

Processing and Properties of Polymers Modified by Clays

Douglas L. Hunter, Karl W. Kamena,
and Donald R. Paul

Abstract

Layered smectite nanoclays are being developed for incorporation into a variety of host polymer systems. Nanoscopic phase distribution can impart enhanced stiffness at low addition levels and improve barrier and flame-retardant properties. When combined with other inorganic and organic modifiers, nanoclays can provide synergies to generate the desired formulation properties and cost/performance characteristics. Developments with existing nanoclay products using conventional amine chemistries are described for thermoplastic, thermoset, and rubber formulations. Nanoclays are demonstrating unique, multidimensional performance and processing capabilities. Commercial applications are emerging in a variety of diverse markets ranging from automotive to packaging.

Nanoclays and Host Polymers

"Nanoclay" is a term often used when referring to a clay mineral with a phyllosilicate or sheet structure having dimensions on the order of 1 nm in thickness. The mineral base can be natural or synthetic and is hydrophilic. The clay surfaces can be modified with specific chemistries to render them organophilic and therefore compatible with organic polymers. When small quantities are added to a host polymer, the resulting product is often termed a clay-polymer nanocomposite.¹⁻⁵

Host polymers can be thermoplastic or thermoset, commodity or engineering/specialty plastics, crystalline or amorphous. Nanocomposite preparation can be done at the monomer stage by using *in situ* polymerization (e.g., polyamides and thermosets), by solution-blending organoclays with polymers, by mixing polymer latices with aqueous suspensions of unmodified clays, and finally by melt-compounding organoclays with thermoplastics.

Nanoclay Sources, Structure, and Properties

Many nanoclays are based on a clay classified as montmorillonite⁶⁻⁸ (Figure 1a),

a natural clay mineral of the smectite family that traces its origins to volcanic ash deposited millions of years ago in ancient brine seas where it slowly underwent alteration processes. Although montmorillonite is found in vast deposits around the world, it is always found with impurities such as gravel, shale, limestone, quartz, and feldspar, among others. This mixture of materials is known as bentonite (Figure 1b), and the montmorillonite is separated from the raw ore primarily through aqueous separation processes. The unique characteristic of the smectite clay minerals, including montmorillonite, that sets them apart from other clay minerals is their ability to swell in water.

Montmorillonite is classified as magnesium aluminum silicate, and each individual platelet has a thin-foil morphology, as shown in Figure 1a. The platelets are irregular in overall shape, with aspect ratios generally in the 50–150 range. A side view of a platelet reveals a uniform thickness of 0.94 nm, resulting in an extremely large surface area of $\sim 750 \text{ m}^2/\text{g}$.

Each montmorillonite platelet or sheet is a 2:1 layered structure consisting of silica

tetrahedral layers bonded to an inner alumina octahedral layer, as illustrated in Figure 2 by a molecular model of a small portion of a platelet. Other metals such as magnesium or iron can replace some of the aluminum atoms in the octahedral layer, or aluminum can replace a silicon atom in the tetrahedral layer and establish a charge deficiency. The resulting negative charge on the surface will attract any positive ions (cations), such as calcium or sodium ions, to neutralize the charge.

The cations on the clay surface can be easily exchanged for other cations. A measure of this capacity is commonly referred to as the cation exchange capacity (CEC) and is usually expressed as milliequivalents of cations per 100 g of clay.

It should be understood that each montmorillonite deposit found in nature is unique. Particle size, shape, and charge are different, and the replacement elements and positioning in either the octahedral or tetrahedral layers can have a significant effect on the characteristics and performance of the specific montmorillonite. Also, the impurities composing the overall bentonite deposit can be very different; removing non-montmorillonite impurities is essential to the overall performance of

