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Sudip Ray a & Allan J. Easteal a

a Center for Advanced Composite Materials and Department of Chemistry, The University of Auckland, Auckland, New Zealand

Published online: 19 Jul 2007.

To cite this article: Sudip Ray & Allan J. Easteal (2007) Advances in Polymer-Filler Composites: Macro to Nano, Materials and Manufacturing Processes, 22:6, 741-749, DOI: 10.1080/10426910701385366

To link to this article: http://dx.doi.org/10.1080/10426910701385366
Advances in Polymer-Filler Composites: Macro to Nano

SUDIP RAY AND ALLAN J. EASTEAL

Center for Advanced Composite Materials and Department of Chemistry, The University of Auckland, Auckland, New Zealand

It has been long known that polymers can be mixed with clay minerals, however, the ideas of microcomposites have been expanded recently to a new and emerging class of clay-filled polymers, called Polymer-Clay Nanocomposites (PCN), which has experienced the real breakthrough early in the past decade only. This is a novel class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range with very low filler loading (usually 2–6% by weight). Due to the unique structure, specifically the high aspect ratio of these mineral fillers, the resultant high surface area provides similar reinforcing performance to that of traditional minerals and fibers used in polymers and yet does not increase density, since loading levels are low. Because of the nanometer size of the particles, which is smaller than the wavelength of visible light, the reinforced polymer remains transparent. Other characteristics of these composites include high barrier performance and improved thermal stability, which make these compounds suitable for many applications. This review aims to provide a brief current overview in exploring this new class of polymer composites.

Keywords Application; Barrier properties; Exfoliation; Flame retardancy; Future market; Intercalation; Layered silicate; Mechanical properties; Modeling; Montmorillonite clay; Nanocomposites; Polymers; Review; Structure; Synthesis.

1. INTRODUCTION

The idea of using particulate fillers in polymeric materials is an old practice. Fillers are added to polymers for a variety of purposes, of which the most important are reinforcement, reduction in material costs, and improvements in processing. Generally, the strength properties can be realized using high filler loading while sometimes sacrificing other properties. However, the Nylon6-clay hybrid developed by the research group in Toyota Central Research and Development Laboratories, Inc., Japan in 1986 revealed the possibility of achieving remarkable improvement in thermal and mechanical properties of the polymeric composite by incorporating a very low loading of clay filler [1]. In a series of experiments, they studied the ability of Na⁺-montmorillonite organically modified by protonated α, ω-aminoacid that was swollen by the ε-caprolactam monomer to initiate ring opening polymerization and obtain Nylon6-based nanocomposites using in situ polymerization [2]. The melt mixing of polymers with clays excluding the use of organic solvents was developed subsequently by Vaia et al. [3]. These initial achievements attracted further investigations and revelations, which showed enhancement of many material properties by nanodispersion of these inorganic layered silicate fillers that could not be obtained by conventional fillers. The commercial importance of this new class of materials has also been driven by an intense analysis of polymeric composites reinforced by these layered inorganic fillers, which have been documented in several books, patents, reviews, journal papers, and so on [4–10].

While the incorporation of microscale and larger inorganic fillers in organic polymers is scientifically well explored, the decrease in size of the inorganic component into the nanodimension and the simultaneous huge increase of the interfacial area resulting in extraordinary material properties requires further investigation. A critical survey of the available literature reveals that the field of nanocomposites is still more focused on exploration than application. The present review gives a brief overview of Polymer-Clay Nanocomposites (PCN) and recent developments in this field comprising nanocomposite structures, synthesis, properties, applications, and future markets, with special attention to their formation and interaction.

