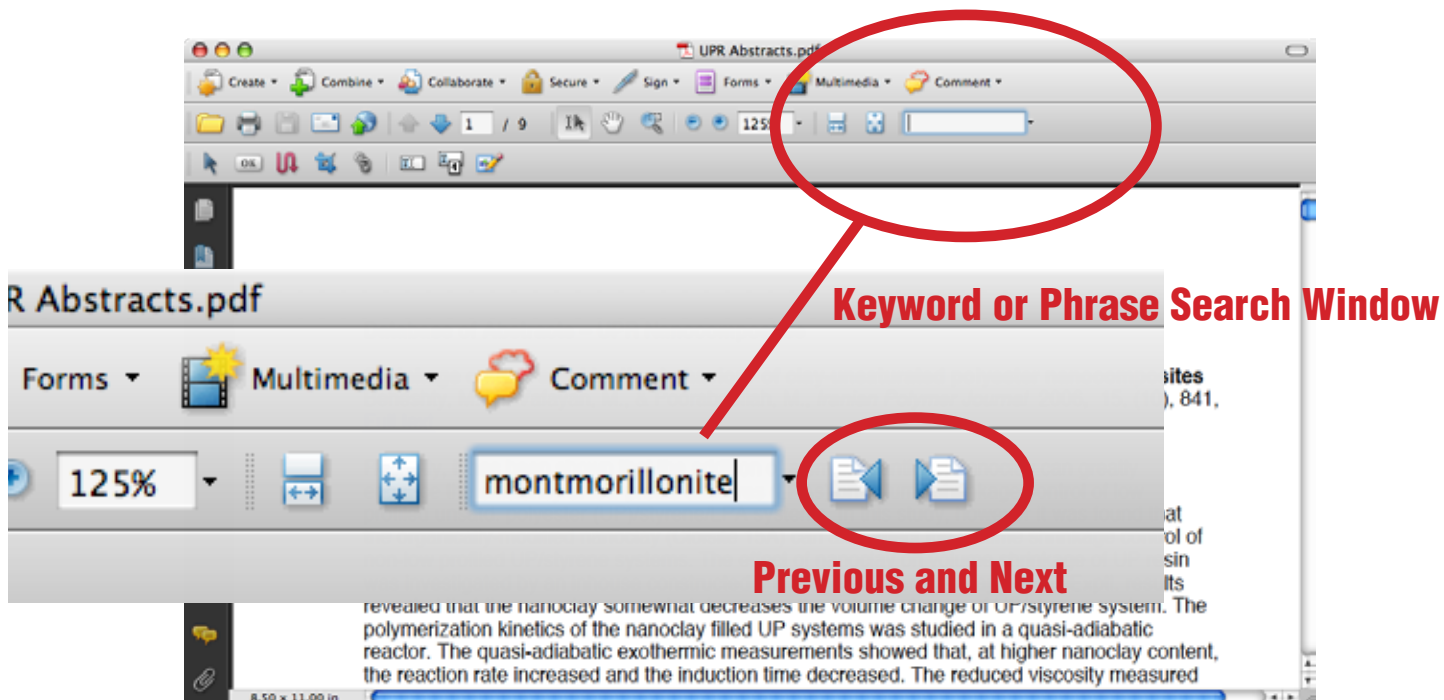
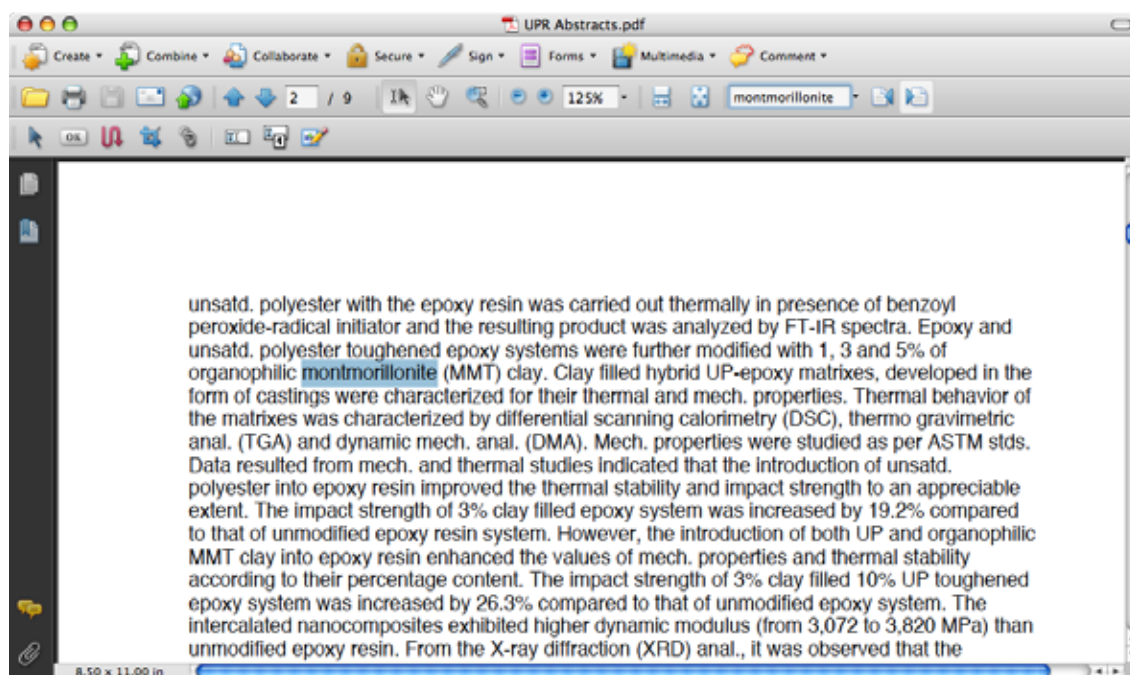


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General Database of Nanocomposite Abstracts

Study of individual Na-montmorillonite particles size, morphology, and apparent charge

A. Cadene, S. Durand-Vidal, P. Turq, J. Brendle, *Journal of Colloid and Interface Science* 285 (2005) 719–730, [Full Text](#)

Size, morphology, and apparent charge of individual Na-montmorillonite particles of natural MX-80 sodium montmorillonite were investigated in the present study by the use of three coupling methods. In the first part of this work, natural and synthetic montmorillonite clays were studied with atomic force microscopy (AFM) and photo-correlation spectroscopy (PCS). Both techniques exhibit the presence of two clay populations with a high dispersion of the length distribution. Microscopic analysis of the system revealed that clay particles could be reasonably approximated at low concentrations to ellipsoidal tactoids about 1.2 nm high. Average dimensions of the first population were typically 320–400 nm long/250 nm wide and 200–250 nm long/120 nm wide for natural and synthetic clays, respectively. The second population exhibits smaller sizes: 65 and 50 nm long and 35 and 25 nm wide for natural and synthetic clays, respectively. The statistics obtained for natural clay were then verified by PCS experiments on sodium montmorillonite suspensions. Both techniques reveal an important length dispersion. However, the relative proportions of the two kinds of particles could not be established properly because of both lack of statistics and limitations of the employed techniques. In the following part, conductivity measurements were performed on dilute montmorillonite clay suspensions. Raw data were then interpreted with the sizes and morphological information gained in the first part of the present work. The apparent charge of the clay sheets was found to be 8% of the structural charge.

Improved Thermal Stability of Crown Ether and Imidazolium Treatments for Polymer Layered-Silicate Nanocomposites

Alexander B. Morgan, J. W. Gilman., Paul C. Trulove, Hugh C. De Long, and Thomas E. Sutto, Leonard J. Chyall, *Flame Retardants* 2002, [Full Text](#)

The thermal stability of the organic treatment present on a layered silicate is of utmost importance in preparing a polymer-layered silicate nanocomposite by melt processing methods. Specifically, the organic treatment must not decompose at temperatures needed for successful polymer processing. Currently used alkyl ammonium treatments for polymer layered-silicate nanocomposites begin decomposition around 200 °C, and many polymers are processed above that temperature. Recent work done in our laboratory has developed two new types of organic treatments for clays, with each having significantly higher thermal stability. The two new types of organic treatments are crown ethers and imidazolium salts. The work presented in this paper shows the thermal properties of this material as well as their ability to be dispersed in a polymer when used to make a nanocomposite.

Nanosopic-Confinement Effects on Local Dynamics

Anastasiadis S.H., Vlachos G, Manias E, Giannelis EP., *Physical Review Letters*, 2000, 84, (5), 915, [Full Text](#)

The segmental dynamics of 1.5-2.0 nm polymer films confined between parallel solid surfaces is investigated with dielectric spectroscopy in polymer/silicate intercalated nanocomposites. The confinement effect is evident by the observation of a mode, much faster than the bulk-polymer alpha relaxation and exhibiting much weaker temperature dependence. This is discussed in relation to either the interlayer spacing restricting the cooperative volume of the alpha relaxation or to the dominance of the more mobile interphase regions as predicted by simulations; the data qualitatively support the former.

Poly(ethylene terephthalate) ionomer based clay nanocomposites produced via melt extrusion

Barber, Grant D.; Moore, Robert B, *Polymer* 46 (2005) 6706-6714, [Full Text](#)

Poly(ethylene terephthalate) ionomer (PETI)/organically-modified montmorillonite clay (OMC) nanocomposites were prepared via melt extrusion. Sulfonated PET containing various incorporations of ionic comonomer and clay modifications were investigated. The random incorporation of ionic functionalities along the PET backbone enhances interactions between the matrix polymer and montmorillonite clay resulting in the creation of polymer-clay nanocomposites exhibiting a predominately exfoliated morphology. The morphology is correlated with mechanical properties and crystallization behavior. It is found that incorporation of clay into the random ionomers leads to increased mechanical properties and slower crystallization rates.

Brominated poly(isobutylene-co-para-methylstyrene) (BIMS)-clay nanocomposites: Synthesis and characterization

Bhowmick, A.; Madhuchanda; Sadhu, Susmita, *Journal of Polymer Science, Part B: Polymer Physics*, 2004, 42, (24), 4489, [Full Text](#)

In this work, prep. and properties of different nanoclays modified by org. amines (octadecyl amine, a primary amine, and hexadecyltrimethylammonium bromide, a tertiary amine) and brominated polyisobutylene-co-p-methylstyrene (BIMS) rubber-clay nanocomposites are reported. The clays and the rubber nanocomposites were characterized with the help of FTIR, TEM, and X-ray diffraction (XRD). The X-ray diffraction peaks obsd. in the range of 3°-10° for the modified clays disappear in the rubber nanocomposites. TEM photographs show predominantly exfoliation of the clays in the range of 12 ± 4 nm in the BIMS. In the FTIR spectra of the nanocomposites, there are common peaks of virgin rubber as well as those of the clays. Excellent improvement in mech. properties like tensile strength, elongation at break, and modulus is obsd. on incorporation of the nanoclays in the BIMS. Structure-property correlation in the above nanocomposites is attempted.

Effect of clay type on morphology and thermal stability of PMMA-clay nanocomposites prepared by heterocoagulation method

Brittain, W. J., Yijin Xu, Chenchen Xue, Ronald K. Eby, *Polymer*, 2004, 45, 3735-3746, [Full Text](#)

Poly(methyl methacrylate) (PMMA)-clay nanocomposites were prepared by a heterocoagulation method. A cationic PMMA emulsion was prepared by emulsion polymerization using a cationic initiator in the presence of free surfactant, cetyl

trimethylammonium bromide (CTABr), followed by mixing with an aqueous clay slurry. Clays used in present research included montmorillonite (MMT), synthetic hectorites and fluorohectorites (with two different sizes). WAXD results and TEM images indicate that the morphologies of these nanocomposites depend on clay colloid stability as well as clay loadings. WAXD and TEM results also indicate the good morphology preservation of the nanocomposites during solution and melt processing. Thermal stability of these nanocomposites was studied by TG–DTG analyses; the mechanism of thermal stability improvement is discussed based on experimental results.

Synthesis and Characterization of PMMA Nanocomposites by Suspension and Emulsion Polymerization

Brittain, William J.; Huang, Zinua; *Macromolecules*, 2001, 34, 3255, [Full Text](#)

PMMA-layered silicate nanocomposites were prepared by in-situ suspension polymerization and emulsion polymerization. For the suspension polymerization, the silicate layers were dispersed individually in water, and we speculate that they are adsorbed on the surface of monomer droplets. For the emulsion polymerization, the nanocomposite was obtained by adding an aqueous dispersion of layered silicate into the polymer emulsion. Wide-angle X-ray diffraction (WAXD) and atom force microscopy (AFM) were used to characterize the structures of the nanocomposites. Analysis of samples from emulsion and suspension polymerization was consistent with an exfoliated structure; after melt pressing, WAXD analysis indicated that both intercalated and exfoliated structures were observed. The exfoliated structure was preserved when organic modifiers that produced tethered polymer chains were used. Compared to a PMMA macrocomposite, the nanocomposites prepared by these methods display glass transition temperatures that are up to 15 °C higher and thermal degradation temperatures that are up to 60 °C higher.

