

White Paper

**Organoclay/Polymer Nanocomposites:
Recent Discoveries of New Enabling
Technologies**

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INTRODUCTION

It is not widely recognized, but polymer/clay nanocomposite development began in the late 1930s with the work of MIT professor E.A. Hauser on latex systems, and the technology for producing highly-dispersible organo-bentonites, was developed by Jordan and colleagues in the 1940s, under the sponsorship of N.L. Industries in an effort to extend the work of Hauser. Except for improvements in processing technology, organo-bentonite technologies have changed very little during the last 60 years. In the 1960s, the J.M. Huber Corporation began work on the development of functional, silane-modified kaolins. These materials provided significant improvements in the mechanical properties of elastomers, and have found wide spread use in commercial products despite their relatively high cost, compared to non-functionalized fillers.

During the 1980s, work on the development of organo-bentonite/polymer nanocomposites was revived simultaneously at the Toyota Central Research Laboratories in Japan and at the Michigan State University by professor Tom Pinnavaia. While improvements in mechanical strength, barrier properties and flame retardancy have since been demonstrated, polymer nanocomposite performance, with very few exceptions, has failed to live up to theoretical expectations.

It has been approximately 25 years since a resurgence in interest in clay/polymer nanocomposites began. And yet the commercial use of these materials remains relegated to niche markets. Theoretical analyses clearly tell us that nano-scale fillers should provide significant advantages in performance over conventional, micro-scale fillers. Where should we look for answers to explain and rectify the discrepancy between theory and practice? First of all, theory regarding the details of the interactions that take place at the mineral/polymer interface and interphase are still in the early stages of development. In surveying the vast scientific and patent literature on clay/polymer nanocomposites, one comes to the conclusion that several pertinent issues have universally been neglected. First and foremost is the fact that our understanding of surfactant self-assembly at clay surfaces is in its infancy, and very few research groups have attempted to treat the clay lattice/clay-surfactant interphase as an integrated system.

In surveying the clay/polymer nanocomposite literature, several key factors become apparent:

- True, x-ray diffraction and transmission electron microscopy are used routinely to measure basal spacings of organoclays, and by inference to determine the conformation of the surfactant's hydrocarbon chains. Other than the effects of the clay's cation exchange capacity on surfactant chain conformation, no one has attempted to study the relationship between the spatial distribution of charge within the clay lattice and self-assembled surfactant structures. All published studies, to date, on nanocomposites are founded on the inherent assumption that the charge centers within the clay are homogeneously distributed within either the octahedral or tetrahedral layer, (octahedral or tetrahedral charge location depends on the type of clay). This is in spite of the fact

that no scientific evidence exists to suggest that this is universally true. In fact, existing experimental data points to the contrary.

- Wetting of the organoclay surface by the polymer is certainly a prerequisite for nanocomposite formation, and yet not a single study exists in the literature in which attempts have been made to measure the critical surface energy of the organoclay surface, despite the fact that existing techniques, such as contact angle measurement, are well suited to the study of these characteristics. Researchers in the field have inherently assumed that the contact angles at the organoclay/polymer interface are zero, despite data to the contrary.
- There has been a lack of recognition within the nanocomposite community that the organoclay structure is in fact a lamellar liquid crystal (LLC). LLCs and Lipid bilayer structures (i.e., lamellar lyotropic liquid crystals, LLLCs) are an intermediate state of matter - immiscible with liquids (i.e., polymer melts) and solids. The physico-chemical properties of these surfactant phases are well known within the surfactant community, and the thermodynamic factors that severely limit the ability of lipid bilayer structures to solubilize significant amounts of organic material by intercalation processes were first discussed in the surfactant literature over 20 years ago, but these properties continue to be overlooked by the organoclay community.