2. LAYERED SILICATES AS FILLERS

Silicates used in the synthesis of PCN are layered with a layer thickness of around 1 nm. The lateral dimensions of these layers can vary up to several microns; consequently, the aspect ratio of these fillers (ratio of length to thickness) is very high, with values greater than 1000. These layers form stacks with a gap between them called the interlayer or the gallery. The inorganic cations within the interlayers can be substituted by other cations. The exchange of metal ions with cationic surfactants, such as bulky alkylation ammonium ions, increases the spacing between the layers and reduces the surface energy of the filler. Consequently, these modified fillers, also called organoclays, are more compatible with polymers and form polymer-layered silicate nanocomposites. Montmorillonite (Mmt), hectorite, and saponite are the most commonly used layered silicates. A schematic representation of the atom arrangements in a unit cell for a three-layer clay, such as Mmt is shown in Fig. 1. The idealized structural formula for Mmt is Mx(Al₄₋ₓMgₓ)Si₄O₉(OH)ₓ, where, M = monovalent cation; x = degree of isomorphous substitution (between 0.5 and 1.3) [8, 9].
Interlayer surface and cation hydration between the structural units is a unique property of these layered silicates. For example, in the structure of Mmt shown in Fig. 1, only a relatively small proportion of the inorganic cations balancing the negative layer charge are located at external crystal surfaces. The majority of these cations are present in the interlayer space between the clay platelets. The thin, negatively charged sheets are held together by the electrostatic forces between alternate layers of bridging cations (e.g., Na\(^+\)); thus bonding between the layers is weak. Also there is a high repulsive potential on the surface of the layers resulting from isomorphous substitution. These two factors contribute to the increase of the spacing between the interlayer (Fig. 1).

The increase in the interlayer spacing, or the degree of expansion of the layers/planes, also depends on the cations located in the interlayer region, i.e., on the basal cleavage. If the interlayer cations are monovalent and strongly hydrated (e.g., Na\(^+\), Li\(^+\)), the interplatelet repulsion will be stronger and the degree of platelet separation will be larger [11].

3. Nanocomposite structures

Three main types of composites can be obtained when a layered silicate is dispersed in a polymer matrix. The type of composite depends on the nature of the components used including the polymer matrix, layered silicate, and organic cation. If the polymer cannot intercalate between the silicate sheets, a microcomposite is obtained. Beyond this traditional class of polymer-filler composites, two types of nanocomposites can be obtained:

- a) Intercalated structure: In this case, extended polymer chains are intercalated (sandwiched) between the silicate layers which form a multilayer structure of alternating polymeric and inorganic layers.

- b) Exfoliated or delaminated structure: These are obtained when the silicate layers are completely separated from each other and dispersed in the continuous polymer matrix.

These structures are schematically presented in Fig. 2. Usually, the structure of nanocomposites can be characterized by two complementary analytical techniques, i.e., Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). SAXS is used to identify intercalated structures by determination of the interlayer spacing with the help of Bragg’s law. Intercalation of the polymer chains increases the interlayer spacing and it should cause a shift of the (001) diffraction peak towards a lower angle. However, if the spacing between the layers becomes too large, this (001) diffraction peak will disappear in the X-ray diffractograms, which implies complete exfoliation of the layered silicates in the polymer matrix. In this case, TEM is used to identify the exfoliated silicate layers. However, TEM provides only two-dimensional projection of the three-dimensional clay morphology. Moreover, both these methods cannot be used to estimate the orientation of clay layers in the matrix. Very recently, Nishioka et al. [12] performed structural analysis of a model PCN using an organophilic Mmt dispersed in poly(ethylene-co-vinylacetate) (EVA), by Transmission Electron Microtomography (TEMT). The above technique was found to be a promising tool to obtain three-dimensional...
ADVANCES IN POLYMER-FILLER COMPOSITES

![Diagram](https://via.placeholder.com/150)

**Figure 2.**—A) Polymer matrix; B) layered silicate clay filler; C) conventional polymer clay microcomposite; D) PCN, where layered silicate clay filler present in the polymer matrix in i) aggregated, ii) intercalated, iii) partially exfoliated, and iv) completely exfoliated form.

spatial arrangement of clay layers in the matrix, which could be very useful for structure-property relationship studies.