Nanostructure and Properties of Polysiloxane-Layered Silicate Nanocomposites

Burnside, Shelly D.; Giannelis, Emmanuel P; *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 38, 1595–1604 (2000), [Full Text](#)

The relationship between nanostructure and properties in polysiloxane layered silicate nanocomposites is presented. Solvent uptake (swelling) in dispersed nanocomposites was dramatically decreased as compared to conventional composites, though intercalated nanocomposites and immiscible hybrids exhibited more conventional behavior. The swelling behavior is correlated to the amount of bound polymer (bound rubber) in the nanocomposites. Thermal analysis of the bound polymer chains showed an increase and broadening of the glass-transition temperature and loss of the crystallization transition. Both modulus and solvent uptake could be related to the amount of bound polymer formed in the system.

Polyurethane/clay nanocomposites foams: processing, structure and properties

Cao, X., et al; *Polymer*, 2005, 46, (3), 775, [Full Text](#)

Polyurethane (PU)/montmorillonite (MMT) nanocomposites were synthesized with organically modified layered silicates (organoclays) by in situ polymerization and foams were prepared by a batch process. Clay dispersion of polyurethane nanocomposites

was investigated by x-ray diffraction and transmission electron microscopy. The morphol. and properties of PU nanocomposites and foams greatly depend on the functional groups of the organic modifiers, synthesis procedure, and mol. weight of polyols because of the chemical reactions and phys. interactions involved. Silicate layers of organoclay can be exfoliated in the PU matrix by adding hydroxyl and organotin functional groups on the clay surface. The presence of clay results in an increase in cell d. and a reduction of cell size compared to pure PU foam. In the polyurethane with high mol. weight polyol, a 6 °C increase in Tg, 650% increase in reduced compressive strength, and 780% increase in reduced modulus were observed with the addition of 5% organically treated clays. Opposite effects were observed in PU nanocomposite foams with highly crosslinked structure. The interference of the H-bond in the presence of clay is probably the reason.

Cell development in microcellular injection molded polyamide-6 nanocomposite and neat resin

Chandra, A., Gong, S., Turng, L. & Gramann, P., *Annual Technical Conference - Society of Plastics Engineers*, 2004, [Full Text](#)

The effects of nanoclay addition into polyamide-6 (PA-6) neat resin and processing parameters on cell d. and size in microcellular injection molded components were investigated. The analyses were performed on the sprue section of standard ASTM D 638-02 tensile bars molded based on a fractional four factorial, three-level, L9 Taguchi design of expts. (DOE) with varying melt temperature, injection speed, super critical fluid (SCF) concentration, and shot size. It was found that the presence of nanoclay greatly reduced the cell size and increased the cell d. when compared to neat resin processed under identical molding conditions. In addition, cell size distribution at the sprue center was, in general, the largest, gradually decreasing towards the skin for both neat resin and nanocomposite. Finally, in contrast to neat resin, in which shot size and injection speed were important to cell d. and all molding parameters affected cell growth, the cell size and d. for nanocomposite only depended strongly on shot size.

Effect of alkyl quaternary ammonium on processing discoloration of melt-intercalated PVC-montmorillonite composites

Chaoying Wan, Chaoying; Zhang, Yong; Zhang, Yinxi; *Polymer Testing*, 2003, 23, 299, [Full Text](#)

The effects of alkyl quaternary ammonium on the processing thermal stability of poly (vinyl chloride)/alkyl quaternary ammonium modified montmorillonite (PVC/OMMT) composites were investigated. PVC/sodium montmorillonite (MMT) composites were prepared for comparison. The intercalated PVC/OMMT composites exhibited a non-terminal rheological behavior, and showed better mechanical properties and higher thermal degradation stability than the PVC/MMT composites. However, under identical melt processing conditions, the PVC/OMMT composites were observed to discolor from light yellow to pink with increasing OMMT content, while the PVC and PVC/MMT composites kept good processing stability. It is suggested that the decomposition of alkyl quaternary ammonium modifier and the following catalytic effects on the dehydrochlorination of PVC were the main reasons for the discoloration of the PVC/OMMT composites. Discoloration of all the composites was investigated by UV-visible spectroscopy, yellowness index and haze measurement. All the composites were

characterized and tested using wide angle X-ray diffraction, transmission electron microscopy, infrared spectroscopy, solution ¹H nuclear magnetic resonance spectroscopy, tensile testing, notched Izod impact testing and thermogravimetric analysis as well as ARES rheometrics.

Fracture Properties of Nanoclay-Filled Polypropylene

Chen Ling, Sreekumar Pisharath, *Journal of applied polymer science*, 2002, 88, (14), 3298, [Full Text](#)

Maleic anhydride-modified polypropylene was compounded with commercially available surface-modified montmorillonite in a twin-screw extruder. Recompounding ensured the removal of visible tactoids from the extrudate but TEM and XRD techniques showed nonuniform dispersion of clay platelets. In this study, we investigated the mechanical and fracture properties of nanoclay-filled polypropylene. Emphasis was placed on the fracture characterization of the clay-filled polypropylene. Tensile strength and stiffness increased steadily with an increase in the clay loading. The toughness of compounded materials was characterized using rigorous fracture mechanics. J-integral fracture resistance decreased with an increase in the clay content. The resistance against stable crack growth was compared using the slopes derived from the J-R curve and the tearing modulus concept. A significant amount of crack growth resistance was evident in the nanoclay-filled polypropylene as opposed to other brittle nanocomposites such as the nylon-clay systems

Compatibilizing effect of maleated polypropylene on the mechanical properties and morphology of injection molded polyamide 6/polypropylene/organoclay nanocomposites

Chow, W.; Karger-Kocsis, J.; Apostolov, A.A.; Ishiaku, U.S., *Polymer*, 2003, 44, (24), 7427, [Full Text](#)

Polyamide 6/polypropylene (PA6/PP = 70/30 parts) blends containing 4 phr (parts per hundred resin) of organophilic modified montmorillonite (organoclay) were prepared using twin screw extruder followed by injection molding. Maleated polypropylene (MAH-g-PP) was used to compatibilize the blend system. The mechanical properties of PA6/PP nanocomposites were studied through tensile and flexural tests. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to assess the fracture surface morphology and the dispersion of the organoclay, respectively. X-ray diffraction (XRD) was used to characterize the formation of nanocomposites. The thermal properties were characterized by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The dynamic mechanical properties of PA6/PP nanocomposites were analyzed by using dynamic mechanical thermal analyzer (DMTA). The strength and stiffness of PA6/PP nanocomposites were improved significantly in the presence of MAH-g-PP. This has been attributed to the synergistic effect of organoclay and MAH-g-PP. The MAH-g-PP compatibilized PA6/PP nanocomposites showed a homogeneous morphology supporting the compatibility improvement between PA6, PP and organoclay. TEM and XRD results revealed the formation of nanocomposites as the organoclay was intercalated and exfoliated. A possible chemical interaction between PA6, PP, organophilic modified montmorillonite and MAH-g-PP was proposed based on the experimental work.

Polyamide- and polycarbonate-based nanocomposites prepared from thermally stable imidazolium organoclay

Cui, L.; Bara, J. E.; Brun, Y.; Yoo, Y.; Yoon, P. J.; & Paul, D. R.; *Polymer*, 2009, 50, (11), 2492, [Full Text](#)

This paper explores the possible advantages of the more thermally stable imidazolium-based organoclay over a more conventional ammonium-based organoclay for facilitating exfoliation and minimizing polymer matrix degradation in melt blended polyamide 6 (PA-6) and polycarbonate (PC) nanocomposites. The thermal stability of the two organoclays was evaluated by TGA analyses. The extent of clay exfoliation was judged by anal. of the morphol. and tensile modulus of these nanocomposites formed using a DSM Microcompounder, while the extent of color formation and mol. weight change were used to evaluate polymer matrix degradation. For PA-6 and PC nanocomposites, the use of the imidazolium organoclay only produced slight differences in both exfoliation and mol. weight change, although the imidazolium organoclay is remarkably more thermally stable than the ammonium organoclay.

Processing and morphological development of montmorillonite epoxy nanocomposites

Chenggang Chen and David Curliss, *Institute of Physics Publishing*, 2003, Nanotechnology 14, [Full Text](#)

Polymer-layered silicate nanocomposites are new hybrid polymeric materials with nanometre thick layered silicates that generally show improvement over the properties of polymeric materials. This paper reports that synthesized organolayered silicates can be used to make epoxy nanocomposites. The nanocomposites were characterized by wide-angle x-ray diffraction, small-angle x-ray scattering (SAXS) and transmission electron microscopy. The studies on in situ SAXS and differential scanning calorimetry were carried out to gain an understanding of the morphological development of a nanocomposite during processing. The storage and glass transition temperature of the nanocomposite were also studied by dynamic mechanical analysis.

Creep and physical aging behaviour of PA6 nanocomposites

D.P.N. Vlasveld, H.E.N. Bersee, S.J. Picken, *Polymer* 46 (2005) 12539–12545, [Full Text](#)

The creep and physical aging behavior of various types of PA6 nanocomposites and unfilled PA6 are described. After annealing far above T_g the samples were quenched to room temperature and tested after various ageing times. The creep compliance shows a significant reduction with the addition of exfoliated layered silicate to the matrix polymer. The shape of the creep curves of the nanocomposites is similar to unfilled PA6 and time-ageing time superposition is possible with all materials. The shift rate for superposition is in the same range, but slightly higher in nanocomposites. The creep behavior of nanocomposites conditioned with an equilibrium amount of moisture and dry samples at elevated temperatures shows that the effect of nanofillers is much stronger under these conditions.

Nanocomposite matrix for increased fibre composite strength

D.P.N. Vlasveld, H.E.N. Bersee, S.J. Picken, *Polymer* 46 (2005) 10269–10278, [Full Text](#)

A new type of three-phase thermoplastic composite has been made, consisting of a main reinforcing phase of woven glass or carbon fibres and a PA6 nanocomposite matrix. Nanocomposites have the potential to improve the matrix dominated flexural and compressive strength by increasing the matrix modulus. Good quality fibre composites have been made with several types of PA6 nanocomposite and unfilled PA6 in combination with glass and carbon fibre reinforcement. Flexural tests on commercial PA6 fibre composites have shown the decrease of the flexural strength upon increasing temperature and this has been compared with the decrease of the matrix modulus. The nanocomposites used in this research have moduli that are much higher than unfilled PA6, also above T_g and in moisture conditioned samples. The strength of glass fibre composites can be increased by more than 40% at elevated temperatures and the temperature range at which a certain minimum strength is present can be increased by 40-50 °C. Carbon fibre composites also show significant improvements at elevated temperatures, although not at room temperature. The advantage of the use of nanocomposites instead of other polymers to improve the fibre composite properties is that the properties can be improved without any change in the processing conditions.

The interlayer swelling and molecular packing in organoclays

D.R. Paul, Q.H. Zeng, A.B. Yu, G.Q. Lu, *Journal of Colloid and Interface Science* 292 (2005) 462–468, [Full Text](#)

Understanding the interlayer swelling and molecular packing in organoclays is important to the formation and design of polymer nanocomposites. This paper presents recent experimental and molecular simulation studies on a variety of organoclays that show a linear relationship between the increase of d -spacing and the mass ratio between organic and clay. A denser molecular packing is observed in organoclays containing surfactants with hydroxyl-ethyl units. Moreover, our simulation results show that the head (nitrogen) groups are essentially tethered to the clay surface while the long hydrocarbon chains tend to adopt a layering structure with disordered conformation, which contrasts with the previous assumptions of either the chains lying parallel to the clay surface or being tilted at rather precise angles.

Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites

Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R., *Polymer*, 2001, 42, (23), 9513, [Full Text](#)

Polymer layered silicate nanocomposites have been studied for nearly 50 yr, but few refs. deal with the importance of how the organoclay was processed into the plastic of choice. Many articles focus on the importance of the chem. used to modify the surface of the clay, usually montmorillonite, without including the role of processing. This paper demonstrates the importance of both the chem. of the clay surface and how the clay was melt processed into the thermoplastic. Two different clay treatments were added to polyamide 6 using four different types of extruders with multiple screw designs. The mixts. of organoclay and polyamide 6 were characterized by X-ray diffraction, transmission electron microscopy, and mech. property tests. The degree of dispersion is

interpreted in terms of the residence time distribution in the extruder and the intensity of shear. A model for organoclay delamination in a polymer melt is proposed that envisions the role of both shear and time.

Effects of stress on the exfoliation of polystyrene nanocomposites

Dolgovskij, M.; Macosko, C. W., Annual Technical Conference - Society of Plastics Engineers, [Full Text](#)

Polystyrene/organoclay nanocomposites were prepared by melt blending in a vertical co-rotating twin-screw mixer. Monodisperse polymers having mol. weight 18,000 and 49,000 were investigated. Low mol. weight polystyrene was chosen to take advantage of the high viscosity near T_g , allowing temperature variation to provide for several orders of magnitude of viscosity and to correspondingly change the shear stress. Melt rheol. was the primary tool used to determine the extent of exfoliation in the nanocomposite samples. The highest amount of exfoliation at low clay loading occurred in the low mol. weight matrix favoring low temperature. A bimodal polystyrene matrix facilitated dispersion, but the low mol. weight component compromised the final modulus.

