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Polymer–Clay Nanocomposites

3.1 Introduction

The mystery of the nano-world has been progressively unraveled in recent years. The nanometer scale is simply a range between micro and molecular dimensions. The sciences in these two-dimensional ranges have been well explored by materials scientists and chemists. Materials science and chemistry are often engaged in research on the nanometer scale, for example, the dimensions of crystal structures. The well-known nanometer-scale technologies developed within materials science and chemistry in the past may not be reasonably regarded as nanotechnology. The real interest in and ultimate goal of nanotechnology is to create revolutionary properties and functions by tailoring materials and designing devices on the nanometer scale. In this respect, polymer–clay nanocomposites (PCNs) are an archetypical example of nanotechnology.

According to the International Union for Pure and Applied Chemistry (IUPAC) (Work et al., 2004), a composite material is defined as “a multicomponent material comprising multiple different (non-gaseous) phase domains in which at least one type of phase domain is in a continuous phase.” IUPAC also extends its definition to nanocomposite materials as those composites “in which at least one of the phases has at least one dimension of the order of nanometers.” Based on these definitions, a plethora of systems can be classified among these materials, the dispersions of nanosized objects of different nature—such as metal particles or carbon nanotubes—or intercalated/exfoliated layered minerals in continuous/polymeric phases being prime examples. PCNs fall in the last category of the examples cited above.

The mixing of nanoparticles with polymers to form composite materials has been practiced for decades. For example, the clay-reinforced resin known as Bakelite was introduced in the early 1900s as one of the first mass-produced polymer–nanoparticle composites, and fundamentally transformed the nature of practical household materials. Even before Bakelite, nanocomposites were finding applications in the form of nanoparticle-toughened automobile tires prepared by blending carbon black, zinc oxide, and/or magnesium sulfate particles with vulcanized rubber. Despite these early successes, the broad scientific community was not galvanized by nanocomposites until the early 1990s, when reports by Toyota researchers revealed that adding a clay mineral to nylon produced a fivefold increase in the yield and tensile strength of the material (Kojima et al., 1993; Usuki et al., 1993). Subsequent developments have further contributed to the surging interest in polymer–nanoparticle composites. In particular, the growing availability of the nanoparticles of precise size and shape, such as fullerences, carbon nanotubes, inorganic nanoparticles, dendrimers, and bio-nanoparticles, and the development of instrumentation to probe small length scales, such as scanning force, laser scanning fluorescence, and
electron microscopes, have spurred research aimed at probing the influence of particle size and shape on the properties of polymer–nanoparticle composites.

The subject of hybrids based on layered inorganic compounds such as clay has been tackled for a considerable time, but the area has enjoyed a resurgence of interest and activity owing to the massive industrial exploitation of Nylon6-clay PCNs in the automotive industry by the Toyota Corporation (Okada and Usuki, 2006), and to the exceptional properties exhibited by PCNs (LeBaron et al., 1999; Pinnavaia and Beall, 2000; Sinha Ray and Okamoto, 2003; Utraki, 2004; Zeng et al., 2005; Balazs et al., 2006; Chen et al., 2008). These systems offer a number of material parameters that can be controlled or fine-tuned to achieve a given ultimate property; these include the type of clay, the choice of the clay pretreatment, the selection of the polymeric matrix, and, last but not least, the method by which the polymer is incorporated in the nanocomposite. The last of these is, in turn, dictated by the processing conditions available and whether the end user is an integrated polymer manufacturer or a specialist processor.

As part of this renewed interest in nanocomposites, researchers also began seeking design rules that would allow them to engineer materials that combine the desirable properties of nanoparticles and polymers. The ensuing research revealed a number of key challenges in producing nanocomposites that exhibit a desired behavior. The greatest stumbling block to the large-scale production and commercialization of nanocomposites is the dearth of cost-effective methods for controlling the dispersion of the nanoparticles in polymeric hosts. The nanoscale particles typically aggregate, which negates any benefits associated with the nanoscopic dimension. Another hurdle to the broader use of nanocomposites is the absence of structure–property relationships. Because increased research activity in this area has only spanned the past decade, there are limited property databases for these materials (Ajayan et al., 2003). Thus, greater efforts are needed to correlate the morphology of the mixtures with the macroscopic performance of the materials. Establishing these relationships requires a better understanding of how cooperative interactions between flexible chains and nanoscopic solids can lead to unexpected behavior, like the improved mechanical behavior of clay-reinforced nylon.

### 3.2 Clay Minerals

#### 3.2.1 Clay Types and Structures

Common clay minerals possess variability in their constitution, as expected for many naturally occurring compounds. Importantly, the composition and purity of given clay can exert an influence on the final properties of the corresponding PCN. These minerals represent a wide class of compounds, also known as layered materials, which can be defined as "crystalline materials wherein the atoms in the layers are cross linked by chemical bonds, while the atoms of adjacent layers interact by physical forces" (Schoonheydt et al., 1999). Clays are generally classified by structure as allophane, kaolinite, halloysite, smectite, illite, chlorite, vermiculite, attapulite-palygorskite-sepiolite, and mixed layered minerals (Grim, 1968). The most used clays for the production of PCNs can be substantially grouped into three main categories:

- **2:1 type**: These minerals belong to the smectite family, and present a crystal structure consisting in nanometer thick layers (also called platelets) of alumina octahedrons sheets sandwiched between two silica tetrahedrons sheets (Figure 3.1a). The stacking of the layers results in a van der Waals gap between the layers. The isomorphic substitution of aluminum (Al) with magnesium (Mg), iron (Fe), lithium (Li) in the octahedrons sheets, and/or silicon (Si) with Al in the tetrahedrons sheets gives each three-sheet layer an overall negative charge, which is counterbalanced by exchangeable metal cations residing in the interlayer spaces, also called galleries, such as sodium (Na), calcium (Ca), Mg, Fe, and Li.

- **1:1 type**: These clays consist of layers that are made up by alternating Al octahedrons and Si tetrahedrons sheets, respectively. As no isomorphic substitution occurs, each layer bears no charge. Therefore, except for crystallization and humidity water molecules, cations, and anions are never found in the interlayer galleries, and the layers are held together by a hydrogen bond network between the hydroxyl (–OH) groups in the octahedrons sheets and the oxygen atoms of the adjacent tetrahedrons layers.