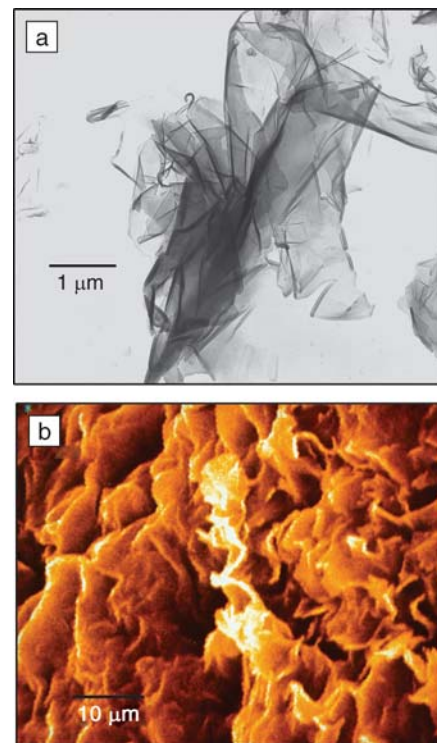


Figure 1. (a) Transmission electron microscopy image of refined montmorillonite. (b) Scanning electron microscopy image of bentonite rock.

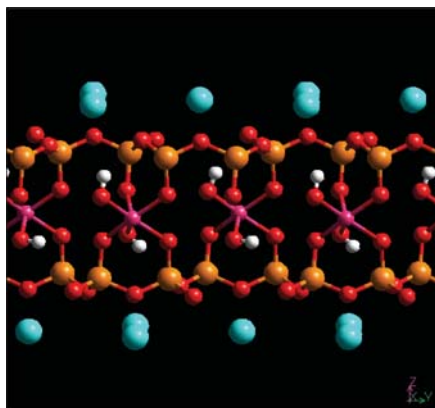


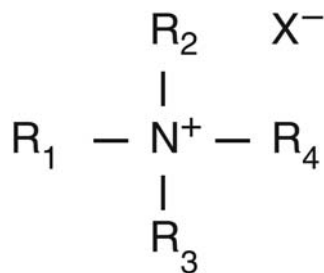
Figure 2. Molecular model of the edge of a montmorillonite platelet, showing the cations (e.g., Na^+ or Ca^{2+}) in blue, the silicon-oxygen tetrahedral layers in orange and red, and the aluminum-oxygen-hydroxyl octahedral layers in magenta, red, and white, respectively.

the montmorillonite in a nanocomposite, because impurities cannot be reduced to nanoscopic particle sizes.

The focus of this article is nanocomposites based on natural clay minerals, but synthetic nanoclays can also be used in nanocomposites. Synthetic clays may be prepared using a variety of chemical sources to provide the necessary elements such as silicon, oxygen, aluminum, magnesium, and others. Natural clays would appear to have an inherent raw material cost advantage, but the ability to control purity, charge density, and particle size is an appealing objective.

Nanoclay Chemistries and Functionalities

Unmodified, natural, and purified montmorillonite clays are extremely hydrophilic and fundamentally incompatible with hydrophobic organic polymers. The conventional way to prepare an organoclay is to replace the sodium ions on the surface of the sheets with an organic cation, often referred to as a surfactant, such as a quaternary ammonium salt (quat), as shown in Structure 1. The pendant groups on the quat may be hydrogen atoms or methyl, benzyl, hydroxyethyl, or other groups with one or two relatively long alkyl tails (generally 16–22 carbons) derived from natural fatty acids like those from cocoa, tallow, rapeseed, and other oils. The ion exchange is typically done in a very dilute, purified aqueous solution. During the reaction, the clay loses its hydrophilicity and becomes oleophilic, at which point it precipitates from the aqueous phase and is filtered, dried, milled, and packaged.



Structure 1. General structure of a quaternary ammonium salt. R is an organic group and X is an anion.

