis *et al.*, 2002), PET (Wang *et al.*, 2001), PP (Usuki *et al.*, 1997) etc., have been synthesized by this route. Being comparatively easier than the *in situ* route, the development of the melt blending route brought polymer-clay nanocomposites closer to commercialization.

Solution synthesis: Aranda and Ruiz (1992) reported PEO/montmorillonite nanocomposites can be prepared by dissolving PEO in a suitable solvent which also swells the montmorillonite. In this method for synthesizing polymer-clay nanocomposites, the polymer is first dissolved in a solvent and then modified clay is added to it. The solvent used in this technique should dissolve the polymer and also swell the clay layers. The mechanism for the formation of nanocomposites by this technique involves two steps. 1) Swelling of the clay layers by the solvent and then 2) intercalation of the polymer chains into the expanded clay galleries by displacing the solvent molecules out of the gallery.

After the solvent is completely displaced out of the galleries, the system is heated till all the solvent evaporates. On removal of all the solvent it has been observed that the intercalated clay remains intact, resulting in polymer-clay nanocomposite. Various

polymer-clay nanocomposites, using polymers like poly-vinyl acetate (Strawhecker and Manias, 2000), PE (Jeon *et al.*, 1998) and PEO (Choi *et al.*, 2001), have been synthesized using this route.

Although no studies involving measurements of the nanocomposite properties after a certain period of time (in order to study the aging behavior of the nanocomposite) is reported, it is believed that once the clay is dispersed by a certain distance from the neighboring platelet so that no VanDer Waals interactions are present, the clay layers would not collapse back and deteriorate the properties.

Although this route can be used to synthesize nanocomposites from polymers with little or now polarity, from a commercial point of view, this route involves use of organic solvents in a large amount, which is environmentally unfriendly and economically prohibitive. Also it is believed that a small amount of solvent remains in the final product at the polymer-clay interface thus creating weaker interfacial interaction between the polymer and the clay surfaces (Jin *et al.*, 2002).

Dispersion in polymer-clay nanocomposites: Most of the studies on nanocomposites have used x-ray diffraction and transmission electron microscopy to study the type of dispersion present in the sample. The explanation of these techniques with their advantages and disadvantages are discussed as follow:

Characterization techniques for determining dispersion of clay: TEM and X-Ray Diffraction (XRD) are the most widely used techniques to determine the dispersion of the clay platelets in the polymer matrix. Some studies have used either Small Angle X-ray Scattering (SAXS) or wide-angle x-ray scattering or both together to get data on dispersion and orientation of the clay platelets in the polymer matrix.

Transmission Electron Microscopy (TEM): The micrograph is of a commercially available nylon-clay nanocomposite and was obtained from the nanocomposite database at Equistar Chemicals (Fig. 5). The dark lines in the micrograph are the dispersed clay layers in the polymer matrix. It is seen that the clay is dispersed as a stack of clay layers with the total stack thickness of approximately 2-5 nm and containing 2-5 clay platelets. Although TEM is a technique that gives a clear picture of the morphology of the nanocomposite, good sample preparation techniques for TEM are pivotal. Very thin cross-sections (40-50 nm) of the nanocomposite are required to get a good quality image. For this reason the nanocomposite needs to be microtomed cryogenically. Microtoming of a material in to very thin sections

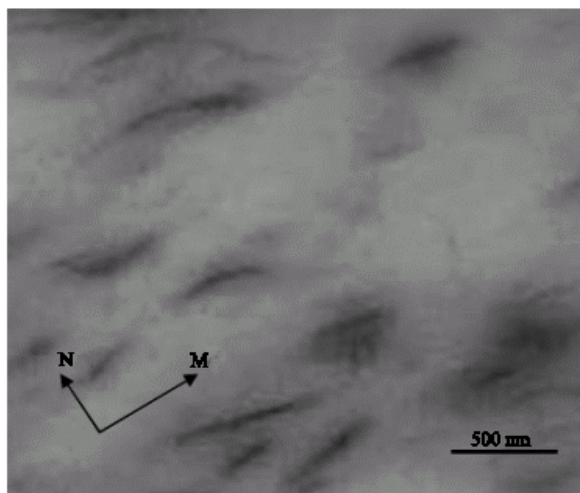


Fig. 5: Transmission electron micrograph of a nylon-clay nanocomposite showing planar projection of the orientation of clay platelets (dark lines) in the polymer matrix. Micrograph obtained from the nanocomposite database at Equistar Chemicals.

(40-50 nm) and heating of the sections in the TEM column by the high-energy electron beam could have an effect on the morphology of the material. Also, TEM gives only a planar projection of the orientation of the clay platelets (Fig. 5) and thus performing TEM along a single cross section of the sample could give misleading results regarding the orientation of the clay platelets in the polymer matrix. Performing TEM on all the 3 different faces of a sample, even though extremely tedious, could give a rough idea of the 3-d orientation of clay layers but still could be misleading as it is very difficult to identify the sample direction, without making some assumptions, when viewing the cross-section in the microscope at 100,000 times magnification, at which the clay layers are clearly visible.

X-Ray Diffraction (XRD): XRD gives quantitative data on the dispersion of the clay platelets. The clay platelets are arranged periodically in an intercalated system and thus a reflection from the clay platelets is observed in the XRD pattern. As more and more polymer chains enter the clay gallery, the clay spacing increases, shifting the clay peak to lower angles ($2\theta < 2^\circ$).

The separation of the clay platelets also decreases the periodicity and hence reduces the intensity of the clay peak. For an exfoliated system the clay platelets are randomly dispersed and no clay peak is observed in the XRD pattern. But the lack of a Bragg's peak in the diffraction pattern does not necessarily mean that the clay

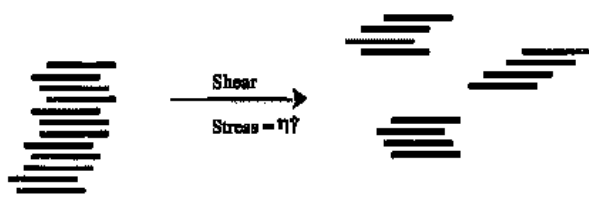
is exfoliated. A disordered and immiscible sample, or other factors like low concentration of the clay in the region where the x-ray beam hits a non-uniformly dispersed sample, could fail to produce a Bragg's reflection (Morgan and Gilman, 2003). It is also difficult to get diffraction data from thin nanocomposite films when a reflection mode diffractometer is used. Thus XRD can be used to characterize as incompatible or intercalated system but could possibly give misleading data on the exfoliation.