- **Layered silicic acids**: This class of clays is mainly composed of silica tetrahedrons sheets characterized by different layer thickness. Basically, their structures are composed on layered silicate networks and interlayer hydrated alkali metal cations.

Smectite clays such as montmorillonite (MMT, Figure 3.1b) are probably the most common types of clay used for nanocomposite formation. The main composition of layered silicates are SiO2 (30%–70%), Al2O3 (10%–40%), and H2O (5%–10%). The intralayer space of these distinctive materials include the –OH sandwich groups of the octahedral aluminum-hydroxyl sheets and the oxygen of the tetrahedral silicate sheets: the crystal consists of alternating cations planes and negatively charged silicate sheets in the ratio 2:1. Their fundamental building blocks are Si(OH)4, silicon–oxygen tetrahedral (T-network), and M(OH)2 octahedra (O-network), with M = Mg2+, Al3+, Fe3+, and Fe2+ (Figure 3.1c).

Depending on their size, cations may be fully or partially incorporated in the free space between the tetrahedral, producing contracting forces between the layers, in addition to the dispersion forces between the silicon–oxygen tetrahedra in the silica sheets and the electrostatic (Coulombic) forces between the negative charges on opposite layers and the cations in between. Some trivalent Al cations are substituted by Mg2+ in MMT; as mentioned above, these isomorphic substitutions result in an overall negative charge on the mineral which
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is counterbalanced by the presence of external cations (mainly Na\(^+\)) in the interlayer galleries. Depending on the valence state of exchangeable ions, the lattice may remain electrically neutral (pyrophyllite and talc groups) or may bear a net negative charge (from 0.25 to 0.6 in smectites up to 1 in micas). In contrast to those in mica, the cations in smectites can readily be exchanged, in particular, for transition-metal ions, and the cation-exchange capacity of smectites attains 0.64–1.50 meq/g. The interlayer space (galleries) of many layered minerals with T-O-T structures contain water molecules, which are involved in mineral formation and prevent collapse, a complete sticking of the layers to one another. In natural Na-MMT-type smectite clays, the parameters of the interlayer space are determined by the crystal structure of the aluminosilicate. The general formula of dioctahedral minerals (pyrophyllite, MMT, muscovite, vermiculite, and others) formed by Al octahedra can be represented as 
\[ \text{Si}_{8-x} \text{M}_{x}(\text{Al}_{4-y} \text{M}_{y})_6(\text{OH})_4 \text{O}_{20}(\text{H}_2\text{O})_n \] and that of trioctahedral minerals based on Mg octahedral (talc, saponite, biotite, hectorite, vermiculite, and others) is 
\[ \text{Si}_{8-x} \text{M}_{x}(\text{Mg}_{6-x})_6(\text{OH})_4 \text{O}_{20}(\text{H}_2\text{O})_n \]. The smectites capable of swelling, such as MMT, HECT, and saponite, are of special interest for intercalation chemistry. Vermiculites and micas (muscovite and others) swell far less readily. The crystal structures of some layered silicates are shown schematically in Figure 3.1d.

The principal characteristics leading to the exploitation of smectite clays in the preparation of PCNs are

- Their swelling ability, with the consequent potential to host even big molecules as polymers between their layers (intercalation chemistry).
- Optimal balance between strength, stiffness, and flexibility. In this respect, each single clay platelet can be considered as a rigid inorganic polymer with a molecular mass (approx. \(1.3 \times 10^8\)) considerably higher than that of typical commercial polymers. Hence, PNCs with very low clay loadings (e.g., 5% weight) can achieve the same final properties of conventional composites.
- High aspect ratio of the individual platelets. The key parameters of layered silicates are the distance from a T-network to its analog in one of the neighboring layers, \(d\), and the thickness of the interlayer space, \(\Delta d\). The interlayer spacing in clay minerals depends on the size of

![Figure 3.1](image-url)
exchangeable cations and the amount of water in the interlayer space. For example, the interlayer spacing is \(1.18\) nm in anhydrous Na‘MMT and increases to \(1.25, 1.50–1.55\), and even \(1.80–1.90\) nm upon the incorporation of mono-, bi-, and trimolecular water layers into the interlayer space. The crystals of clay minerals unite in fine flakes, ribbons, or tubes (sometimes of colloidal size), which tend to aggregate, producing secondary porous structures: hexagonal platelets in kaolinite, poorly defined shapes in MMT, thin elongated platelets (\textit{laths}) in hectorite, and others. The longitudinal size of disk-like clay particles depends on the preparation procedure: clays prepared by grinding typically consist of plate-like particles ranging in longitudinal size from 0.1 to \(1.0\) \(\mu\text{m}\). Since colloidal clay particles have very large aspect ratios, delaminated clays offer extremely large specific surfaces and are nanostructured. This is a necessary condition for good intercalation properties and the enhanced performance of composites. Therefore, although layered silicates are not nanoparticles per se, the thickness of the clay layers of the order of \(1\) nm, the high aspect ratios (typically \(100–1500\)), and the large surface areas (\(700–800\) \(\text{m}^2/\text{g}\)) (Theng, 1979; Pinnavaia, 1983; Pinnavaia and Beall, 2000) render the clay platelets truly nanoparticulate objects.

- High natural abundance and, hence, low cost. Clays are ubiquitous in nature, and constitute relatively cheap feedstocks with minimal limitation on supply.

### 3.2.2 Clay Surface Modification

As mentioned earlier, the interlayer spacing in anhydrous Na-MMT is about \(1.0\) nm. Each layer is separated from its neighbors by a spacing determined by the interlayer van der Waals forces and forms an interlayer space or gallery. Whereas the Na–O bond length is typically \(0.21–0.22\) nm, it is increased to \(0.36\) nm in the galleries. Since the Coulomb electrostatic force is inversely proportional to the square of the distance between the charges, the cation–oxygen bond strength is reduced by \(\sim 60\%\). As a result, the galleries may contain a large amount of water molecules, which, coupled with the clay sheet surface change and the presence of ions, ultimately contributes to render these substances highly hydrophilic species and, therefore, poorly compatible with a wide range of nonpolar, organic molecules such as polymers. A necessary prerequisite for the successful formation of a PCN is therefore the alteration of the clay polarity to make the clay \textit{organophilic}. Their unique layered structure, coupled to their high intercalation ability, allow these minerals to be easily modified to be compatible with polymers. Further, the relatively low layer charge unbalance (ranging from \(0.2\) to \(0.6\)) results in weak van der Waals and electrostatic forces between neighboring layers, rendering the interlayer cations quite mobile and interchangeable. A simple and most popular way to produce an organophilic clay from a normally hydrophilic clay is therefore to exchange the interlayer cations with organic cations such as alkylammonium ions. Thus, for example, in MMT the Na‘ ions in the clay galleries can be exchanged for dimethyl, bis(hydrogenated tallow) quaternary ammonium chloride (2M2HT, i.e., \((\text{CH}_3)\text{N}((\text{C}_{18}\text{H}_{37})\text{H})\text{Cl}\) see Figure 3.2a) according to the following reaction:

\[
\text{Na}^+ – \text{MMT} + 2\text{M2HT} \rightarrow 2\text{M2HT} – \text{NH}_3^+ – \text{MMT} + \text{NaCl}
\]