The quat chemistry can be varied to produce dozens of organoclays. By modifying the surface polarity of the clay, the function of the ammonium ions is to thermodynamically alter the interaction with the polymer to assist in delamination of the clay platelets. Figure 3 shows molecular models of a typical organoclay according to early concepts⁹ (Figure 3a) and more recent understanding (Figure 3b).¹⁰

In nonpolar polyolefin systems, a primary issue yet to be fully resolved is the identification of a chemistry (or combination of chemistries) that will provide a thermodynamic driving force for exfoliation. The most fruitful approaches have involved incorporating polarity into the polymer matrix by copolymerization, grafting, or blending; the most attractive option has been to use maleic anhydride-grafted polyolefins as compatibilizers in combination with a well-selected organoclay.

Another function of the quat chemistry is to weaken the inherent van der Waals forces attracting adjacent sheets of montmorillonite to facilitate delamination. Although it has been suggested that increasing the

d-spacing between the sheets is desirable, empirical evidence would suggest a larger *d*-spacing is less important than improving compatibility between the polymer, the silicate surface, and the surfactant used to modify the clay.

Historically, nanoclays based on montmorillonite have been used in aqueous and organic solvent formulations to modify rheology in a thixotropic manner.¹¹ Typical application areas include paints and coatings, consumer care products, inks, ceramics and refractories, drilling fluids, greases, and polyester and epoxy composites. Because of montmorillonite's tremendous surface area of 750 m²/g, just a few percent of completely dispersed platelets "solvate" in the liquid, creating a functional network and imparting the desired rheological properties to the system.

Preparation and Processing Considerations

Although nanocomposites can be prepared by a number of methods, much of the research and development activity leading to commercial interest is based on melt-compounding, for both manufacturing flexibility and economic considerations. Once the nanocomposite has been successfully prepared with good nanoclay dispersion and exfoliation, additional processing by normal extrusion and injection-molding methods are both applicable and may improve the efficiency of those downstream processing steps.

Preparing polyolefin-based nanocomposites is similar to preparing other types of nanocomposites but is more difficult because of the nonpolar nature of polyolefins and the lack of a thermodynamic driving force for exfoliation. Studies suggest that a combination of (1) chemistries used to

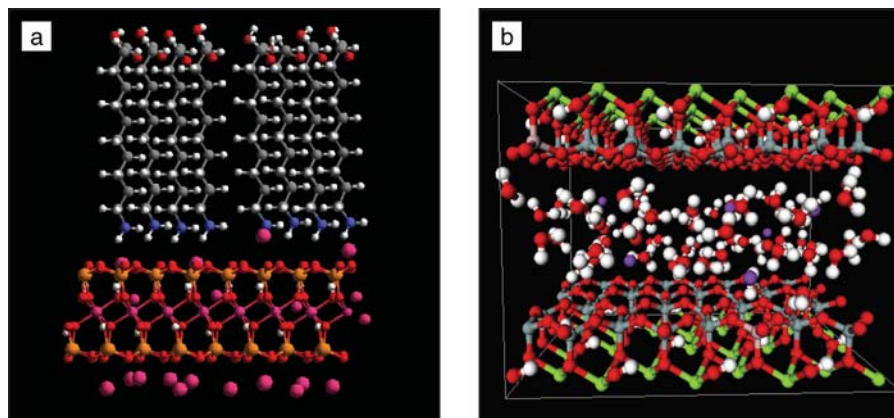


Figure 3. Two different models for organoclays. (a) Quaternary ammonium alkyl tails (gray) perpendicular to the platelet.⁹ (b) More recent computer modeling shows the alkyl tails in a more random conformation between the platelets with some degree of entanglement.¹⁰

modify the clay surface, (2) compatibilizers such as maleated polypropylene, and (3) processing conditions will markedly increase the degree of dispersion and exfoliation of the nanoclay and thus enhance the properties and performance characteristics of the nanocomposites.