In situ Synthesis of Poly(ethylene terephthalate)/layered Silicate Nanocomposites

Doris Pospiech, A. K., Hartmut Komber, Dieter Voigt, Dieter Jehnichen, Jan Müller, Andreas Janke, Thorsten Hoffmann and Bernd Kretzschmar, *High Performance Polymers* 2007; 19; 565, [Full Text](#)

The goal of the work presented here was to develop nanocomposites consisting of layered silicates and poly(ethylene terephthalate) (PET). Two nanocomposite preparation methods were compared: first, the usual melt compounding technique, and second, in-situ synthesis of PET in presence of different types of layered silicates. Montmorillonite (MMT) without and with organophilic modification was employed as layered silicate. In most cases, PETs with acceptable properties (molecular weight and discoloration) were synthesized in presence of different MMTs although the molecular weights of the in-situ PETs were lower than the control sample. These materials were used as masterbatch for PET nanocomposites with 5 wt.% inorganic content. The exfoliation in both types of nanocomposites was not complete, but they showed a good distribution of clay within the polymer matrix.

Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties

E. Manias, L. Wu, K. Strawhecker, B. Lu, and T. C. Chung, *Chem. Mater.*, 2001, (13), 3516, [Full Text](#)

The synthetic routes and materials properties of polypropylene/montmorillonite nanocomposites are reviewed. The nanocomposite formation is achieved in two ways: either by using functionalized polypropylenes and common organo-montmorillonites, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates. All the hybrids can be formed by solventless melt-intercalation or extrusion, and the resulting polymer/inorganic structures are characterized by a coexistence of intercalated and exfoliated montmorillonite layers. Small additions typically less than 6 wt % of these nanoscale inorganic fillers promote concurrently several of the

polypropylene materials properties, including improved tensile characteristics, higher heat deflection temperature, retained optical clarity, high barrier properties, better scratch resistance, and increased flame retardancy.

Polymer-Silicate Nanocomposites: Model Systems for Confined Polymers and Polymer Brushes

E. P. Giannelis, R. Krishnamoorti and E. Manias; *Advances in Polymer Science - Polymers in Confined Environments*, 1999, [Full Text](#)

The static and dynamic properties of polymer-layered silicate nanocomposites are discussed, in the context of polymers in confined spaces and polymer brushes. A wide range of experimental techniques as applied to these systems are reviewed, and the salient results from these are compared with a mean field thermodynamic model and non-equilibrium molecular dynamics simulations.

Effect of Melt Processing Conditions on the Morphology and Properties of Nylon 6 Nanocomposites

F. Chavarria, R. K. S., D.L. Hunter, D.R. Paul, *POLYM. ENG. SCI.*, 47:1847–1864, 2007, [Full Text](#)

Nylon 6 (PA-6) organoclay nanocomposites were prepared by melt processing using three different twin screw extruders (TSEs). The effect of mixing conditions, feed port location, residence time, and number of extrusion passes on the morphology and mechanical properties of the nanocomposites were examined. Wide-angle X-ray scattering, transmission electron microscopy (TEM), and mechanical property data are reported. Particle analyses were performed on the TEM images to quantitatively characterize the extent of exfoliation. The amount of shear and the mixing conditions created by TSEs have a significant effect on the morphology and properties of PA-6 nanocomposites. Morphology and mechanical property results show that (1) melting the polymer before coming into contact with the organoclay followed by a low level of shear and (2) maintaining a medium level of shear throughout the extruder with a longer residence time lead to extremely high platelet dispersion and matrix reinforcement for PA-6 nanocomposites. Nanocomposites formed in a DSM microcompounder showed similar morphologies and modulus trends as those obtained with conventional TSEs; thus, this microcompounder is a good alternative for nanocomposite research especially when only small amounts of material are available.

Extrusion processing of TPO nanocomposites

Fasulo, Paula D.; Rodgers, William R.; Ottaviani, Robert A.; Hunter, Douglas L.; *Polymer Engineering and Science*, 2004, 44, (6), 1036, [Full Text](#)

Nanocomposites are a class of materials that use mol.-sized reinforcing the polymer matrix. These materials blend an polymer to produce a composite with phys. and mech. properties better than their conventionally filled counterparts but at lower loadings. Occasionally, when the processing conditions are not compaction of the filler materials can occur. This agglomeration filler can affect the final properties of the composite by

effective filler concn. and by the creation of stress risers agglomerates. This paper addresses the role of extrusion relates to the dispersion of the organoclay filler.

Effect of organoclay structure on nylon 6 nanocomposite morphology and properties

Fornes, T. D., Yoon, P. J., Hunter, D. L., Keskkula, H., & Paul, D. R., *Polymer*, 2002, 43, (22), 5915, [Full Text](#)

A series of org. amine salt-modified montmorillonites was prepd. Each organoclay was melt-mixed with high mol. wt. nylon 6 using a twin screw extruder; some also were mixed with low mol. wt. polymer. WAXS, TEM and stress-strain behavior were used to evaluate the effect of amine structure on nanocomposite morphol. and phys. properties. The effects on modulus, yield strength and elongation at break are discussed. Overall, the nanocomposites based on high mol. wt. nylon 6 exhibited higher extents of platelet exfoliation and better mech. properties than those formed from low mol. wt. polyamide, regardless of the organoclay used.

Nylon-6 nanocomposites from alkylammonium-modified clay: the role of alkyl tails on exfoliation

Fornes, T. D.; Paul, D. R.; Hunter, D. L.; *Macromolecules*, 2004, 37, (5), 1793, [Full Text](#)

Nylon-6-organoclay nanocomposites were prepd. by melt processing via twin-screw extrusion for the purpose of comparing the effect of the no. alkyl groups attached to the nitrogen of the org. modifier on the level of organoclay exfoliation. Wide-angle X-ray scattering and transmission electron microscopy techniques were employed to assess the morphol. developed in each type of nanocomposite, while stress-strain diagrams were used to evaluate mech. property performance. Nanocomposites derived from an organoclay having no alkyl tails in the quaternary cation result in an immiscible morphol., consisting primarily of unexfoliated clay particles, whereas those derived from an organoclay having one alkyl tail in the quaternary cation lead to a well-exfoliated morphol. Increasing the no. of alkyl tails to two produced a mixed structure comprised of a large fraction of clay stacks intercalated with polymer as well as a fraction of dispersed clay platelets. The extent of mech. reinforcement parallels the degree of exfoliation. Overall, the results may be explained by the competition between the effects of platelet-platelet interactions and the interaction of the polymer with the organoclay platelet.

Modeling properties of nylon 6/clay nanocomposites using composite theories

Fornes, T.D.; Paul, D.R.; *Polymer*, 2003, 44, (17), 4993, [Full Text](#)

The reinforcement of nylon 6 by layered aluminosilicates (LAS) and glass fibers was examined using the composite theories of Halpin–Tsai and Mori–Tanaka. Theoretical comparisons show that exfoliated LAS offer superior reinforcement to glass fibers owing to the filler's high modulus, high aspect ratio, and its ability to reinforce in two directions. The effect of incomplete exfoliation of simple stacks of LAS on nanocomposite modulus was also examined. Increasing the number of platelets per stack and the gallery spacing between platelets results in a dramatic decrease in reinforcing efficiency. The predictions were benchmarked against experimental data for nylon 6 nanocomposites based on organically modified montmorillonite and glass fibers. The quantitative determination of

the morphology of the nanocomposites is non-trivial due to the large distribution of filler shapes and sizes present. Thus, a detailed experimental procedure for determining the aspect ratio of the nanocomposites is reported. The composite theories satisfactorily capture the stiffness behavior of both types of composites. Furthermore, experimental heat distortion temperatures and those predicted from modeling the dynamic mechanical properties of nanocomposites are in reasonable agreement.

Preparation and mechanical properties of intercalated PP/OMMT nanocomposites

Gaidukov, S.; Maksimov, R.D.; Kalnins, M.; Zicans, J.; *J. Phys.: Conf. Ser.* 93 (6pp) J., 2007, [Full Text](#)

The preparation of polymer nanocomposites by melt compounding polypropylene (PP) with organically modified montmorillonite using maleic anhydride modified PP as compatibilizer is described. Compositions with organomontmorillonite content 0, 5, 10 wt.% were prepared and tested. Data on the influence of organomontmorillonite content on the tensile stress–strain curves, elastic modulus, strength, and ultimate elongation of the nanocomposites are obtained. The concentration dependences of elastic properties of materials with differently oriented plate like nanoparticles analyses taking into account hierarchical structure features of nanocomposites is considered. Theoretical analysis results are compared with experimental data. The presence of unexfoliated particles in the form of multilayer packages must be taken into account. The results of an investigation of hardness, impact strength, and thermal properties of polymer nanocomposites are presented. Tension creep tests were performed to predict nanocomposites long term deformation behaviour.

Improved Thermal Stability of Organically Modified Layered Silicates

Gilman, J. W. et. al., *Clays and Clay Minerals*, Vol. 52, No. 2, 171-179, 2004, [Full Text](#)

Bromide-containing impurities were found to decrease the thermal stability of quaternary alkyl ammonium-modified layered silicates. Improved purification procedures completely removed bromide and led to a 20°C to >100°C increase in organic modified layered silicate thermal stability. Using mass spectrometry and thermal and electrochemical analysis, N,N-dimethyl-N,N-di octadecyl quaternary ammonium-modified montmorillonite and fluorinated synthetic mica were found to degrade primarily through elimination and nucleophilic attack by these anions. The nature of residual bromides was identified and quantified, and the efficiency of removing these anions was found to be solvent dependent; sequential extraction, first ethanol then tetrahydrofuran, gave the best results. This exhaustive extraction method represents a viable alternative to the use of expensive, more thermally stable onium treatments for layered silicates.

Polymer Layered Silicate Nanocomposites: Thermal Stability of Organic Cationic Treatments

Gilman, J. W.; Morgan, A. B.; Harris, R. H., Jr.; Trulove, P. C.; DeLong, H. C.; Sutto, T. E.; *Polymeric Materials Science and Engineering*, Vol. 83, 59-60, 2000, [Full Text](#)

Nanocomposites result from the combination of materials with different properties at the nanometer scale. Some examples of these include: polymers combined with layered-silicate, polymers combined with nano-silica, hybrid materials prepared by sol-gel methods and POSS nanocomposites. All these materials exhibit many such as improved

thermal stability, reduced improved mechanical properties; etc. However, for successful preparation of nanocomposites, and for their subsequent incorporation into end-products, nanocomposites must maintain their unique chemical and physical properties during processing. We report here our recent results, which show improved thermal stability (140 deg C higher) for new organic cationic treatments used to compatibilize layered silicates with polymers and monomers. This work was motivated by concern about processing degradation, which we observed in polymer/montmorillonite (MMT) nanocomposites.

Self-Passivation of Polymer-Layered Silicate Nanocomposites

Hao Fong, Jeffrey H. Sanders, Derek Lincoln, Andrew J. Vreugdenhil, Weidong Liu, John Bultman, and Chenggang Chen, *Chem. Mater.*, 2001, 13 (11), pp 4123–4129, [Full Text](#)

Nanoscale dispersion of only a few weight percentage of layered silicate (montmorillonite) in nylon 6 and epoxy results in the formation of a uniform passivating and self-healing inorganic surface region upon exposure to oxygen plasma. The enrichment of inorganic is compositionally graded with respect to the surface and is due to the preferential oxidation of the polymer from the nanocomposite and the corresponding enhancement of the nanoscale layered silicate on the surface. The structure of the inorganic region is turbostratic, with an average distance between layered silicates of 1–4 nm. This ceramic-like silicate layer provides an overcoat to the nanocomposite and can significantly retard the penetration of oxygen plasma. Thus, layered silicate containing nanocomposites may enhance the survivability of polymeric materials in aggressive oxidative environments, such as atomic oxygen in low earth orbit (LEO). The formed inorganic region was characterized chemically and morphologically by X-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared (ATR), transmission electron microscopy (TEM), and X-ray scattering.

Clay locked phase morphology in the PPS/PA66/clay blends during compounding in an internal mixer

Hao Zou, h Hong Tan, Ke Wang, Rongni Du, Qiang Fu, *Polymer* 47 (2006) 6–11, [Full Text](#)

In this communication, we will demonstrate, by using poly(p-phenylene sulfide) (PPS)/polyamide66 (PA66) blends as an example, the clay can not only affect the phase morphology in immiscible polymer blends, but also frozen in the phase inversion. By adjusting the processing method, an inversed phase, where the minor component PA66 forms the continue phase and the major component PPS forms the dispersed phase, is observed for the first time. This is explained as due to the locking effects of clay layers on the phase development. The result is interesting and also very important, which provides a new way to control the phase morphology and phase inversion in immiscible polymer blends by using clay.

