

# Polypropylene Nanocomposites

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## 1. Introduction

The possibility of manufacturing nano-composites materials with tailored properties at low cost has gained much interest. In fact, there is already more than two decades of research on those materials. Particular interest has been paid to clay nano-platelets and their composites with non-polar thermoplastic polyolefin matrixes, namely polypropylene (PP).

Imagine an industrialist and his design team relatively aware of the developments in the research with nano-fillers asking themselves: What can we do with nano-composites and make a net profit up to the 'promises' of the current state of the art? Research announced potential areas of interest for practical applications include mechanical performance, toughness improvement, surface hardening, fire retardancy, or, solvent and permeability reduction. However there remains the problem of how a company could set up the facility for compounding, and guarantee proper dispersion and minimization of health hazards. One should bear in mind that for industrial dissemination conventional equipments should be used and compounding achieved through in-line mixing of virgin resins and nanoclay master batches. Since the seventies polypropylene has been seen as the wonder engineering-commodity material with widespread application in numerous technical applications.

Current masterbatches are mainly based on thermoplastic polyolefin and anhydride functionalized PP as a compatibilizer. In principle, filling with a low incorporation level of nanoclay (typically less than 5%), makes PP adequate to applications with engineering requirements. Nevertheless, only well-dispersed and well-exfoliated nanoparticles can lead to the expected improvement of properties. The nanoparticle dispersion and exfoliation is usually assumed to be achieved during masterbatching, but the suppliers of master batches request a relatively high price. Underlining these evidences poor exfoliation was a common feature in moldings obtained using industry achievable processing conditions. There is an evident interest of bringing the benefits of nanocomposites at the laboratory scale to cost competitive industrial products. However the first available information leaves a number of treads that research could well follow, for example. Which level of exfoliation should be required to viable master batches? Is there any scope for hybrid compounding, i.e. combining particulate nanoclays with fibre reinforcements? Are there only a few niches of application for nanocomposites? Have nanofillers any chance of being full exfoliated within non polar matrixes? Do these nanocomposites will require alternative routes of processing? Should novel compatibilizers be developed in order to avoid unavoidable reagglomeration during injection molding? (Frontini & Pouzada, 2011).

## 2. Nanotechnology growth predicted

Nanocomposites, defined as polymers bonded with nanoparticles to produce materials with enhanced properties, have been in existence for years but are recently gaining momentum in mainstream commercial packaging use (Butschli 2004). The United States is leading in nanotechnology research with over 400 research centers and companies involved with over \$3.4 billion in funding. Europe has over 175 companies and organizations involved in nanoscience research with \$1.7 billion in funding. Japan is also very involved in research with over 100 companies working with nanotechnologies (Anyadike, 2005). Globally, the market for nanocomposites is expected to grow to \$250 million by 2008, with annual growth rates projected to be 18-25% per year (Principia, 2004). The global market for nanotechnology products was worth an estimated \$11.7 billion in 2009. The market is projected to grow to more than \$15.7 billion in 2010 and nearly \$26.7 billion in 2015 at a compound annual growth rate (CAGR) of 11.1% from 2010 to 2015 (bccresearch, 2010).

## 3. What does nanocomposites really mean?

Perhaps it is necessary to make clear the terms “hybrids” and “nanocomposites” before the discussion of the nanocomposites, since it is somewhat ambiguous to identify whether materials fall into “nanocomposites” or not. The most wide-ranging definition of a hybrid is a material that includes two moieties blended on the molecular scale.

Commonly the term “hybrids” is more often used if the inorganic units are formed in situ by the sol-gel process (Kickelbick, 2007). Meanwhile, use of the word “nanocomposites” implies that materials consist of various phases with different compositions, and at least one constituent phase (for polymer/silica nanocomposites, that phase is generally silica) has one dimension less than 100 nm. A gradual transition is implied by the fact that there is no clear borderline between “hybrids” and “nanocomposites” (Kickelbick, 2007).

Expressions of “nanocomposites” seem to be very trendy, and although the size of the silica particles is above 100 nm, the composites are often called “nanocomposites” in some literature. Organic/inorganic composite materials have been extensively studied for a long time. When inorganic phases in organic/inorganic composites become nano sized, they are called nanocomposites. Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processibility). Moreover, they usually also contain special properties of nanofillers leading to materials with improved properties.

A defining feature of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in interfacial area as compared with traditional composites (Balazs et al., 2006; Caseri & Nalwa, 2004; Caseri, 2006, 2007; Schadler, 2003; Schadler et al., 2007; Schaefer & Justice, 2007; Winey & Vaia, 2007; Krishnamoorti & Vaia, 2007).

The next time you look at a car, you could be looking at nanotechnology without even realizing it. For the past several years, car companies have been using nanocomposites instead of plastic to make certain car parts. In 2001, Toyota started using nanocomposites to make bumpers for their cars. In 2002, General Motors (GM) made nanocomposite “step-assists” - external running boards that help people get into and out of cars - an option on

the 2002 Chevrolet Astra and the GMC Safari (The Future of Automotive Plastics, 2003). Nanocomposites are lighter, stiffer, less brittle, and more dent- and scratch-resistant than conventional plastics. Some nanocomposites are also more recyclable, more flame retardant, less porous, better conductors of electricity, and can be painted more easily (Leaversuch & Buchholz, 2003).

#### 4. How nanocomposites work?

Polymer nanocomposites are constructed by dispersing a filler material into nanoparticles that form flat platelets. These platelets are then distributed into a polymer matrix creating multiple parallel layers which force gases to flow through the polymer in a “torturous path”, forming complex barriers to gases and water vapour, as seen in **Figure 1**. As more tortuosity is present in a polymer structure, higher barrier properties will result. The permeability coefficient of polymer films is determined using two factors: diffusion and solubility coefficients:

$$P = D \times S.$$

Effectively, more diffusion of nanoparticles throughout a polymer significantly reduces its permeability. According to the Natick Soldier Center of the United States Army, “the degree of dispersion of the nanoparticles within the polymer relates to improvement in mechanical and barrier properties in the resulting nanocomposite films over those of pure polymer films”. Nanoparticles allow for much lower loading levels than traditional fillers to achieve optimum performance. Usually addition levels of nanofillers are less than 5%, which significantly impact weight reduction of nanocomposite films. This dispersion process results in high aspect ratio and surface area causing higher performance plastics than with conventional fillers (Brody, 2003).