Unless an integrated approach to address each of these issues is initiated, the performance of clay/polymer nanocomposites will forever fail to live up to theoretical expectations. In this White Paper, an outline for an integrated approach to addressing these problems is presented. Initial findings, by the author, indicate that clay/polymer nanocomposite performance can indeed live up to expectations, and what's more surprising, performance beyond current theoretical predictions is indeed attainable.

AN INTEGRATED APPROACH TO DESIGNING MINERAL/POLYMER NANOCOMPOSITES

Work initiated at Argonne National Laboratory's Chemical Engineering Division, and now relocated to the University of Illinois at Chicago, Department of Earth and Environmental Sciences, has treated the clay/surfactant/polymer constituents as an integrated system. Organoclays, are normally prepared from clays possessing a significant ion exchange capacity. The naturally hydrophilic surface is rendered compatible with organic solvents and hydrophobic polymers by an onium ion exchange process, wherein exchangeable Na^+ ions are replaced by hydrophobic surfactants, such as dimethyl dihydrogenated tallow ammonium ions. The individual clay platelets are approximately 10 Å thick, highly flexible, have aspect ratios of approximately 100-500, and surface areas on the order of 750 – 800 $\text{m}^2 \text{g}^{-1}$.

All existing organoclay technology has focused exclusively on modification of the basal surfaces of the clay platelets. The only exceptions are work done at Argonne (see for example Chaiko, U.S. Patent 6,790,896; 2004) and Southern Clay Products (Powell, U.S. Patent 6,730,719; 2004). A lack of attention to the properties of the clay edge has been rationalized by the fact that the basal surface of smectite clays comprises over 95 % of the total surface area of the clay. Hence, any effect that the edge surface might exert on dispersion behavior was believed to be insignificant. However, organically-modified clay platelets have a tendency to stack in ordered arrays called booklets (i.e., LLC structures). This stacking means that prior to exfoliation, the contribution of the edge surface area to the total area is not insignificant. Figure 1 illustrates some common features of LLLCs and organoclay LLCs.

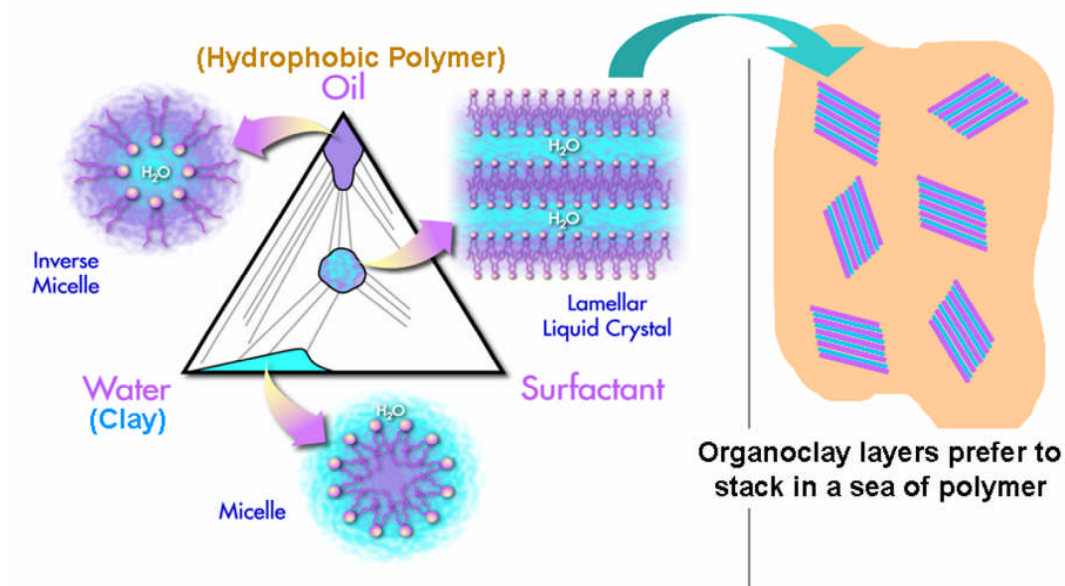


Fig. 1 Phase equilibria of oil/water/surfactant systems and their analogy to organoclay/polymer equilibria. The LLC phase is isolated within the center of the phase diagram and is connected through thermodynamic equilibrium by tie lines to the bulk organic phase (i.e., polymer). The modest size of the LLC domain indicates that these types of phases have a very limited ability to solubilize organics via intercalation (i.e., ≤ 6 wt%).