Rheological characterization of polystyrene–clay nanocomposites to compare the degree of exfoliation and dispersion

Harris, J.; et al, *Polymer*, 2005, 46, (20), 8641, [Full Text](#)

Polymer–clay nanocomposites are of great interest due to their improvement in certain material properties relative to virgin polymer or conventional composites. For example, compared to conventional materials, Nylon 6/montmorillonite nanocomposites demonstrated significant improvements, including high strength, high modulus and high heat distortion temperature. Because viscoelastic measurements are highly sensitive to the nanoscale and mesoscale structure of polymeric materials, when combined with X-ray scattering, electron microscopy, thermal analysis, and mechanical property measurements, they will provide fundamental understanding of the state and mechanism of exfoliation of the layered silicate (clay) in a polymer matrix. In addition, understanding rheological properties of polymer nanocomposites is crucial for application development and understanding polymer processability.

The objective of this research is to develop a rheological technique to analyze the clay morphology in nanocomposite. Previous work has demonstrated the utility of the rheological technique to differentiate (qualify) the degree of exfoliation/dispersion. This report utilizes findings from the earlier work to further map out the structure-rheological response of polystyrene nanocomposites with various composition, clay types, and dispersion; and to quantify the key parameter that dominates the characteristic rheological response. This report explored a series of polystyrene (PS)–clay nanocomposites with 1,2-dimethyl-3-n-hexadecyl imidazolium (DMHDI) organically modified clays. These PS nanocomposites investigated here demonstrated a change of pattern in dynamic mechanical spectrum, as a function of the degree of exfoliation, from typical polymer response to a terminal response of $[G'\omega, G''\omega]$, then to a pattern with double crossover frequencies, and finally to a solid-like response with $G' > G''$ in all frequency ranges. We showed that the number of particles per unit volume is a key factor determining the characteristic response of nanocomposites.

In addition, the rheological response of PS–clays nanocomposite made from DMHDI modified clay combined with high-energy sonication (characterized as exfoliated by XRD and TEM) was compared with that of nanocomposites made by dimethyl, benzyl hydrogenated tallow (2MBHT) modified clay. We found that PS nanocomposites made by DMHDI-modified clay with high-energy sonication are better dispersed than the nanocomposites made previously using 2MBHT-modified clay. We also showed that the glass transition temperatures were not very sensitive to the degree of dispersion.

The key finding of this research is that rheological measurements are complimentary to traditional polymer nanocomposite analysis techniques, and they may also serve as an analytical tool by itself (under appropriate conditions), now that some fundamental behavior has been identified.

The effect of nanoclays on the processibility of polyolefins

Hatzikiriakos, Savvas G.; Rathod, Nimish; Muliawan, Edward B.; *Polymer Engineering and Science*, 2005, 45, (8), 1098, [Full Text](#)

The influence of a new processing additive (particles of organically modified nanoclays) on the processibility of polyolefins in extrusion is studied. The equipment used includes an instron capillary rheometer with two types of dies, namely capillary dies and special annular dies (Nokia Maillefer wire coating crosshead) attached to the rheometer. Ziegler Natta and metallocene polyethylenes and one polypropylene were tested using these two pieces of equipment. It was found that the nanoclay additive had a significant effect

on the extrudate appearance of polyethylene. It eliminates surface melt fracture and postpones the critical shear rate for the onset of gross melt fracture to significantly higher values depending on resin type, temperature, and additive concentration (typically 0.05 to 0.5 wt%). To explain the possible mechanism for the effect of the additive on the processibility of the resins, shear and extensional rheol. measurements were carried out for the pure resins as well those loaded with the nanoclay additives. It seems that the presence of nanoclays suppresses the development of extensional stresses to such high levels that can cause melt fracture phenomena. Finally, it was found that the combination of nanoclays with traditional processing aids such as fluoropolymers produce an enhanced processing aid that can increase the critical shear rates for the onset of melt fracture to levels much higher than the individual constituents when they are used independently.

Montmorillonite-thermoset nanocomposites via cryo-compounding

Hilmar Koerner, Ashley Tan, Lawrence Drummy, Peter Mirau, Richard Vaia, *Polymer*, Volume 47, Issue 10, 3 May 2006, Pages 3426-3435, [Full Text](#)

For organically modified montmorillonite (OMM)-epoxy nanocomposites, maximal montmorillonite dispersion is found to depend synergistically on the mechanical processing history of the resin mixture and the chemistry at the OMM surface. Specifically, Cloisite 30A (quaternary ammonium OMM) and I30.E (primary ammonium OMM), each containing surfactants with different catalytic effects on the curing chemistry of Epon 862, are compared. Irrespective of the OMM, conventional solvent-free processing methodologies, including sonication, result in an inhomogeneous distribution of OMM on the micron scale. Even though the primary ammonium alkyls within I30.E enhance intragallery reactivity, this only results in extensive swelling of tactoids (interlayer distance ≈ 10 -20 nm), and thus retention of layer-layer correlations, leading to 'hybrid' micron scale reinforcing particles, not nanoscale dispersion of individual layers. In contrast, sub-ambient temperature (cryo) compounding had substantial impact on the ability to reduce tactoid and agglomerate size and increase homogeneity of dispersion for Cloisite 30A. The reactivity near Cloisite 30A is similar to that in the bulk and thus localized gelation around the layer-stacks does not retard particulate refinement. In all cases, alteration of the global epoxy network structure was ruled out by FTIR and NMR measurements. For nanocomposites with similar OMM content, however, the final thermal-mechanical properties does not coherently relate to one characteristic of the morphology. The coefficient of thermal expansion (TOTg) and hardness (TITg) depend only weakly on morphology, where as the glass transition temperature depends strongly on the extent of OMM dispersion and interfacial chemistry. In general, the inter-relationships between mechanical processing, OMM surface chemistry and the desired property enhancements are not linear and thus must be considered in light of a final application to evaluate the optimal 'nanocomposite' fabrication methodology to achieve maximal benefit.

Nanocomposites formed from linear low density polyethylene and organoclays

Hotta, S., & Paul, D. R., *Polymer*, 2004, 45, (22), 7639, [Full Text](#)

Polyethylene-clay nanocomposites were prep'd. by melt compounding varying amts. of LLDPE, maleated LLDPE and two organoclays. The two types of organoclay were selected to show the effect of the alkyl groups of the organic modifier on the exfoliation

and improvement of mech. properties. In addition, the rheol. properties and gas permeability of the nanocomposites were investigated. Both the melt viscosity and melt tension (melt strength) increased with increasing clay and maleated LLDPE content.

Processing and Properties of Polymers Modified by Clays

Hunter; Douglas L.; Kamena. Karl W.; Paul, D. R., *MRS Bulletin - Volume 32 - April 2007*, [Full Text](#)

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.

Morphology and gas barrier properties of polyethylene-based nanocomposites

Jacquelot, E.; Espuche, E.; Gerard, J. F.; Duchet, J.; Mazabraud, P.; *Journal of Polymer Science, Part B: Polymer Physics*, 2005, 44, (2), 431, [Full Text](#)

Nanocomposites were processed by melt blending 2 ref. matrixes, a metallocene polyethylene and a low d. maleic anhydride-grafted polyethylene with an organo-modified montmorillonite. It was shown that the introduction of a maleated polyethylene compatibilizer was required to improve the clay nanoplatelet dispersion in the metallocene polyethylene-based nanocomposites. Increasing the montmorillonite content led to a significant increase of the barrier properties. Interfacial agents such as oxidized paraffins were shown to be more effective to reduce the gas permeability than maleated polyethylene and the dependence of the gas transport properties was discussed not only as a function of the clay dispersion but also as a function of the clay/compatibilizer and compatibilizer/matrix interactions.

Thermoset-Layered Silicate Nanocomposites. Quaternary Ammonium Montmorillonite with Primary Diamine Cured Epoxies

Janis M. Brown and Richard A. Vaia, *Chem. Mater.*, 2000, 12 (11), pp 3376–3384, [Full Text](#)

The role of various quaternary ammonium-modified montmorillonites in epoxy/diamine nanocomposite formation is examined to further refine the criteria for selection of organic modifiers necessary to enable fabrication of thermoset resins containing nanoscale dispersions of inorganic phases. Utilization of a hydroxyl-substituted quaternary ammonium modifier affords flexibility to combine both catalytic functionality, which increases the intragallery reaction rate, with enhanced miscibility toward both reagents. The rheological implications of these processing techniques are discussed with regards to using thermoset nanocomposites as a matrix in conventional fiber reinforced composites. The use of a low-boiling solvent to enhance mixability and processability of the initial mixtures is shown not to alter the structure or properties of the final nanocomposite. Also, the use of autoclave techniques enabled fabrication of high-quality

specimens containing up to 20 wt % organically modified layered silicate (OLS). Finally, exfoliated and partially exfoliated epoxy/diamine nanocomposites were produced with enhanced heat-distortion temperature and increased flammability resistance.

Effect of Platelet Dispersion on the Load Transfer Efficiency in Nanoclay Composites

Jialin Tsai, C.T. Sun; *Journal of Composite Materials*, 2003, 38, (7), 567, [Full Text](#)

Load transfer efficiency of nanoclay platelets in a polymer matrix was investigated. Both tactoid nanocomposites and uniformly dispersed nanocomposites were considered. The unit cell suitable for modeling the load transfer from the surrounding matrix to nanoclay platelets using a shear lag model was discussed. The load transfer efficiency in the nanocomposite was characterized by the effective length of the platelet carrying the saturated stress. For tactoid nanocomposites the platelets were held together in clusters by the ionic bond which was simulated using an elastic interphase with a low shear stiffness. It was demonstrated that well dispersed platelets in the polymer matrix can significantly enhance the load transfer efficiency.

Estimation of Stresses Required for Exfoliation of Clay Particles in Polymer Nanocomposites

Nitin K. Borse, Musa R. Kamal, *POLYM. ENG. SCI.*, 49: 641-650, 2009, [Full Text](#)

The dispersion of clay in a polymer matrix is influenced by two factors: the choice of organic treatment for the clay and the processing or mixing method. Maximum benefits are achieved when the platelets are well dispersed or exfoliated. Exfoliated nanocomposites are formed when the individual clay layers break off the agglomerated particles or tactoids and are either randomly dispersed in the polymer (a disordered nanocomposite) or left in an ordered array. It is suggested that size reduction of clay particles and platelet delamination occur by erosion or surface peeling. A model based on the classical theories of interparticle interactions was formulated for the exfoliation of the clay platelets in a polymer matrix. The model involves the estimation of the binding energy and the adhesive force between the platelets in a clay particle, which indicate the forces required for breaking apart or delamination of clay particles. Then, the shear force required for breakup or delamination of the tactoids is estimated and compared to the hydrodynamic shear forces available during processing.

Effect of maleated polyethylene on the crystallization behavior of LLDPE/clay nanocomposites

Kim, Y. C., *Polymer Journal*, 2006, 38(3), 250, [Full Text](#)

The crystallization behavior and microstructure of linear low density polyethylene (LLDPE)/modified montmorillonite (20A) composites containing maleic anhydride grafted polyethylene (MA-g-PE) were investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and transmission electron microscope (TEM). The dispersion of 20A in LLDPE matrix depended on the amount of MA-g-PE. The degree of super cooling reduced when 20A was introduced into LLDPE with MA-g-PE. The Avrami analysis shows that the nonisothermal crystallization process of the LLDPE/20A composites followed the Avrami equation with Avrami exponent value in the range of 2.75-3.97. The activation energies

calculated by Kissinger method were 986 kJ/mol for LLDPE, 949 kJ/mol for PE-A5MA0, 1445 kJ/mol for PE-A5MA5, and 1581 kJ/mol for PE-A5MA20. The activity of nucleation of PE-A5MA0 was 0.75 but the values of the composites with MA-g-PE were in the range of 0.37-0.56. These behaviors can be interpreted by the fact that the loading of MA-g-PE in LLDPE/20A composites enhances the dispersion of clay in LLDPE matrix and the good dispersion of 20A affects the degree of super cooling and the nucleation activity of silicate.

Melt-extensional properties and orientation behaviors of polypropylene layered silicate nanocomposites

Koo, Chong Min; Kim, Jong Hyun; Wang, Ki Hyun; Chung, In Jae; *Journal of Polymer Science, Part B: Polymer Physics*, Volume Date 2005, 43, (2), 158, [Full Text](#)

Polypropylene-layered silicate nanocomposites consisting of three components-pure polypropylene, maleated polypropylene, and organically modified silicate-were prepared by the melt-intercalation method to investigate melt-extensional properties such as melt strength, neck-in test, and orientation behavior. The nanocomposites showed an enhanced tensile modulus, enhanced storage modulus, much enhanced melt tension, and reduced neck-in during the melt processing as compared with neat polymer. The uniaxial drawing induced the silicate surface to align parallel to the sheet surface. The c and a* axes of the polypropylene crystals were bimodally oriented to the flow direction, and the b axes were oriented to the thickness direction. The bimodal orientation of the polypropylene crystal was enhanced with the concentration of silicates.