Upon this treatment, and depending on the chemical structure of the clay surface organic modifier, the clay becomes more compatible with a given polymer, being it thermoplastic, thermosetting, or elastomer. The resulting modified clay is also often commonly referred to as an organoclay. A further, important aspect of clay surface treatment with organic salts is that to accommodate the long, hydrophobic chains within the silicate galleries, the interlayer space must increase with respect to the pristine mineral. For instance, interlayer space \(\Delta d\) in natural MMT is equal to \(11.8\) \(\text{Å}\). After Na‘ exchange with 2M2HT, \(\Delta d = 24.2\) \(\text{Å}\) (see Figure 3.2b). This increased interlayer space leads to a twofold advantage in the preparation of a MMT-based PCN: (1) the interlayer binding forces are reduced and (2) the insertion, diffusion, and accommodation of the bulky polymeric chains (or their monomeric precursors) are facilitated.

**FIGURE 3.2** (a) Stick-and-ball molecular model of dimethyl, dehydrogenated tallow quaternary ammonium chloride (2M2HT), where tallow stands for a mixture of C18 (\(\sim 65\%\)), C16 (\(\sim 30\%\)), and C14 (\(\sim 5\%\)). Atom color code: gray, C; blue, N; white, H, light green, Cl. (b) 3D molecular model of the organoclay obtained by ion-exchanging interlayer sodium cations with 2M2HT. The 2M2HT molecules are portrayed as CPK spheres, with atom color code as in (a). The MMT sheets are represented as polyhedrons, with the same atom coloring used in Figure 3.1.
3.3 Polymer–Clay Nanocomposites

Classification

Nanocomposites are commonly defined as materials consisting of two or more dissimilar materials with well-defined interfaces, at least one of the materials being nanostructured (having structural features ranging in size from 1 to 100 nm) in one, two, or three dimensions. The same refers to the spacing between the networks and layers formed by polymeric and inorganic components. Nanocomposites include materials in which monomer or polymer molecules are incorporated as guests into host lattices. Hosts may be both natural materials and compounds prepared by various synthetic techniques and possessing well-defined intercalation properties. The physicochemical properties of such composites are governed by the distribution of reinforcing constituents (fibrous, dispersion-toughened, or layered structures).

Depending on the strength of the interfacial tension between the polymeric matrix and the layered silicate (modified or not), the resulting PCNs can be categorized into three types, depending on the extent of the separation of the silicate layers (see Figure 3.3):

1. **Intercalated nanocomposites**: In these PCNs, the polymer chains are inserted between the layers of the clay such that the interlayer spacing d is expanded, but the layers still bear a well-defined relationship to each other.

2. **Exfoliated nanocomposites**: In an exfoliated PCN, the layers of the clay have been completely separated, and the individual mineral sheets are randomly distributed throughout the polymeric matrix.

3. **Conventional composites (microcomposites)**: A third alternative is constituted by the dispersion of whole clay particles (tactoids) within the polymer matrix, but this simply represents the use of clay as conventional filler in the formation of a microcomposite.

The synthetic route of choice for making a PCN depends on whether the final material is required in the form of an intercalated or exfoliated hybrid (Pinnavaia and Beall, 2000). Many different factors can exert a control whether a particular PCN can be synthesized as an exfoliated or an intercalated system. Since the presence of either structure can lead to dramatically different characteristics in the ultimate properties of the final clay nanocomposite, it is of utmost importance to be able to understand and control these factors, which include the exchange capacity of the clay, the characteristics of the solvent medium, and the chemical nature of the interlayer cations (onium ions). With a thorough modification of the clay surface polarity, onium ions will allow a thermodynamically favorable penetration of the polymer into the intergallery region. The ability of onium ions to assist in clay delamination depends on the nature of its substituents (long vs. short chains, fully apolar vs. partially polar substituents, etc.). The efficiency in loading capacity of the onium ions onto the clay surface also plays a pivotal role, and it should be borne in mind that a commercial organoclay might not have the optimum loading for a given application. The other types of clay surface modifiers can be employed, depending on the nature of the clay surface (e.g., for positively charged clays such as hydroxide, negatively charged surfactants can be employed) and the polymer choice, such as ion-dipole interactions, silane coupling agents, and block copolymers.

A customary example of ion-dipole interactions is the intercalation of small molecules into the clay galleries. The entropically driven displacement of the small molecules then provides a route to polymer intercalation. The unfavorable interaction of clay edges with polymers can be overcome by use of silane coupling agents to modify the edges. These can be used in conjunction with the onium-ion-treated organoclay. An alternative approach to compatibilizing clays with polymers is based on the use of block or graft copolymers where one component of the copolymer is compatible with the clay and the other with the polymer matrix. This is similar in concept to the compatibilization of polymer blends. A typical block copolymer would consist of a clay-compatible hydrophilic block and a polymer-compatible hydrophobic block. The block length must be controlled and must not be too long. The high degrees of exfoliation are claimed using this approach.