A nanoclay in its dry form consists of particles approximately 8–10 μm in diameter containing more than 1 million individual montmorillonite platelets. Conventional theory supposes that during the extrusion process, the polymer gradually enters the galleries between the platelets, and the distance between the platelets, the d -spacing, begins to expand until the van der Waals forces are overcome and the platelets are no longer linked together. We would propose,¹² however, that the exfoliation mechanism is more of a shearing process whereby hundreds or thousands of tactoids (particles that appear as spindle-shaped bodies under a polarizing microscope) composing the 8–10- μm particles are separated by a combination of mechanical and chemical forces, reducing them to smaller ribbons. Individual platelets peel from the ribbons to complete the exfoliation process. Figure 4a

schematically illustrates this process, and Figures 4b and 4c show evidence for this mechanism from transmission electron microscopy (TEM) images taken in the early stages of exfoliation of an organoclay in a nylon-6 matrix.

For polypropylene-based nanocomposites, incorporation of maleated polypropylene into the formulation appears to aid in the dispersion and exfoliation process, apparently by acting as a compatibilizing agent with the clay edges, which are very different in character from the clay surfaces. The clay edges are also called broken-bond surfaces,⁸ and, for example, the silica tetrahedral edge can have the functional groups Si-O⁻, Si-OH, or Si⁺, depending on pH.

As a general comment, during commercial scaleup of a thermoplastic polyolefin (TPO) nanocomposite product, we encountered a number of production issues, many of which were related to feeding a small amount of nanoclay (3–5% by weight of the bulk polymer) to attempt good distribution and dispersion. Clay agglomeration¹³ can occur when clay particles are exposed to both increased temperature and pressure and can result during the feeding of

nanoclay to make a nanocomposite. It can be a significant issue because agglomerates can account for a tremendous amount of individual clay platelets that cannot be exfoliated and benefit the overall polymer matrix. It must be stressed that when adding a small amount of nanoclay to a polymer, every step must be taken to maximize homogeneous distribution and microdispersion to facilitate the separation of tactoids and to ensure the proper temperature and pressure are attained to create shear conditions favoring exfoliation. We analyzed extruder screws for exfoliation by x-ray and TEM and showed that exfoliation occurs early in the extrusion process. When there is a strong enough affinity between the polymer and organoclay, this process may occur more or less spontaneously, given enough time; this is illustrated for Cloisite 93A¹⁴ in PA6 held statically in a heated press under 69 MPa pressure for up to 120 min in Figure 5.