Influence of Layered Silicates on the Phase-Separated Morphology of PS–PVME Blends

Koray Yurekli, Alamgir Karim, Eric J. Amis, and Ramanan Krishnamoorti; *Macromolecules*, 2003, 36, (19), 7256–7267, [Full Text](#)

The influence of the disk diameter of nanometer thick anisotropic layered silicates on the phase-separated morphology of a near-critical polystyrene (PS)–poly(vinyl methyl ether) (PVME) blend was examined using atomic force microscopy. Films with comparable amounts of thermodynamically equivalent nanoparticles varying only in lateral disk diameters were examined using a temperature gradient method and showed dramatic differences in late-stage morphology. The blends with small disk diameter (30 nm and 0.5 μm) nanoparticles exhibit a pinning of domain sizes and demonstrate an increase in the number of domains with a higher fraction of near circular structures. On the other hand, for layered silicates with large disk diameters (10 μm), the nanoparticles do not affect the morphology of the phase-separated structure and only accelerate the phase separation kinetics. The extent of domain pinning increases with increasing silicate content and results in smaller domains at higher concentrations of silicate.

The effects of processing and organoclay properties on the structure of poly(methyl methacrylate)clay nanocomposites

Kyle R. Ratinac, Lin Ye, Allan S. Jones, Simon P. Ringer, *Polymer*, 47 (2006) 6337-6361, [Full Text](#)

A variety of nanocomposites were synthesised by bulk polymerisation of methyl methacrylate (MMA), and also by extrusion of poly(methyl methacrylate) (PMMA). These were characterised by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). We applied image analysis to the TEM images of these PMMA/clay nanocomposites to quantify their structures; an analysis was made of the resulting parameters to determine which were most useful for quantifying the microscale and nanoscale structures. Frequently, these quantitative results differed from those expected on the basis of WAXD, demonstrating the limitations of using diffraction data as the sole measure of nanocomposite structure. By combining the quantitative parameters from TEM with the WAXD data, we have explored the effects of processing conditions and organoclay properties on final nanocomposite structure. Factors examined included the effect of the reactivity of the surface modifiers, platelet size, the incorporation of excess modifier within the organoclay, and bulk polymerisation versus extrusion.

Preparation of natural rubber–montmorillonite nanocomposite in aqueous medium: evidence for polymer–platelet adhesion

L.F. Valadares, F. Galembeck, *Polymer* 47 (2006) 672–678, [Full Text](#)

Nanocomposites of natural rubber latex and layered silicates are prepared by a mild dispersion shear blending process. The results of X-ray diffraction (XRD) and transmission electron microscopy (TEM) show that clay particles are well dispersed in the dry latex and the platelets have a preferential orientation, forming translucent nanocomposites. These show tensile mechanical properties analogous to those obtained with vulcanized rubber as well as an increased solvent resistance, which is expected considering that there is significant adhesion between clay lamellae and rubber. Nanocomposite swelling is strongly anisotropic. Natural rubber properties may thus be strongly modified by nanocomposite formation producing unprecedented combinations of properties.

Applications of Nanoparticles in Polymeric Foams

Lee, J. L., The Ohio State University, all rights reserved.

A great deal of interest in recent years because they possess high potential to achieve significant property improvement when a small amount of nanoparticles are added to the polymer matrices. Plastic foams, on the other hand, represent a group of lightweight materials that have been used widely in a variety of industries with a market value of US\$2 billion in 2000. However, the foam applications are limited by their inferior mechanical strength and poor surface quality and dimensional stability. Novel nanocomposite foams based on the combination of functional nanoparticles and supercritical fluid foaming technology may lead to a new class of materials that are lightweight, high strength, and multifunctional.

Effect of organoclay purity and degradation on nanocomposite performance, Part 1: Surfactant degradation

Lili Cui, D.L. Hunter, P.J. Yoon, D.R. Paul; *Polymer*, 49 (2008) 3751–3761, [Full Text](#)

The alkylammonium surfactants used to form commercial organoclays are known to begin to degrade at temperatures below the typical melt processing temperatures of

some polymers. In this study, the thermal stability and degradation of various surfactants and their corresponding organoclays were investigated. Several factors, such as surfactant type and excess surfactant in the organoclay, that affect the thermal stability of surfactants on organoclays are explored. Nuclear magnetic resonance (NMR) spectroscopy was used to analyze the decomposition products. Thermogravimetric analysis (TGA) was used as the primary method to characterize the thermal stability of these surfactants and organoclays; the neat surfactants lose mass more rapidly, at a given temperature, than the corresponding organoclay. Washing the organoclay with methanol proved to be an effective way to remove the excess surfactant from the clay galleries. Such purification generally improves the thermal stability of the as-received organoclays. Depending on the availability of residual halide anions in the organoclay, the organoclays decompose via either SN2 nucleophilic substitution or Hoffmann elimination pathways.

Effect of organoclay purity and degradation on nanocomposite performance, Part 2: Morphology and properties of nanocomposites

Lili Cui, D.L. Hunter, P.J. Yoon, D.R. Paul; *Polymer*, 2008, 49, 3762–3769, [Full Text](#)

Part 1 of this series showed that the purification level and surfactant loadings of organoclays significantly affect their thermal stability; the higher rate of degradation of as-received commercial organoclay is primarily a result of excess surfactant that is intentionally or unintentionally part of the commercial organoclay. Polypropylene nanocomposites and nylon 6 nanocomposites were formed through melt processing to assess the practical consequences, in terms of nanocomposite formation and performance, of using a purified version of the organoclay with no excess surfactant and a lower rate of thermal degradation versus using the as-received organoclay. The properties and morphology of polymer–clay nanocomposites based on both as-received and purified organoclays were evaluated by TEM, WAXS, and mechanical testing. The results from the different techniques were generally consistent with each other suggesting that the differences in thermal stability of organoclays do not appear to have a significant effect on the morphology and properties of the nanocomposites formed from them.

Morphology and properties of nanocomposites formed from ethylene-vinyl acetate copolymers and organoclays

Lili Cui, Xiaoyan Ma, D.R. Paul; *Polymer*, 2007, 48, 6325, [Full Text](#)

A series of ethylene-vinyl acetate copolymers, EVA, containing 0–40% VA and three organoclays, M2(HT)2, M3(HT)1 and (HE)2M1T1, were melt processed to explore the relationship between the polarity of the polymer matrix and the organoclay structure on the extent of exfoliation and properties of the resulting nanocomposites. The degree of exfoliation of the nanocomposites was evaluated by TEM, WAXS, and mechanical testing. Quantitative particle analyses of TEM images were made to give various averages of the clay dimensions and aspect ratio. The results from different techniques were generally consistent with each other. These EVA copolymer nanocomposites show dramatically improved exfoliation of the organoclay as the VA content is increased. Nanocomposites based on the organoclay with two alkyl tails always gave better exfoliation than those based on the organoclays with a single tail at all VA levels;

however, the relative advantage of the two tails versus one tail seems to diminish with increased VA level. The predictions of tensile modulus using a simple composite model based on Halpin–Tsai equations show rather good agreement with the experimental data.

Quantitative Analysis of Montmorillonite Platelet Size by Atomic Force Microscopy

Harry J. Ploehn, Chunyan Liu, *Ind. Eng. Chem. Res.* 2006, 45, 7025-7034, [Full Text](#)

This work focuses on the use of atomic force microscopy (AFM) for quantitative analysis of the size of suspended, exfoliated platelet materials. In particular, we study a model material montmorillonite (MMT) clays and use tapping-mode AFM with image analysis software to quantify the distributions of MMT platelet thickness and aspect ratio. X-ray diffraction (XRD), transmission electron microscopy (TEM), and AFM confirm that, upon dispersion in water, MMT particles exfoliate into stable platelet suspensions, as is well known. We use dry weight analysis, dynamic light scattering (DLS), and AFM to assess the impact of sample preparation procedures for exfoliation and obtaining high-quality AFM images. Unexfoliated MMT and other contaminant particles can be removed by low-speed centrifugation; however, large exfoliated platelets are increasingly removed as centrifugal acceleration increases. Dilution of MMT suspensions with acetone prior to deposition onto mica leads to high-quality AFM images with many isolated platelets. Quantitative analysis of the data from many AFM images shows that the distribution of MMT platelet thickness is narrow and centered near 1.0 nm. The distribution of platelet aspect ratio closely follows a log-normal distribution, which has not been previously reported in the literature for MMT. We find that the average aspect ratio measured by AFM correlates linearly with the effective spherical particle diameter measured by DLS.

High-Performance Filaments from Compatibilized Polypropylene/Clay Nanocomposites

M. Joshi, et al; *Journal of Applied Polymer Science*, 2006, 102, 2164, [Full Text](#)

Polypropylene (PP)/nanoclay composite filaments were produced by melt spinning and characterized to study the effect of the compatibilizer and the role of the nanoclay in improving the physical properties. The compatibilizer was maleic anhydride grafted PP. Clay loadings up to 1 wt % with up to 3 wt % compatibilizer were explored. There was a significant improvement in the tensile, thermal, and dynamic mechanical properties and creep resistance of PP/nanoclay composite filaments over neat PP filaments at very low clay loadings of 0.25-0.5 wt % and a compatibilizer/clay ratio of 2:1. The properties were correlated to the morphology of the nanocomposite filaments, which was investigated with differential scanning calorimetry, X-ray diffraction, and transmission electron microscopy.

On significant retention of impact strength in clay-reinforced high-density polyethylene (HDPE) nanocomposites

M. Tanniru, Q. Yuan, R.D.K Misra, *Polymer* 47 (2006) 2133–2146, [Full Text](#)

The mechanical response of clay-reinforced polyethylene nanocomposite is investigated and the behavior compared with the un-reinforced polyethylene under identical

conditions of processing. The micromechanism of plastic deformation during impact loading of neat polyethylene and clay-reinforced polyethylene nanocomposite are studied with scanning electron microscopy (SEM). The impact strength of composites is linked to structural studies by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and transmission electron microscopy (TEM) and SEM observations. The addition of clay to polyethylene retains adequately high-impact strength in the investigated temperature range of K40 to C70 8C. The micromechanism of deformation is altered from a combination of craze and drawing of fibrils in neat polyethylene to microvoid coalescence-fibrillated process in the nanocomposite. The aspects related to micromechanism of deformation are discussed.

Electrospinning of poly(MMA-co-MAA) copolymers and their layered silicate nanocomposites for improved thermal properties

M. Wang, G.C. Rutledge, *Polymer* 46 (2005) 3407–3418, [Full Text](#)

Copolymers consisting of methyl methacrylate (MMA) and methacrylic acid (MAA) and their layered silicate nanocomposites were electrospun to form fibers with diameters in the sub-micron range. The presence of MAA increased the T_g and thermal stability of the copolymers through formation of anhydrides upon heating. Fibers of uniform diameters were obtained for the poly(MMA-co-MAA) copolymers and nanocomposites containing montmorillonite (MMT), while protrusions were observed on the electrospun fibers from nanocomposites containing fluorohectorite (FH). The electrospinnability of copolymer solutions and nanocomposite dispersions predicted based on both rheological analyses and conductivity measurements correlates well with the experimental electrospinning observations. Dispersion of clays within the nanocomposites improved the electrospinnability of the nanocomposite dispersions. MMT is predominantly exfoliated and well distributed within the fiber and oriented along the fiber axis. Char formation was observed when the MMT-containing fibers were heated above the decomposition temperature, indicating a potential for reduced flammability and increased self-extinguishing properties, whereas the FH-containing materials disintegrated into either film or powder form.

Effects of Organoclays on Morphology and Thermal and Rheological Properties of Polystyrene and Poly(methyl methacrylate) Blends

M.Y. Gelfer, Hyun H. Song, Lizhi Liu, Benjamin S. Hsiao, Benjamin Chu, Miriam Rafailovich, Mayu Si, Vladimir Zaitsev, *Journal of Polymer Science Part B: Polymer Physics*, 2002, 41, (1), 44, [Full Text](#)

Morphology, thermal and rheological properties of polymer-organoclay composites prepared by melt-blending of polystyrene (PS), poly(methyl methacrylate) (PMMA), and PS/PMMA blends with Cloisite® organoclays were examined by transmission electron microscopy, small-angle X-ray scattering, secondary ion mass spectroscopy, differential scanning calorimetry, and rheological techniques. Organoclay particles were finely dispersed and predominantly delaminated in PMMA-clay composites, whereas organoclays formed micrometer-sized aggregates in PS-clay composites. In PS/PMMA blends, the majority of clay particles was concentrated in the PMMA phase and in the interfacial region between PS and PMMA. Although incompatible PS/PMMA blends remained phase-separated after being melt-blended with organoclays, the addition of organoclays resulted in a drastic reduction in the average microdomain sizes (from 1-1.5

m to ca. 300-500 nm), indicating that organoclays partially compatibilized the immiscible PS/PMMA blends. The effect of surfactant (di-methyl di-octadecyl-ammonia chloride), used in the preparation of organoclays, on the PS/PMMA miscibility was also investigated. The free surfactant was more compatible with PMMA than with PS; the surfactant was concentrated in PMMA and in the interfacial region of the blends. The microdomain size reduction resulting from the addition of organoclays was definitely more significant than that caused by adding the same amount of free surfactant without clay. The effect of organoclays on the rheological properties was insignificant in all tested systems, suggesting weak interactions between the clay particles and the polymer matrix. In the PS system, PMMA, and organoclay the extent of clay exfoliation and the resultant properties are controlled by the compatibility between the polymer matrix and the surfactant rather than by interactions between the polymer and the clay surface.