3.4 Preparation Methods of Polymer–Clay Nanocomposites

The correct selection of the modified clay is essential to ensure the effective penetration of the polymer or its precursor into the interlayer spacing of the clay and result in the desired exfoliated or intercalated product. Substantially, there are three main methods for preparing PCNs:

1. **Intercalation of polymer from solution**. This approach is of interest from various viewpoints. Note, first of all, that it is effective at producing organic–inorganic multilayer composites. Owing to the unusual physical chemistry of the intercalation processes involved, it offers the possibility of improving the physical and mechanical properties of many
systems and fabricating electron-conducting materials, e.g., for reversible electrodes. Among the most widespread nanocomposites are polyolefin-MMT, nylon-layered silicates, and epoxy-clay hybrid nanomaterials. This process is based on the choice of a solvent system in which the polymer is soluble and the silicate layers are swellable. The clay is first swollen in a suitable solvent, such as water, chloroform, or toluene. When the polymer and silicate solution are mixed, the polymer chains intercalate and displace the solvent adsorbed within the silicate galleries. Upon solvent removal, the intercalated structure remains, resulting in the corresponding PCN (see Figure 3.4). Generally speaking, for the overall process in which the polymer chains are exchanged with the previously intercalated solvent in the clay galleries, a negative variation of the Gibbs free energy $\Delta G$ is required, i.e., $\Delta G = \Delta H - T \Delta S < 0$, where $\Delta H$ represents the enthalpic contribution $\Delta G$ and $T \Delta S$ is the entropic variation associated to the given process. In this case, the driving force for polymer intercalation into layered silicate from solution is the entropy gained by solvent molecules’ release, which compensates for the decrease of entropy of the confined, intercalated chains (Vaia and Giannelis, 1997a). From the application standpoint, however, this method involves the extensive use of solvent. Therefore, exception made for water-soluble polymers (e.g., poly(ethylene oxide), PEO), this procedure is usually environmentally unfriendly and economically prohibitive.

2. **In situ intercalative polymerization method.** The most intriguing type of intracrystalline chemical reaction is the incorporation of monomer molecules into the pores of a host structure, followed by controlled internal transformations into polymer, oligomer, or hybrid-sandwich products (post-intercalative transformations). Monomers intercalated into a clay mineral migrate along its galleries, and, initiated by heat, radiation, or an appropriate agent, polymerization occurs within its layers (see Figure 3.5).

This approach is often also called “ship-in-the-bottle” polymerization, and the monomer molecules incorporated through displacement reactions form new hydrogen bonds and other types of intercalation compounds with the host. The simplest way of intercalating polymers into inorganic structures is by producing hybrid nanocomposites via a one-step emulsion polymerization of conventional monomers (most frequently, styrene, methyl methacrylate, and acrylonitrile) in the presence of various organophilic minerals. The physical processes underlying intercalation via emulsion polymerization are as follows. The basis of the swelling characteristic of clays in aqueous systems containing monomer micelles 2–10 nm in size allows the micelles to penetrate into swollen MMT layers. At the same time, the monomer drops forming during solution polymerization are very large ($10^2$–$10^4$ nm) and are simply adsorbed or bound to the surface of MMT particles. The earliest example of PCN was actually produced via this method by Toyota Motors for the synthesis of MMT-nylon6 nanocomposite, which remains the most studied and well-characterized system to date.

3. **Melt intercalation method.** This technique involves annealing (statically or under shear) a mixture of the polymer and organoclay above the polymer softening point. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. A range of nanocomposites with structures from intercalated to exfoliated can be obtained, depending on the degree of the penetration of the macromolecular chains in the interlayer spaces (see Figure 3.6). So far, experimental results point to the fact that the outcome of polymer intercalation depends critically on silicate functionalization and constituent interactions. Undoubtedly, an optimal starting interlayer structure in the organoclay (e.g., a suitable number and size of compatibilizer chains per clay unit area) and the right

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**FIGURE 3.4** Schematic view of PCN formation via polymer intercalation from solution. The black bars are MMT layers, the green dots represent solvent molecules, and the red lines symbolize polymer chains.

**FIGURE 3.5** Schematic view of PCN formation via in situ intercalative polymerization. The black bars are MMT layers, the red dots represent monomeric species, and the red lines symbolize polymer chains.
balance of polar/hydrophobic interactions between the polymer chains and the organoclay are two key issues for a successful melt intercalation process. Contrary to process (a), in which entropy is claimed to be the driving force leading to PCN formation, in melt intercalation the enthalpic component ($\Delta H$) of the Gibbs free energy ($\Delta G$) seems to govern the system thermodynamics (Vaia and Giannelis, 1997b). In fact, in this case the entropy loss associated to the confinement of the polymer melt within the silicate galleries is compensated by the entropy gain of the aliphatic chains of alkylammonium cations associated to the concomitant layer separation, resulting in a net entropy change $\Delta S \approx 0$. The favorable enthalpy is due to the increase in favorable interaction energy between the polymer and the organoclay, due to the formation of weak, hydrogen-like bonds, dipole–dipole, and van der Waals interactions. Overall, this method has great advantages over both processes (a) and (b). In fact, (1) it is environmentally benign as no solvent is employed, and (2) it is totally compatible with current polymer industrial processes such as extrusion or injection molding. Accordingly, the melt intercalation technique has become the standard for the preparation of PCNs.

To date, both thermoset and thermoplastic polymers have been incorporated into nanocomposites, including polyamides (i.e., nylons), polyolefins (e.g., polypropylene, PP), polystyrene (PS), epoxy resins, polyurethanes, polyimides, and poly(ethylene terephthalate, PET). However, the development of a compatibilizer chemistry is the key to the expansion of this nanocomposite technology beyond the systems where success has been achieved. Also, polar functionalities such as hydroxyl groups (–OH) can be introduced into the onium salt clay surface modifier to improve the compatibility between the polymer and the mineral via the formation of intermolecular hydrogen bond networks. Similarly, chemistry alterations might be needed for the intercalation/exfoliation of different polymers in different clay minerals. For instance, the intercalation of PP into organomodified MMT is achieved only after maleic anhydride is grafted onto the polymer chain. For the preparation of nanocomposites from high temperature engineering thermoplastics, a major limitation in the use of conventional organoclay is the thermal instability of the alkylammonium species during processing. To overcome this hurdle, imidazolinium or phosphonium salts represent more stable, valid alternative choices as their use lead to an increase in the degradation temperature of the organoclay from 200°C to 300°C to >300°C. Finally, wholly synthetic organoclay could be employed when exceptional thermal stability is required by the processing conditions.

