5.10 Polymer-Layered Silicate Nanocomposites

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5.10.1 Introduction and Historical Perspective

Composites comprised of a polymer matrix and inorganic fillers are one of the most important and significant engineering materials in today’s society [1]. Examples include the use of glass fibers or carbon black dispersed throughout a polymer host. Such materials are of great interest because they usually display significant improvements in mechanical properties, and often other properties such as barrier and fire-retardancy, over and above that of the pure polymer. One of the most significant developments in the past two decades or so has been nanocomposite materials in which at least one component has nanoscale dimensions [2,3]. One of the best examples of such materials are polymer-layered silicate nanocomposites (PLSNs) [4–8]. In PLSNs, the large surface-to-volume ratios of the inorganic component leads to significant improvements in properties and, perhaps most importantly, these nanocomposites often avoid the usual trade-offs in properties integral to macroscopic filled composites.

Historically, the addition of silicates to polymeric materials goes back at least 50 years. Throughout the 1960s, there was significant effort in examining the production of PLSNs (although they were not known by that name at the time) by several workers, notably by Blumstein [9–12] and Solomon and Swift [13], who were primarily interested in the chemistry of polymerization in the presence of clays. During the 1970s, it was reported by Unitika Ltd., that layered silicates can be added to nylon materials [14]. This is an early example of the significant contribution from industrial researchers in the field.

Not withstanding the fact that polymer–silicate composites had been studied for several decades, the genesis of the modern PLSNs can be traced to the seminal work done at Toyota Central Research and Development Laboratories in the late 1980s [15]. They first demonstrated the significant improvement of several properties on the inclusion of only small percentages of silicate into nylon [16–19]. They polymerized intercalated ε-caprolactam in montmorillonite (MMT) to produce a nylon 6 (N6)-clay nanocomposite [16–19]. This resulted in
the silicate layers being uniformly dispersed within the polymer matrix, and resulted in the composite material having improved physical properties compared with virgin polymer. For example, the nanocomposite material showed an increase in tensile strength by 55% with only 4.2 wt.% of MMT [19]. The significance of these results is further compounded when it is noted that these improvements were obtained with only a few percent of silicate present.

Since the publication of these papers from the Toyota group, there has been an enormous push toward the development of new PLSN-based materials, not only from an industrial viewpoint of making products but also to answer more academic questions regarding the nanoeffect present in these materials. This review will concentrate on these developments in PLSNs since the Toyota publications. It is not intended to be a comprehensive treatise, but discusses the most salient aspects of PLSNs, including preparation methods, structure, and properties.

5.10.2 Basic Structures of Layered Silicates and Polymers
5.10.2.1 Layered Silicate Structure

Layered silicates are from the smectite family of clays, and include MMT, hectorite, and saponite. Varieties of distinct silicates are either found naturally or can be synthesized, and are distinguished by the location and type of cations present in the oxygen framework. As shown in Figure 1, they consist of two silica tetrahedral sheets fused to an edge-shared octahedral sheet, typically aluminum or magnesium hydroxide. Periodic stacking of the layers forms a lattice, with each layer of approximately 1 nm thickness. Weak van der Waals forces hold the stack together. Small molecules or macromolecules can be inserted (intercalated) between the layers under appropriate conditions. The lateral dimensions vary from 300 Å to several microns depending on the specific silicate, and each layer can nominally be treated as a disk. A negative surface charge is present on the layers because of isomorphic substitution of the tetrahedral silicon or the octahedral aluminum and magnesium. The net charge deficiency is typically compensated by cations, such as Na⁺, K⁺, and Ca²⁺, in the interlayer galleries.

The interlayer spacing between the silicate layers is quite hydrophilic and normally hydrated unless heated to several hundred degrees Celsius. Modification of the interlayer spacing can be achieved through the use of alkyl-ammonium or alkyl-phosphonium cations in cation exchange reactions. The result of this is that the interlayer spacing becomes more hydrophobic; furthermore, the organic modifiers may contain a variety of functional groups, thereby providing access to a wide range of chemistries and properties. Such functionalities can include polymerizable groups (e.g., vinyl) or initiating groups.