A novel approach to high performance elastomer by using clay

Ma, J., Xiang, P., Mai, Y., Zhang, L.Q.; *Macromolecular Rapid Communications*, 2004, 25, (19), 1692, [Full Text](#)

A novel method was developed to prepare an exfoliated styrene butadiene rubber (SBR)/clay nanocomposite with a strong interface between the clay layers and the rubber. An exfoliation mechanism was proposed and verified based on X-ray diffraction (XRD)/transmission electron microscopy (TEM) analyses of the intercalation/exfoliation phenomena after each step of the process. The significant improvements of mech. properties may give the first evidence that both exfoliation and a strong interface play critical roles in nanoreinforcement.

Origins of the Materials Properties Enhancements in Polymer/Clay Nanocomposites

Manias, E.; *Nanocomposites 2001, Delivering New Value to Plastics*, [Full Text](#)

Understanding the structure/property relations in polymer/clay nanocomposites is of great importance in designing materials with desired properties. Along these lines, a critical overview is attempted on the physical and molecular origins of material properties enhancements in polymer/clay hybrid nanocomposites. A comparative discussion of mechanical, thermal, optical, and ammiability properties across various polymers focuses on those properties that are universally improved. In general, such properties originate from the nature of the layered inorganic fillers and from their nano-dispersion in a polymer. In contrast, other properties are determined by the particular/distinctive interactions between a specic polymer with the filler; such attributes can not be transferred from one polymer system to another. We shall try to distinguish between these two classes of properties, and provide some insight into which properties can be improved concurrently across a wide range of polymers.

Polymer Layered Silicate Nanocomposites: A Review

Mittal, V., *Materials*, 2009, (2), 992, [Full Text](#)

This review aims to present recent advances in the synthesis and structure characterization as well as the properties of polymer layered silicate nanocomposites.

The advent of polymer layered silicate nanocomposites has revolutionized research into polymer composite materials. Nanocomposites are organic-inorganic hybrid materials in which at least one dimension of the filler is less than 100 nm. A number of synthesis routes have been developed in the recent years to prepare these materials, which include intercalation of polymers or pre-polymers from solution, *in-situ* polymerization, melt intercalation etc. The nanocomposites where the filler platelets can be dispersed in the polymer at the nanometer scale owing to the specific filler surface modifications, exhibit significant improvement in the composite properties, which include enhanced mechanical strength, gas barrier, thermal stability, flame retardancy etc. Only a small amount of filler is generally required for the enhancement in the properties, which helps the composite materials retain transparency and low density.

Study of the Factors Influencing the Exfoliation of an Organically Modified Montmorillonite in Methyl Methacrylate/Poly(methyl methacrylate) Mixtures

Morven McAlpine, John J. Liggat, Richard A. Pethrick, David Pugh, Ian Rhoney, *Journal of Applied Polymer Science*, Vol. 99, 2614-2626 (2006), [Full Text](#)

The factors that affect the dispersion of exfoliated organically modified montmorillonite in a solution of poly(methyl methacrylate) in methyl methacrylate are explored. Exfoliation of montmorillonite in the solution is achieved with the assistance of ultrasound, and rheological measurements indicate a very significant increase in the viscosity, a dramatic shear thinning behavior, and a finite yield stress, all of which are direct consequences of the exfoliated state of the clay platelets. A number of factors, including the sonication power, clay loading, use of a swelling agent, and moisture content of the modified montmorillonite, are found to influence the exfoliation process. The effect of addition of a range of titanate coupling agents (LICA-01, 12, 38, 44, and 97) on the viscosity of the nanoclay dispersions was investigated. It was found that LICA-44 had the effect of reducing the viscosity of the exfoliated montmorillonite dispersion without apparently influencing the extent of the exfoliation. Molecular modeling, UV-visible and Fourier transform infrared spectrometry were used to investigate the possible reasons for efficacy of this LICA. The LICA appears to act through a combination of steric effects and the presence of certain charges on the organic molecule. The magnitude of the negative charges on elements of the LICA appears to influence its ability to bind to the clay and also its ability to reduce the viscosity of the nanoclay. This article indicates how the apparently conflicting requirements of achieving a highly exfoliated state and also maintaining a viscosity low enough for processing can be effectively

Clay-Polymer Nanocomposites Formed from Acidic Derivatives of Montmorillonite and an Epoxy Resin

Muh S. Wang, et al; *Chem. Mater.*, 1994, 6 (4), pp 468-474., [Full Text](#)

A new type of clay-polymer nanocomposite has been prepared by the spontaneous selfpolymerization of an epoxy resin, the diglycidyl ether of bisphenol A (DGEBA), and the concomitant delamination (exfoliation) of acidic forms of montmorillonite at elevated temperatures. The epoxide polymerization-clay delamination temperature (PDT) was dependent on the heating rate and the nature of the clay-exchange cation. H^+ , NH_4^+ , and acidic onium ions of the type $[H\sim N(CH\sim), ICOOH]^+$, $[H_3N(CH_2)_nNH_2]^+$, $[H_3N(CH_2)_nNH_2]^+$, and $[H_sN-(CH_2)_n\sim\sim CH(\sim n)]^{+6}$ and 12) facilitated the polymerization-delamination process over the temperature range 198-287 °C. In general,

the PDT increased with decreasing cation acidity and decreasing basal spacing of the clay. Evidence for nanocomposite formation was provided in part by a dramatic liquid-to-powder transformation of the clay-e oxide mixture upon formation of the polyether. The delamination of montmorillonite into 9.6- 8: layers was further confirmed by transmission electron micrographs, which revealed interlayer separations up to - 2000 Å and by the absence of clay reflections in the X-ray powder diffraction patterns. Differential scanning calorimetry studies of a polyether nanocomposite containing 5 wt % [H₃N(CH₂)₁₁COOH]⁺-montmorillonite indicated the heat of reaction and activation energy for the organoclay-catalyzed polymerization reaction to be 228 and 108 kJ/mol, respectively.

Tribological behaviour of clay – thermoset polyester nanocomposites

P. Jawahar, M. Balasubramanian, *Wear*, 2005, 261, (7-8), 835, [Full Text](#)

Clay – thermoset polyester nanocomposites and conventional clay filled composites are produced using organo-modified clay as the reinforcement and unmodified inorganic clay as filler, respectively. Composites are prepared with clay contents of 1 wt.%, 3 wt.% and 5 wt.%. Tribological property of the nanocomposite system is studied to assess the influence of nanoclay and compared with conventional clay filled composites. The wear test is carried out on a pin-on-disc tribometer with the composite pin sliding over a disc made of tool steel. The coefficient of friction and wear loss decreases significantly on addition of organoclay, whereas for conventional clay filled composites wear loss and coefficient of friction increases with increase in inorganic clay content. The nanocomposites exhibit a maximum of 85% improvement in wear resistance and 35% decrease in coefficient of friction. The highest wear resistant and least coefficient of friction is observed in the nanocomposite with a clay content of 3 wt.%.

Nanocomposite polymer films containing carvacrol for antimicrobial active packaging

Paola Persico, V. A., Cosimo Carfagna, Pierfrancesco Cerruti, Mario Ferrocino, Gianluigi Mauriello, *Polymer Engineering and Science*, 2009, Volume 49 Issue 7, Pages 1447 - 1455, [Full Text](#)

Nanocomposite films based on low-density polyethylene (LDPE) containing carvacrol were prepared and characterized with the aim to get antimicrobial active packaging. Organo-modified montmorillonite (MMT) was used as filler. The weak interaction between LDPE and clay led to the formation of intercalated systems. On the other hand, strong interaction between carvacrol and organosilicate allowed a good dispersion of the oil into the clay galleries, promoting the swelling of MMT stacks and a higher polymer/clay interface. As a result, carvacrol was protected against thermal degradation and its release from the films was efficiently delayed. Moreover, outstanding thermal oxidative stability as well as improved oxygen barrier properties were detected in the nanocomposite containing carvacrol. The presence of clay and carvacrol also increased LDPE crystallinity, due to an enhanced nucleation activity, while the mechanical properties of the films were slightly affected. The antimicrobial properties of carvacrol containing films were tested, showing a significant activity against several bacterial strains, which is preserved in presence of the clay.

Properties of bulk-polymerized thermoplastic polyurethane nanocomposites

Pattanayak, A. J., Sadham C., *Polymer*, 2005, 46, 3394, [Full Text](#)

The thermal, rheological, and mechanical properties of bulk-polymerized thermoplastic polyurethane nanocomposites of reactive and non-reactive layered silicate clay were characterized as a function of the state of dispersion of particles. True exfoliated nanocomposites were produced by mixing reactive clay particles with polymer chains carrying residual isocyanate groups. On the other hand, non-reactive clay particles yielded only intercalated composites. Most significant improvement in mechanical properties were obtained when clay particles were fully exfoliated, e.g. 110% increase in tensile modulus, 170% increase in tensile strength, 110% increase in tear strength, 120% increase in fracture toughness, and 40% increase in abrasion resistance over pristine polyurethane with 5 wt% clay. In addition, the terminal dynamic rheological data showed strong dependence on the clay content, indicating substantial hindrance to chain relaxation by tethering clay particles. The peak location and the area under the peak of hydrogen-bonded carbonyl showed two distinct zones of temperature dependence, which indicate additional hydrogen bonding between polymer chains and organic modifier of reactive clays.

Comparison of Nanocomposites Prepared from Sodium, Zinc, and Lithium Ionomers of Ethylene/Methacrylic Acid Copolymers

Rhutesh K. Shah and D. R. Paul, *Macromolecules*, 2006, 39, 3327-3336, [Full Text](#)

Morphology and mechanical properties of nanocomposites prepared by melt mixing a montmorillonite-based organoclay with lithium, sodium, and zinc ionomers of poly(ethylene-co-methacrylic acid) are presented here. The effect of the type of neutralizing cation on the melt rheology and organoclay exfoliation efficiency of the ionomers was examined using transmission electron microscopy, wide-angle X-ray scattering, DSM axial-force rheometry, and stress-strain analysis. Nanocomposites prepared from the sodium and the zinc ionomers displayed much better exfoliation of the organoclay and superior levels of reinforcement compared to equivalent nanocomposites prepared from the lithium ionomer. On the basis of the detailed experimental analysis, the lower levels of organoclay exfoliation observed in the nanocomposites prepared from the lithium ionomer are suggested to be a result of irreversible exchange of quaternary ammonium ions (of the organoclay) for the very small lithium ions (of the polymer) that can enter the montmorillonite lattice structure.

The development of structure in a melt blended polypropylene organo-clay nanocomposites

Read, M. D.; Harris, J. D.; Samson, R. R., *Annual Technical Conference - Society of Plastics Engineers*, 2004, 2, [Full Text](#)

The development of structure was evaluated for a melt blended polypropylene organo-clay nanocomposites on a co-rotating intermeshing twin-screw extruder. The development of structure was investigated by evaluating the degree of dispersion of the clay platelets as a function of distance (or shear history) down the length of a specially designed clam-shell extruder. The dispersion was characterized by optical and TEM microscopy, x-ray diffraction, and mech. property testing. The results show the

development of structure from the initial large agglomerates to the final mixture of exfoliated and intercalated platelets.

Nanocomposites from poly(ethylene-co-methacrylic acid) ionomers: effect of surfactant structure on morphology and properties

Rhutesh K. Shah, D.L. Hunter, D.R. Paul, *Polymer* 46 (2005) 2646–2662, [Full Text](#)

A detailed study of the structure–property relationships for nanocomposites prepared using melt processing techniques from a sodium ionomer of poly(ethylene-co-methacrylic acid) and a series of organoclays is reported. Transmission electron microscopy, X-ray scattering, stress-strain behavior, and Izod impact analysis were used to evaluate the nanocomposite morphology and physical properties. Four distinct surfactant structural effects lead to improved levels of exfoliation and higher stiffness for these nanocomposites: higher number of alkyl tails on the amine rather than one, longer alkyl tails instead of shorter ones, use of 2-hydroxy-ethyl groups as opposed to methyl groups on the ammonium ion, and an excess amount of the amine surfactant on the clay instead of an equivalent amount. These trends are opposite of what has been seen in nylon 6 based nanocomposites but are similar to those observed in nanocomposites formed from LDPE and LLDPE. Although some organoclays were exfoliated better than others, none of the ionomer-based nanocomposites exhibited exfoliation levels as great as those seen in nylon 6 nanocomposites; nevertheless, these nanocomposites offer promising improvements in performance and may be particularly interesting for barrier applications.

Characterisation of thermoset laminates for cosmetic automotive applications: Part III - Shrinkage control via nanoscale reinforcement

Schubel, P.; Michael S.; Warrior, Nicholas A.; Rudd, Chris D., *Composites, Part A: Applied Science and Manufacturing*, 2006, 37A, (10), 1757, [Full Text](#)

Exfoliated clays were examd. as a means to control resin shrinkage within styrene based unsatd. polyester resins via a so-called nanocomposite. Two clays (Cloisite 10A and Garamite 1958) were investigated and compared to a conventional low profile additive (polyvinyl acetate) with calcium carbonate filler at various loadings. A suitable exfoliation process was established using in-situ, intercalative polymn. followed by measurement of volumetric shrinkage and glass transition temp. A series of hybrid matrixes consisting of clay and PVAc were used to impregnate random E-glass preforms via RTM. The laminates were monitored for changes in volumetric shrinkage and subsequent changes in surface quality of pre- and post-painted surfaces. Residual volatile org. compds. (VOCs) were monitored for each system. Tensile, flexural and impact properties were compared to the base resin and a conventional low profile matrix. The results suggest that the exfoliated clay systems work synergistically with conventional additives to reduce shrinkage and residual VOCs while in many cases improving properties above the level of the base resin.