### 3.5 Polymer–Clay Nanocomposite Characterization Methods

#### 3.5.1 Wide-Angle X-Ray Diffraction and Transmission Electron Microscopy

The archetypical experimental technique employed to characterize the structure of PCNs is wide-angle x-ray diffraction (WAXD) analysis, mainly due to its ease of use and widespread availability (LeBaron et al., 1999; Biswas and Sinha Ray, 2001). By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the PCN structure (intercalated or exfoliated) may be identified. For example, in an exfoliated PCN, the extensive layer separation associated with the delamination of the original clay layers in the polymer matrix results in the eventual disappearance of any coherent x-ray diffraction (XRD) from the randomly distributed silicate sheets (compare Figure 3.7a and d). On the contrary, for intercalated PCN structures, the finite layer expansion associated with polymer penetration into the clay galleries results in the appearance of a new basal reflection corresponding to the larger gallery heights (Figure 3.7b). Although WAXD undoubtedly offers a convenient and precise method to determine the interlayer spacing in organoclays (pristine and after modification with, for instance, alkylammonium salts) and in intercalated PCNs (from 1 up to 4 nm), this technique does not allow any speculation about the spatial distribution of the clay platelets or the eventual presence of structural inhomogeneities in the system. Further, some clays (organically modified or not) do not present themselves as well-resolved WAXD peaks; accordingly, peak broadening/shifting and/or intensity decrease may be difficult to detect systematically.

On the other hand, transmission electron microscopy (TEM) allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defects present in a given PCN by direct observation (see Figure 3.7e through g). However, care must be taken in order to ensure a representative cross section of the sample. The coupling of WAXD and TEM nowadays constitutes the essential tool for evaluating PCN structures (Morgan and Gilman, 2003).

#### 3.5.2 Nuclear Magnetic Resonance

Solid-state $^1$H and $^{13}$C NMR (nuclear magnetic resonance) could be used, in principle, to gain a deeper insight about the morphology, surface chemistry, and, to a limited extent, the dynamics of exfoliated PCNs, although only recently a reliable method for tracking the increase of the interlayer distance $d$ as exfoliation proceeds has been developed (Bourbigot...
et al., 2003). The methodology relies on the measurements of the proton longitudinal relaxation time $T_1$ under two effects: the paramagnetic character of the silicate (e.g., MMT) that directly reduces $T_1$ of nearby protons, and spin diffusion, by which the locally enhanced relaxation propagates to more distant protons. The application of this method is actually limited to amorphous PCNs, in which there is no possibility of change in crystallinity, as this would strongly affect the relaxation time.

### 3.5.3 Differential Scanning Calorimetry

Many of the polymers used to produce PCNs are semi-crystalline. Accordingly, the dispersion of high surface energy clay sheets in such polymer matrices can provide heterogeneous nucleation sites for crystallization. One way to estimate crystallinity in a given PCN is to compare the melting temperature of the actual system with that of a well-known crystalline polymer sample. The fraction of crystalline material is proportional to the measured enthalpy, after the obvious correction for the mineral mass fraction (Chen and Evans, 2006). Another use of differential scanning calorimetry (DSC) measurements is the estimation of the amount of intercalated polymers by a combination of multiple runs (Chen and Evans, 2005). When a mixture of clay and polymer is run on the DSC twice, the first run allows the polymer to intercalate and the second run only gives the endotherm for melting the excess (or free) polymer since the gallery contents are assumed to behave as they were amorphous. This endotherm is subtracted from the melting enthalpy corresponding to the initial mass of the polymer to provide the amount of amorphous intercalated polymer. Figure 3.8 shows an example of successive DCS runs for a system composed by poly(ethylene glycol) (PEG) and MMT. The first run exhibits an endotherm corresponding to the polymer melting and the superposing, although somewhat delayed, exotherm due to polymer adsorption and intercalation. On the contrary, the second run features only the melting endotherm.

![Figure 3.7](image_url)
Finally, DSC experiments can be profitably exploited to verify the nature of the thermodynamic driving forces underlying intercalation/exfoliation. As discussed above, DSC observations, for instance, confirmed that the reduction in free energy on intercalation is a compromise between a significant enthalpic change and entropic change for clays with interlayer solvent (e.g., solution intercalation), and primarily from an enthalpic change for PCN produced in the absence of solvent (e.g., melt intercalation).

3.5.4 Computer Simulation Techniques

In recent years, computer-based simulation techniques play an ever-increasing role in the design and a priori prediction of new material properties, and in drawing the guidelines for experimental work and characterization (Zeng et al., 2008). In particular, in the complex world of PCNs, computational chemistry and simulation techniques have proved to be extremely useful in addressing the following, topical issues:

- Thermodynamics and kinetics of PCN formation.
- Hierarchical characteristics of the structure and dynamics of PCNs, which span from molecular to meso- up to microscale, with special emphasis on the molecular structures and dynamics at the interface level between the inorganic nanoparticles and the polymeric chain matrices.
- The influence exerted by the presence of the nanoparticles on the flow properties of the pristine polymeric matrices, a critical issue in PCN production and processing.
- The molecular origins lying at the bases of the enhanced macroscopical properties exhibited by PCNs.

Roughly speaking, the most common computational techniques employed so far in the simulation of PCNs can be classified into three main levels:

(i) Fully atomistic simulations, which span length scales of the order of a few nanometers and time scales of the order of a few nanoseconds, and include validated methods such as molecular dynamics (MD) and Monte Carlo (MC) techniques (Allen and Tildesley, 1989);

(ii) Mesoscale level simulations, in which the length scale is extended up to hundreds of nanometers and the time scale may reach up to hundreds of microseconds. These recent computational techniques substantially include Brownian dynamics (BD) (Carmesin and Kremer, 1988), dissipative particle dynamics (DPD) (Hoogerbrugge and Koelman, 1992), and mean-field density functional theory (MFDF) (Altevogt et al., 1999);

(iii) Microscale simulations, which basically refer to the well-known micromechanical and finite-element method (FEM) calculations.

Modeling at level (i) usually employs atoms, molecules, or their ensembles as basic constituents, and the techniques of election are MD and MC. MD generates the time evolution of a given system of interacting particles from which the equilibrium (and nonequilibrium) structures, energetic, and thermophysical properties can be estimated by means of the application of the fundamental laws of statistical mechanics. Contrary to MD, which is a deterministic method, the stochastic MC technique uses random numbers to generate a sample population of configuration for a given molecular system, from which, by resorting to the adoption of suitable probabilistic or statistical models, the equilibrium properties can be determined.