Small and wide angle x-ray scattering (SAXS and WAXS): SAXS and WAXS when used together give data on both dispersion and orientation of clay platelets and various other structural features in a polymer-clay nanocomposite. Scattering data from both, molded samples and thin films can be obtained. Recent studies have obtained data on the 2-d orientation of clay platelets and polymer structures in a nanocomposite system, which could be misleading (Varlot *et al.*, 2002).

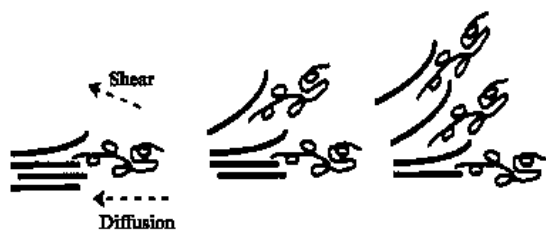
Most of the studies present by Hambrir *et al.* (2001), Fomes *et al.* (2001), Oya *et al.* (2000) Beyer and Eupen (2001) and Gilman (1999) propose that the dispersion of the clay platelets play an important part in tuning the property enhancements in PLSN systems. For this reason a review on the factors affecting the dispersion and the mechanism of property enhancement based on dispersion of clay is presented here.

Factors effecting dispersion of clay platelets: The presence of positive ions on the surface makes the clay platelet hydrophilic and thus incompatible with many polymers. The organophilicity of the clay platelets is increased by exchange of these ions with organic cations (alkyl ammonium ions) on treating it with ammonium salts (surfactants). These treated clays are called organically modified layered silicates (OLS's). The dispersion of these OLS's in the polymer matrix depends on a number of factors some of which are explained here.

Molecular weight of the polymer: Fomes *et al.* (2001) proposed a model for explaining the mechanism of exfoliation of clay layers, from an initially present stack of clay layers, by the stepwise skewing of the clay platelets, followed by peeling, one-by-one, of the silicate layers off the silicate stack under the influence of shear forces. A schematic of the skewing/peeling and diffusion mechanism as proposed by Fomes *et al.* (2001) (Fig. 6). The intercalation/exfoliation of clay platelets was shown to be a combination of two mechanisms the breaking up of large clay stacks into smaller stacks of fewer and fewer clay platelets under the influence of large shear forces (Fig. 6a) and the diffusion of the polymer molecules into



(a) Shearing of platelet stacks leads to smaller tactoids



(b) Platelet peel apart by combined diffusion/shear process

Fig. 6: Mechanism of intercalation/exfoliation of the clay platelets by the polymer (Fornes *et al.*, 2001)

the clay galleries (Fig. 6b). They also showed that higher the molecular weight of the polymer matrix, higher was its melt viscosity; greater was the stress exerted on the stack of clay platelets and lesser was the number of platelets left in the stack.

Although the mechanism of intercalation/exfoliation by breaking of large clay crystals into smaller ones (Fig. 6a) and then peeling of each platelet one after one seems possible, the bending of the ends of clay layers (Fig. 6b) in order to allow the intercalation of polymer chains seems unlikely. Most likely the whole clay platelets at the top and at the bottom of a clay crystal would just separate out one after another by skewing under the influence of shear force since this would require less energy than that required for bending the ends of the clay layers and hence their ionic bonds with the neighboring platelets.

Increase in the molecular weight decreases the diffusion of polymer chains ($D \sim 1/M^2$) (Strobl, 1997) into the clay galleries and hence should decrease the rate of hybrid formation. Thus, in a nanocomposite system, the rate of hybrid formation depends on the type of mechanism, which dominates. For example, Ishida *et al.* (2000) observed a decrease in the degree of intercalation/exfoliation on increase in the molecular weight of the base resin.

They prepared the nanocomposites by manually mixing the polymer melt and clay. Due to the lower degree of shear involved, the mechanism of the diffusion of

polymer chains dominated the intercalation process and hence the degree of intercalation/exfoliation decreased with the increase in molecular weight. Fornes *et al.* (2001) observed an increase in the degree of intercalation/exfoliation with molecular weight in nylon-clay nanocomposites. The nanocomposites were made by extruding a mixture of polymer and clay through a twin-screw extruder. Due to the higher degree of shear involved the breakup of large stacks into smaller ones took place and hence increased the rate of hybrid formation. Thus the molecular weight of the base resin affects the rate of hybrid formation by two different mechanisms and the actual rate depends on the combinatory effect of both the mechanisms.

Thermodynamic interactions: Vaia and Giannelis (1997a) proposed a mean-field model to explain the intercalation of polymer molecules in an organo-clay. They propose that changes taking place in both entropy and enthalpy by the addition of organo-clay into the polymer matrix play an important role in determining the degree of intercalation/exfoliation in the nanocomposite system.

From an entropic point of view Vaia and Giannelis, (1997a) propose that the intercalation of polymer chains in the clay gallery decreases its entropy due to polymer confinement and thus decreases the overall entropy and thus the free energy, of the system which is unfavorable for further polymer intercalation. But Vaia and Giannelis, (1997a) also propose that this decrease in entropy can be balanced by the increase in entropy of the alkyl-ammonium chains on the surface of the clay layers due to increased gallery height. The increase in the entropy depends on the gallery height which in turn depends on the interlayer packing density of the alkyl ammonium (aliphatic) chains (Vaia and Giannelis, 1997b). Interlayer packing density is the number of aliphatic chains of the surfactant present per unit area of the surface of the silicate layer. At very low packing densities the aliphatic chains display mono/bilayer arrangement while at very high packing densities they display solid-like fully extended arrangement (Vaia and Giannelis, 1997b; LeBaron *et al.*, 1999).

At both low and very high packing density the aliphatic chains have comparatively less conformational freedom and thus the total entropy increase is not high enough to balance the decrease in entropy by polymer confinement and is thus unfavorable for polymer intercalation (Vaia and Giannelis, 1997a). At intermediate range of packing densities the chains adopt pseudo-trilayer arrangements which have comparatively higher conformational freedom and thus balance the decrease in entropy by polymer confinement, resulting in a net entropy change near zero (Vaia and Giannelis, 1997a).

Thus the hybrid formation by melt intercalation now depends on the enthalpic interactions between the polymer and clay surfaces which can be increased by polymer and clay surface functionalization (Vaia and Giannelis, 1997b). By experiments they also showed that the outcome of polymer intercalation depends on the silicate functionalization and constituent polar interactions between the clay and the polymer.