Fig. 1. Idealized Oriented Layered Nanoparticle

#### 5. The most commonly used nanoparticles

Different types of fillers are utilized, the most common is a nanoclay material called montmorillonite—a layered smectite clay. Clays, in a natural state, are hydrophilic while polymers are hydrophobic. To make the two compatible, the clay’s polarity must be modified to be more “organic” to interact successfully with polymers (Hay & Shaw, 2000; Ryan, 2003). One way to modify clay is by exchanging organic ammonium cations for

inorganic cations from the clay's surface (Sherman,1999). Additional nanofillers include carbon nanotubes, graphite platelets, carbon nanofibers, as well as other fillers being investigated such as synthetic clays, natural fibers (hemp or flax), and POSS (polyhedral oligomeric silsesquioxane). Carbon nanotubes, a more expensive material than nanoclay fillers which are more readily available, offer superb electrical and thermal conductivity properties. The major suppliers for nanoclays are Nanocor and Southern Clay. Inorganic nanoscale building nanoparticles of metals (e.g., Au, Ag), and metal oxides (e.g.,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  which  $\text{SiO}_2$  is viewed as being very important.

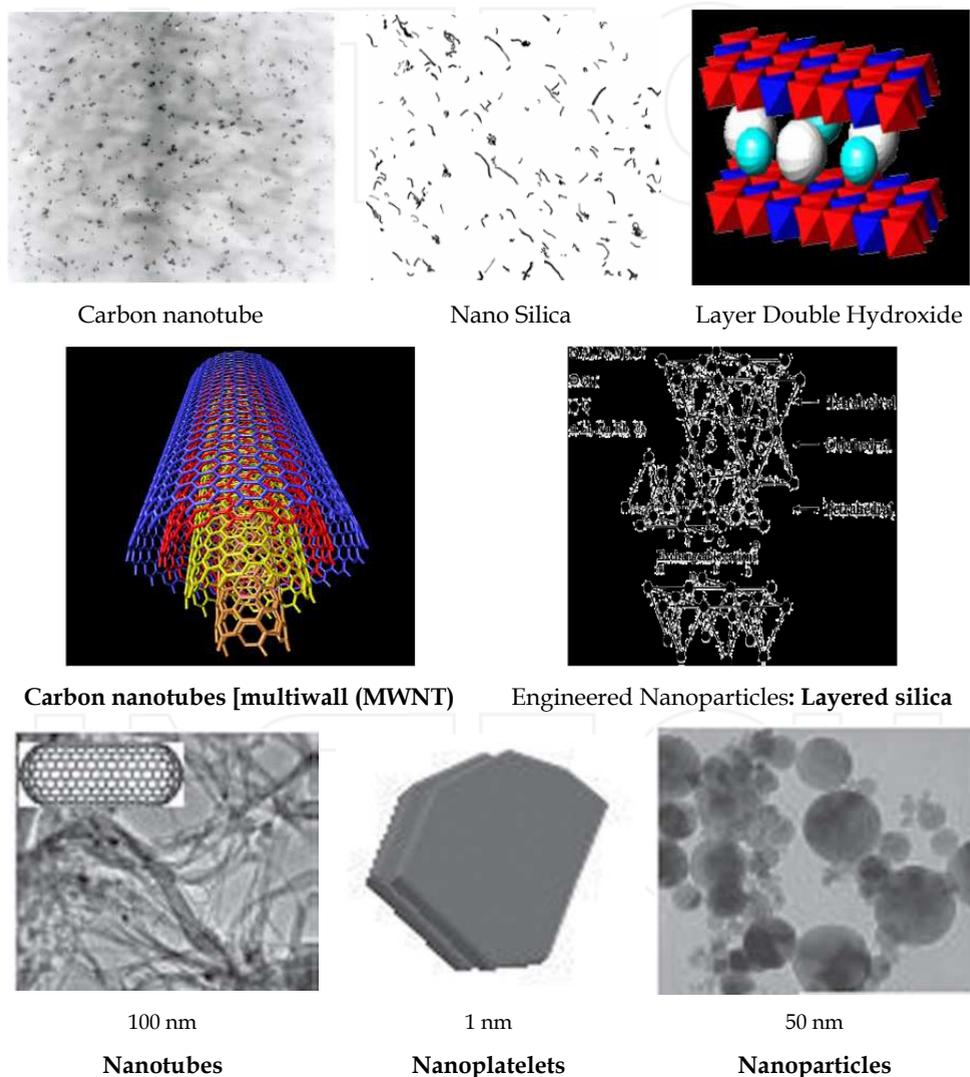


Fig. 2. The most common used of nanoparticle

Using polypropylene, polyethylene, and other polymers reinforced with natural minerals such as calcium carbonate, zeolite, mica, and talc combined with efficient coupling agents has proven to be a successful technology to obtain tailored reinforcement and optimize the cost to property balance. One important material used as filler is the talc mineral since it has unique reinforcing features as softness, lubricity, excellent wetting and dispersion in plastics, and other organics. Talc is a hydrated magnesium silicate mineral widely used in polymers as reinforcing filler. Its plate-like structure provide the talc-filled materials with tailored properties to be used in some industrial and commercial applications such as in refrigerators jackets, packaged components, blocking of infrared in agricultural films, and in automotive and appliance markets. Talc-filled polypropylene composite has low specific gravity and combines excellent chemical resistance with low cost (Zihlif & Ragosta, 2003; Tripathi & Pillia, 1994; Hijleh et al.,2000; Mahanwar et al.,2006; Xie et al.,2001; Chen, 2004; Hajji et al. 1999; Kojima et al., 1993). **Figure 2.**

## 6. Polymer nanocomposite synthesis

The synthesis of polymer nanocomposites is an integral aspect of polymer nanotechnology. By inserting the nanometric inorganic compounds, the properties of polymers improve and hence this has a lot of applications depending upon the inorganic material present in the polymers. Solvent casting is one of the easiest and less time consuming methods for the synthesis of polymer nanocomposites.

There are three common methods used to enhance polymers with nanofillers to produce nanocomposites: melt compounding, in-situ polymerization and the solvent method.