Intuitively, given the dimension involved in real PCNs, simulations at this level are mainly directed toward the study and characterization of the thermodynamics of the formation of PCNs, their detailed molecular structures, and the energetic of interactions between the different PCN components (e.g., MMT, onium salt, and polymer). The application of computer-based simulation techniques at level (ii)—or the mesoscale level—aims at filling the gap between detailed atomistic and coarse continuum level, and avoid their shortcomings. In the specific field of PCNs, mesoscale simulation recipes have been employed to study the structural evolution, the microphase structure, and the phase separation of these systems. Of two most popular mesoscale techniques, DPD and DFT, the former is a particle-based method in which the basic unit is no longer a single atom or molecule but a molecular assembly (e.g., an entire particle or a set of linked monomer in a polymer chain). Three main forces act simultaneously upon DPD particles in their motion and interactions, i.e., a conservative force, a dissipative force, and a random force. As these forces are pair wise additive, and the particle momentum is conserved, the system macroscopic behavior directly incorporates Navier–Stokes hydrodynamics.

Finally, level (iii)—or the continuum model level—is known and applied since long, and substantially obeys the fundamental laws of continuity (from mass conservation), equilibrium (from Newton’s second law and momentum conservation), conservation of energy (from first law of thermodynamics), and
Continuum methods relate to the deformation of a continuous medium to the external forces acting on the medium, and the resulting stresses and strains. Computational approaches at this level range from simple closed-form analytical expressions to micromechanics and complex structural mechanics calculations based on beam and shell theories. The most popular technique so far employed in PCN characterization is FEM, which is a general numerical method for obtaining approximate solutions in space to initial-value and boundary-value problems, including time-dependent processes. It uses preprocessed mesh generation, which enables the model to fully capture the spatial discontinuities of highly inhomogeneous materials, and also to incorporate nonlinear tensile relationships into analysis.

Despite the importance of understanding the molecular structure and nature of PCN materials, their behavior can be homogenized with respect to different aspects which can be observed at different length and time scales. Typically, the macroscopic behavior of a given PCN is usually explained by totally ignoring its discrete atomic and/or molecular structure, and assuming that the material is continuously distributed throughout its volume. In other words, the continuum material is conceived to have an average density and being subjected only to body forces such as gravity and surface forces. Clearly, as we have seen so far, this is not the case for PCNs, where complex structures coexist at different time/length scales. Therefore, the very actual concept of multiscale molecular modeling and simulation comes into play, with the ambitious goal of bridging the models and simulation techniques for PCNs (and for many other complex nanostructure systems as well) across the entire range of length and time scales involved. In this way, computer-based techniques are expected to address first the mesoscopic behavior of PCNs starting from detailed atomistic simulations and then transfer the obtained information to the continuum level. In other terms, the challenge for multiscale modeling is to move, as seamless as possible, from one scale to another so that all the parameters, properties, and topologies obtained at one (lower) scale can be transferred to the next (higher) scale. In the special case of PCNs, the ultimate target is to be able to predict, with a high degree of confidence, their hierarchical structures and behavior, and to capture all the phenomena taking place on length scales that typically span 5–6 orders of magnitudes and time scales encompassing a dozen of orders of magnitude. Figure 3.9 summarizes this concept and gives a graphical, clear view of the multiscale modeling approach to PCNs based on MD [level (i)], DPD [level (ii)], and FEM calculations [level (iii)] (Scocchi et al., 2007a,b).

### 3.6 Properties of Polymer–Clay Nanocomposites

Nanomaterials additives can provide many property advantages in comparison to both their conventional filler counterparts and base polymers. Properties that have been shown to undergo substantial improvements include:

- Mechanical properties (e.g., strength, modulus, and dimensional stability)
- Decreased permeability to gases, water, and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Electrical conductivity
- Chemical resistance
- Biodegradability
- Optical clarity in comparison to conventionally filled polymers

In addition, it is important to recognize that nanoparticle/fibrous loading confers significant property improvements...
with very low loading levels, traditional nanoparticle additives requiring much higher loadings to achieve similar performance. This, in turn, can result in substantial weight reductions (of obvious importance for various military and aerospace applications) for similar performances, greater strength for similar structural dimensions, and, for barrier applications, increased barrier performance for similar material thickness.

3.6.1 Mechanical Properties

The enhancement in mechanical properties of PCNs can be ascribed to the high rigidity and aspect ratio of the clay nanoparticles, coupled with the good affinity between the polymer and the organoclay. To say, stronger interface interactions significantly reduce the stress concentration point upon repeated distortion which easily occurs in conventional nanocomposites (e.g., those reinforced by glass fibers), and thus leads to weak fatigue strength. As an example, for polyamide–MMT PCNs tensile strength improvements have been reported to be around 40% at room temperature and 20% at 120°C, while for the Young modulus an improvement of 70% and 200% at the same temperatures was reported (Kojima et al., 1993). On the contrary, in the case of the apolar polymers such as polypropylene or polystyrene, only a slight enhancement in tensile stress was observed. This disappointing result was ascribed in part to the lack of an efficient interfacial adhesion between the apolar PP or PS chains and the polar clay surface, and indeed the use of a PP modified by maleic anhydride led to an improvement of the system tensile behavior (Hasegawa et al., 1998).

Generally speaking, however, the enhancement of the mechanical properties of PNCs strongly correlates with the ultimate structure of the material, and many investigations dealt with comparative analyses of results obtained from intercalated and exfoliated PCN structures. When considering the same (or very close) loading values, an exfoliated PCN structure often exhibits both higher elastic modulus and tensile strength, by virtue of the good dispersion and the high moduli of the clay platelets. At the same time, however, an exfoliated PCN can present a lower toughness with respect to the corresponding intercalated system. So, again taking Nylon6 as a proof-of-concept PCN, it has been verified that the impact strength of this polymeric material with the inclusion of 10% (by weight) of nanoclay decreased from approximately 7 to 3.2 kJ/m² and 4.3 kJ/m² for the exfoliated and intercalated PCN, respectively (Dasari et al., 2007). These experimental evidences have been rationalized on the basis of the formation of submicron voids associated with intercalated clay tactoids.

3.6.2 Barrier Properties

The gaseous barrier property improvement that can result from the incorporation of relatively small quantities of nanoclay materials is shown to be substantial. Many data concur to show that oxygen transmission rates in PCNs can be as low as 50% of that of the unmodified polymer. In addition, studies have shown that PCNs have excellent barrier properties against other gases (e.g., nitrogen and carbon dioxide), water, hydrocarbons, and other organic solvents such as alcohols, toluene, and chloroform. The main factors contributing to the barrier property enhancement are both the amount of clay incorporated into the polymer matrix and the aspect ratio of the filler particle. In particular, the aspect ratio is shown to have a major effect, with high ratios (and hence high tendencies toward filler incorporation at the nanolevel) quite dramatically enhancing barrier properties.