Polymer-clay interaction: As explained in the earlier section it was shown by (Vaia and Giannelis, 1997a) that functionalization of the clay surfaces is very critical for polymer intercalation into the clay galleries. Presence of functional groups on the surface of the clay layers easily intercalate polar polymers but do not favor intercalation of non-polar polymers like polyethylene (PE) and polypropylene (PP). Addition of a compatibilizer like maleated polyolefin oligomer increases the interaction between the clay surface and the non-polar polymer. This increase in interaction originates from the strong hydrogen bonding between the maleic anhydride groups and the oxygen atoms on the clay surfaces (Liu and Wu, 2001). Increased interaction between the two, acts as a driving force for the intercalation of the compatibilizer into the clay galleries. The bulky nature of the maleated polyolefin oligomer increases the clay-spacing and decreases the interactions between the clay layers which in turn favor the intercalation of the base resin (PE/PP). Increasing the polarity of the compatibilizer increases the interactions between the clay and the polymer and hence the degree of intercalation/exfoliation (Vaia and Giannelis, 1997b).

Property enhancements based on clay dispersion

Mechanical properties: Varlot *et al.* (2002) studied the injection molded samples of both intercalated and exfoliated nylon 6-clay nanocomposites. Both the systems showed an increase in the storage modulus, which increased monotonically with the clay content. Compression modulus and strain was found to be different along different faces of the sample and was maximum for the faces along the injection axis of the sample. The compression modulus and strain along the same face increased with increase in the filler content. An exfoliated system had higher values of tensile modulus than an intercalated one and the modulus increased with increase in the filler content. The variation in the compression modulus and strain along different directions could be due to the preferential orientation of the clay platelets along the injection axis of the sample. The higher values of the tensile modulus in the exfoliated sample as compared to the intercalated sample could be due to the increased surface area of the clay platelets in contact with the polymer.

Brune and Bicarano (2002) developed a model to predict the effects of incomplete exfoliation on the tensile modulus of nanocomposite systems. In an incompletely exfoliated nanocomposite the stacks of clay layers (tactoids), with polymer intercalated in their galleries, are called pseudoparticles in their study. For nanocomposites containing pseudoparticles, they modified the Halpin-Tsai equation as the stack of clay layers now behave as a single large particle which has decreased aspect ratio and decreased effective elastic modulus. Due to the decreased aspect ratio and elastic modulus of the filler, the relative modulus of the nanocomposite having pseudoparticles, with respect to a nanocomposite with exfoliated clay layers is lower. This model thus theoretically supports the experimental observation of Varlot *et al.* (2002) that exfoliated nanocomposites have significantly higher properties than a intercalated nanocomposite.

Kojima *et al.* (1993b) studied the mechanical properties of nylon 6-clay nanocomposites prepared using organically modified montmorillonite (NCH) and synthetic (NCHP) clays. TEM showed that both nanocomposites were exfoliated. The nylon 6-clay hybrid (NCH) was superior in strength and modulus to nylon 6. The flexural strength of NCH at 120°C was double than that of nylon 6. The flexural and tensile modulus was 4 times and 3 times that of nylon 6 respectively. This contradicts (Brune and Bicerano, 2002) statement that the clay platelets are flexible. Nylon 6-clay hybrids (NCHP) prepared using synthetic clay had properties better than nylon 6 but not better than NCH. This difference in the mechanical properties could be due to the smaller aspect ratio of the synthetic clay as compared to montmorillonite clay and the direct relationship between the aspect ratio and modulus as shown theoretically by (Brune and Bicerano, 2002).

Degradation properties: Zanetti *et al.* (2001) investigated the degradation properties of PP-clay nanocomposites. A 50°C increase in the temperature at which thermal degradation starts was observed as compared to the homopolymer. A decrease in the rate at which degradation and weight loss proceeded was also observed. They relate this increase in the thermal stability in the nanocomposites to the decrease in rate of transport of volatile products in and out of the sample. The decrease in the transport could be due to the labyrinth effect (complex arrangement of the silicate layers which increases the tortuous path) that increased the barrier to the flow of the degradation volatiles and physical adsorption of the volatile products on the surface of the silicate layers.

Liang and Yin (2003) also studied the degradation properties of poly (etherimide) (PEI)-clay nanocomposites. From XRD and TEM results they claim that the montmorillonite was exfoliated in the polymer matrix. They observed a moderate increase in the temperature of onset of thermal degradation by addition of organo-clay to the nanocomposite. The onset temperature of thermal degradation increased from 522°C for PEI to 534°C for the PEI-clay nanocomposite containing about 10 wt. % organo-clay. They mention that montmorillonite has higher thermal stability and the layer structure of montmorillonite exhibited a greater barrier to the flow of small molecules generated during the thermal decomposition of PEI matrix.

Thermal properties: Liang and Yin (2003) also studied the thermal stability of PEI and PEI-clay nanocomposites. They observed a significant decrease in the coefficient of thermal expansion (CTE) of PEI by addition of clay to it. The CTE of PEI decreased from $2.37 \times 10^{-5} \text{ K}^{-1}$ for PEI to $1.33 \times 10^{-5} \text{ K}^{-1}$ for PEI containing 10 wt% organo-clay. They propose the reduced segmental motion of the PEI matrix by addition of clay to it as the reason for the decrease in the CTE.

Yoon *et al.* (2002) studied the thermal expansion behavior of nylon 6 nanocomposites. TEM analysis showed that the clay layers were exfoliated in the polymer matrix. They studied the coefficient of thermal expansion for injection molded Izod bars. They observed a decrease in the CTE along the Flow Direction (FD) and the Transverse Direction (TD) when compared to nylon 6 containing no clay. They observed that the CTE decreases more along the FD than along the TD and suggest non-uniform platelet orientation along the FD, since perfect alignment of the clay layers in an isotropic polymer matrix should yield equal CTE along both FD and TD. They also showed that nanocomposites made from high molecular weight polymer had higher degree of exfoliation (higher aspect ratio) and thus lower CTE and the nanocomposites made from lower molecular weight polymer had lower degree of exfoliation (lower aspect ratio) and thus higher CTE even though it was lower than the base resin.

The effect of molecular weight on the degree of exfoliation has been explained earlier.

Flame resistance: Beyer and Eupen (2001) and Gilman (1999) investigated the flammability of ethylene-vinyl acetate (EVA)-clay nanocomposites. The EVA-clay nanocomposites were found to have better flame retardant properties. It was observed that the intensity of the peak of heat release decreased by 47% for a nanocomposite

containing 5 wt. % of the modified montmorillonite when compared to the pure EVA. The decrease in the intensity of the peak of heat release indicates a reduction of the burnable volatiles, which indicates the flame-retardant effect due to the presence of clay. Such properties are further improved by the fact that the peak of heat release is spread over a much longer period of time. This improvement in the flame-retardant properties is due to char formation during the nanocomposite combustion. The clay layers act as reinforcement to the char produced and thus forms a thick insulating, non-burning material that reduces the emission of the volatile material into the flame area. The silicate layers thus play an active part in decreasing the transport of volatile products and hence improving the flame-retardant properties.