### 4. Nanocomposite Synthesis

Several strategies can be used to prepare PCN. Three processes are mainly used:

a) In situ intercalative polymerization: The layered silicates are allowed to swell by absorption of a liquid monomer, or a monomer solution. The monomer migrates into the galleries of the layered silicate, so that polymerization can occur within the intercalated sheets. Polymerization can be initiated either by heat or radiation, by diffusion of a suitable initiator, or by an organic initiator, or catalyst fixed through cationic exchange inside the interlayer before swelling by the monomer. Examples: In situ polymerization of Nylon6, Nylon12, polypropylene (PP), polyethylene terephthalate (PET), etc. with organomodified Mmt [7–9].

b) Intercalation by solvent-method: The approach is similar to that used in the in situ intercalative polymerization method. First, the organoclay is swollen in a nonpolar solvent, e.g., toluene. Then the polymer, dissolved in the solvent, is added to the solution and intercalates between the clay layers. The final step consists of removing the solvent by evaporation, usually under vacuum. The major advantage of this method is that intercalated nanocomposites can be synthesized based on polymers with low or even zero polarity. Examples: solution intercalation of PP, polystyrene (PS), polymethylmethacrylate (PMMA) etc. with organomodified Mmt [7–9].

c) Melt intercalation: The layered silicate is mixed with the polymer matrix in the molten state. If the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form intercalated, and/or exfoliated nanocomposite.

In this technique, no solvent is required. Examples: PS, polyurethane (PU), etc. with organomodified Mmt [7–9].

### 5. Nanocomposite Properties

Clay fillers have a great disadvantage in their inherent tendency to form aggregated structures on a submicron scale (Fig. 2B). Hence the mechanical properties of each individual layer in clay particles cannot be utilized effectively while they are incorporated in the polymer matrix. Much effort has been devoted to breaking down clay particle aggregates into individual particles to form micro-sized filler reinforced polymers [13], as shown in Fig. 2C. Usually, high clay loading leads to improvement of the modulus at the cost of strength and toughness of the polymer composites. However, the concept behind PCN is to split not only clay aggregation but also to separate the individual silicate layers in the polymer matrix, as demonstrated schematically in Fig. 2D. As a result, the interfaces between clay layers and the polymer are considerably increased, while the number of reinforcing components also increases significantly because each clay particle contains hundreds or thousands of layers. In consequence, a wide range of engineering properties can be appreciably improved with a low level of filler loading.

The experimental results available so far show enormous improvements in different material properties as compared to pristine polymer, with a low level of filler loading, usually 2–6 wt%. At such a low filler loading, polymers such as Nylon-6 show significant improvement in mechanical properties, e.g., an increase in Young’s modulus of 105%, in tensile strength of 49%; in thermal properties e.g., heat distortion temperature of 146% [14]. Other improved physical and engineering properties include the ability to promote fire retardancy [15], barrier resistance such as gas and liquid permeability, and solvent swelling [16] and ionic conductivity [17].

Properties of PCN are highly correlated with their microstructure. Clays are generally highly hydrophilic and therefore incompatible with quite a few polymer types. The way in which the clay polarity is changed has a major effect on the nanocomposite form, i.e., intercalation vs. exfoliation. Although exfoliation has been the ultimate aim because this morphology is expected to lead to spectacular improvements in nanocomposite properties, often one obtains partial exfoliation and intercalation (Fig. 2D). Most published work dealing with the morphology of the nanocomposite systems only present a very general overview without in-depth details. The chief deduction derived is that the exfoliated structures have been achieved supported only by incidental facts. To indicate the exfoliation, the XRD patterns with a disappearance of interlayer spacing diffraction peak and/or TEM images showing expanded inter-gallery spacing of the clay layers have been provided. The degree of exfoliation usually varies from system to system. Interestingly, in most of the reports no attempt was made to estimate the degree of exfoliation. The fully exfoliated nanocomposite or high degree of exfoliation has been claimed only in very few cases [18, 19]. Extensive studies of the factors which control whether a particular organo clay hybrid can be synthesized.
as an intercalated or exfoliated structure demonstrate that by modifying the surface polarity of the clay, onium ions allow thermodynamically favorable penetration of polymer precursors into the interlayer region. The ability of the onium ion to assist in delamination of the clay depends on its chemical nature such as its polarity. Not only the exchange capacity of the clay but also the type of polymer matrix can determine the level of property enhancement. For example, polyamides (e.g., Nylon6, Nylon66) and polyesters are good candidate matrices for the hybrid clay to accomplish tremendous enhancement in mechanical properties. On the other hand, polyolefins, due to their incompatibility with the organo-hybrid clays, are not so suitable. However, judicious introduction of polarity in these compounds can make them useful. For example by use of compatibilizers, e.g., maleic anhydride grafted polyethylene (PEgMA) and polypropylene (PPgMA) blended with polyethylene (PE) and PP, respectively, show some spectacular improvements [20, 21].