Multiscale micromechanical modeling of polymer-clay nanocomposites and the effective clay particle

Sheng, N., Boyce, M.C., Parks, D.M., Rutledge, G.C, Abes J.L., Cohen, R.E., *polymer*, 2003, (10), [Full Text](#)

Polymer/clay nanocomposites have been observed to exhibit enhanced mechanical properties at low weight fractions W_c of clay. Continuum-based composite modeling reveals that the enhanced properties are strongly dependent on particular features of the second-phase 'particles'; in particular, the particle volume fraction ϕ_p ; the particle aspect ratio $\delta L/t$; and the ratio of particle mechanical properties to those of the matrix. These important aspects of as-processed nanoclay composites require consistent and accurate definition. A multiscale modeling strategy is employed to account for the hierarchical morphology of the nanocomposite: at a lengthscale of thousands of microns, the structure is one of high aspect ratio particles within a matrix; at the lengthscale of microns, the clay particle structure is either (a) exfoliated clay sheets of nanometer level thickness or (b) stacks of parallel clay sheets separated from one another by interlayer galleries of nanometer level height, and the matrix, if semi-crystalline, consists of fine lamella, oriented with respect to the polymer/nanoclay interfaces. Here, quantitative structural parameters extracted from XRD patterns and TEM micrographs (the number of silicate sheets in a clay stack, N ; and the silicate sheet layer spacing, d_{001}) are used to determine geometric features of the as-processed clay 'particles', including L/t and the ratio of ϕ_p to W_c : These geometric features, together with estimates of silica lamina stiffness obtained from molecular dynamics simulations, provide a basis for modeling effective mechanical properties of the clay particle. In the case of the semi-crystalline matrices (e.g. nylon 6), the transcrystallization behavior induced by the nanoclay is taken into account by modeling a layer of matrix surrounding the particle to be highly textured and therefore mechanically anisotropic. Micromechanical models (numerical as well as analytical) based on the 'effective clay particle' were employed to calculate the overall elastic modulus of the amorphous and semi-crystalline polymer-clay nanocomposites and to compute their dependence on the matrix and clay properties as well as internal clay structural parameters. The proposed modeling technique captures the strong modulus enhancements observed in elastomer/clay nanocomposites as compared with the moderate enhancements observed in glassy and semi-crystalline polymer/clay nanocomposites. For the case where the matrix is semi-crystalline, the proposed approach captures the effect of transcrystallized matrix layers in terms of composite modulus enhancement, however, this effect is found to be surprisingly minor in comparison with the 'composite'-level effects of stiff particles in a matrix. The elastic moduli for MXD6-clay and nylon 6-clay nanocomposites predicted by the micromechanical models are in excellent agreement with experimental data. When the nanocomposite experiences a morphological transition from intercalated to completely exfoliated, only a moderate increase in the overall composite modulus, as opposed to the expected abrupt jump, was predicted.

Diffusion Behavior in Polymer-Clay Nanocomposites

Sorrentina, A.; Vittoria, V., *J Polym Sci Part B: Polym Phys*, 2005, 44, 265, [Full Text](#)

This paper reviews our previous studies on the diffusion behavior in polymer/clay nanocomposites. A geometric model for predicting the effective diffusivity through this type of systems as a function of clay sheets orientation, volume fraction, polymer/clay interaction, and aspect ratio is proposed. Model predictions are compared to the effective diffusivity generated using random walk simulations as well as with predictions obtained from already existing theoretical models. Fair agreement is found between the model prediction and the results of numerical simulations. With respect to the already existing theoretical models, the present mathematical derivation seems more adequate

to describe diffusion behavior in conventional nanocomposites systems (i.e. when fillers present very low values of volume to surface ratio). Experimental diffusion tests are discussed and interpreted with the aid of the proposed model. In addition to the aspect ratio and clay concentration, the polymer clay interactions as well as the sheets orientation are the factors controlling the barrier properties of polymer-layered silicate nanocomposites. Good agreement was found in the case of samples containing exfoliated clay, whereas the model fails in the case of micro-composites, in which the inorganic lamellae are agglomerated in clusters.

Nylon 6 nanocomposites: the effect of matrix molecular weight

T. D. Fornes, P. J. Yoon, H. Keskkula and D. R. Paul, *Volume 42, Issue 25, Pages 09929-09940*, 2001, [Full Text](#)

Organoclay nanocomposites based on three different molecular weight grades of nylon 6 were prepared by melt processing using a twin screw extruder. Mechanical properties, transmission electron microscopy, wide-angle X-ray diffraction, and rheological measurements were used to characterize the three types of composites. Tensile modulus and yield strength were found to increase with increasing concentration of clay, while elongation at break decreased. Izod impact strength was relatively independent of clay content for the higher molecular weight composites, but slightly decreased with increasing clay content for the lowest molecular weight polyamide. In general, nanocomposites based on the higher molecular weight polyamides yielded superior composite properties, having higher degrees of clay exfoliation, higher stiffness and yield strength values, and marginal loss of ductility as compared to nanocomposites based on the low molecular weight polyamide. Differences in properties between the three types of composites were attributed to differences in melt rheology. Capillary and dynamic parallel plate data revealed sizeable differences in the levels of shear stress between each nanocomposites system. A mechanism for exfoliation during melt mixing is outlined.

Extensional flow mixer for polymer nanocomposites

Tokihisa, M.; Sakai, T.; Utracki, L. A.; Sepehr, M.; Simard, Y., *Polymer Engineering and Science*, 2006, 46, (8), 1040, [Full Text](#)

The extensional flow mixer (EFM) was used in industry, for e.g., homogenization of reactor products, polymer blending, incorporation of plasticizer, etc. Recently, several labs. attempted to use EFM for dispersing organoclay in a molten polymer. Thus, usually EFM was mounted on a twin-screw extruder equipped with a gear pump. The use of EFM resulted in improved dispersion and performance - more significant in polyamide or thermoplastic polyester - and marginal in a polyolefin or polystyrene. Recently, to improve EFM efficiency, the com. EFM-3 was modified by redesigning the convergent-divergent plates that engender the extensional flow. The two mixers, EFM-3 and the new EFM-N, were evaluated using a single-screw extruder. Two systems were examined: (1) polyamide-6 (PA-6) with Cloisite-15A (C15A) and (2) polypropylene with maleated-PP and C15A. The compounded samples were injection-molded, and then tested for the degree of dispersion and mech. performance. The results showed superiority of EFM-N. Compounding PA-6 with C15A in a single-screw extruder with EFM-N exfoliated the organoclay, producing polymeric nanocomposites with high performance, comparable or better than that of a com. nanocomposite produced by polycondensation of E-caprolactam in the presence of clay, preintercalated with reactive cations.

Solid-State NMR Investigation of Paramagnetic Nylon-6 Clay Nanocomposites. 1. Crystallinity, Morphology, and the Direct Influence of Fe³⁺ on Nuclear Spins

Vanderhart, D. L., Asano, A. and Gilman, J. W., *Chemistry of Materials* 2001; 13(10): 3781-3795., [Full Text](#)

Several exfoliated nylon-6/clay nanocomposites (NnC's) were investigated and compared with pure nylon-6 using solid-state NMR, both proton and ¹³C. NnC's had nominally 5 mass % clay and were generated both by blending and by in situ polymerization (IsP). Most of the studied NnC's contained layered, naturally occurring montmorillonite clays having nonstoichiometric amounts of nonexchangeable Mg²⁺ and Fe³⁺ ions that substitute into octahedral Al³⁺ sites along the midplane of the 1-nm-thick clay layers. The Fe³⁺ ions impart a useful paramagnetism to the clay. Each Mg²⁺ ion leaves an embedded negative charge that must be neutralized with some cation at the surface of the clay. All clays were initially treated with a cationic so-called organic modifier (OM), often a substituted ammonium ion, which increases the clay layer spacing, attaching ionically to the surface of the clay layers. Clay is found to promote growth of the ζ -crystalline phase of nylon-6 for both blended and IsP NnC's; R-crystallites are characteristic of the pure nylon-6. Stability of the ζ -phase to annealing at 214 °C was investigated. Conversion of ζ - to R-crystallinity during annealing was minimal, except for an injection-molded IsP NnC, which had been exposed to a temperature of 295 °C during molding. This high processing temperature produced an irreversible change. An attempt was made to understand, at least qualitatively, the nature of the spectral density of magnetic fluctuations associated with the paramagnetic Fe³⁺ sites in the clay. For this purpose, we looked directly at the influence of Fe³⁺ on the ¹³C and proton observables in organically modified clays (OMC). We agree with other investigators that the spectral density of paramagnetic fluctuations at the surface of the clay is determined mainly by spin-exchange interactions between Fe³⁺ sites; thus, the spectral density can be altered by changing the Fe³⁺ concentration. Moreover, we find that the spectral density is very wide, having strong contributions all the way from mid-kHz fluctuations to MHz fluctuations near the proton Larmor frequencies. Significant variations in the R/ ζ ratio were also observed in the injection-molded disk, which reflect either a processing-induced heterogeneity in clay dispersion or a significant variation in cooling history from region to region. Proton spin diffusion and multiple-pulse methods were utilized to compare morphologies for a diamagnetic NnC and nylon-6 with the same thermal histories. Long spacing, crystallinity, and the mobility of the noncrystalline nylon-6 segments are very similar for NnC's and nylon-6.

Solid-State NMR Investigation of Paramagnetic Nylon-6 Clay Nanocomposites. 2. Measurement of Clay Dispersion, Crystal Stratification, and Stability of Organic Modifiers

Vanderhart, D. L., Asano, A. and Gilman, J. W., *Chemistry of Materials* 2001; 13(10): 3796-3809, [Full Text](#)

In this second paper of a two-part series dealing mainly with NMR characterization of nylon-6/clay nanocomposites (NnC's) having nominally 5 mass % clay, measurements with application to processing are featured. The paramagnetism of the montmorillonite clays, discussed in the first paper, allowed us to use the corresponding spin-diffusion-moderated reduction in longitudinal proton relaxation time, T₁ H, for two purposes,

namely, to rank the quality of clay dispersion in NnC families with the same formulation and to investigate morphological stratification of the nylon-6 R- and ζ -crystallites with respect to the clay surface. In a group of three NnC's with the same formulation but different melt-blending conditions, variations in T1 H correlated well with previously published TEM assessments of the quality of the clay dispersion. Also, in a set of samples from an injection-molded, in situ polymerized NnC disk where strong variations in R/ ζ ratios were observed, it was found that these differences did not arise from processing-induced inhomogeneities in clay concentration; rather, variations in cooling histories throughout the disk was the more probable cause. In these latter samples, well-defined stratification of the ζ -phase (versus the R-phase) crystallites nearer the clay surface did not occur until after annealing at 214 °C. We also examined the dependence of NnC T1 H's on the static field of the measurement. It is clear that the magnitude of the paramagnetic contribution to T1 H is a function of field and of Fe³⁺ concentration in the clay. Trends support the notion that spin-exchange interactions between the electrons on different Fe³⁺ ions largely define the spectral density of magnetic fluctuations near the clay surface. Some attention was, therefore, given to optimizing Fe³⁺ concentrations for the best NnC characterization. Finally, we investigated the chemical stability of a particular organic modifier (OM), which is used to pretreat the clay prior to melt blending. The OM, dimethyl, dehydrogenated-tallow ammonium ion, was followed in the process of blending this modified clay with nylon-6 at 240 °C. It was found that when such a clay surface was exposed to the nylon-6 during blending, most of the OM on that surface decomposed, releasing a free amine with one methyl and two tallow substituents. However, subsequent melting at 240 °C produced no further decomposition. The implication is that the combination of temperature and shear stress in blending causes decomposition, not just temperature alone. The susceptibility to chemical decomposition varied strongly with the OM. Ironically, extensive decomposition of the OM did not result in poor mixing; in fact, as judged by T1 H, the NnC with the best dispersion of clay also had the most extensively degraded OM. The implications of this degradation for the physical properties have not been explored in detail.

Prediction of the overall moduli of layered silicate -reinforced nanocomposites- part I: basic theory and formulas

Wang, J., & Pyrz, R., *Composites Science and Technology*, 2003, 64, (7-8), 925, [Full Text](#)

This part of the two-part paper presents the basic theory and formulas for the prediction of the overall moduli of layered silicate -reinforced polymeric nanocomposites. In view of the morphol. of the composites and the anisotropic nature of layered silicate, formulas for the overall moduli of composite materials reinforced with transversely isotropic spheroids are derived in this part using the Mori-Tanaka method. These formulas are then used to examine the influences of the anisotropy and aspect ratio of the transversely isotropic spheroids on the overall moduli of the composite materials. It is found that the overall moduli of the composite materials reinforced with transversely isotropic spheroids are predominated by the stiffness of the spheroids in the direction of their major axis, especially for the cases of small and large aspect ratios. The predictions based upon the Mori-Tanaka method are also compared with approx. formulas in the literature for isotropic thin oblate spheroids. It is found that these approx. formulas agree well with the Mori-Tanaka predictions at low volume fractions of the reinforcement.