During the late 1990s, new surfactant designs were developed at Argonne National Laboratory and synthesized by Solutia (St. Louis) in support of the nanocomposite work at Argonne. These hydrophobic surfactants are high-molecular-weight diphosphonates, which are capable of selectively treating the clay edge to render it hydrophobic. As this organoclay technology developed further, the unique edge treatment was found to offer a much greater benefit than simply modifying the wetting characteristics of the clay edge. The hydrocarbon chains, dangling from the edge of the platelets, provided the capability for producing entirely new nano-phase structures based on interactions between the platelet edges and the basal surfaces. When this new organoclay chemistry was coupled with a novel processing approach, the organoclays were found to self-assemble into fractal structures. During the transition from a lamellar-type stacking arrangement to a fractal arrangement, the organoclay loses all color, becomes transparent, and becomes readily dispersible in organophilic solvents and polymers by the simple application of heat and low-shear mixing. Neat Organoclays in the 'fractal fluid' state, will flow with a minor application of pressure. In the absence of any added solvents, plasticizers, or polymers, the neat organoclay can be fashioned into completely transparent, colorless, highly flexible, fractal fluid sheets, which are 'plastic-like' at room temperatures and pressures (see Fig. 2). Fractal fluids are distinguished from nanofluids which are comprised of nanoscale particle dispersions in a liquid phase. Fractal fluids can be prepared using amorphous surfactants in place of ditallow amines to provide fluid-like flow at low temperatures (e.g., -50 °C).

Because of the edge-face stacking arrangement, these new nanomaterials offer the possibility for producing nano-scale films and coatings that are completely impermeable to gases and liquids. The impermeable nature of the fractal fluid, coupled with its low yield stress, suggests that these nanomaterials will find applications as highly corrosion-resistant, dry lubricants, especially useful in high vacuum conditions. The discovery of the fractal fluid state is truly the first significant advancement in organoclay chemistry since the 1940s.