The extraordinary enhancements in the mechanical properties even at very low loading of clay fillers in PCN documented in several literatures was presumably due to an efficient load transfer from the polymer matrix to the dispersed clay particles depending on several factors like polymer-clay interaction, degree of clay dispersion, extent of intercalation and exfoliation of the clay platelets in the polymer matrix, etc. Much research work has been already devoted to improve the mechanical properties but minimal information is available to understand the reinforcing mechanism of the layered silicates. In an early attempt, Vaia and Giannelis developed a mean-field, lattice-based model of polymer melt intercalation in organically modified layered silicates and applied it to styrene derivative polymers [22]. Later, Meneghetti and Qutubuddin [23] applied such a model for other polymers with different polarity, namely, PMMA, PP, and poly(ethylene oxide). They found that the nature of each polymer controls significantly the intercalation of the system. Chen [24] has recently reviewed the interaction mechanisms and the behavior of intercalated polymer in clay galleries. Zhu and Narh [25] have proposed a numerical simulation model, which is comprised of three phases, namely, polymer matrix, an interlayer, and clay platelets, to predict the modulus of clay reinforced polymer nanocomposites. Fertig and Garnich [26] proposed a finite element micromechanics model to generate parametric micromechanics data for a locally orthotropic three-phase PCN material that describes the stiffness properties of a group of aligned clay flakes with surrounding interphase suspended in a polymer matrix. Sheng et al. [27] demonstrated a multiscale modeling strategy to account for the hierarchical morphology of the nanocomposite. The proposed model relates the overall mechanical properties of PCN to those of the polymer matrix and of the dispersed clay particles, considering the influence of polymer matrix modulus, clay modulus, clay loading, degree of exfoliation, and clay aspect ratio. In another report, Scocchi et al. [28] presented a multiscale molecular modeling, bridging the gap between atomistic and mesoscopic simulation for PCN design. The dissipative particle dynamics was adopted as the mesoscopic simulation technique and the interaction parameters of the mesoscopic model were estimated by mapping the corresponding energy values obtained from atomistic molecular dynamics simulations. The predicted structure of the Nylon6 PCN system considered was in excellent agreement with previous experimental and atomistic simulation results [28]. Loo and Gleason [29] showed that FTIR could be used in situ to monitor the clay’s response to deformation relative to the polymer matrix. Katti et al. [30] estimated molecular interactions in organically modified clay and PCN using photoacoustic Fourier Transmission Infrared (FTIR) spectroscopy, XRD and computational molecular dynamics. The hydrogen bond and ionic bond interaction between functional end groups of organic modifier and surface oxygen of clay sheet lying in the interlayer clay gallery in the PCN were revealed by FTIR. In another current study, Kalra et al. [31] reported the results of molecular dynamics simulations to obtain the vibrational spectrum of a model Mmt clay as a function of microstrain in the clay platelet. The spectral shifts for various states of microstrain was determined by comparing the calculated spectra obtained in the absence of applied deformation to that obtained in the presence of tensile strain along different directions in the plane of the clay platelet. They compared the experimental results of Loo and Gleason [29] with theoretical values obtained by using vibrational data to relate macrostrain to frequency shifts in the clay vibration spectrum, Eshelby’s analysis to relate macrostrain to microstrain in the clay particles themselves, and molecular dynamics modeling