Barrier properties: The enhancement of barrier properties is believed to depend on the degree of exfoliation of the clay platelets. In the fully exfoliated state, individual clay platelets have the highest aspect ratio possible and thus the highest barrier improvement is expected. Kojima *et al.* (1993a) studied the barrier of nylon-montmorillonite and nylon-saponite (synthetic clay) nanocomposites to water. Both nylon-montmorillonite and nylon-saponite nanocomposites had better barrier to water than nylon homopolymer. The higher aspect ratio of montmorillonite compared to saponite, made nylon-montmorillonite nanocomposites more resistant to water absorption than nylon-saponite nanocomposites.

Most of the studies explained above have related the property enhancement to the dispersion and/or the aspect ratio of the clay platelets. Properties mentioned above depend on the transport of some material in and out of the sample and thus, the enhancement in these properties will depend on the orientation of the clay platelets in the sample. For this reason recent studies have proposed that along with the dispersion, the orientation of the clay platelets should be considered to understand the true relation between morphology and property enhancement.

Rheological properties: Understanding the rheological properties of PLSN's is of significant interest for the design of customized polymer-clay systems with enhanced mechanical, thermal, flame resistance and barrier properties. Various factors like polymer-filler interaction, filler-filler interaction and the dispersion and orientation of filler could influence the viscoelastic properties of the polymer matrix (Krishnamoorti *et al.*, 2001). The response of the presence of clay in the polymer matrix, either as intercalated or exfoliated structures, to external flow is essential in their processing (Krishnamoorti and Yurekli,

2001). For this reason recent studies have focused on studying the rheological properties (Krishnamoorti *et al.*, 2001; Galgali *et al.*, 2001; Lele *et al.*, 2002) of the polymer matrix on addition of clay to it. Krishnamoorti *et al.* (2001) studied the response of polystyrene-1,4 polyisoprene block copolymer/clay nanocomposites to steady shear as a part of their study about the effect of clay on the rheological properties of polymer-clay nanocomposites. The steady shear data for the intercalated nanocomposites showed non-Newtonian behavior in the low shear rate region where the polymer without clay shows Newtonian behavior.

Increasing the clay content was shown to enhance the shear-thinning behavior of the nanocomposite system. Significant improvement of the zero shear viscosity in the nanocomposite system was observed. Additionally, they observed that the viscosity of the nanocomposite systems approached that of the polymer at high shear rates. Significant improvement of the zero shear viscosity in the nanocomposite system was attributed to the confinement of the polymer chains in the clay galleries. The enhanced shear thinning behavior and the viscosities comparable to that of the polymer at high shear rates was attributed to the ability of the anisotropic silicate layers to orient with the application of shear flow. This ability of the anisotropic clay layers to orient with the shear flow was observed by Krishnamoorti and Giannelis (1997). Similar effects of the presence of clay on the rheological properties were observed by Galgali *et al.* (2001) and Lele *et al.* (2002) on different polymer systems.

ORIENTATION STUDIES OF POLYMER-CLAY NANOCOMPOSITES

Although studies Hambir *et al.* (2001) and Zhang *et al.* (2000) have mentioned that true nanocomposites and significant property enhancements are obtained only when the clay disperses as single platelets (exfoliation) in the polymer matrix, there are some studies (Nam *et al.*, 2001) which have observed enhancements in properties just by intercalating the clay platelets with the polymer chains. Thus the type of dispersion of the clay platelets into the polymer matrix does not seem to be the only governing factor in tuning the property enhancements in nanocomposites. Recent studies mention that along with dispersion, orientation of the clay platelets plays a major role in tuning some property enhancements in PLSN systems. Kojima *et al.* (1995) concluded that the orientation of the clay platelets affected the strength of the nanocomposite along different sample directions. Krishnamoorti *et al.* (2001) proposed that the orientation of the clay platelets could

affect the viscoelastic properties of the nanocomposite. Recently a few studies have focused on the effect of shear on the orientation of the clay platelets and the polymer unit cells in PLSN systems.

Kojima *et al.* (1995) studied the effect of shear on the orientation of clay platelets and polymer unit cells as a function of depth in a 3 mm thick injection molded samples of nylon-clay nanocomposite. Depending on the shear involved the clay platelets and the unit cell (020) or (110) lattice planes oriented in different directions. Due to the high shear involved in the region of the sample close to the surface of the mold, both clay platelets and polymer unit cell (020) or (110) lattice planes were found to orient along the flow direction. In the bulk of the sample the clay platelets and the polymer unit cell (020) or (110) lattice planes were found to orient perpendicular to each other due to lower shear rate. The clay platelets were found to govern the orientation of the polymer unit cells due to hydrogen bonding between the ammonium cations at the end of nylon-6 molecules and the ionic sites on the montmorillonite monolayer.

Fong *et al.* (2002) studied clay dispersion and orientation in nylon-clay nanocomposite films and fibers using XRD and TEM. Films were cast and fibers were electrospun from solution. The effect of shear on the orientation of clay platelets and polymer unit cells in electrospun nylon-clay nanocomposite fibers was also studied. They found that the fibers had layered silicates aligned with layer normal perpendicular to the fiber axis and polymer crystallite (020) planes aligned with normal parallel to the fiber axis implying orthogonal orientation between clay platelets and polymer crystallite (020) planes.

RHEOLOGY AND ORIENTATION OF COLLOIDAL DISPERSION OF CLAY PLATELETS

Understanding the rheological properties of PLSN's is important in order to control orientation of platelets and their structure-property relationship. For this reason recent studies have focused on studying their rheological properties. Addition of clay and its interaction with the polymer was shown to have a significant effect on the rheological properties. The nanocomposites showed higher melt viscosities and greater shear thinning (Galgali *et al.*, 2001; Lele *et al.*, 2002). Thus the literature requires a true understanding of the role played by the dispersed phase (clay layers) on the polymer melt. A explanation of the effect of the addition of spherical or non-spherical colloidal particles on the rheological properties of dispersion as follows:

Einstein proposed an additive expression for the viscosity of a dilute dispersion of solid spheres based on Stokes law (Strobl, 1997). According to his model,

$$\eta' = \eta (1 + 2.5 \phi + \dots) \quad (7)$$

where:

ϕ = Volume fraction of the dispersed phase
 η' and η = Viscosities of the suspension and the solvent respectively.