5.10.2.2 PLSN Structure: Degree of Silicate Layer Dispersion

There are two idealized structures in PLSN materials (excluding immiscible systems, which normally should not be regarded as nanocomposites), as depicted in Figure 2 [20]. These are (1) intercalated materials, where the organic polymer is present within the inorganic silicate layers (i.e., a well-ordered and structured arrangement exists), and (2) exfoliated materials, where the organic polymer host matrix contains delaminated silicate crystallites (i.e., disordered and well dispersed). Notice that in the exfoliated case the surface area between organic and inorganic is increased compared with the intercalated materials. This is speculated to lead to greater enhancement of physical properties of exfoliated composites when compared with similar intercalated materials. It should be pointed out, however, that many polymer–nanocomposite materials are not simply only exfoliated or just intercalated – they often tend to have mixtures of structures [21]. Also shown in Figure 2 are typical data from different idealized PLSN structures collected from transmission electron microscope (TEM) and X-ray diffraction (XRD). These are the most common techniques used to analyze structures in PLSNs. In particular, the TEM images show the silicate layers (the dark areas) are increasingly dispersed from the immiscible case to the exfoliated case. In an exfoliated nanocomposite, XRD spectra do not have a characteristic peak due to the regular stacking of the silicate layers.

5.10.2.3 Polymers Used in PLSNs

There are a large number of polymers that have been used in the fabrication of PLSNs. A small subset of these include polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl pyridine), polyacrylonitrile, poly(acrylic acid), poly(vinyl alcohol), poly(N-vinyl pyrrolidone), poly(N-vinyl carbazole),...
Polyethylene, poly(ethylene terephthalate) (PET), nylons (polyamides), polysters, epoxy resins, poly(lactide), poly(ε-caprolactone), polycarbonates, and polysiloxanes. Reviews published by several authors, including Alexandre and Dubois [4], Ray and Okamoto [7], Giannelis et al. [8], and more recently by Paul and Robeson [20], Pavlidou and Papaspyrides [22], and Chen et al. [23] further account for these and other materials.

5.10.3 Synthetic Methods

There are three main methods of PLSN synthesis: in situ polymerization, solution intercalation, and melt processing (or melt blending). A fourth method, using sol–gel techniques, can in principle be applied but is not utilized often because of the higher temperatures needed and the tendency of the inorganic component to aggregate. Each of the three main approaches may yield exfoliated, intercalated, or a mixed of exfoliated and intercalated structures. The degree of exfoliation versus intercalation depends on a host of experimental conditions, such as monomer type, solvents, temperatures, etc.

5.10.3.1 In Situ Polymerization

There are various approaches to in situ polymerization, with each one relying on the addition of monomer, either neat or in solution, to the silicate layers to swell or even exfoliate the silicate layers before polymerization occurs. The earliest example of highly exfoliated nanocomposites from this method was that from the Toyota Central Research and Development Laboratories [16–19]. They swelled MMT modified with α, ω-amino acids, of the structure $H_nN^+\{\text{CH}_2\}_n\text{CO}_2\text{H}$, with $n = 2–6, 8, 11, 12$, and 18, with ε-caprolactam monomer (above its 70°C melting temperature). N6 PLSN was formed by initiating the polymerization. Exfoliated PLSNs were formed when the amount of modified MMT was less than 15 wt.%, but intercalated systems formed when it was between 15 and 70 wt.%. Further work demonstrated that it was possible to perform the in situ polymerization and yield exfoliated nanocomposites without the need for the silicate organic modifier. Many other workers have subsequently investigated the production of polyamides using the in situ polymerization approach (see Ref. [22] for a more comprehensive listing up to 2008).

One of the most-studied in situ polymerizations is the amine-catalyzed epoxy resin formation [24]. Both Pinnavaia and coworkers [25–27] and Vaia and coworkers [28] have examined this system in detail. Although these polymerizations and subsequent structures are quite complex, Wang and Pinnavaia [27] pointed to the importance of the rate of polymerization within the silicate layer galleries (intragallery) relative to the polymerization rate outside of the layers (extragallery). If the intragallery polymerization was able to proceed at a rate comparable to, or in excess of, the extragallery rate, then exfoliation is thought to occur more readily. Since the curing of the epoxy resin is amine-catalyzed, it was proposed that primary and acidic intragallery ammonium ions, present to organically modify the clay, also catalyze the reaction, thus providing an acceptable rate of polymerization within the silicate layers that leads to exfoliation. Secondary and tertiary ammonium ions are not as effective as catalysts, and therefore do not lead to exfoliation. Vaia and coworkers [28] showed that including hydroxy functionality into the surfactant silicate modifier leads to increased intragallery catalytic activity and better miscibility between the components.

Many vinyl monomers have also been polymerized in the presence of (normally organically modified) silicates. Early examples included the synthesis of PS and PMMA–MMT nanocomposites through radical polymerization. The organic modification of the silicates has most often been performed using ammonium-based surfactants that can be nonpolymerizable, polymerizable, or radical initiators. Initial work by Akelah and Moet [29] demonstrated that intercalated nanocomposites could be formed, with the degree of silicate dispersion being dependent on the organic modifier used.