1. **Melt compounding - or processing** - of the nanofillers into a polymer is done simultaneously when the polymer is being processed through an extruder, injection molder, or other processing machine. The polymer pellets and filler (clay) are pressed together using shear forces to help with exfoliation and dispersion (Brody, 2003; Zihlif & Ragosta, 2003).
2. **In-situ polymerization**, the filler is added directly to the liquid monomer during the polymerization stage.
3. **The solution method**, fillers are added to a polymer solution using solvents such as toluene, chloroform and acetonitrile to integrate the polymer and filler molecules <sup>(19)</sup>. Since the use of solvents is not environmentally-friendly, melt processing and in-situ polymerization are the most widely used methods of nanocomposite production.

As pointed out( Tripathi &Pillia,1994) nanocomposite systems can be prepared by various synthesis routes, thanks to the ability to combine different ways to introduce each phase. *The organic component can be introduced as:*

- i. A precursor, which can be a monomer or an oligomer,
- ii. A preformed linear polymer (in molten, solution, or emulsion states), or
- iii. A polymer network, physically (e.g., semi crystalline linear polymer) or chemically (e.g., thermosets, elastomers) cross-linked.

*The mineral part can be introduced as:*

- i. A precursor (e.g., TEOS) or
- ii. Preformed nanoparticles.

Organic or inorganic polymerization generally becomes necessary if at least one of the starting moieties is a precursor.

## 7. Polypropylene nanocomposites

Polypropylene (PP) is a versatile material its use has significantly penetrated numerous sectors of the manufacturing, medical, and packaging industries. Polymer clay nanocomposites are multiphase organic/inorganic hybrid materials pioneered by researchers at Toyota, (Kojima et al., Usuki et al., 1993) which may exhibit significantly improved mechanical, flammability, and permeability properties relative to the base polymer matrix at very low clay loading. Although first demonstrated for nylon, polymer clay nanocomposites have since been prepared for a range of thermoplastic and thermoset polymers. However, the development of PP/clay nanocomposites poses special challenges because of polypropylene's hydrophobicity.

The reinforcement of polypropylene and other thermoplastics with inorganic particles such as talc and glass is a common method of material property enhancement. Polymer clay nanocomposites extend this strategy to the nanoscale. The anisometric shape and approximately 1 nm width of the clay platelets dramatically increase the amount of interfacial contact between the clay and the polymer matrix. Thus the clay surface can mediate changes in matrix polymer conformation, crystal structure, and crystal morphology through interfacial mechanisms that are absent in classical polymer composite materials. For these reasons, it is believed that nanocomposite materials with the clay platelets dispersed as isolated, exfoliated platelets are optimal for end-use properties.

Recent research has generated advances in polypropylene nanocomposites that are sufficient to motivate new technological applications. For example, PP-based nanocomposites have been developed for application as exterior automotive components (Sherman, 1999) Cone calorimetry measurements of peak heat release rate from maleated/PP nanocomposites with 4% loading are reduced by 75% relative to the pure polymer (Gilman et al., 2000). These improvements are relevant to applications requiring reduced flammability. Yet, relative to other thermoplastic nanocomposites, such as nylon 6, the improvement in end-use properties for polypropylene nanocomposites has been modest. In addition, noting that many synthesized PP nanocomposites are likely to exist as nonequilibrium structures, research into the aging and rejuvenation of these mesoscale structures is warranted. Furthermore, better methods to characterize the full distribution and hierarchy of structural states present in PP nanocomposites are required because, for example, rare aggregates can seriously compromise nonlinear mechanical properties such as toughness, yield stress, and elongation at break. Finally, the interaction between clay platelets and polymer crystallization requires further attention because these interactions are likely a significant determinant of the end-use properties of polypropylene nanocomposites.

## 8. What is organoclay?

Organoclays are manufactured by modifying bentonite with quaternary amines, a type of surfactant that contains a nitrogen ion. The nitrogen end of the quaternary amine, the

hydrophilic end, is positively charged, and ion exchanges onto the clay platelet for sodium or calcium. The amines used are of the long chain type with 12-18 carbon atoms. After some 30 per cent of the clay surface is coated with these amines it becomes hydrophobic and, with certain amines, organophilic.



Fig. 3.

## 9. The nature of organoclays

The main component of organoclay is bentonite, a chemically altered volcanic ash that consists primarily of the clay mineral montmorillonite. The bentonite in its natural state can absorb up to seven times its weight in water, after treatment can absorb only 5 to 10 per cent of its weight in water, but 40 to 70 per cent in oil, grease, and other sparingly-soluble, hydrophobic chlorinated hydrocarbons. As the organoclay is introduced into water, the quaternary amine is activated and extends perpendicularly off the clay platelets into the water. A chlorine or bromine ion is loosely attached to the carbon chain. Since the sodium ions that were replaced by the nitrogen are positively charged, they bond with the chlorine ion, resulting in sodium salt that is washed away. The result is a neutral surfactant with a solid base, which is the organoclay. The hydrophilic end of the amine dissolves into the oil droplet because "like dissolves like," thus removing that droplet from water. Because the partition reaction takes place "outside" of the clay particle (in contrast to adsorption of oil by carbon, which takes place inside its pores), the organoclay does not foul quickly.

Organophilic clay can function as a prepolisher to activated carbon, ion exchange resins, and membranes (to prevent fouling), and as a post polisher to oil/water separators, dissolved air flotation (DAF) units, evaporators, membranes, and skimmers. Organophilic clay powder can be a component or the main staple of a flocculent clay powder. They are excellent adsorbers for the removal of oil, surfactants, and solvents, including methyl ethyl ketone, t-butyl alcohol (TBA), and others.

## 10. Layered silicate / polypropylene nanocomposites

Layered silicate/polymer nanocomposites were first reported in 1950 as a patent literature (Carter et al.,1950) . However, it was not popular until Toyota researchers began a detailed

experimentation in the year of 1996 on the nylon 6/clay nanocomposites (Kojima et al., 1993). In recent years, nanocomposites received a great interest in academic, governmental and industrial studies (Kojima et al., 1993). The improvements in thermal, mechanical and flammability properties of clay/polymer nanocomposites are significantly higher than those achieved in traditional filled polymers. Up to now, these systems have experienced some success for several kinds of polar polymers. However, for polymers with low polarity, such as polyolefins, the improvements are not very significant due to the low compatibility between the clay and the polyolefins.