In general, best barrier effects can be achieved in polymer nanocomposites with fully exfoliated clay minerals, and such evidences can be justified considering the Nielson labyrinth tortuous path model (see Figure 3.10), according to which, once a film of PCN is formed, the sheet-like clay layers orient in parallel with the film surface (Nielsen, 1967). As a result, the diffusing species have to travel a longer way around the impermeable clay platelets than in the corresponding pristine polymer matrix when they traverse an equivalent film thickness.

A further note of interest here is that the improvement of the barrier properties in PCN materials does not involve the chemistry of the systems, as it is practically independent of the nature of the gas/liquid diffusing molecules.

3.6.3 Thermal Stability and Heat Distortion Temperature

Upon heating, polymer molecules start to degrade and, finally decompose, as temperature is increased above a certain critical value, specific for each polymeric species. The thermal stability of a polymer is usually determined via thermogravimetric experiments, in which a weighted sample of polymer is gradually heated and the weight loss upon heating, due to the formation of volatile products (e.g., CO₂, H₂O, NH₃), is recorded. The higher thermal stability experimentally verified for PCNs can be related, in analogy with the barrier properties, by the
presence of the dispersed clay platelets, which create a hindered path for the diffusion of the volatile species and assist the formation of char after thermal decomposition. Another important thermal behavior is the heat resistance upon external loading, which is quantified by the so-called heat distortion temperature (HDT). For example, HTD was found to increase from 65°C for pure nylon to 152°C for the corresponding PCN material (Kojima et al., 1993).

3.6.4 Flame Retardancy

The ability of nanoclay incorporation to reduce the flammability of polymeric materials is a battle-horse application of these systems. Indeed, flammability behavior can be restricted in polymers such as PP with as little as 2% nanoclay loading, the effect resulting substantially from very low heat release rates obtained upon the incorporation of nanomaterials. Although conventional microparticle filler incorporation together with the use of flame-retardant agents would ultimately minimize flammability behavior, this is usually accompanied by reduction in various other important properties. With the PCN approach, this is usually achieved while maintaining or even enhancing other properties and characteristics.

The flame retardancy effect is evaluated by quantifying the reduction in the peak of the heat release rate (HHR). As examples, by the addition of 10% organoclay the average HHR of PS decreases by 21% with respect to the pristine polymer (Zheng and Wilkie, 2003) or, more impressively, the HHR of nylon6 made fabric was reduced by 40% with addition of only 5% of organoclay (Bourbigot et al., 2002). The molecular explanation for this characteristic property of PCN finds its roots in the carbonaceous char layers that form when the organic material burns and the structure of the clay minerals. The multilayered clay structures act as excellent insulators and mass transport barriers. Char formation and clay structure thus concord to impede the escape of the decomposed volatiles for the interior of the remaining polymeric matrix. A word of caution, however, must be spent on the fact that the presence of organic surface modifiers has also been shown to be able to catalyze thermal degradation and, hence, act somewhat against the flame retardancy. Therefore, the ultimate flame retardancy property of a given PCN results as a balance between these two counteracting effects.

3.6.5 Electrical Conductivity

Intuitively, being ionic substances clay minerals exhibit peculiar electrical properties. Indeed, although overall a layered clay can be considered as an insulator, the hydrated cationic species present in the interlayer spaces, being quite mobile, can guarantee a notable ionic conductivity of the system. Furthermore, the intercalation of neutral species could affect the hydration shells of these interlayer ions, resulting in a significantly modified ionic mobility and, hence, in altered electrical conductivity and other electrical parameters. As an example, PEO-based PCNs show a remarkably increased ionic conductivity with respect to the pristine clay materials, and this conductivity increases with increasing temperature. The maximum conductivity in the direction parallel to the clay layer is of the order of $10^{-5}$–$10^{-4}$ S/cm (Ruiz-Hitzky et al., 1995). Other parameters that play a pivotal role in these properties are the eventual presence of crystalline phase within the polymeric matrices. In fact, while in conventional polymer/salt systems the ionic conductivity is strongly influenced by the presence of polymeric crystallites, ion-pair formation, and the mobility of the counterions, it is not so in PCNs. Indeed, here the counterions (i.e., the negatively charged clay layers) are substantially immobile and, hence, ion-pairs and anion-complexed cation interactions cannot take place.

3.6.6 Chemical Resistance

Water- or chemicals-laden atmosphere has long been regarded as one of the most damaging environments which polymeric materials can encounter. Thus, the ability to minimize the extent to which water/chemical is adsorbed can be a major advantage. Indeed, nanoclay incorporation can reduce the extent of water/chemical adsorption in a polymer matrix, and this effect again is bound to the clay particle aspect ratio: increasing aspect ratio is found to diminish substantially the amount of water/chemical adsorbed and, hence, water/chemical transmission to the underlying substrate. Thus, application in which contact with water or moist environment is likely could clearly benefit from the use of materials incorporating nanoclay particles.

3.6.7 Biodegradability

In an era in which environmental protection is becoming a must, and recycling and/or biodegradability are two keywords, PCN materials constituted by organoclays and biodegradable polymeric matrices have proven to be outstanding systems by virtue of their improved biodegradability. The first biodegradable PCNs reported were based on organically modified MMT as mineral and poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA) as matrices. The remarkably improved biodegradability of these PCNs was substantially attributed to the catalytic role of the organoclay in the biodegradation mechanism.

3.6.8 Optical Properties

The presence of filler incorporation at nano-levels has also been shown to have significant effect on the transparency and haze of films. In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. With polymers characterized by a significant amount of crystalline fractions (e.g., polyamides and PET), this effect has been attributed to the modification in the crystallization behavior brought about by the nanoclay particles, the spherulitic domain dimensions being considerably smaller. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparent materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics. An ability to resist
high velocity impact combined with substantially improved abrasion resistance has also been verified.

### 3.7 Applications of Polymer–Clay Nanocomposites

The fact that polymer–clay nanocomposites show concurrent improved performances in various material properties at very low filler content, together with the ease of preparation through simple processes, opens up a new dimension for plastic and composite materials.

Generally speaking, the enhancement of the material properties highlighted above has paved the way for a substantial exploitation of PCN-based systems in industrial applications. For instance, the mechanical property improvements have resulted in major interest in numerous automotive and general/industrial applications. These include potential for utilization and as mirror housing on various vehicle types, door handles, engine covers, and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housing, mower hoods, and covers for portable electronic equipment such as mobile phones, pagers, and so on.