Thus an increase in the viscosity of the dispersion on addition of the solid spheres is expected. Changing the shape of the dispersed particles from spherical to ellipsoidal or similar shapes in which one of the axes is longer than the other (e.g., clay platelets), makes the model more complex. For a suspension of asymmetric particles the viscosity would depend on the orientation of the particles with respect to the flow direction (Simha, 1940). Due to this dependence of the viscosity of the suspension on the orientation of the particles modified the Einstein's equation for a suspension containing asymmetric particles. The equation proposed by Simha (1940) and Larson (1999) for the macroscopic viscosity, η' , of the suspension of asymmetric particles is written as follows.

$$\eta' = \eta (1 + v\phi) \quad (8)$$

where, v according to Eq. 7 for solid spheres is 2.5 and is larger for asymmetric particles. For disc-shaped particles v is written as follows (Simha, 1940; Larson, 1999).

$$v = A/\tan^{-1}(A) \quad (9)$$

where:

A = The aspect ratio, i.e., ratio of the diameter (D) to the thickness (t), of the particle.

Inclusion of v ($v > 2.5$) along with the volume fraction ϕ in the Einstein's equation could mean that the presence of asymmetric particles in a suspension possibly increases the effect of the volume fraction on the viscosity of the suspension as compared to that by the presence of spherical particles of same volume fraction. This behavior of asymmetric particles can be explained as follows.

v is directly proportional to the aspect ratio as seen in Eq. 9 and so it can be written as $v \sim A = D/t$. The volume fraction of the filler is $\phi = D^2 tN/\phi_s$, where, N is the number of asymmetric particles and ϕ_s is the total volume of the suspension. Product of ϕ and v yields $V^* \sim D^3 N/\phi_s$, which is the volume fraction of spheres of diameter D in

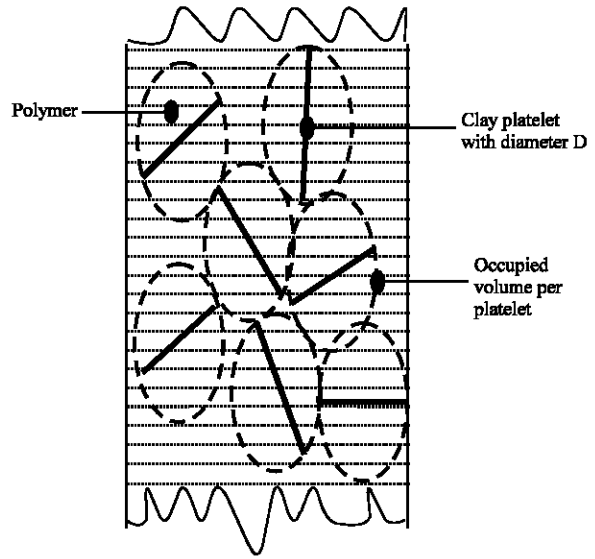


Fig. 7: The morphology of a polymer-clay nanocomposite showing the increase in the occupied volume fraction of the filler due to its asymmetric nature

a suspension. The product of v and ϕ therefore increases the effect of volume fraction on the viscosity of the suspension since the asymmetric particles of diameter D now possibly behaves as having occupied the volume equal to that which would have been occupied by spheres of the same diameter (Fig. 7).

Simha's modification to Einstein's equation takes care of the asymmetric nature of ellipsoidal filler particles. In a shearing flow if the particle long axis is inclined to the plane of deformation (the plane parallel to the flow) then the particle will rapidly rotate initially and then slowly till its long axis is parallel to the plane of deformation. The angle of rotation depends on the quantities like shear rate, the time of shearing and the aspect ratio of the particles (Tanford, 1967). The Jefferies orbit that relates these quantities for ellipsoidal filler particles is:

$$\tan \theta_t = p \tan [\text{shear rate} * t / (p + 1/p)] + \tan \theta_0 \quad (10)$$

where, θ_t , θ_0 are the angles of the axis of symmetry of the filler particles measured in the clockwise direction from the flow direction at time t and time zero respectively and p is the aspect ratio (Tanford, 1967). Therefore control of the shear rate and the time of shear can control the amount of rotation/orientation.

The Jefferies equation is good only for dilute concentrations of the dispersed particles. At higher loading of clay platelets in a PLSN system, the tendency of the particles to form a percolating network arises (Galgali *et al.*, 2001; Lele *et al.*, 2002). Galgali *et al.* (2001)

studied the creep behavior of PP-clay nanocomposite containing 9 wt% clay as apart of their study on the rheological response of polymer nanocomposites. They propose that the frictional interaction between the clay layers could be one reason for the solid like rheological behavior of the nanocomposite systems. Although no evidence either by microscopy or XRD was shown, they propose that at high clay loadings (~9 wt. %) small amount of clay layers exfoliate and form networks between the intercalated clay tactoids finally producing a percolating network. By studying the response of viscosity of the nanocomposite system to shear stress they observed that, the nanocomposite creeps at low stresses in a Newtonian manner, possibly due to the presence of percolating network, followed by apparent yielding at about 1000 Pa, in which the viscosity drops by 3 orders of magnitude in a very narrow range of shear stress. They also propose that above the yield stress, the percolating structure starts to break down and the clay layers start to align along the direction of stress which causes the material to flow to greater extents. Thus to study the orientation in PLSN's the stress on the material should be greater than the apparent yield stress.

Opposing this orientation, randomization of these particles can take place by Brownian motion under the influence of temperature. The ratio of shear energy to thermal energy is a measure of the tendency to thermally randomize. This ratio is called the Rotational Peclet number (Pe) which is given as:

$$Pe = 4 \tau d^3 / 3 k_B T \quad (11)$$

where, τ is the shear stress, d is the diameter of the disc shaped particle, k_B is the Boltzmann's constant and T is the temperature. Particles will orient with shear only when $Pe > 1$ (Tanford, 1967). Therefore, for clay platelets of average diameter 500 nm and considering a temperature of 200°C, the platelets will randomize due to Brownian motion if $\tau < 10^{-5}$ Pa. In a twin-screw extruder, which is the most commonly used instrument to process polymers, the stress acting on the material is high ($>> 10^5$ Pa) and hence the particles will orient and the degree of orientation can be controlled by controlling the shear rate. Processing parameters which affect the shear rate are screw speed, shearing time, temperature of the melt, die-gap and gap between the screw and the barrel etc. Thus an extruder can be used to study the effect of the effect of the processing conditions on the orientation and the property enhancements. Although studies of the rheology of PLSN's are present in the literature, the literature lacks studies relating the effect of the processing conditions on the orientation and the property enhancement.