One of the most commonly used organophilic layered silicates is derived from montmorillonite (MMT). Its structure is made of several stacked layers, with a layer thickness between 1.2-1.5 nm and a lateral dimension of 100- 200 nm (Marchant & Krishnamurthy ,2002; Moore & Reynolds ,1997) . These layers organize themselves to form the stacks with a regular gap between them, called interlayer or gallery. The sum of the single layer thickness and the interlayer represents the repeat unit of the multilayer material, called d-spacing or basal spacing (d001), and is calculated from the (001) harmonics obtained from X-ray diffraction patterns. The clay is naturally a hydrophilic material, which makes it difficult to exfoliate in a polymer matrix. Therefore, the surface treatment of silicate layers is necessary to render its surface more hydrophobic, which facilitates exfoliation. Generally, this can be done by ion-exchange reactions with cationic surfactants, including primary, secondary, tertiary and quaternary alkylammonium cations (Fornes et al., 2002; Le Pluart et al.,2002). This modification also leads to expand the basal spacing between the silicate layers due to the presence of alkyl chain intercalated in the interlayer and to obtain organoclay (OMMT).

Polypropylene (PP) is one of the most widely used plastics in large volume. To overcome the disadvantages of PP, such as low toughness and low service temperature, researchers have tried to improve the properties with the addition of nanoparticles that contains polar functional groups. An alkylammonium surfactant has been adequate to modify the clay surfaces and promote the formation of nanocomposite structure. Until now, two major methods, i.e., in-situ polymerization( Ma et al., 2001; Pinnavaia, 2000) and melt intercalation (Manias et al.,2001) have been the techniques to prepare clay/PP nanocomposites. In the former method, the clay is used as a catalyst carrier, propylene monomer intercalates into the interlayer space of the clay and then polymerizes there. The macromolecule chains exfoliate the silicate layers and make them disperse in the polymer matrix evenly. In melt intercalation, PP and organoclay are compounded in the molten state to form nanocomposites.

As the hydrophilic clay is incompatible with polypropylene, compatibilization between the clay and PP is necessary to form stable PP nanocomposites. There are two ways to compatibilize the clay and PP. In the first approach, the enthalpy of the interaction between the surfactant and the clay is reduced. In the second approach, a compatibilizer, such as maleic anhydride grafted PP (PPgMA) can be used(Manias et al.,2001). The clay is melt compounded with the more polar compatibilizer to form an intercalated master batch. The master batch is then compounded with the neat PP to form the PP nanocomposite.

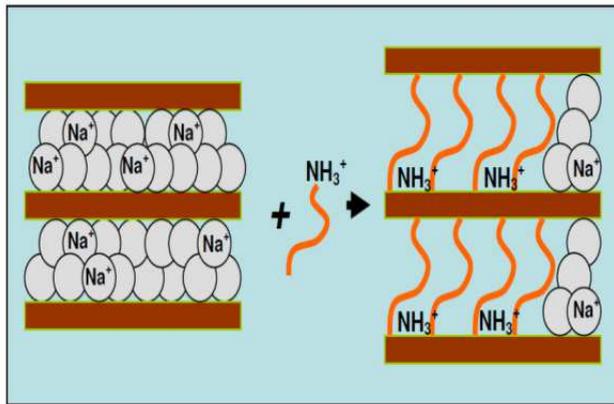


Fig. 4.a. Ion Exchange Reaction between Na-MMT and Alkyl Ammonium Molecules

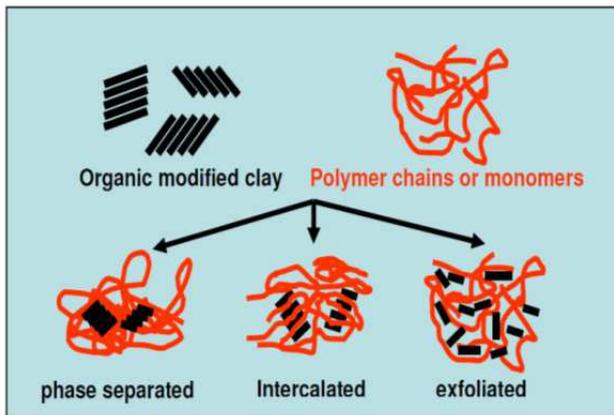


Fig. 4.b. Three main morphology achievable in nanocomposite structure

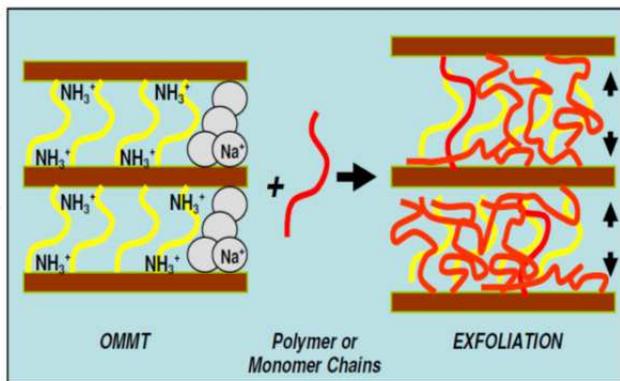


Fig. 4.c. Microstructural Development during Melt Intercalation Process

Mixtures of clay platelets and polymer chains compose a colloidal system. Thus in the melt state, the propensity for the clay to be stably dispersed at the level of individual disks (an exfoliated clay dispersion) is dictated by clay, polymer, stabilizer, and compatibilizer potential interactions and the entropic effects of orientational disorder and confinement. An isometric dimension of clay platelets also has implications for stability because liquid crystalline phases may form. In addition, the very high melt viscosity of polypropylene and the colloidal size of clay imply slow particulate dynamics, thus equilibrium structures may be attained only very gradually. Agglomerated and networked clay structures may also lead to nonequilibrium behavior such as trapped states, aging, and glassy dynamics.

Clay structure in polymer nanocomposites can be characterized as a combination of exfoliated platelets and intercalated tactoids. Clays themselves are layered silicate minerals with charged surfaces neutralized by interlayer counterions. Unless a liquid crystalline order disorder transition occurs, the exfoliated structure is spatially and orientationally disordered and the clay is dispersed at the level of individual disks. Intercalated clay retains interlayer ordering, at least within a particular tactoid; however, intergallery spacing is increased relative to natural clay because stabilizing surfactants, compatibilizers, and/or matrix polymers are infiltrated within the clay galleries. In the extreme case of clay/polymer matrix immiscibility, intercalation spacing not much greater than the clay and its counterion indicates negligible penetration of polymeric or compatibilizing species between clay layers. Clay platelets or tactoids themselves comprise the mesoscale structure of nanocomposites. Possible structures include that of a dispersed suspension, a percolated network, or a liquid crystal with orientational order. The hierarchy of possible states is depicted in **Figure 5**.