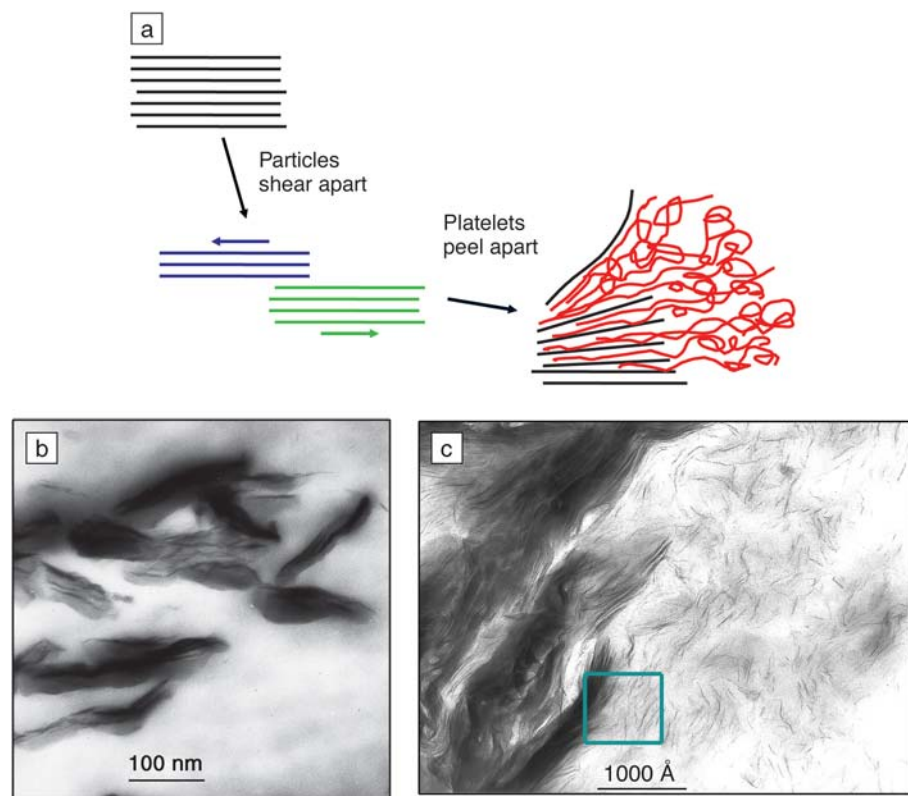


Figure 4. (a) Shearing-peeling mechanism for exfoliation of montmorillonite platelets in a polymer. Red ribbons are polymers penetrating between the platelets. (b), (c) Transmission electron micrographs showing evidence for the combination of (b) shearing tactoids to a consistent thickness and (c) peeling platelets off a tactoid. (Reprinted from Reference 12 with permission from Elsevier.)

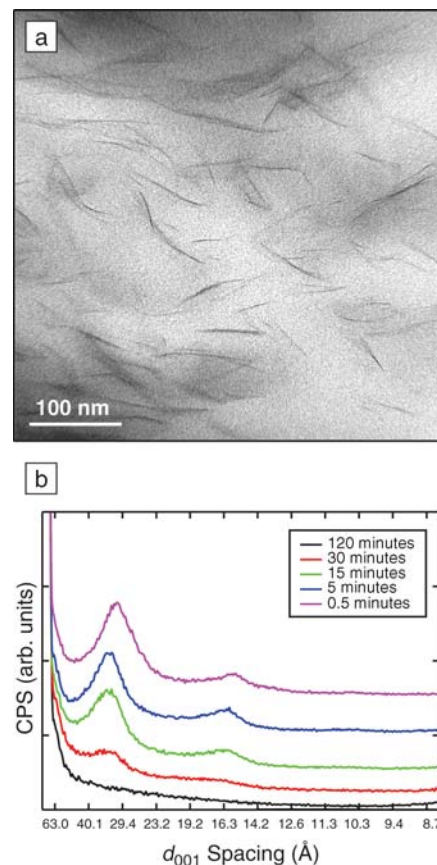


Figure 5. Evidence for static exfoliation of Cloisite 93A in PA6 as seen (a) by TEM and (b) by the evolution of x-ray scans with time in the melt. CPS is counts per second.

The process of moving from laboratory concept to production of commercial nanocomposites is beginning to become significant, especially as production engineers develop the necessary handling and processing parameters required to consistently prepare the same product.

Applications and Commercial Developments

In thermoset composites, nanoclays can be considered for a variety of functionalities, including improved syneresis control, improved dispersion of low-profile additives, decreased settling of fillers, improved surface appearance, improved processability, and better flow despite increased low shear rate viscosity. It would also appear that lower shrinkage can result, thereby enabling lower-density formulations. In transportation applications where the energy cost is particularly significant, lower mass can be an important benefit.

Interestingly, thermoset formulations have always been a combination of chemistries, fillers, additives, and curing agents, and nanoclays have been considered as one more synergistic ingredient to be used as a part of the whole. On the other hand, the development mindset in thermoplastics considers nanoclays as the single or primary inorganic additive. More recently, however, researchers are reporting developments based on synergy and combinations of additives. A producer of nylon products, for example, has commercialized a line of barrier resins that include nanoclay as the primary barrier and an active resin that serves as an oxygen scavenging agent; the two concepts work together to provide excellent barrier properties.

Similarly, early developments in the area of flame-retardant polymers focused on the use of nanoclays as the primary additive to impart flame-retardant performance to the host polymer. Products that have been commercialized or are in the late stages of the development process, however, employ a small amount of nanoclays (up to 5%) in combination with conventional additives such as magnesium hydroxide or aluminum trihydrate. Nanoclays promote extensive char formation, and the resulting synergies provide a flame-retardant polymer system with enhanced mechanical performance. Several companies are employing this approach in the wire and cable market.