APPLICATIONS

The nanocomposites have already been used widely in the various fields of injection molding, e.g., engine cover, timing belt cover, oil reservoir tank and fuel hose in automobile industries, floor adjuster and handrail in the construction fields and various connectors in the electrical fields. Nanocomposite nylon6-Clay Hybrid (NCH) shows a high modulus and high distortion temperature (Okada *et al.*, 1987). The timing belt covers made from NCH by injection molding was the first example of industrialized use of polymer-clay nanocomposites. NCH has also a high gas barrier property because of the nanometer level dispersion of silicate layers (Messersmith and Giannelis, 1995), so it has a wide range of applications in the food packaging films. As mentioned above, the increased mechanical properties and dimension stability makes the Nanocomposites convenient to be used as high value construction materials.

They are highly stable against aggressive chemicals, so they can also be implemented in corrosive protective coatings.

Due to the decreased permeability for gases and water, as well as for hydrocarbons, they have a wide range of applications in packaging and automotive industries. In high temperature areas, such as internal combustion engines, because of good thermal stability, flame retardancy and HDT; nanocomposites are more attractive and promising than other conventional materials.

These materials have a good perspective of application for the near future in daily life. Through the nano-clay reinforcement we expect a new dimension in the polymer technology. The production of the high-tech composites like carbon-carbon composites is extremely expensive and labour-intensive, therefore the art of composites may be considered as another alternative solution. By the extrusion technology, lower labour-intensive mass production lines are expected.

DISCUSSION

Poor barrier to hydrocarbons and lower stiffness to impact ratio of polyethylene's has restricted its application in certain packaging/handling and automotive applications respectively. Reports on improvement in mechanical, thermal, barrier and flame retardant properties of a polymer by addition of 2-6 wt. % organo-clay have drawn tremendous attention due to significant property enhancement without a significant increase in weight. This modified thermoplastic system is called polymer layered-silicate nanocomposite system.

Depending on the interaction between the polymer and the surface of the organoclay and few other factors like the polymer molecular weight, type of treatment on the surface of clay layers and the processing conditions, different degrees of dispersion and thus different levels of property enhancement are obtained. The dispersion of the clay layers can be quantitatively and qualitatively studied using XRD and TEM respectively with each of the techniques having their own merits and demerits.

Most of the previous studies have related the property enhancement to the dispersion of the clay platelets. Properties like barrier, thermal stability and flammability depend on the transport of some material in and out of the sample and thus, the enhancement in these properties will depend on the orientation along with the dispersion of the clay platelets in the sample. For this reason recent studies have started focusing on the effects of both dispersion and orientation on the property enhancement.

In injection molded nylon-clay nanocomposite samples, Kojima *et al.* (1995) found that the polymer crystallites either align parallel (high shear region) or perpendicular (low shear region) to the clay platelets. Contrary to Kojima *et al.* (1995) observation, Fong *et al.* (2002) observed that polymer crystallites align perpendicular to the clay platelets in nylon-clay electro spun fibers where exceedingly high shear rates are expected. Varlot *et al.* (2002) observed that in intercalated nylon-clay nanocomposites, the clay platelets aligned with normal both parallel and perpendicular to the thickness of an injection molded sample consistent with Kojima *et al.* (1995). Although it is clear that the polymer lamellae align in different directions depending on the type of deformational cumulative shear strain and shear rate, the relationship of clay platelet orientation to the orientation of other structural units, such as the polymer unit cells and polymer lamellae still remains unclear.

The application of nanocomposites is currently limited to polar polymer like nylons, EVA's (ethylene-vinyl acetate) etc. In order for a major impact PLSN's should be applied to non-polar systems like polyolefins which are the most widely consumed thermoplastics. As mentioned earlier, polyolefins being non-polar show poor compatibility with modified clays. Many researchers (Wang *et al.*, 2001; Kodgire, 2001) reported on the dispersion of clay platelets in polyolefins by addition of a compatibilizer such as maleated polypropylene or polyethylene. Although previous studies showed the effect of compatibilizer on property enhancement in polyolefin nanocomposites, the literature lacks a clear picture of the effect of compatibilizer on the orientation/dispersion of the clay platelets and the effect

of this clay orientation on the orientation of other structural units like, polymer unit cells and polymer lamellae.

Although studies on the rheology of PLSN's are present in the literature it lacks studies relating the effect of the rheology and the processing conditions on the orientation and the property enhancement.

CONCLUSIONS

Polymer/clay nanocomposites are materials that display rather unique properties, even at low clay content, by comparison with more conventional mineral-filled polymers. Nanocomposites have a number of advantages over traditional polymer composites. Conventional composites usually require a high content (>10 wt%) of the inorganic filler to impart the desired mechanical properties. Such high filler levels increase the density of the product and can cause deterioration in properties through interfacial incompatibility between the filler and the organic matrix.

Processability also worsens as filler content increases. In contrast, nanocomposites show enhanced thermal and mechanical properties with even a small amount of added clay because the nanoscale dimensions of the clay particles yield a large contact area between the polymer and the filler. The structure of clays, with layers of high aspect ratio, also imparts excellent barrier properties, which in turn provides low gas permeability and enhanced chemical resistance and flame retardancy. This new type of materials, based on smectite clays usually rendered hydrophobic through ionic exchange of the sodium interlayer cation with an onium cation, may be prepared via various synthetic routes comprising exfoliation adsorption, *in situ* intercalative polymerization and melt intercalation. The whole range of polymer matrices is covered, i.e., thermoplastics, thermosets and elastomers.

Nanocomposites are subject of current interest because of their unusual magnetic, optical, electronic properties, which often different from their bulk properties. The reasons for these are confinement of electronic and vibrational excitation, quantum size effect and large surface to volume ratio. Although Nanocomposites have received attention from both theoretical and experimental standpoints, the greatest challenge at present is to find out an effective synthesis procedure. The fundamental challenges in nanostructured materials are ability to control the scale (size) of the system, understand the influence of the size of building blocks in nanostructured materials as well as the influence of microstructure on the physical, chemical and

mechanical properties of this material and transfer of developed technologies into industrial applications including the development of the industrial scale of synthesis methods of nanomaterials and nanostructured systems.