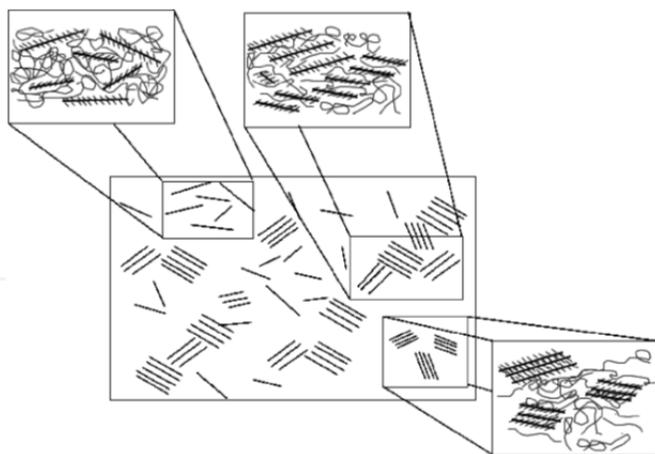


Fig. 5. Schematic of the hierarchy of clay structures in polypropylene nanocomposites of mixed morphology. Clay tactoids and exfoliated platelets comprise the mesoscale morphology. The internal intercalation structure of clay tactoids is determined by the compatibilizer and compounding conditions. (View this art in color at [www.dekker.co](http://www.dekker.co))

Polypropylene (PP) is widely used for many applications due to its low cost, low density, high thermal stability and resistance to corrosion. Blending polypropylene with clays to form nanocomposites is a way to increase its utility by improving its mechanical properties.

Layered silicates dispersed as a reinforcing phase in polymer matrix are one of the most important forms of hybrid organic-inorganic nanocomposites. MMT, hectorite, and saponite are the most commonly used layered silicates. Layered silicates have two types of structure: tetrahedral-substituted and octahedral substituted figure 6. In the case of tetrahedrally substituted layered silicates the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can react interact more readily with these than with octahedrally-substituted material.

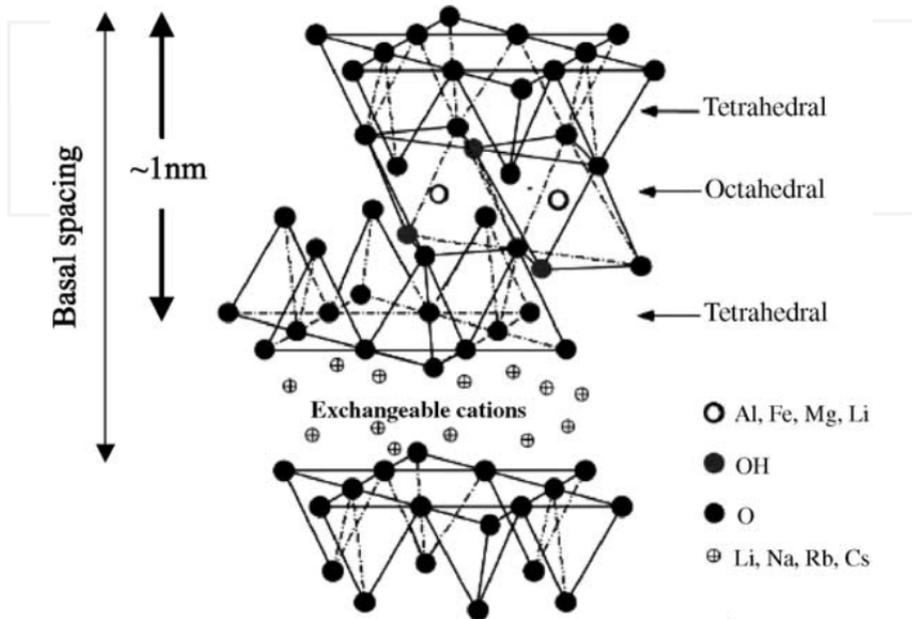


Fig. 6. Structure of Layered Silicates

Compared to conventional composites, polymer layered-silicate (PLS) nanocomposites have maximized polymer-clay interactions since the clay is dispersed on a nanometer scale.

**There are three general methods for the preparation of polymer/ silica nanocomposites according to the starting materials and processing techniques:** blending, sol-gel processes, and in situ polymerization.

*Blending* is generally just mixing of the silica nanoparticles into the polymer; *sol-gel process* can be done in situ in the presence of a preformed organic polymer or simultaneously during the polymerization of the monomer(s); and *in situ polymerization* involves the dispersion of nanosilica in the monomer(s) first and then polymerization is carried out.

Layered silicate/polypropylene nanocomposites were prepared by melt intercalation method. Homopolymers PP alone and maleic anhydride-grafted polypropylene (PPgMA) as a compatibilizer were used as the matrix. Clay ( $\text{Na}^+$  montmorillonite, MMT) particles were used to obtain silicate nano-layers within the PP matrix. Structural modification of MMT

using hexadecyltrimethyl ammonium chloride (HTAC) was applied to obtain organophilic silicates (OMMT) (Kıvanç, 2006). The most recent methods to prepare polymer-layered-silicate nanocomposites have primarily been developed by several other groups. In general these methods (shown in **Figure 7**) achieve molecular level incorporation of the layered silicate (e.g. montmorillonite clay or synthetic layered silicate) in the polymer by addition of a modified silicate either to a polymerization reaction (in situ method), (Usuki et al., 1993, 1997; Lan & Pinnavaia, 1994) to a solvent-swollen polymer (solution blending), Jeon et al., 1998) or to a polymer melt (melt blending) (Giannelis, 1996; Fisher et al., 1998). Additionally, a method has been developed to prepare the layered silicate by polymerizing silicate precursors in the presence of a polymer (Carrado & Langui, 1999)