A more conventional nanocomposite development has focused on TPO for automotive applications. Many organizations are in the process of developing clay/polyolefin nanocomposites with varying degrees of success. A number of commercial products have been introduced. While no one is yet claiming full exfoliation and complete

technical success, competitive products are evolving, and newer and improved products are certain to emerge.

One example of an emerging product is from Basell Polyolefins, who, in conjunction with General Motors (GM) R&D and Southern Clay Products, has developed a line of nano-TPO resins. The first product was for a General Motors M-Van step assist in August 2001, and in February 2004, GM announced a second application, side trim moldings for their Impala line. This was quickly followed with additional trim and panel applications for the Hummer H2 sport utility vehicle. In each of these cases, the nanocomposite replaced a TPO formulation containing high loadings of talc. Figure 6 compares the relative efficiency of adding montmorillonite platelets versus talc particles for increasing modulus and reducing the coefficient of thermal expansion (CTE). It takes about four times more talc than montmorillonite to achieve the same level of property improvement.^{15,16}

General Motors R&D has been a visible and active promoter of polyolefin as well as other types of nanocomposites. Their interest is based on a variety of factors:

- Mass savings
- Lower specific gravity
- Lighter weight, which requires less adhesive for attachment
- A large processing window
- Consistent physical and mechanical properties
- Elimination/reduction of "tiger striping" (a type of color defect in extruded or molded components)
- Improved appearance
- Improved knit line appearance
- Improved colorability and painting
- Sharper feature lines and grain patterns
- Improved scratch/mar resistance
- Low temperature ductility
- Improved recyclability

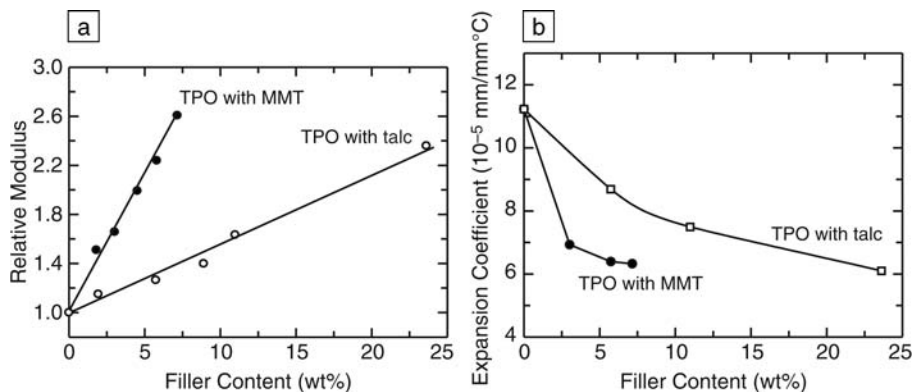


Figure 6. (a), (b) Comparison of the effect of adding montmorillonite (MMT) and talc to a thermoplastic olefin (TPO) on modulus and coefficient of thermal expansion. (Reprinted from References 15 and 16 with permission from Elsevier.)

One of the more remarkable but perhaps unappreciated characteristics of nanoclays is their effect on improving the melt strength of thermoplastics. As is the case with thermosets, a higher melt strength of a given thermoplastic may enable the incorporation of other beneficial additives and, perhaps, unique processing techniques and parameters. One commercial product based on this property is nylon/glass fiber/nanoclay, which because of the higher melt strength of the formulation, can be blow-molded into large parts with high rigidity and strength.