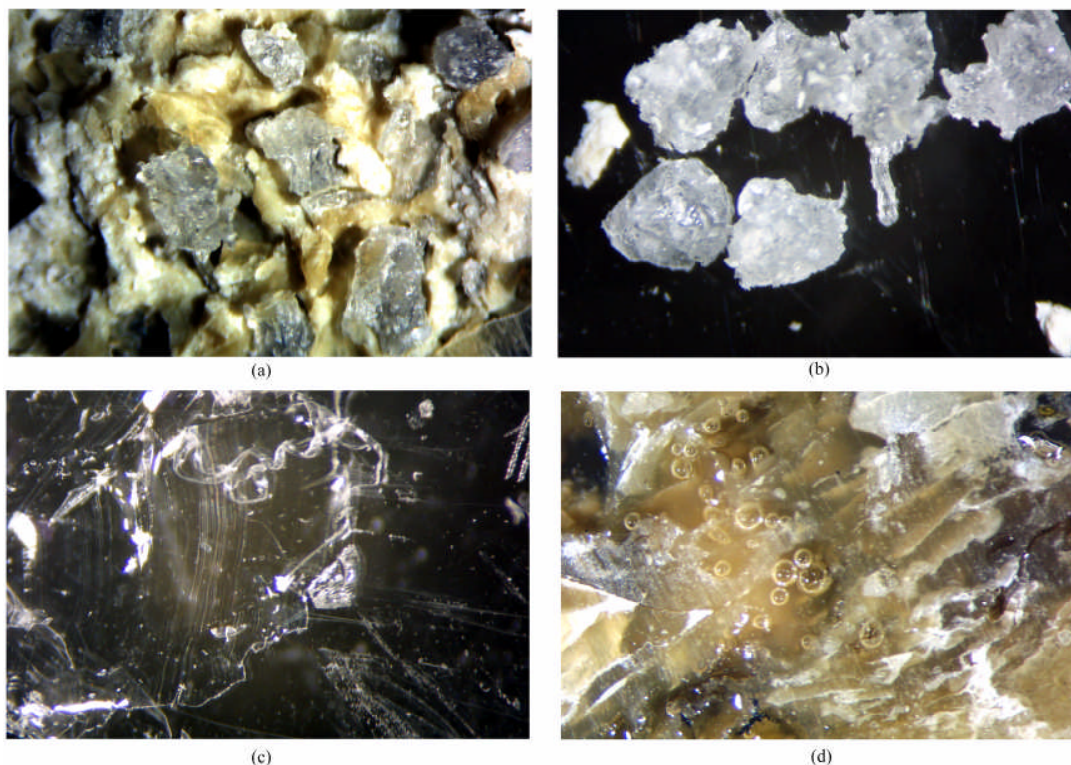


Fig. 2. Transformations of organoclays into a 'fractal fluid', produced by isostatic compression: a) a colorless clay phase with a fractal structure is condensed from the initial, yellow-green organoclay in the absence of any solvents or polymers, b) isolated particle sizes are 1-2 mm, c) uniaxial compression of the fractal fluid at 120 °C produces colorless, transparent, and flexible films, d) trapped gas bubbles in the condensed fractal-fluid phase – the gas was trapped by rapidly reducing gas pressure from 3,000 psi to 1 atm during the preparation of the fractal-fluid phase.

Developments in clay edge treatment and process technology were followed by further developments at the University of Illinois at Chicago in new organoclay characterization techniques. New concepts of describing the organoclay surface in terms of a hydrophilic/lipophilic balance (HLB), coupled with new techniques to map the spatial distribution of the charge centers within the clay crystal lattice have been developed in my laboratory, and indicate that naturally occurring clays, such as Wyoming bentonites, possess a bimodal distribution in the area associated per base exchange site. The bimodal distribution has peak distribution loci at approximately 5 nm^2 and 0.8 nm^2 . It was discovered that almost 50 % of the clay surface, primarily segregated within these 5 nm^2 domains, remains hydrophilic, even after complete base exchange with ditallow ammonium ions. Because of the bimodal distribution in the area per base exchange site, surfactants tend to self-assemble into hemi-micelle structures (see Fig. 3). Furthermore, experimental data relating organoclay swelling behavior to surfactant structure, indicate that the surface HLB is minimized when the chain area of the surfactant exactly matches the average area per base exchange site. Unfortunately, the molecular areas of commonly used ditallow quaternary amines are slightly mismatched with the 0.8 nm^2 exchange sites. This leads to an undesirable increase in the surface HLB value and inhibits intercalation processes. But the key factor preventing the full exfoliation of organoclays in polyolefins is the heretofore unrecognized need to treat the clay surface with surfactant combinations that have molecular areas matching the 5 nm^2 and 0.8 nm^2 base exchange sites. When surfactant combinations are used to treat a Wyoming bentonite, the resulting organoclay becomes fully

dispersible in hydrophobic oligomers and polymers, without the need for admixture with compatibilizing agents, such as maleated oligomers. These recent findings provide a more complete explanation of published data (see for example, Vaia and Giannelis, *Macromolecules* **1997**, *30*, 8000-8009) regarding organoclay intercalation processes and a new understanding of past difficulties in preparing polyolefin nanocomposites.