The first production of an exfoliated PS-based PLSN was reported by Weimer et al. [30], who used nitroxide-mediated polymerization (NMP) to synthesize PS initiated from a silicate-bound alkoxyamine initiator (Scheme 1). This produced a well-dispersed PS nanocomposite in addition to low polydispersity PS because of the use of NMP. The other so-called living or controlled radical polymerizations [31], such as vinyl-mediated polymerization [32], atom transfer radical polymerization [33–35], and reversible addition–fragmentation chain transfer [36] polymerization have also been successful in making PLSN materials wherein the polymer has predictable molecular weight and low polydispersity. Block copolymer PLSNs have also been achieved [35,37].
Other forms of polymerizations have been used to create PLSNs. Advincula and coworkers [38] examined the use of anionic polymerization of styrene. Polyolefins have been made using Ziegler–Natta types of catalysts or other coordinating catalysts such as metallocenes [39–42], which are often intercalated into the layered silicate structure. However, ionic polymerizations suffer from inherent high reactivity and susceptibility to moisture, and interest in the preparation of polyolefin-based PLSNs has primarily been in melt processing.

### 5.10.3.2 Solution Intercalation/Exfoliation

Layered silicates are well known to be dispersible in an appropriate solvent. By adding a polymer to the dispersed layered silicate and then removing the solvent one can make a PLSN that is in some cases exfoliated, but normally the silicate layers reform a (semi)ordered stack, thus yielding an intercalated PLSN. A drawback of this approach being commercially useful is the use of large quantities of solvents, particularly if they are organic, although water has potential.

Since most layered silicates disperse well in aqueous solutions, the solution intercalation/exfoliation method is an obvious choice for water-soluble polymers. For example, PLSNs comprised of poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), and poly(N-vinyl pyrrolidone) have all been used to make intercalated PLSNs [4]. Typically polar organic solvents, such as acetonitrile, various alcohols, N,N-dimethylformamide, and acetone, result in adequate dispersions of the clay and also facilitate the dissolution of a wide range of polymers. This is especially the case with organically modified silicates.

Some polymers are inherently difficult to dissolve in common solvents and thus a solution containing the layered silicate and a prepolymer can be used. An example of such polymers are poly(imide)s. The Toyota Research group demonstrated that well-dispersed poly(imide)-based nanocomposites could be made from organically modified MMT (it was treated with dodecylammonium hydrochloride) and poly(imide) precursors poly(amic acid) and 4,4′-diaminophenyl ether [43].

A third method of using solution intercalation/exfoliation to make PLSNs is based on emulsion polymerization [44–46]. In such preparations, the silicates are dispersed in an aqueous medium, along with water-insoluble monomer and surfactant which are normally present in an emulsion polymerization. Once the polymerization has been realized, the water and other volatiles are removed, yielding the resulting PLSN. In most cases, the PLSN has an intercalated structure. Early work using this method was based on PMMA [44] and PS [45], and subsequently applied to other polymers such as epoxies [47] and other monomers [48–50].

### 5.10.3.3 Melt Processing

Melt processing is, as the name suggests, simply based on the thorough mixing of silicates within a polymer...
melt and subsequent cooling. In most cases, an intercalated nanocomposite is formed. This process has industrial appeal—it avoids the use of monomers and/or solvents, uses production equipment commonly found in commercial facilities (e.g., extruders), and has flexibility in the formulation of the PLSN. However, in practice, thermodynamic and entropic factors may work against the intercalation of the polymer into the interlayer spacing of the silicate [51–53]. A broad picture of melt processing would paint the process of polymer chains moving into the confined space between layers; this would have an entropic penalty, and the affinity between the polymer and silicate may not provide sufficient enthalpy to overcome the loss in freedom the polymer experiences. However, modeling of melt processing has shown that there is a variety of other aspects that should be considered [51,54,55]. In fact, in organically modified clays the loss in entropy experienced by the polymer chains is (at least) somewhat offset by the gain in entropy experienced by the alkyl chains in the organic modifier.

Significant progress in both the understanding of melt processing and its application for the production of a variety of PLSNs based on many polymers has been made in recent years [20,22]. In some cases, the appropriate conditions that result in significant amounts of exfoliation have been found. However, these successes are normally based on more polar polymers, such as polyamides. The less polar polymers, including polyolefins such as polypropylene and polyethylene, the degree of mixing is limited. However, it has been found that the inclusion of small amounts of maleic anhydride grafted to polypropylene [56] or polyethylene [57] can lead to significantly enhanced mixing. The use of swelling agents, monomers or volatile solvents that help disperse the silicate layers during mixing, also improves PLSN production [20,22].