to relate microstrain to frequency shifts in the clay vibration spectrum, and checked the internal consistency for these three methods. The theoretically predicted values of −1.6 to −2.2 cm$^{-1}$% macrostrain and the theoretical modulus of 1.12 GPa for the composite obtained by Kalra et al. were in good agreement with the previously reported experimentally measured values of −1.25 cm$^{-1}$% macrostrain and 1.12 GPa modulus respectively by Loo and Gleason [29]. Rao and Pochan [32] reported the mechanics of PCN using a designed copolymer latex, comprising butyl acrylate, styrene, methacrylamide, and 2-acrylamido-2-methylpropane sulfonic acid sodium salt to control its interaction with the surface of Mmt clay (Cloisite Na$^+$) and to keep glass-transition temperature ($T_g$) of the copolymer lower than room temperature. The role of butyl acrylate and styrene was mainly to adjust the $T_g$ of the material; methacrylamide was designed to form hydrogen bonds with the surface oxygen of the clay platelet and the anionic sulfonic salt was used to separate the polymer from the surface to extend the intercalation spacing. The anionic charge on the polymer helped in stabilizing and preventing the agglomeration of the formed nanophases. The methacrylamide and the sulfonic salt further helped in the self-dispersion of the latex in water with a hydrophilic surface. Noticeable reduction in the chain mobility in the nanocomposites was noted by dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA) studies. The enhancement in modulus values was found to be related with the volume of the added clay as well as the volume of the constrained polymer. Modeling based on Mooney’s equation proposed that the nanocomposite modulus enhancement could be determined by the high aspect ratio of the intercalated
clay and the strong interfacial strength, in the form of the Einstein coefficient, when the modulus of the matrix phase was much lower than that of the clay. Thus the improvement in mechanical and thermal properties in PCN could be explained by the formation of intercalated clay phase which acted as an unmeltable crystalline phase nanocomposites with strong interfacial interactions resembled to that of semicrystalline polymers. Kim et al. [33] presented the results of the numerical analysis of the equilibrium thermodynamic miscibility using one- and two-dimensional models based on the self-consistent mean-field theory. In the limit, the two-dimensional model reproduced the one-dimensional model published results. The adopted two-dimensional model considers the presence of four PNC components: solid clay platelets, low molecular weight intercalant, polymeric matrix, and end-functionalized compatibilizer. The simulations, with realistic values of the binary interaction parameters, were analyzed for potential exfoliation of PNC with a polyolefin as the matrix. The simulation results show that intercalation and exfoliation is expected within limited ranges of the independent variables. The presence of a bare clay surface, e.g., generated by thermal decomposition of intercalant or extraction by molten polymer has a strong negative effect on the dispersion process. The simulation successfully identified the most influential factors, e.g., optimum ranges of the compatibilizer and the intercalant concentration. In a very recent study, Hbaieb et al. [34] compared two-dimensional to three-dimensional finite element studies. Due to its simplicity, the two-dimensional model is often used but it does not accurately predict the stiffness. The established mechanics-based composite stiffness models, such as the Morie–Tanaka was found to predict reasonably accurate stiffness of clay nanocomposites whose volume fraction was less than about 5% for aligned particles but underestimated the stiffness at higher volume fractions. On the other hand, for randomly oriented particles the Morie–Tanaka model overestimated the stiffness of clay nanocomposites.