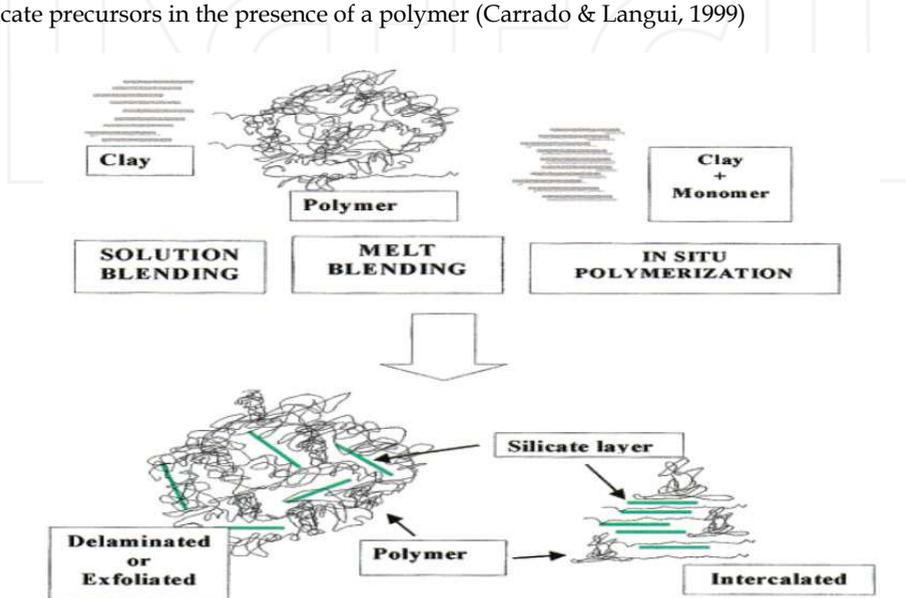


Fig. 7. Schematic representation of various methods (Solution blending, melt blending, and in situ polymerization). The delaminated (or exfoliated) and intercalated morphologies are shown.

Two terms (intercalated and delaminated) are used to describe the two general classes of nanomorphology that can be prepared. *Intercalated structures* are self assembled, well-ordered multilayered structures where the extended polymer chains are inserted into the gallery space between parallel individual silicate layers separated by 2-3 nm (see **Figure 8**). *The delaminated (or exfoliated)* structures result when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations (Lan & Pinnavaia, 1994). In the delaminated cases the interlayer spacing can be on the order of the radius of gyration of the polymer; therefore, the silicate layers may be considered to be well-dispersed in the organic polymer. The silicate layers in a delaminated structure may not be as well-ordered as in an intercalated structure. Both of these hybrid structures can also coexist in the polymer matrix; this mixed nanomorphology is very common for composites based on smectite silicates and clay minerals (Kroschurtz, 1993).

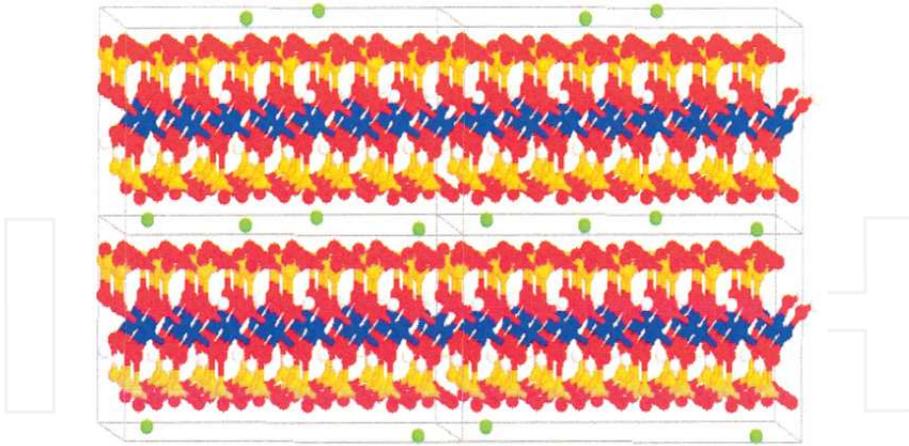


Fig. 8. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na<sup>+</sup> cations in the interlayer gap or gallery. The octahedral (O<sub>h</sub>) alumina layer is shown as blue aluminum atoms surrounded by red oxygen atoms. The tetrahedral (T<sub>d</sub>) silicate layers are shown as yellow silicon atoms surrounded by red oxygen atoms. Hydrogen atoms are white and sodium (Na<sup>+</sup>) cations are shown in green.

The very large commercial importance of polypropylene (PP) has also been driving an intense investigation of PP composites reinforced by particulates, fibers, and layered inorganic fillers (Karger, 1995; Karian, 1999). In particular, in the case of layered inorganic fillers, talc and mica had been traditionally attracting the most interest (Karian, 1999). However, recent advances in polymer/clay and polymer/silicate nanocomposite material (Alexandre & Dubois, 2000; Giannelis et al., 1998) have inspired efforts to disperse montmorillonite-based fillers in PP. (Kato et al., 1997; Kawasumi et al., 1997; Hasegawa et al., 1998; Oya et al., 2000; Wolfet al., 1999; Reichert et al., 2000; Manias et al., 2000).

Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays, (Theng, 1979, 1974) the field of polymer/silicate nanocomposites has gained large momentum recently. Two were the major findings that pioneered the revival of these materials: First, the report of a nylon-6/montmorillonite material from Toyota research, (Kojima et al., 1993; Kojima et al., 1993) where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Second, Giannelis et al. found that it is possible to melt-mix polymers with clays without the use of organic solvents (Vaia et al., 1993). Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements of many materials properties by the nanodispersion of inorganic silicate layers. Where the property enhancements originate from the nanocomposite structure, these improvements are generally applicable across a wide range of polymers (Alexandre & Dubois, 2000). At the same time, there were also discovered

property improvements in these nanoscale materials that could not be realized by conventional fillers, as for example a general flame retardant characteristic (Gilman et al., 2000) and a dramatic improvement in barrier properties (Strawhecker & Manias, 2000; Xu et al., 2001).

Montmorillonite (mmt) is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge (Theng, 1979, 1974). The mmt crystal lattice consists of 1-nm-thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedra). Isomorphous substitution within the layers (for example,  $Al^{3+}$  replaced by  $Mg^{2+}$  or  $Fe^{2+}$ ) generates a negative charge defined through the charge exchange capacity (CEC) and for mmt is typically 0.9-1.2 mequiv /g depending on the mineral origin. These layers organize themselves in a parallel fashion to form stacks with a regular van der Waals gap between them, called interlayer or gallery. In their pristine form their excess negative charge is balanced by cations ( $Na^+$ ,  $Li^+$ ,  $Ca^{2+}$ ) which exist hydrated in the interlayer. Obviously, in this pristine state mmt is only miscible with hydrophilic polymers, such as poly (ethylene oxide) and poly(vinyl alcohol) (Strawhecker & Manias, 2000; Vaia et al., 1995). To render mmt miscible with other polymers, one must exchange the alkali counterions with cationic-organic surfactants, such as alkylammoniums (Alexandre & Dubois, 2000; Giannelis et al., 1998).