Paul and coworkers [20,58] have offered a mechanism for organoclay dispersion in melt processing, as depicted in Scheme 2. In this scenario, the shear forces help peel back the silicate layers, and if the affinity between the polymer and organically modified silicate surface is sufficiently high, then a well-dispersed system is obtained. As might be expected, there are many different factors that can alter the degree of dispersion, including polymer type, organic modifier, silicate type, temperature, extruder, and screw design.

5.10.4 Characterization and Properties of PLSN Structures

5.10.4.1 Structure of Modified Silicates

5.10.4.1.1 XRD and TEM

The two most common methods of structure characterization in PLSNs are XRD and TEM [22,59,60]. XRD analysis in particular is relatively easy to perform, but there are several caveats that must be kept in mind when analyzing PLSN samples in this way [59]: (1) foremost is that the sensitivity of XRD is low, and can depend on several parameters that may not be optimized; (2) XRD is not quantitative; and (3) XRD is normally used to detect the absence of a peak. However, XRD cannot be used as conclusive proof of an exfoliated structure, in part because of the problems mentioned immediately above. With these qualifications in mind, XRD can be a useful technique to provide a quick analysis of the nanocomposite and to determine if further work is warranted.

TEM, however, is extremely useful in providing a direct way of determining nanocomposite morphology. Visualization from TEM can not only be qualitative, but, with some extra effort, it can also yield quantitative data with regard to the extent of exfoliation and/or
intercalation. However, as with all TEM analyses, to provide a complete picture of the sample morphology, images should be taken at various magnifications and several places within the sample.

There are other analytical methods that have been used to determine PLSN structure that have not been used as much as XRD and TEM primarily because of their need for a high degree of expertise and/or the lack of instrumental access. These techniques include solid-state nuclear magnetic resonance spectroscopy [61–63], small-angle X-ray scattering [64,65], and neutron scattering [66].

5.10.4.2 Thermal and Mechanical Properties of PLSNs

5.10.4.2.1 Mechanical properties

The improvement in mechanical properties is a significant driving force behind the development of PLSNs. As mentioned above, the original Toyota publications indicated significant increases in tensile strength with only small amounts of clay [17,18]. These improvements are a result of the reinforcement action of the silicate layers within the polymer matrix. Paul and Robeson [20] have suggested that most of the mechanical improvements observed in PLSNs can be modeled effectively by regular composite theories, and that there is no need to include any special nanoeffects in the model. In any case, because such models are based on parameters such as filler aspect ratio, volume ratio, and orientation (note that filler particle size does not qualify as a factor), PLSNs do show larger improvements in a variety of properties at the same filler content compared to other filler types. For example, as shown in Figure 3, the modulus of a thermoplastic olefin (TPO) increases at a greater rate when MMT compared with talc, which is a common filler used in TPO composite formulations [67]. However, it must be stressed that the degree of improvement is closely linked to the degree of exfoliation and mixing, thus is dependent on the many parameters discussed above with regard to nanocomposite morphology.

The study of the melt rheology of PLSN not only yields vital information for the production of PLSNs, but can also be used to obtain fundamental data that can shed light on structure–property–processing relationships [68–72]. The addition of layered silicates normally changes the rheological properties significantly, particularly at low shear rate. Sample preparation and degree of interaction/connectivity between the silicate and polymer can also significantly alter the melt rheology. As an example, Krishnamoorti and Giannelis [70] studied the melt rheology of N6 silicate nanocomposites in which the polymer chain ends where tethered to the silicate layers (Figure 4). Such linear viscoelastic studies show that there is a change from liquid-like behavior to pseudo-solid-like behavior as the silicate content increases, and high shear rates lead to orientation of the silicate layers.

Other mechanical properties, such as stress at break (the ultimate strength of the material before failure), elongation at break and impact strength tend to be reduced when layered silicates are added, although there are exceptional cases [20]. Furthermore, decreases in these properties are expected and observed in most composite materials; in the case of PLSNs, this effect may be reduced. There is enough evidence to show that these reductions are more significant when the polymer is below its glass transition temperature ($T_g$).