An example of improved melt strength is shown in Figure 7, which shows the melt strength of linear low-density polyethylene (LLDPE) with Cloisite 20A. Again, it is seen that the addition of montmorillonite leads to an increase in melt tension, but a decrease in drawability. An optimal level of montmorillonite is about 1%. These results also show that as the ratio of linear low-density polyethylene grafted with maleic anhydride (LLDPE-g-MA) to Cloisite 20A is increased with the montmorillonite level held constant at ~4.7%, the melt strength increases because of the resulting improved exfoliation. A ratio of about 0.5 gives the best balance of drawability and melt tension.¹⁷

When nanoclay particles are added to a phase-separated polymer blend, the size of the dispersed phase can be dramatically reduced, as recently observed in blends of polypropylene,¹⁵ polyamide,¹⁸ and polystyrene¹⁹ with elastomers. The rubber particle size in such blends is determined by a balance between the rates of droplet breakup and the coalescence of droplets; it has been proposed that the nanoclay particles interfere with the process of droplet coalescence such that smaller rubber particles are produced.^{15,18} Rubber particle size is a key parameter in controlling toughness, and this effect of nanoclay

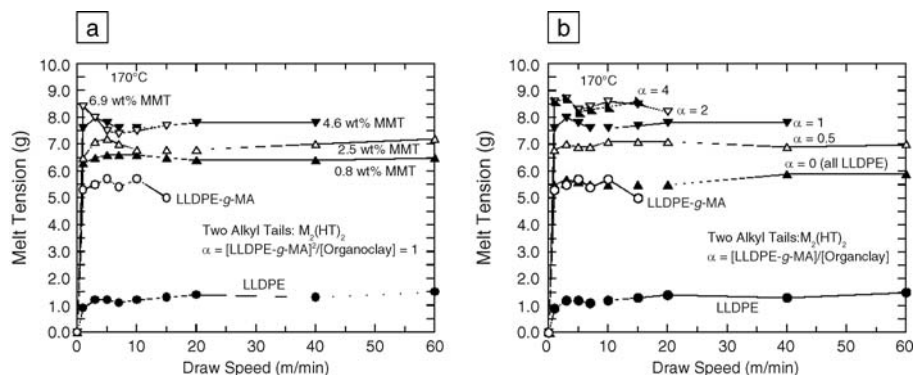


Figure 7. Melt strength for LLDPE nanocomposites containing Cloisite 20A. In (a), the amount of montmorillonite was varied at a fixed ratio of LLDPE-g-MA/Cloisite 20A, whereas in (b), the LLDPE-g-MA/Cloisite 20A ratio α was varied at a constant montmorillonite concentration of $\sim 4.7\%$. (Reprinted from Reference 17 with permission from Elsevier.)

particles on polypropylene/rubber blends leads to a dramatic increase in toughness in such TPO materials.¹⁵

In addition to thermoset and thermoplastics, rubber formulations are being developed based on nanoclays in combination with other additives. As is the case with thermosets, rubber formulations are a complex recipe, and nanoclays are perceived more as synergistic additives than replacements.

ExxonMobil has announced improvements of about 35% in air impermeability of a tire inner liner by using less than 10 wt% organoclay in brominated isobutylene *p*-methylstyrene copolymers.²¹ Some additional improvements are also possible if the improved air impermeability is taken advantage of by reducing the gauge of the inner liner; these advantages include reduced tire weight, lower tire operating temperature, and potential improvement in factory mixing and calendaring rates and potential cure time rates. These improvements to tire customers and the tire manufacturer are not possible by other compounding means.

Next-Generation Clay Nanocomposites

Although it is likely that additional nanocomposites will be developed and introduced as commercial products during the next several years, it is also apparent that conventional technologies using natural clays, quaternary amine chemistries,

and existing polymer bases have some limitations.

Concurrent with the development of first-generation polyolefin nanocomposites, Southern Clay Products and other industry and research-based organizations are studying the fundamentals of nanocomposites. Whereas nature has provided an excellent starting point—natural montmorillonite clays—these natural materials can lack consistency in terms of particle shape, charge density, and charge positioning. Programs are underway to change the clay treatment chemistry using out-of-the-box approaches to make the organoclay more compatible with different types of resins, polymers, and rubbers. The quaternary amine chemistries required to modify the natural clay surfaces to make them more compatible with nonpolar polyolefin structures have inherent thermal stability limitations,²² and once they have served the purpose of helping to exfoliate the individual clay platelets, the chemistry has no further function and can have deleterious effects on the final nanocomposite. Designing clays that would not require large quantities of added compatibilizing chemistries would have obvious benefits.