## 11. Production of layered silicate/polypropylene nanocomposites

The production of polypropylene nanocomposites is shown in Figure 9. The homopolymer PP was fed into Haake two-roll mixer at 190 °C. After melting of the PP in 1 min, clay particles in the amounts of 3, 5 and 10 wt. % were added into molten PP and the mixing was continued for 10 min in the mixer. The blended samples were collected and left for cooling. After cooling, the blends were pressed into 100 mm x 100 mm samples having a



Fig. 9. Processing Stages for Clay/PP Nanocomposites

thickness of 1 mm using a hot press at 190°C. The tensile specimens were prepared by a pneumatic cutter and then the samples were left for two days to complete crystallization.

Kıvanç I\_İK 2006

## 12. Techniques used for the characterization of polypropylene/nanocomposites

Generally, the structure of nanocomposites has typically been established using WAXD analysis and transmission electron micrographic (TEM) observation. Due to its easiness and availability WAXD is most commonly used to probe the nanocomposite structure (Giannelis, 1996; Giannelis et al., 1999; LeBaron et al., 1999; Vaia et al., 1999; Biswas & Sinha, 2001) and occasionally to study the kinetics of the polymer melt intercalation (Vaia et al., 1996). By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. For example, in an *exfoliated nanocomposite*, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for *intercalated nanocomposites*, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1–4 nm), little can be said about the spatial distribution of the silicate layers or any structural non-homogeneities in nanocomposites.

Additionally, some layered silicates initially do not exhibit well-defined basal reflections. Thus, peak broadening and intensity decreases are very difficult to study systematically. Therefore, conclusions concerning the mechanism of nanocomposites formation and their structure based solely on WAXD patterns are only tentative. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization.

However, special care must be exercised to guarantee a representative cross-section of the sample. The WAXD patterns and corresponding TEM images of three different types of nanocomposites are presented in **Figure 10**. Both TEM and WAXD are essential tools (Morgan & Gilman, 2003) for evaluating nanocomposite structure. However, TEM is time-intensive, and only gives qualitative information on the sample as a whole, while low-angle peaks in WAXD allow quantification of changes in layer spacing. Typically, when layer spacing exceed 6–7 nm in intercalated nanocomposites or when the layers become relatively disordered in exfoliated nanocomposites, associated WAXD features weaken to the point of not being useful. However, recent simultaneous small angle X-ray scattering (SAXS) and WAXD studies yielded quantitative characterization of nanostructure and crystallite structure in N6 based nanocomposites (Mathias et al., 1999).

Very recently, (Bafna et al., 2003) developed a technique to determine the three-dimensional (3D) orientation of various hierarchical organic and inorganic structures in a PLS nanocomposite. They studied the effect of compatibilizer concentration on the orientation of various structures in PLS nanocomposites using 2D SAXS and 2D WAXD in three sample /camera orientations.

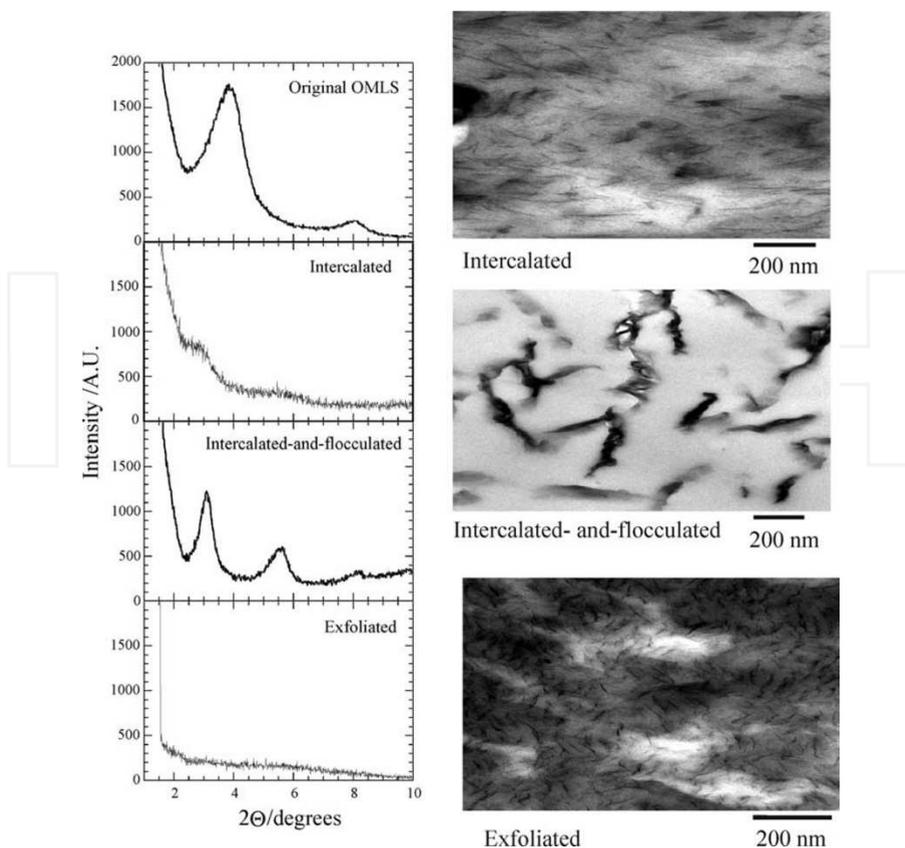


Fig. 10. (a) WAXD patterns and (b) TEM images of three different types of nanocomposites