REFERENCES

- Alexander, J. and P. Dubois, 2000. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mat. Sci. Eng.*, 28: 1-63.
- Aranda, P. and E. Ruiz-Hitzky, 1992. Poly (ethylene oxide)-silicate intercalation materials. *Chem. Mat.*, 4: 1395-1403.
- Bafna, A., G. Beaucage, F. Mirabella and S. Mehta, 2003. 3D hierarchical orientation in polymer-clay nanocomposite films. *Polymers*, 44: 1103-1115.
- Beker, O., L. Varley and G. Simon, 2002. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high functionality epoxy resins. *Polymers*, 43: 4365-4373.
- Beyer, G. and K. Eupen, 2001. Nanocomposites of layered silicate and EVA copolymer-new synthesis route, flame retardancy and potential electrical applications. *Proc. Nanocomposites*, Chicago, IL.
- Brindley, G. and G. Brown, 1980. Crystal structure of clay minerals and their X ray identification. *Mineralog. Soc. London*, pp: 227-232.
- Brune, D. and J. Bicerano, 2002. Micromechanics of nanocomposites: Comparison of tensile and compressive elastic moduli and prediction of effects of incomplete exfoliation and imperfect alignment on modulus. *Polymers*, 43: 369-387.
- Choi, H., S. Kim, Y. Hyun and M. Jhon, 2001. Preparation and rheological characteristics of solvent-cast poly (ethylene-oxide)/montmorillonite nanocomposites. *Macromol. Rapid Commun.*, 22: 320.
- Davis, C., L. Mathias, J. Gilman, D. Schiraldi, J. Shields, P. Trulove, T. Sutto and H. Delong, 2002. Effects of melt-processing conditions on the quality of poly(ethylene terephthalate) montmorillonite clay nanocomposites. *J. Polym. Sci., Polym. Phys.*, 40: 2661-2666.
- Esfandiari, A.H., H. Nazokdast, A.S. Rashidi and M.E. Yazdanshenas, 2007. Investigation of Effect of Organoclay and Compatibilizer on Microstructure and Mechanical Properties of PP/PA6/Montmorillonite Nanocomposite. 6th International Conference of Textile Science (TEXSCI 2007), Liberec, Czech Republic, Book of Abstracts, pp: 31-32.
- Feng, Y. and R.G. Nelson, 2002. PMMA/Silica and Polyethylene/Silica Nanocomposites Prepared via Extrusion. In: *Proc. Nanocomposite 2002*, San Diego, CA.
- Fong, H., W. Liu, C. Wang and R. Vaia, 2002. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. *Polymers*, 43: 775-780.
- Fornes, T., P. Yoon, H. Keskkula and D. Paul, 2001. Nylon 6 nanocomposites: The effect of matrix molecular weight. *Polymers*, 42: 9929-9940.
- Galgali, G., C. Ramesh and A. Lele, 2001. A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites. *Macromolecules*, 34: 852-858.
- Giannelis, E.P., 1993. Polymer-layered silicate nanocomposites: *In situ* intercalative polymerization of ϵ -caprolactone in layered silicate. *Chem. Mater*, 5: 1064-1066.
- Giannelis, E.P., R. Krishnamoorti and E. Manias, 1999. Polymer-silicate nanocomposites: Model Systems for confined polymers and polymer brushes. *Polymers Confined Environ.*, 138: 107-147.
- Gilman, J., 1999. Flammability and thermal stability studies of polymer layered silicate (clay) nanocomposites. *Applied Clay Sci.*, 15: 31-49.
- Gonzalez-Nunez, R., H. Padilla, D. De Kee and B. Favis, 2001. Barrier properties of polyamide-high density polyethylene blends. *Polym. Bull.*, 46: 323-330.
- Gopakumar, T., J. Lee, M. Kontopoulou and J. Parent, 2002. Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites. *Polymers*, 43: 5483-5491.
- Hambir, S., N. Bulakh, P. Kodgire, R. Kalgaonkar and J. Jog, 2001. PP/clay nanocomposites: A study of crystallization and dynamic mechanical behavior. *J. Polym. Sci., Polym. Phys.*, 39: 446-450.
- Hasegawa, N., M. Kawasumi, M. Kato, A. Usuki and A. Okada, 1998. Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-modified polypropylene oligomer. *J. Applied Polym. Sci.*, 67: 87-92.
- Ishida, H., S. Campbell and J. Blackwell, 2000. General approach to nanocomposite preparation. *Chem. Mat.*, 12: 1260-1267.
- Jeon, H., H. Jung, S. Lee and S. Hudson, 1998. Morphology of polymer/silicate nanocomposites. *Polym. Bull.*, 41: 107-113.
- Jin, Y., H. Park, S. Im and S. Kwak, 2002. Polyethylene/clay nanocomposites by *in situ* exfoliation of montmorillonite during Ziegler-Natta polymerization of ethylene. *Macromol. Rapid Commun.*, 23: 135-140.