A number of investigations have shown that PCN have a lower permeability than that of the corresponding virgin polymer. For example, Honeywell claimed that Nylon6 with 2% nano-clay could achieve three times the oxygen barrier of unfilled Nylon6 while 4% nano-clay confers a six-fold improvement, retaining most of its existing favorable characteristics like toughness, clarity, and oil/grease resistance [35]. That makes Honeywell’s Aegis™ NC nano-Nylon a candidate for medium-barrier bottles and films, those offering around 0.5 to 1 cc/mil/day oxygen transmission rate (OTR). In addition it also shows almost double stiffness, higher HDT (heat distortion temperature), and improved clarity for nano-Nylon6 packaging. In the case of Imperm™ compound from Nanocor, an inherent gas barrier of 0.35 cc/mil/day results from addition of a nano-clay to amorphous MDX6 Nylon from Mitsubishi Chemical. Used as the core of a three-layer PET bottle, Imperm™ could reduce OTR by a hundred fold compared with that of neat PET. It is being used in a 16-oz, nonpasteurized beer bottle in which the Imperm™ core (10% of bottle thickness) reportedly ensures a 28.5-week shelf life. Imperm™ can adhere to PET without tie layers while maintaining sufficient clarity to meet requirements for the amber bottle [28].

This phenomenon can be explained by considering the clay sheets as impermeable obstacles in the path of the diffusion process. In a well exfoliated and dispersed state, individual clay platelets are believed to increase the barrier properties by creating a maze or ‘tortuous path’ (Figure 3) that retards the progress of gas and vapor molecules through the polymer matrix. Very recently, Sorrentino et al. [36] reviewed and proposed a geometric model for predicting the effective diffusivity through PCN as a function of clay sheet orientation, volume fraction, polymer clay interaction, and aspect ratio. Xu et al. [37] analyzed the effects of clay layers on the barrier properties of PCN containing impermeable and oriented clay layers. Using the relative permeability theory in combination with the detour theory, new relative permeability expressions were reported that helped in investigating the relative permeability as a function of lateral separation, layer thickness, gallery height, layer length, and layer volume fraction. It was found that intercalated and/or incomplete exfoliated structures and dispersed tactoids with several layers can effectively enhance the barrier properties of the materials. The chain-segment immobility factor was developed to briefly discuss the chain confinement from clay layers. The results showed that the chain confinement enhanced the barrier properties of the intercalated nanocomposites.

Nanoclays also has proved effective as a flame retardant. Flame retardancy is normally evaluated by the reduction of the peak of heat release rate (HRR). For example, Gilman et al. [38] found that peak HRR for Nylon6, PS, and PPgMA nanocomposites could be reduced by 50%–75% using MMT based organically treated layered silicates. In commercial flame retardant applications, nanoclays act as synergists with either halogenated or nonhalogenated flame retardants. In halogenated systems, nanoclays can partially replace brominated flame retardant to reduce cost. Nonhalogenated flame retardant systems often contain high levels of mineral flame retardants such as alumina trihydrate (ATH) or magnesium hydroxide [Mg(OH)₂] that tend to reduce strength properties. Nanoclays can replace a portion of the mineral flame retardant, which also improves the physical properties of the compound. For example, Germany’s Süd-Chemie offers modified nanoclays called Nanofil as flame retardants [39]. They have already developed halogen-free
Li-batteries, includes the development of systems for application in solid-electrodes for electrochemical devices. The interest in polymer-clay nanocomposites for applications involving conducting polymers, e.g., polyaniline and polypyrrole, as well as precursors of conducting materials, has been tested as active phases in polyacrylonitrile, etc. [42]. These layered silicates can also effectively contribute to flame retardancy in EVA/PE wire and cable compounds containing new Nanofil SE 3000 nanoclay. Only 3% to 5% of this nanoclay loading improves flame retardancy to the extent that the loading of alumina trihydrate or magnesium hydroxide flame retardants can be reduced from 65% to about 52% by weight. Incorporation of such nanoclay could also improve mechanical properties, and smoother cable and higher extrusion speeds.

In general, fire retardancy involves a high-performance carbonaceous-silicate char, which builds up like a barrier (Fig. 4) on the surface during burning, i.e., pyrolysis and combustion. This barrier is thought to be responsible for the improvement in flame retardancy, which insulates the underlying material and reduces the mass loss rate of decomposition products. Recently, Lewin critically reviewed the whole procedure [40]. According to his study, gradual precipitation of the Mmt on the surface is not simply due to the gasification of the polymer; rather the migration or convection of the Mmt to the surface could be attributed mainly to the lower surface free energy of the Mmt.

Apart from improvements in the properties considered above, these hybrid clays also find use in enhancing the rate of biodgradation of biodegradable polymers, for example, polylactide (PLA) [41]. According to the studies carried out by SinhaRay et al. [41], the biodegradability of PLA can be controlled by suitable selection of modified clay. Encouraging results are also observed with other biodegradable polymers such as poly(e-caprolactone), poly(3-hydroxy butyrate), thermoplastic starch, cellulose, chitosan, etc. [42].