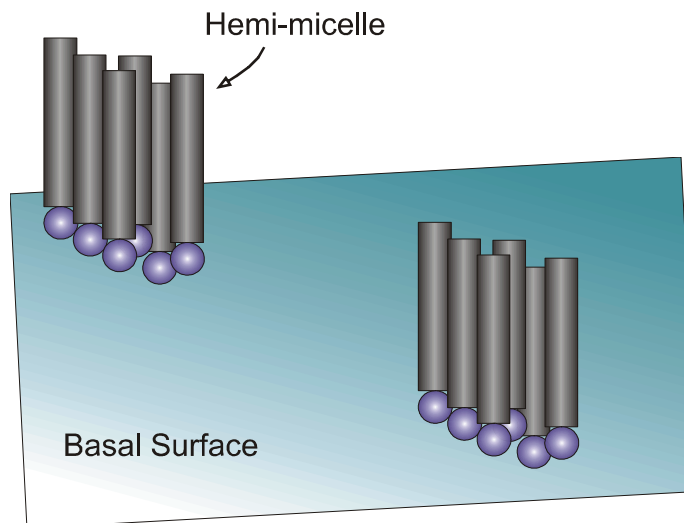


Fig. 3. Self-assembly of surfactant hemi-micelles at the clay surface due to segregation of the clay's lattice charge.

For example, exfoliation of newly developed organoclays in HDPE results in the production of a colorless and completely transparent nanocomposite, with no low-angle scattering of visible light. With the organoclay platelets acting as a polymer nucleating agent, the normal polymer spherulite size is reduced from approximately 50 μm to the nanoscale, thereby resulting in the extraordinary clarity of the material, with no loss in polymer crystallinity. Furthermore, water vapor transmission is reduced by approximately 70 % with only 0.3 wt% clay loading! This clay loading is more than a factor of ten lower than the loadings recommended by leading companies such as Nanocor and Southern Clay Products. More importantly, this is the first time that any reduction at all in the water vapor transmission across HDPE films has been observed.

The performance of the HDPE nanocomposite can be traced to several factors relating to the surface properties of the new organoclay design. The commercially available, high-molecular-weight surfactant used to treat the 5 nm^2 exchange sites results in: 1) a significant reduction in the surface HLB value, 2) an increase in the critical surface tension of the organoclay, 3) matching the melt/freeze transitions of the organoclay with those of the polymer, and 4) disruption of the LLC structure. Matching the surface tension of the organoclay coating to that of the polymer melt, permits the organoclay to remain wetted by the polymer as the melt cools to room temperature. The fact that the C_{50} hydrocarbon tail of the high-molecular-weight surfactant inhibits the tendency of organoclays to stack and form booklets (i.e., LLCs) is supported by x-ray diffraction measurements showing the complete loss of 1-dimensional reflections from the pure organoclay.

It should be noted that experimental data indicate that specific interactions between O_2 and H_2O and the clay surface are not operative. Analysis of gas transport data indicate that the increase in barrier (and mechanical strength) is due to the introduction of a tortuous diffusion path around the impermeable clay platelets, coupled with hindered diffusion – a result of the reduced thickness in the amorphous interphase surrounding the nano-scale polymer spherulites.

Coupling of these two mechanisms results in barrier performance significantly greater than what is theoretically predicted with a tortuous diffusion mechanism alone.