The excellent barrier characteristics exhibited by PCNs have resulted in considerable employment of nanoclay composites for food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals, and boil-in-the-bag foods, and also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion process for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite formulations would be expected to enhance considerably the shelf life of many types of foods.

The ability of nanoclay incorporation to reduce solvent transmission through polymers highlights the possibility of the application of PCN systems as both fuel tank and fuel line components for cars. Of further interest for this type of application, the reduced fuel transmission characteristics are accompanied by significant material cost reduction. And, last but not least, the optical clarity coupled with the flexibility and resistance properties have and currently still are opening new avenues for the employment of PCNs in the micro/electronics industry for special applications such as light-emitting devices (LEDs).

Besides these well documented applications, arising by the direct exploitation of the peculiar PCN properties, a list of promising applications of PNCs in important and to-the-edge fields, chosen among the plethora of many other available, will be briefly outlined and discussed.

#### 3.7.1 PCNs as Rheology Modifiers

Rheological modifiers control the flow properties of liquid systems such as paints, inks, emulsions, or pigment suspensions by increasing the medium viscosity, or impart thixotropic flow behavior to liquid system. Several dispersion procedures are used for conventional organoclays; however, they all can be described by two general methods: (1) pre-gel addition and (2) dry addition. The pre-gel method is based on the preparation of a 10%–15% organoclay dispersion in a suitable solvent using a high-speed disperser and a polar activator. The direct addition of organoclays involves adding the organoclay as a dry powder prior to, or during, the grind phase in the manufacturing process. The polar activator is then added and the dispersion continued. The function of polar activators is to disrupt the weak van der Waals forces which tend to hold the clay platelets together. Once these platelets are separated, it allows the organic functional groups to free themselves from the close association with the clay surface, and to solvate in the organic liquid for which they clearly have high affinity.

The rheological properties of a paint system are enhanced by a small addition of organoclays either by pre-gel or dry addition. The gel formation prevents pigment settling and sagging on vertical surfaces, and thus ensures that the proper thickness of the coating is applied. They also guarantee good leveling for the removal of brush marks and storage stability even at high temperatures.

PCNs are also employed in the formulation of printing inks. Here, the role played by these nanocomposites is manifold, ranging from adjusting the consistency of the inks to the desired values, to avoiding pigment sedimentation, providing good color distribution and desired film thickness, reducing the level of mist, and controlling of tack, water pickup, and dot gain control.

Thickening lubricating oils additivated by PCNs can produce especially high temperature-resistant lubricating greases, with enhanced working stability and water resistance. Such greases are typically used for lubrication in foundries, mills, and on high-speed conveyors, as well as in agriculture, automotive, and mining applications.

Finally, the performance of cosmetics is enhanced by the use of PCNs, where they allow good color retention and coverage for nail lacquers, lipsticks, and eye shadows. They have been tested to be nonirritant for both skin and eye contact.

#### 3.7.2 Drug Delivery

The continuous development of new controlled drug delivery systems is driven by the need to maximize therapeutic activity while minimizing negative side effects. One class of drug delivery vehicle that has received more attention in recent years is layered materials that can accommodate polar organic compounds between their layers and form a variety of intercalated compounds. Because the release of drugs in drug-intercalated layered materials is potentially controllable, these new materials have a great potential as a delivery host in the pharmaceutical field. Calcium MMT, for instance, has been used extensively in the treatment of pain, open wounds, colitis, diarrhea, hemorrhoids, stomach ulcers, intestinal problems, acne, anemia, and a variety of other health issues. Not only does MMT cure minor problems such as diarrhea and constipation through local application, but it has also been shown to act on all organs as well.
3.7.3 Wastewater Treatment

The use of PCNs in wastewater treatment has become common in industry today. PCNs exhibit a synergistic effect with many commonly utilized water treatment unit processes, including granular-activated charcoal, reverse osmosis, and air strippers. Although granular-activated carbon is particularly effective at removing a large range of organic molecules from water, it is very poor for removing large molecules such as humic acid and wastewaters containing emulsified oil and grease. Polymer–clay nanocomposites have proven to be the technology of choice for treating oily wastewaters. Humic acid is one of the common contaminants in potable water and is difficult to remove with conventional flocculation techniques commonly used for drinking water treatment, and activated carbon is very ineffective due to its weak interaction with humic acid. If humic acid is not removed from drinking water, subsequent chlorination produces unacceptable levels of trihalomethanes which are known carcinogens.

3.8 Conclusions

Significant progress in the development of polymer–clay nanocomposites has been made over the past 15 years. During these years of intense labor in this field, the advantages and limitations of this (nano)technology have become clear. The data shown in Table 3.1, reporting the expected market size of PCN-based materials in 2009, clearly justify such scientific and technological efforts. However, we have a long way to go before we understand the mechanisms of the enhancement of the major engineering properties of polymers and can tailor the nanostructure of these composites to achieve particular engineering properties. The use of organoclays as rheological modifiers is one of the oldest methodologies in industries, and is currently extensively used worldwide. The development of polar activator free PCNs in last 10 years made tremendous impact in the field of paint, ink, and greases. Although the field of nanoclays as drug vehicle for controlled release is one of the born age areas in medicinal application, PCNs have revealed a great potential as compared to polymer and carbon nanotubes for these sophisticated yet fundamental applications. The use of PCNs is still enjoying an expansion in water treatment applications. PCNs operate via partitioning phenomena and have a synergistic effect with activated carbon and other unit processes such as reverse osmosis. They have proven to be superior to any other water treatment technology in applications where the water to be treated contains substantial amounts of oil, grease, or humic acid. The commercial application of organoclays to trihalomethane control in drinking water has not yet occurred. However, with increasing concerns about the carcinogenic effects of these halogenated substances, the commercialization of this technology could be around the corner.

To date, one of the few disadvantages associated with nanoparticle incorporation has concerned toughness and impact performance. Clearly, this is an issue which would require consideration for application where impact loading events are likely to occur. In addition, further research is necessary to develop a better understanding of formulation/structure/property relationships, better routes to platelet exfoliation and dispersion, and so on. To quote Richard P. Feynman, “there is plenty of space at the bottom” also for further improving the structures and, hence, the performances of these extremely fascinating materials.

References