5.10.4.2.2 Thermal and flame-retardant properties

Most PLSNs exhibit improved thermal properties, meaning that a nanocomposite is more stable thermally than the pristine polymer. This is normally measured by sample mass loss as a function of increasing temperature and by determining a degradation onset temperature. While increases in stabilization are normally by tens of degrees, there are reports of stabilization well over 100°C [22,73]. Improvements are quite dramatic with low levels of silicate, and tend to level off after a loading of only few percent of silicate. Increases are also seen in the heat distortion temperature.
Thermal expansion coefficients are typically lowered when layered silicates are added to polymer. These are a measure of dimensional changes, with larger coefficients indicating a greater propensity for dimensional changes. Normally, low coefficients are preferred. With PLSNs, the high aspect ratio silicate platelets provide extra dimensional stability by resisting the expansion or contraction in the polymer matrix. Larger differences in the moduli of the silicate and polymer lead to larger changes in thermal expansion coefficients.

PLSNs also show improved flame-retardant properties, with reports of some materials being self-extinguishing. According to Gilman and Kashiwagi [74], the flame-retardant property of PLSN stems from the collapse of the nanocomposite structure, which results in a layered carbon–silicate reinforcing structure that leads to improved char performance. The char forms a protecting layer around the remaining material, and thus slows flame propagation to nearby areas.

**5.10.4.3 Other Properties**

**5.10.4.3.1 Gas-barrier properties**

An application of significant interest for PLSNs has been for use as a gas-barrier material. The lowering of gas permeability in PLSNs is a result of the high aspect ratio of the dense layered silicate material [5, 75]. When well mixed in the polymer matrix, these layers form a torturous path for the gas molecules through which to pass; various models have been developed that account reasonably accurately for the lower permeability [75]. As an example, Choi et al. [76] examined oxygen (O₂) permeability through the polyester PET and MMT nanocomposites made via in situ polymerization using an intercalated Ti-based catalyst. The O₂ permeability of samples with 1–5 wt.% MMT were studied, with the permeability being lowered by approximately 10–15 times. However, various gases do not always behave the same in a given nanocomposite; the permeability of moisture in the study by Choi et al. did not significantly change. Osman et al. [77] also found that O₂ and water vapor transmission varied according to different mechanisms in epoxy–MMT nanocomposites.

**5.10.4.3.2 Electrical properties**

The addition of Li-MMT to poly(ethylene oxide) has been shown by Vaia et al. [78] to increase the ionic conductivity. This is a result of the reduction in crystallization of the polyelectrolyte since crystalites reduce conductivity. Conducting polymers, such as poly(aniline)-dodecylbenzenesulfonic acid, have been shown to have increased conductivities when layered silicates are added [79].

**5.10.4.3.3 Compatibilization of polymer blends**

Layered silicates have been successful in improving blends of polymers through reducing interfacial tension and providing a finer morphology. This latter parameter directly correlates with crystallinity, and thus many mechanical properties. Several types of PLSN blends have been studied: PS/PMMA [80], polycarbonate/PMMA [81], and poly(vinylidene fluoride)/nylon 6 (PVDF/N6) [82], to name a few. In the PVDF/N6 case, the best results were obtained when organically modified MMT was blended with the N6 and then this nanocomposite compounded with the PVDF. This gave a blend nanocomposite that was tougher, stronger, and stiffer compared to the non-nanocomposite blend. As shown in Figure 5...
the silicate layers in this nanocomposite blend are not only dispersed in the N6 phase, but also reside at the interface of the two polymers. This reinforces the N6 phase and reduces the PVDF domain size.

**Figure 5** TEM micrographs of (a) PVDF/N6 30:70 blend and (b) 30:70 blend with 5% 30B. SEM micrographs of fracture surfaces of (c) PVDF/N6 30:70 blend and (d) blend with 5% 30B. Inset in (b) shows some clay residing the PVDF/N6 interface. Reproduced from Vo LT and Giannelis EP (2007) Compatibilizing poly(vinylidene fluoride)/nylon-6 blends with nanoclay. Macromolecules 40: 8271–8276. Copyright (2007), with kind permission of the American Chemical Society.

**5.10.5 Conclusions**

The development of PLSNs over the past 20 years has led to a myriad of improved properties, and importantly also many commercial products. Examples of such products include the first application of a timing belt cover in the Toyota Camry in the late 1980s and early 1990s. Additionally, General Motors have used poly(olefin)-based PLSN in an exterior running board. There are many nonautomotive applications, such as butyl rubber-based PLSN that was developed for use as the lining inside tennis balls by InMatt LLC. This technology improved pressure retention through increased barrier properties. While such developments themselves are noteworthy, there are still many factors that are not well understood in PLSN systems. The basis of many of the questions that still need to be addressed is the surface interaction between the silicate layers, modifier (if any) and polymer. On a more macroscopic level, much more work needs to be done to understand structure–processing–property relationships. Thus, with more work at both fundamental and applied levels, PLSNs will continue to garner much interest in the foreseeable future.

**References**

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