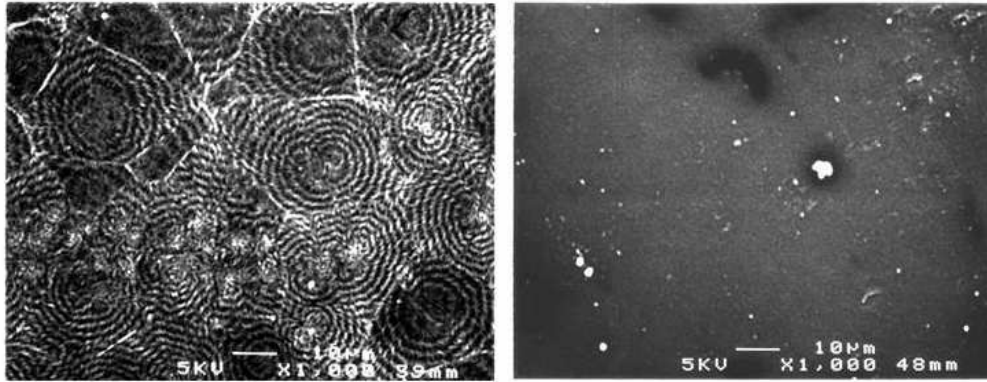


Fig. 4. SEM images of the HDPE reference (left) and the nanocomposite (right). Except for some surface debris, the nanocomposite surface is completely void of any surface structures, including spherulites.

IMPROVING MECHANICAL PROPERTIES

It has been approximately 25 years since a resurgence in interest in clay/polymer nanocomposites began. And yet the commercial use of these materials remains relegated to niche markets. Theoretical analyses clearly tell us that nano-scale fillers should have significant advantages in mechanical performance over conventional, micro-scale fillers, yet this is not always the case.

In Table 1 mechanical performance, measured by dynamic mechanical thermal analysis (DMTA), of a polypropylene homopolymer with 5 wt% organoclay is compared with the performance of a conventional filler (i.e., talc) and with a surfactant-treated talc. The treated talc was prepared by edge treatment of the talc platelets using a long-chain, alkyl diphosphonate developed at Argonne National Laboratory. The Toyota data, for the organoclay/polymer nanocomposite, show an increase in storage modulus at temperatures ranging from -40 °C to 80 °C. However, the use of a conventional talc filler at 5 wt% loading provides mechanical improvements that are just as good as the nanocomposite. Furthermore, the edge-treated talc, at the same filler loading as the nanocomposite, outperforms the nanocomposite!

Additional data show that low concentrations (i.e., ≤ 5 wt%) of treated talc are capable of increasing the flex modulus in polypropylenes to nanocomposite levels, with simultaneous increases in impact strength – something that existing polyolefin nanocomposites have failed to achieve. Clearly, it is possible to significantly enhance the mechanical performance of mineral/polymer composites by proper surface treatment of meso- and micro-scale fillers. Imagine what can be achieved with properly designed nano-scale fillers.

Table 1. DMTA analysis of mineral-filled (5 wt%) polypropylene homopolymer

T, °C	Relative Storage Modulus		
	Nanocomposite*	Conventional Talc**	Treated Talc**
-40	1.15	1.11	1.41
20	1.30	1.29	1.62
80	1.37	1.52	1.76

*Nanocomposite data are from Toyota (Kawasumi, et al., *Macromolecules* **1997**, 30, 6333-6338)

**Talc data are from Argonne National Laboratory (Chaiko and Niyogi, unpublished data)

CONCLUSIONS

For the first time since their inception in the 1930s and 1940s, mineral/polymer composites and nanocomposites are reaching a new plateau in performance. These advances have been achieved by taking an integrated approach to the design of new organoclay chemistries. The exciting discovery of fractal fluid nanostructures significantly broadens the range of possible applications for organoclays and mineral fillers, and offers a glimpse into future directions in polymer nanocomposite nanotechnology. Newly discovered fractal fluid systems provide new insights into the interfacial physics of small particle systems that should lead to improved performance of other systems such as bonded ceramics. With realignment of nanocomposite research funding, potential, near-term applications of fractal fluid systems include:

- Nanoscale films and coatings, that are impermeable to gases and liquids, including hydrogen, hydrocarbons, chemical warfare agents, etc.
- Coatings for dry-machining based on organoclay fractal fluids
- Fractal fluid lubricants for use in spacecraft and satellite applications under high vacuum conditions
- Fire retardants for aircraft applications
- Composite structures for aerospace applications
- Novel nano-structures for photonics and non-linear optics
- Polymer nanocomposites