These layered silicates can also effectively contribute to ionic conductivity in PCN, which could be useful for electrochemical applications. Progress in this area was achieved by Parfitt and Greenland [43] in 1990 via intercalation of poly(ethylene oxide) in Li-smectites to produce Li single-ion conductors. Nanocomposites involving conducting polymers, e.g., polyaniline and polypyrrole, as well as precursors of conducting materials, e.g., polyacrylonitrile, have been tested as active phases of electrodes for electrochemical devices. The interest in polymer-clay nanocomposites for application in solid-state electrochemical devices, mainly in rechargeable Li-batteries, includes the development of systems for electrolytes and electrodes [44]. Other than thermal and mechanical properties the nanocomposites show good ionic conductivity at room temperature. With increase in exfoliated morphology the ionic conductivity improves, since more Li cations are mobile and available for conduction [45]. Application of the melt-intercalation approach developed by Vaia et al. [3] allows a greater disorganization in the nanocomposites as well as the incorporation of Li salts that can contribute to the conductivity of the systems [16]. The combination of clays with biopolymers to develop stable systems capable of tunable ion-exchange capacity for the fabrication of ion sensors has recently gained attention [44].

Currently research work is directed toward improving the properties of foam by incorporation of nanoclays. For thermoplastic foams, it was found that clay-filled nanocomposites could effectively reduce the cell size and increase the cell density [46]. Thus an exfoliated PS nanocomposite can produce foam with a cell size five times smaller than that of the pure PS foam [47]. Thermal insulation and ageing properties of PU foam have been found to be improved by incorporation of nanoclay [47]. Another advantage of PCN is that the optical properties of the polymer are not significantly affected. The thickness of individual clay layers is of the order of a nanometer, which is much smaller than the wavelength of visible light: as a result, well exfoliated PCN is optically clear in visible light [48].

6. Nanocomposite applications and future markets

Several potential applications have been identified so far:

- Automobiles: gasoline tanks, bumpers, interior and exterior panels.
- Construction: building sections, structural panels.
- Aerospace: flame retardant panels, high performance components.
- Electronics and electrical: printed circuit boards, electric components.
- Food packaging: containers, wrapping films.
- Coatings and pigments.

Amongst these, the automotive sector provided the motivation for the first commercial application for polymer nanocomposites of any type [49]. In 1991, Toyota in collaboration with Ube commercialized a Nylon6 nanocomposite moulding composition for timing belt covers. Soon after that development, Unitika introduced another Nylon6 nanocomposite in an engine cover on Mitsubishi’s Gasoline Direct Injection (GDI) engines. These early Nylon nanocomposites were expensive and proved unable to retain their position in the highly competitive automotive markets. The materials are no longer used for these applications. Instead, the main focus for polyamide nanocomposites has now switched to applications requiring high gas barrier properties in both automotive and packaging markets. Ube is developing Nylon12-clay nanocomposites for automotive fuel lines and fuel system components that require very high barrier properties to meet future emissions standards [45].
Nanocomposites based on PP and other polyolefins also find use in this automotive application. General Motors (GM) and Basell have already claimed the application of polyolefin-clay nanocomposites as a step assistant component for GMC Safari and Chevrolet Astro vans. Noble Polymers has developed PP-clay nanocomposites for structural seat backs in the Honda Acura.

Other than automotive applications, PCN have been used to improve barrier resistance in beverage applications. Alcoa CSI has applied multilayer PCN as barrier liner materials for enclosure applications. Honeywell has developed commercial Nylon6-clay nanocomposite products, Aegis™ NC resin for drink packaging applications [50]. Mitsubishi Gas Chemical and Nanocor have jointly developed Nylon-MXD6 nanocomposites for multilayered PET bottle applications. Avella et al. [51] prepared biodegradable starch-clay nanocomposite films for food packaging applications by homogeneously dispersing Mmt via polymer melt processing. Very recently, Ray et al. [52] reviewed the potential use of PCN in food packaging application.

In addition to the improvement of mechanical properties of plastic materials, nanocomposites also afford materials with functionality for conductivity, membranes, corrosion protection, and fire retardant behavior. This includes the possibility of preparing thin layers, which is crucial for many electrochemical devices such as solid state battery or selective electrode components. Very recently Aranda et al. [44] reviewed the possibility of using polymer and biopolymer-clay nanocomposites in electrochemical and electroanalytical applications.