Summary

Clay/polymer nanocomposites are in the early stages of technology development but are beginning to have considerable commercial importance. Although there are

some limitations to current technologies and products, R&D programs are accelerating and are expected to foster a number of new approaches.

Traditionally, the focus has been on the development and preparation of nanocomposites, with nanoclays being the principal non-polymer ingredient. Increasingly, however, we are seeing the development of polymer systems using a variety of modifier agents to generate the desired properties and cost/performance characteristics. Nanoclays are demonstrating unique, multidimensional capabilities to synergistically enhance overall polymer system performance.

References

1. E.P. Giannelis, *Appl. Organomet. Chem.* **12**, 675 (1998).
2. P.C. LeBaron, Z.W. Wang, T.J. Pinnavaia, *Appl. Clay Sci.* **15**, 11 (1999).
3. J.M. Garces et al., *Adv. Mater.* **12**, 1835 (2000).
4. M. Alexandre, P. Dubois, *Mater. Sci. Eng.* **28**, 1 (2000).
5. S.S. Ray, M. Okamoto, *Prog. Polym. Sci.* **28**, 1539 (2003).
6. H. van Olphen, *An Introduction to Clay Colloid Chemistry* (Wiley, New York, 1977).
7. R.E. Grim, *Clay Mineralogy* (McGraw-Hill, New York, 1968).
8. S. Yariv, H. Cross, *Organo-Clay Complexes and Interactions* (Marcel Dekker, New York, 2002).
9. G. Lagaly, *Naturwissenschaften* **68**, 82 (1981).
10. E. Hackett, E. Manias, E.P. Giannelis, *J. Chem. Phys.* **108**, 7410 (1998).
11. J.W. Jordon, F.J. Williams, *Kolloid-Zeitschrift* **137**, 40 (1954).
12. H.D. Dennis et al., *Polymer* **42**, 9513 (2001).
13. P.D. Fasulo, W.R. Rodgers, R.A. Ottaviani, D.L. Hunter, *Polym. Eng. Sci.* **44**, 1036 (2004).
14. Technical information about Cloisite nanoclays can be found at www.nanoclay.com.
15. H. Lee, P.D. Fasulo, W.R. Rodgers, D.R. Paul, *Polymer* **46**, 11673 (2005).
16. H. Lee, P.D. Fasulo, W.R. Rodgers, D.R. Paul, *Polymer* **47**, 3528 (2006).
17. S. Hotta, D.R. Paul, *Polymer* **45**, 7639 (2004).
18. B.B. Khautua, D.J. Lee, H.Y. Kim, J.K. Kim, *Macromolecules* **37**, 2454 (2004).
19. A. Karim, K. Yurekli, R. Krishnamoorti, *Proc. NATAS Annu. Conf. Thermal Analysis and Applications* **29**, 114 (2001).
20. M.Y. Gelfer, H.H. Song, L. Liu, B.S. Hsiao, B. Chu, M. Rafailovich, M. Si, V. Zaitsev, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 44 (2003).
21. B. Rodgers, R.W. Webb, W. Weng, *ACS Rubber Div. Meet.*, paper 58 (November 2005).
22. W. Xie et al., *Chem. Mater.* **13**, 2979 (2001). □

MRS FUTURE MEETING

2007 FALL MEETING

November 26-30

Exhibit: November 27-29

Boston, MA

Meeting Chairs:

Duane Dimos
Sandia National
Laboratories
dbdimos@sandia.gov

Mary Galvin
Air Products and
Chemicals, Inc.
galvinme@airproducts.com

David Mooney
Harvard University
mooneyd@deas.harvard.edu

Konrad Samwer
Universitaet Goettingen I.
Physikalisches Institut
ksamwer@gwdg.de