Prediction of the overall moduli of layered silicate-reinforced nanocomposites— part II: analyses

Wang, J.; Pyrz, R., *Composites Science and Technology*, 2003, 64, (7-8), 035, [Full Text](#)

In this part of the two-part paper, the basic theory and formulas presented in Part I are applied to various montmorillonite silicate-reinforced polymeric nanocomposites. Considering the microstructural characteristics of composites containing intercalated silicate stacks, a hierarchical model is also proposed in this part to predict the overall moduli of these composites. Theor. predictions are compared with exptl. data for isotropic composites. It is found that for the chosen elastic constns. of montmorillonite silicate, all the exptl. results fall within the Hashin-Shtrikman bounds for two-phase isotropic composite materials, as does the theor. prediction of the hierarchical model. The theor. predictions for the intercalated and exfoliated nanocomposites are close to the exptl. data for the considered cases. This paper also points to the need for further examns. of the so-called constrained region that has been widely mentioned in the literature. A simple model for calculating the overall moduli of composites containing constrained regions around the reinforcements is proposed. This simple model shows that the thickness of platelet-like inhomogeneities plays a very important role in stiffening composites containing constrained regions.

Exfoliated PP-Clay Nanocomposites Using Ammonium-Terminated PP as the Organic Modification for Montmorillonite

Wang, Z. M.; Nakajima, H.; Manias, E.; Chung, T.C.; *Macromolecules*, 2003, (10), [Full Text](#)

The herein experimental results demonstrate the advantage of chain-end-function alized PP (PP-t-NH₃⁺) that seems to adopt a unique molecular structure atop of the clay surfaces and results in an exfoliated montmorillonite structure.

Morphological and Rheological Properties of Polyamide 6/Poly(propylene)/Organoclay Nanocomposites

Wen Shyang Chow, Jozsef Karger-Kocsis, *Macromol. Mater. Eng.* 2005, 290, 1184–1191, [Full Text](#)

Polyamide 6 (PA6)/Poly(propylene) (PP)/organoclay (octadecylamine intercalated montmorillonite) systems with and without compatibilizer (maleated poly-(propylene) and ethylene/propylene-based rubber (PPgMA and EPRgMA, respectively)) were produced by extrusion melt blending and the clay dispersion was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The rheological behaviour of the nanocomposites was determined by various methods, viz melt flow index (MFI), capillary and plate/plate rheological measurements. Attempts were made to trace the rheological parameters that reliably reflect the observed changes in the clay dispersion. It was found that some parameters in the viscoelastic range derived from frequency sweep measurements using a plate/plate rheometer are a suitable indicator for changes in the clay dispersion. High initial viscosity with a strong reduction as a function of frequency was attributed to improved clay exfoliation. The latter was also reflected by a high initial shear storage modulus (G_0) along with its small change with the frequency. Variation of the storage modulus (G_0) as a function of frequency for the

PA6/PP nanocomposites. Note: this figure also indicates how the slopes at low and high shear rates were determined.

Thermal Degradation Chemistry of Alkyl Quaternary Ammonium Montmorillonite

Xie, W., Gao, Z., Pan, W.-P., Hunter, D., Singh, A., & Vaia, R., *Chemistry of Materials* (2001), 13(9), 2979-2990, [Full Text](#)

The thermal stability of organically modified layered silicate (OLS) plays a key role in the synthesis and processing of polymer-layered silicate (PLS) nanocomposites. The nonoxidative thermal degrdn. of montmorillonite and alkyl quaternary ammonium-modified montmorillonite were examd. using conventional and high-resoln. TGA combined with Fourier transform IR spectroscopy and mass spectrometry (TG-FTIR-MS) and pyrolysis/GC-MS. The onset temp. of decompn. of these OLSs was approx. 155 °C via TGA and 180 °C via TGA-MS, where TGA-MS enables the differentiation of water desorption from true org. decompn. Anal. of products (GC-MS) indicates that the initial degrdn. of the surfactant in the OLS follows a Hoffmann elimination reaction and that the architecture (tri-Me or dimethyl), chain length, surfactant mixt., exchanged ratio, or preconditioning (washing) does not alter the initial onset temps. Catalytic sites on the aluminosilicate layer reduce thermal stability of a fraction of the surfactants by an av. of 15-25° relative to the parent alkyl quaternary ammonium salt. Finally, the release of org. compds. from the OLS is staged and is assocd. with retardation of product transfer arising from the morphol. of the OLS. These observations have implications to understanding the factors impacting the interfacial strength between polymer and silicate and the subsequent impact on mech. properties as well as clarifying the role (advantageous or detrimental) of the decompn. products in the fundamental thermodyn. and kinetic aspects of polymer melt intercalation.

Compatibilization of Immiscible Poly(propylene)/Polystyrene Blends Using Clay

Yong Wang, Q. Z., Qiang Fu, *Macromolecular Rapid Communications*, 2002, 24, (3), 231, [Full Text](#)

Inorganic clay was investigated as a compatibilizer for immiscible poly(propylene)/polystyrene blends. A substantial decrease in the number of polystyrene particles was seen after adding small amounts of an organically treated clay (2-5 wt.-%) to the blends. A possible mechanism for this kind of compatibilization is discussed, but these unique and completely new findings need further verification.

Effects of Nanoclay Structure on the Mechanical Properties of EPDM

Yoon, P. J., Fall 170th Technical Meeting of the Rubber Division, American Chemical Society, [Full Text](#)

The chemical structure and amount of organic surfactant are important parameters for the dispersion of organically modified nanoclay in rubber compounds. In this study, organoclays based on montmorillonite (MMT) were compared in ethylene-propylene-diene rubber (EPDM) model compounds. The results showed that dimethyl bis(hydrogenated-tallow) ammonium MMT revealed finer clay morphology as well as greater tensile strength for EPDM nanocomposites. It is suggested that hydrophobic modification aided the exfoliation of platelets during EPDM compounding. The final

morphology of the organoclay via transmission electron microscopy and x-ray diffraction showed finely dispersed tactoids comprised of several platelets. The tensile strength of EPDM composites prepared with organoclays was linearly increased with increasing MMT. This trend continued to a loading of about up to 15 wt%. For less compatible organoclays with EPDM, a pre-dispersed masterbatch was prepared by twin screw extruder. This technique was effective in increasing dispersion in the EPDM matrix. Vulcanization kinetics in peroxide curing was not greatly affected by the presence of organoclay, however, there may be an influence on sulfur cure kinetics due to the attraction between the organoclay and zinc or amine based agents. In addition, the synergetic role of organoclay to silica is discussed. Tensile strength and elongation at break were significantly improved as organoclay replaced silica by MMT at up to 6 %. Dynamic fatigue measured by a DeMattia tester showed that the flexing cycle was exponentially increased with increasing MMT loading in filler amount.

Polycarbonate nanocomposites. Part 1. Effect of organoclay structure on morphology and properties

Yoon, P. J., Hunter, D. L., & Paul, D. R., *Polymer*, 2003, 44, (18), 5323, [Full Text](#)

Polycarbonate nanocomposites were prep'd. by melt processing from a series of organoclays based on sodium montmorillonite exchanged with various amine surfactants. To explore the effects of matrix mol. wt. on dispersion, an organoclay was melt-mixed with a medium mol. wt. polycarbonate (MMW-PC), i.e., lupilon S3000 and lupilon S2000F, and a high mol. wt. polycarbonate (HMW-PC), i.e., lupilon E2000 and lupilon E2000F, using a twin screw extruder. The effects of surfactant chem. structure on the morphol. and phys. properties were explored for nanocomposites formed from HMW-PC. Wide angle x-ray scattering, transmission electron microscopy, and stress-strain behavior were used to investigate the nanocomposite morphol. and phys. properties. The modulus enhancement is greater for nanocomposites formed from HMW-PC than MMW-PC. This trend is attributed to the higher shear stress generated during melt processing. A surfactant having both polyoxyethylene and octadecyl tails shows the most significant improvement in modulus with some of the clay platelets fully exfoliated. However, the nanocomposites formed from a range of other organoclays contained both intercalated tactoids and collapsed clay particles with few, if any, exfoliated platelets.

Polycarbonate nanocomposites: Part 2. Degradation and color formation

Yoon, P. J.; Hunter, D.L.; Paul, D.R., *Polymer 44 (2003) 5341–5354*, 2003, [Full Text](#)

Polycarbonate nanocomposites were prepared using two different twin screw extruders from a series of organoclays based on sodium montmorillonite, with somewhat high iron content, exchanged with various amine surfactants. It seems that a longer residence time and/or broader residence time distribution are more effective for dispersing the organoclay. The effects of organoclay structure on color formation during melt processing were quantified using colorimeter and UV–Vis spectroscopy techniques. Color formation in the PC nanocomposites depends on the type of organoclay and the type of pristine clay employed. Double bonds in the hydrocarbon tail of the surfactants lead to more darkly colored materials than saturated surfactants. The most severe color was observed when using a surfactant containing hydroxyethyl groups and a hydrocarbon tail derived from tallow. Molecular weight degradation of the PC matrix during melt processing produces phenolic end groups which were tracked by UV–Vis

spectroscopy. Greater dispersion of the clay generally led to higher reduction in molecular weight due to the increased surface area of clay exposed; however, for color, the situation is far more complex. Hydroxy-ethyl groups and tallow unit on the surfactant lead to more degradation. A selected series of organoclays based on synthetic clay Laponitew and calcium montmorillonite from Texas (TX-MMT) were also prepared to explore the effects of the clay structure. Laponitew and TX-MMT produce less color formation in PC nanocomposites than montmorillonite probably due to lower content of iron. Dynamic rheological properties support the trends of molecular weight degradation and dispersion of clay.

Rubber toughening of nylon 6 nanocomposites

Young-Cheol Ahn, D. R. Paul, *Polymer* 47 (2006) 2830–2838, [Full Text](#)

The rubber toughening of nylon 6 nanocomposites prepared from an organoclay was examined as a means of balancing stiffness/strength versus toughness/ductility. Nine different formulations varying in montmorillonite, or MMT, and maleated ethylene/propylene rubber or EPR-g-MA rubber content were made by mixing of nylon 6 and organoclay in a twin screw extruder and then blending the nanocomposites with the rubber in a single screw extruder. In this sequence, the MMT platelets were efficiently dispersed in the nylon 6 matrix. The MMT platelets did not penetrate into the rubber phase. The addition of clay affected the dispersion of the rubber phase resulting in larger and more elongated rubber particles. The tensile properties and impact strength of these toughened nanocomposites are discussed in terms of the MMT and rubber contents and morphology. There is a clear trade-off between stiffness/strength versus toughness/ductility.

Melt-processable syndiotactic polystyrene/montmorillonite nanocomposites

Z. M. Wang, J. W. Gilman, E. Manias, *Journal of Polymer Science Part B: Polymer Physics*, 2003, 41, (24), 3173, [Full Text](#)

Monoalkyl- and dialkyl-imidazolium surfactants were used to prepare organically modified montmorillonites with markedly improved thermal stability in comparison with their alkyl-ammonium equivalents (the decomposition temperatures increased by ca. 100 °C). Such an increase in the thermal stability affords the opportunity to form syndiotactic polystyrene (s-PS)/imidazolium-montmorillonite nanocomposites even under static melt-intercalation conditions in the absence of high shear rates or solvents. Upon nanocomposite formation, s-PS exhibited an improvement in the thermal stability in comparison with neat s-PS, and the beta-crystal form of s-PS became dominant. This crystallization response agrees with previous studies of s-PS/pyridinium-montmorillonite hybrids and is tentatively attributed to a heterogeneous nucleation action by the inorganic fillers.

Chaotic Advection as a Basis for New Smart Blending Technology

Zumbrunnen, D., *web article*, [Full Text](#)

As an outcome of studies begun at Clemson University in 1991, a new smart blending technology has been demonstrated at Clemson University (www.ces.clemson.edu/mmpl) that allows specification by technicians via a computer keyboard of desired blend

morphologies or structured distributions among solid additives in extruded plastics. A single smart blending device can readily produce a large variety of structures in polymer blends or composites that can be unattainable with conventional compounding equipment or require post-processing steps and time-consuming iteration. Smart blenders are particularly useful where the emphasis is on structure-property-composition optimization. This new technology is made possible by chaotic advection, a recent advance in fluid mechanics (Aref, 1984). Chaotic advection has two relevant characteristics of general importance to blending. Polymer melt streams in a smart blender become recursively stretched and folded by chaotic motions. Also, the positions of individual parts of a melt diverge exponentially fast over time. The influences of both characteristics can be made to progress to a desired degree and are evident in materials produced. Morphology development and morphology features are consistently repeatable. Recently, smart blending has been characterized as a new area of chaotic advection research that may hold particular promise.