### 13. The development and characterization of polypropylene-clay nanocomposites

The development and characterization of polymer-clay nanocomposites has been a subject of raising interest in the recent years (Vaia et al., 1996). Polymer-layered silicate (PLS) nanocomposites exhibit outstanding properties that are synergistically derived from the organic and inorganic components. The enhanced properties are presumably due to the synergistic effects of nanoscale fillers within the polymer (Kojima et al., 1993). The delamination and dispersion of clays in the polymeric matrix is the key to design nanocomposites. In the ideal conditions, the delamination of the original clay structures, as well as the polymer intercalation in the clay can be achieved. Nanoparticles can significantly improve the stiffness, heat distortion temperature (HDT), dimensional stability, gas barrier properties, electrical conductivity and flame retardancy of polymer with only a 0.1–10 vol.% addition of dispersed nanophase (Wu et al., 2002; Tyan et al., 1999; Lan et al., 1996; Li et al., 2004; Ma et al., 2001; Li et al., 2001; Kawasumi et al., 1997; Usuki et al., 1997; Hasegawa et al., 2000). These performance improvements largely depend upon the spatial distribution,

arrangement of intercalating polymer chains and interfacial interaction between the silicate layers and the polymer (Giannelis, 1996; Giannelis et al., 1999; LeBaron et al., 1999; Ray & Okamoto, 2003). Nanoclays like purified Na<sup>+</sup> or Ca<sup>2+</sup> montmorillonites are inherently hydrophilic in nature, which leads to incompatibility with the hydrophobic polymer matrix with subsequent poor composite properties. Although, the modified clay is miscible with polar polymer like PS, Epoxy, Nylon etc., its dispersion within PE, PP, EVA, ABS etc is unsatisfactory (Komori & Kurada, 2000; Cho & Paul, 2001). Grafting of polar functional groups onto polymer chains has been suggested to improve the properties in PE/clay nanocomposites (Fukushima & Inagaki, 1987).

Therefore, to obtain a nanocomposite with requisite properties, the inorganic clay must be modified with some organic surfactant, usually onium salt or an alkyl amine which, compatibilizes the surface chemistry of the clay and polymer matrix at the interface by replacing the inorganic cation and making the gallery space of the clay sufficiently organophilic to permit the entry of polymer matrix (Fukushima & Inagaki, 1987). PP nanocomposites have been the subject of research since several years (Boeing, 1997; Kurokawa et al., 1997; Kato et al., 1997; Reichert et al., 2000; Hasegawa et al., 1998; Zheng et al., 2001). Various organically modified nanoparticles have been prepared and incorporated within the PP matrix to enhance mechanical and thermal performance. However, the development of PP clay nanocomposites poses special challenges because of polypropylene's hydrophobicity. The dispersion of nanolayers strongly depends on the preparation techniques such as in-situ polymerization, solution blending or melt compounding (Okada et al., 1993; Akelah, 1995; Akelah et al., 1994; Giannelis, 1998; Zilg et al., 1998). Melt intercalation of inorganic clay mineral consisting of layered silicates with polymers is widely used, as it is environmental friendly and does not involve any solvent. Direct melt intercalation method offers convenient techniques for preparation of hybrids, which involve mixing the layered silicates with the polymer matrix above its softening point (Rzaev et al., 2007). However, desired intercalation/ exfoliation of the clay galleries within PP based nanocomposites system poses host of technical issues which needs to be explored and addressed.

#### 14. Future of nanocomposites

By 2009, it is estimated that the flexible and rigid packaging industry will use five million pounds of nanocomposites materials in the beverage and food industry. By 2011, consumption is estimated to be 100 million pounds. Beer is expected to be the biggest consumer by 2006 with 3 million pounds of nanocomposites until carbonated soft drinks bottles are projected to surpass that to use 50 million pounds of nanocomposites by 2011 (Butschli, 2004). Polymer nanocomposites are the future for the global packaging industry. Once production and materials cost are less, companies will be using this technology to increase their product's stability and survivability through the supply chain to deliver higher quality to their customers while saving money. The advantages that nanocomposites offer far outweigh the costs and concerns and with time the technology will be further refined and processes more developed. Research continues into other types of nanofillers (i.e., carbon nanotubes), allowing new nanocomposite structures with different improved properties that will further advance nanocomposite use in many diverse packaging applications.

## 15. Conclusion

The synthesis of polymer nanocomposites is an integral aspect of polymer nanotechnology. By inserting the nanometric inorganic compounds, the properties of polymers improve and hence this has a lot of applications depending upon the inorganic material present in the polymers. The improvements obtained in clay/PP nanocomposite structure can make this commercial thermoplastic polymer more suitable for automotive, construction and packaging applications. Different alkyl ammonium surfactants and compatibilizer was used to produce layered silicate/PP nanocomposites by the same melt intercalation technique.

Polypropylene nanocomposites are still challenging due to the lack of affinity of organophilic PP for hydrophilic clay. The reinforcement of polypropylene and other thermoplastics with inorganic particles such as talc and glass is a common method of material property enhancement. Polymer clay nanocomposites extend this strategy to the nanoscale. The anisometric shape and approximately 1 nm width of the clay platelets dramatically increase the amount of interfacial contact between the clay and the polymer matrix. Thus the clay surface can mediate changes in matrix polymer conformation, crystal structure, and crystal morphology through interfacial mechanisms that are absent in classical polymer composite materials. For these reasons, it is believed that nanocomposite materials with the clay platelets dispersed as isolated, exfoliated platelets are optimal for end-use properties. Yet, relative to other thermoplastic nanocomposites, such as nylon 6, the improvement in end-use properties for polypropylene nanocomposites has been modest. Thus research in the areas of synthesis and, especially, compounding, which are aimed at closing this performance gap, is necessary. Alternatively, improved fundamental understanding of the detailed interactions and chemistry between clays, amine surfactants, and maleic anhydride compatibilizers can help elucidate the complex thermodynamics of clay dispersion. In addition, noting that many synthesized PP nanocomposites are likely to exist as nonequilibrium structures, research into the aging and rejuvenation of these mesoscale structures is warranted. Furthermore, better methods to characterize the full distribution and hierarchy of structural states present in PP nanocomposites are required because, for example, rare aggregates can seriously compromise nonlinear mechanical properties such as toughness, yield stress, and elongation at break. Finally, the interaction between clay platelets and polymer crystallization requires further attention because these interactions are likely a significant determinant of the end-use properties of polypropylene nanocomposites.

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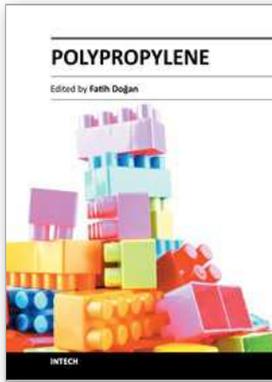
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## **Polypropylene**

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This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

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