- Ke, Y.C. and P. Stroeve, 2005. Polymer-Layered Silicate and Silica Nanocomposites. 1st Edn., Elsevier, Amsterdam, The Netherlands, pp: 39.
- Kodgire, P., R. Kalgaonkar, S. Hambir, N. Bulakh and J. Jog, 2001. PP/Clay nanocomposites: Effect of clay treatment on morphology and dynamic mechanical properties. *J. Applied Polym. Sci.*, 81: 1786-1792.
- Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi and O. Kamigaito, 1993a. Sorption of water in nylon 6-clay hybrid. *J. Applied Polym. Sci.*, 49: 1259-1264.
- Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, 1993b. Mechanical properties of nylon 6-clay hybrid. *J. Mat. Res.*, 8: 1185-1189.
- Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito and K. Kaji, 1995. Novel preferred orientation in injection-molded nylon 6-clay hybrid. *J. Polym. Sci., Polym. Phys.*, 33: 1039-1045.
- Krishnamoorti, R. and P. Giannelis, 1997. Rheology of end-tethered polymer layered silicate nanocomposites. *Macromolecules*, 30: 4097-4102.
- Krishnamoorti, R. and K. Yurekli, 2001. Rheology of polymer layered silicate nanocomposites. *Curr. Opin. Colloid Interface Sci.*, 6: 464-470.
- Krishnamoorti, R., J. Ren and A. Silva, 2001. Shear response of layered silicate nanocomposites. *J. Chem. Phys.*, 114: 4968-4973.
- Larson, R., 1999. *The Structure and Rheology of Complex Fluids*. Oxford University Press, New York, pp: 280-281.
- LeBaron, P., Z. Wang and T. Pinnavaia, 1999. Polymer-layered silicate nanocomposites: An overview. *Applied Clay Sci.*, 15: 11-29.
- Lele, A., M. Mackley, G. Galgali and C. Ramesh, 2002. *In situ* rheo-x-ray investigation of flow-induced orientation in layered silicate-syndiotactic polypropylene nanocomposite melt. *J. Rheol.*, 46: 1091-1110.
- Liang, Z. and J. Yin, 2003. Poly (etherimide)/montmorillonite nanocomposites prepared by melt intercalation. *J. Applied Polym. Sci.*, 90: 1857-1863.
- Liu, X. and Q. Wu, 2001. PP/clay nanocomposites prepared by grafting melt intercalation. *Polymers*, 42: 10013-10019.
- Mehta, S., F. Mirabella, A. Bafna and K. Ruffner, 2004. Thermoplastic olefin/clay nanocomposites: Morphology and mechanical properties. *J. Applied Polym. Sci.*, 92: 928-936.
- Messersmith, P.B. and E.P. Giannelis, 1995. Synthesis and barrier properties of poly(1 -caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. Part A: Polym. Chem.*, 33: 1047-1057.
- Morgan, A. and J. Gilman, 2003. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study. *J. Applied Polym. Sci.*, 87: 1329-1338.
- Nam, P., P. Maiti, M. Okamoto, T. Kotaka, N. Hasegawa and A. Usuki, 2001. A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites. *Polymers*, 42: 9633-9640.
- Okada, A., M. Kawasumi, T. Kurauchi and O. Kamigaito, 1987. Synthesis and characterization of a nylon 6-clay hybrid. *Polym. Prep.*, 28: 447.
- Okada, A. and A. Usuki, 2006. Twenty Years of Polymer-clay nanocomposites. *Macromol. Mat. Eng.*, 291: 1449-1476.
- Okamoto, M., S. Morita, H. Taguchi, Y. Kim, T. Kataka and H. Tateyama, 2000. Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via *in situ* intercalative polymerization. *Polymers*, 41: 3887-3890.
- Okamoto, M., S. Morita and T. Kokata, 2001. Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites. *Polymers*, 42: 2685-2688.
- Okamoto, M., 2006. Recent Advances in Polymer/Layered Silicate Nanocomposites: An overview from science to technology. *Mat. Sci. Technol.*, 22: 756-779.
- Oya, A., Y. Kurokawa and H. Yasuda, 2000. Factors controlling mechanical properties of clay mineral/polypropylene nanocomposites. *J. Mat. Sci.*, 35: 1045-1050.
- Saito, T., M. Okamoto, R. Hiroi, M. Yamamoto and T. Shiroy, 2006. Intercalation of diphenyl sulfide into nano-galleries and preparation of poly (p- phenylene sulfide)- based nanocomposites. *Macromol. Mat. Eng.*, 291: 1367-1374.
- Schon, F., R. Thomann and W. Gronski, 2002. *Macromol. Symp.*, 189: 105-109.
- Sekelik, D., E. Stepanov, D. Schiraldi, A. Hiltner and E. Baer, 1999. Oxygen barrier properties of crystallized and talc-filled poly (ethylene terephthalate). *J. Polym. Sci., Polym. Phys.*, 37: 847-857.
- Simha, R., 1940. The influence of Brownian movement on the viscosity of solutions. *J. Phys. Chem.*, 44: 25.
- Strawhecker, K. and E. Manias, 2000. Structure and properties of poly (vinyl alcohol)/Na⁺ montmorillonite nanocomposites. *Chem. Mat.*, 12: 2943-2949.
- Strobl, G., 1997. *The Physics of Polymers*. 2nd Edn., Springer-Verlag Berlin Heidelberg New York, pp: 285.
- Svoboda, P., C. Zeng, H. Wang, L. Lee and D. Tomasko, 2002. Morphology and mechanical properties of polypropylene/organoclay nanocomposites. *J. Applied Polym. Sci.*, 85: 1562-1570.

- Takahashi, S., M. Taniguchi, K. Omote, N. Wakabayashi, R. Tanaka and A. Yamagishi, 2002. First observation of in-plane X-ray diffraction arising from a single layered inorganic compound film by a grazing incidence X-ray diffraction system with a conventional laboratory X-ray source. *Chem. Phys. Lett.*, 352: 213-219.
- Tanford, C., 1967. *Physical Chemistry of Macromolecules*. John Wiley and Sons, Inc., New York, pp: 333-336.
- Ton-That, M.T., W. Leelapornpisit, L.A. Utracki, F. Perrin-Sarazin, J. Denault, K. Cole and M.M. Bureau, 2006. Effect of Crystallization on Intercalation of Clay-polyolefin Nanocomposites and Their Performance. *Polym. Eng. Sci.*, 46: 1085-1093.
- Usuki, A., M. Kato, A. Okada and T. Kurauchi, 1997. Synthesis of polypropyleneclay hybrid. *J. Applied Polym. Sci.*, 63: 137-138.
- Vaia, R. and E. Giannelis, 1997a. Lattice model of polymer melt intercalation in organically-modified layered silicates. *Macromolecules*, 30: 7990-7999.
- Vaia, R. and E. Giannelis, 1997b. Polymer melt intercalation in organically-modified layered silicates: Model predictions and experiment. *Macromolecules*, 30: 8000-8009.
- Varlot, K., E. Reynaud, G. Vigier and J. Varlet, 2002. Mechanical properties of clayreinforced polyamide. *J. Polym. Sci. Polym. Phys.*, 40: 272-283.
- Wang, K., M. Choi, C. Koo, Y. Choi and I. Chung, 2001. Synthesis and characterization of maleated polyethylene/clay nanocomposites. *Polymers*, 42: 9819-9826.
- Yen, J., C. Fan-Chiang and S. Yang, 1997. Effects of composition of modified polyamide on barrier properties of polyethylene/modified polyamide blends. *J. Applied Polym. Sci.*, 64: 1531-1540.
- Yoon, P., T. Fornes and D. Paul, 2002. Thermal expansion behavior of nylon 6 nanocomposites. *Polymers*, 43: 6727-6741.
- Yoshida, O. and M. Okamoto, 2006. Direct melt intercalation of polylactide chains into nanogalleries: Interlayer expansion and nano-composite structure. *Macromole Rapid Commun.*, 27: 751-757.
- Zanetti, M., G. Camino, P. Reichert and R. Mulhaupt, 2001. Thermal behaviour of poly (propylene) layered silicate nanocomposites. *Macromol. Rapid Commun.*, 22: 176-180.
- Zhang, Q., Q. Fu, L. Jiang and Y. Lei, 2000. Preparation and properties of polypropylene/montmorillonite layered nanocomposites. *Polym. Int.*, 49: 1561-1564.