The cost attractiveness of these novel materials is tempting automotive suppliers, as well as many other industries to carry out further research and invest both in thermoplastic and elastomer markets [50]. GM, Toyota, Ford, and Volvo are known to be actively engaged in nanocomposite research. Bayer, Honeywell, Eastman, Clariant, Showa Denko, and Ube are also likely to continue and expand their involvement. Major polymer producers such as Basell and Dow are expected to become deeply involved over the next few years, facilitating the spread of nanocomposite technology to the market in general and stimulating value creation and volume growth across global markets. A previous survey about the prospective market for PCN by Principia Partners [53] in 2000 found that the world market demand for PCN was relatively small. However, they estimated that there would be huge requirement of these materials in the near future and according to their assessment, nearly 450 million kg nanoclay-reinforced compound would be in production in 2009, along with a steady growth. In a very recent review, Freedonia industry [54] forecast that with the fall of material and production costs of clay-based nanocomposites, clays will rise to account for over half of all nanomaterials demand by 2020.

7. Conclusions

In several instances, PCN has already established potential advantages over conventional polymer filled systems. Surprisingly, even after one and half decades of extensive research there are only a few examples where this new composite system is truly commercialized rather than a subject of academic interest only. It is apparent that in order to reap the full benefit, more fundamental studies should be carried out in the following areas:

- The research work carried out so far is mostly concentrated on sodium montmorillonite clay due to its superior performance in the final property improvements. The other layered aluminosilicates, such as hectorite, vermiculite, or saponite should also be explored and appropriately modified to make them suitable for the nanocomposite applications.
- Only few polymers are found to provide immense property improvement in combination with organoclays. However, it would be worthwhile to study the type of polymer and the influence of molecular weight, molecular weight distribution, crystallinity, end-group concentration, etc. of a broad range of polymers and the possible steps required to modify them in order to achieve higher degree of exfoliation of organoclay and thus on the final properties to further expand the scope in this field.
- Recently, attempts have been made to investigate the structure-property relationship using model polymer-clay system, mostly on Nylon6 and Mmt clay. More detailed understanding of laminates with silicate and polymer is essential, especially their interaction mechanism related to the impending uses for the other polymer-clay systems as well. Although ionic interactions, Hydrogen bonding, and nonbonding interactions has been reported in different PCN systems but further in-depth studies on how these interactions affect the mechanical properties of the nanocomposites and how polymers can be properly designed to have a controlled interaction with the clay nanoplatelets is highly desired.
- Most of the composite theories assume that the filler particles are uniform in size and shape and completely aligned in one direction. However, the layered silicates are usually dispersed randomly in the polymer matrix. Partial exfoliation and curved features in the exfoliated nanoplatelets with dissimilar platelet lengths are a rather common occurrence. Detailed investigations should be carried out considering the above phenomena to bridge the gap between the theoretical and experimental findings.
- Various polymerization techniques have been employed to prepare PCN rather than melt processing, whereas the latter technique is more acceptable to the industries. Thus attention should also be paid to develop simple and effective processing methods for these materials to make them more amenable to industrial applications. Recently Kim et al. [55] demonstrated a novel fabrication method to continuously produce PP/clay nanocomposites using electric melt pipe equipped with a twin-screw extruder without using any compatibilizer to achieve partial intercalation.
- Although the high level of shearing is the driving force for the exfoliation process in the melt processing technique, attention should be paid to aim at achieving higher degree of exfoliation without causing much attrition in the clay platelets.
• Improved thermal stability of nanoclays is also desired to make them suitable for melt processing.
• Interestingly, the nanosilicate platelets have a tendency to orient along the polymer flow direction resulting in a formation of anisotropic structure. Thus the tensile, compressive, barrier properties etc. differ when they are acted parallel versus perpendicular to the platelets. These directionally-dependent properties of oriented nanocomposites need to be further explored and exploited, particularly with regard to the design of applications made by extrusion, injection molding or other flow orienting processes.
• Much less research effort has been devoted to thermoset nanocomposites, which might also provide some distinct advantages. Advantages such as the relatively low coefficient of expansion of thermoset resins when compared to thermoplastics might lead to wide utility of thermoset nanocomposites in the coatings industry.

Even though the present scenario for nanocomposites is somewhat clouded, bright sunny days are sure to follow. The amount of research work carried out globally on these materials both in academia and in industry, on their theoretical as well as applied aspects, indicates that rapid progress in this field will be achieved in near future.

REFERENCES

ADVANCES IN POLYMER-FILLER COMPOSITES