

Layered Silicate Reinforced Polymer Nanocomposites: Development and Applications

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This review provides a rationale for polymer nanocomposites, emphasizing layered (smectic) silicate reinforcements, particularly montmorillonite clay with various surfactant treatments. Considerable attention is given to processing techniques for synthesizing such nanocomposites via compounding in the melt. While briefly covering structural characterization, it focuses on physico-mechanical properties, using examples of nylon as a polar polymer matrix and polypropylene, the continuous phase in a thermoplastic vulcanizate (TPV), as a non-polar polymer matrix. Both polar and non-polar rubber components are considered for the TPV. Thus, the thermodynamic compatibility between a surfactant-treated clay and the polymer matrix as well as the partitioning of the clay reinforcement in a two-phase heterogeneous polymer blend are addressed. Finally, functional performance is reviewed, with an emphasis on automotive applications.

Keywords nanocomposite, montmorillonite, layered silicate, clay, nylon, polypropylene, blend, thermoplastic vulcanizate

Role for Nanocomposites

In order to elevate the mechanical and thermal properties of polymers for enhanced performance in ever-widening applications, organic matrices have been traditionally reinforced with components that are harder, stronger, or stiffer. Such a solid discontinuous phase is generally incorporated into plastics and rubber to enhance mechanical properties, although other physical properties, such as conductivity, optical properties, permeation, and stability could benefit as well. The mechanical enhancements from such reinforcement include increased stiffness and, to some extent, strength, reduced elongation to failure, improved resistance to crack growth and tearing, and, finally, various modifications of dynamic, abrasion, and fatigue properties.

Generally cost-effective micron-scale minerals reinforce by sharing the stress load through shear transfer. However, the relatively large size of the dispersed phase

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requires high reinforcement concentrations that produce poor appearance and difficult processing. A limiting characteristic of such classical composites is the low extent of interaction between the reinforcement and the matrix polymer.

The small size, high surface area, and possibly a high aspect ratio of nanoscale reinforcements potentially allow polymeric composites to exceed classical limitations and display synergistic properties. Reduction of the reinforcing phase size to nanoscale dimensions conceptually produces a hybrid macromolecule of the organic and inorganic components.

New technologies develop slowly in the background before their commercial viability becomes evident. It appears that a point of emergence has now been reached in the case of polymer nanocomposites (PNCs).¹ While admittedly a small sub-sector of the overall field of nanotechnology, PNCs are achieving recognition within the materials industry for their enhanced performance and applicability in polymer and metal replacement. For example, PNC automotive body components bring scratch and rust resistance along with weight savings, embedded nanoparticles in cloth induce stain and water-resistance to clothing, and tennis balls with an interior nanoplatelet coating provide enhanced air retention for extended performance lifetime. The infrastructure is falling into place at the governmental, commercial, investment, and academic levels to support the continuing growth of the nanotechnology industry that includes chemicals, medicines, electronics, photonics, and energy in addition to materials.²

The global market for nanomaterials was considered to be \$23B in 2002 and should have grown to more than \$30B in 2006. Of this total, nanocomposites is expected to account for \$380M – \$1.2B.³ The number of nanotechnology patents issued worldwide has been growing exponentially from less than 500 in 1995 to just under 6,000 in 2003.⁴ The US, Europe, and Japan have invested about equally in the technology development.

Technical aspects of clay nanocomposites are covered in detail in recent books by Pinnavaia and Beall,⁵ Krishnamoorti and Vaia,⁶ and Utracki.⁷ Noteworthy comprehensive review articles have been provided by Legaly,⁸ LeBaron, Wang, and Pinnavaia,⁹ Alexandre and Dubois,¹⁰ and Ray and Okamoto.¹¹ The material below gives a more deliberate treatment to certain representative segments of the general polymer nanocomposites field.

Types of Polymer Matrices

By this point in their development, nanocomposites have been prepared from practically every known polymer. General classes include thermoplastics (along with thermoplastic elastomers) as well as thermosetting plastics and rubber. This review is limited to thermoplastic polymers, including thermoplastic vulcanizate (TPV) elastomers, with an emphasis on model polar (nylon) and non-polar (polyolefin) matrices.

Types of Reinforcements

The original nanoparticles, perhaps, were the carbon blacks used predominantly in the rubber industry. Primary nanoparticles are fused into aggregates measuring 10–100 nm across, which are difficult to further refine in the compounding processes. Thus, a large technology has grown up around the characteristics of these aggregates relative to their reinforcing ability. However, the degree of reinforcement remains below nanoscale potential.

Newer forms of carbon reinforcements as buckyballs, nanofibers, and nanotubes have much greater potential for reinforcement that is now being realized despite their high costs. A high throughput process has recently been implemented to manufacture high purity multiwalled carbon nanotubes (MWCNTs) in bulk at a reduced cost that should serve to accelerate the commercialization of such nanocomposites.

Graphene sheets, which are single layers of graphite, can enhance electrical conductivity and mechanical properties of polymers when delaminated, and effectively dispersed in the matrix. Cost would be lower than for equivalent carbon nanotubes, but delamination continues to be a problem. As with other nanocomposites, some type of surface modification is required in the galleries between the sheets. While this has traditionally been accomplished by acid treatment followed by heating to a high temperature in order to expand the structure through vaporization of the trapped water, newer treatments include chemical functionalization, such as oxidation.

Layered Silicate Mineral Materials for Polymer Reinforcements

Amongst the reinforcing nanostructures that include metal oxide particles, buckyballs and the related nanotubes, nanofibers, sol-gel hybrids, and silsesquioxane cages, the generation of nanoscale platelets in a liquid polymer (or its monomer) through the (partial) delamination of readily available and cost-effective silicate minerals, particularly the 2:1 smectic silicates such as montmorillonite, represents the most reasonable and practical route to polymer nanocomposites today. Exfoliation of the clay bundles, referred to as tactoids, in such layered silicate nanocomposites (LSNs) augments reinforcement by increasing the interfacial area between the clay platelets and the polymer matrix, or alternately by increasing the aspect ratio of residual platelet structures to render them more efficient reinforcements. Such clay fragments feature high surface area (400–700 m²/g) and aspect ratio (>100:1) by combining nanoscale thickness (10 Å) with an equiaxial planar dimension in the range of 100–200 nm. This high aspect ratio can be maintained during compounding and forming operations by the high flexibility of the exfoliated platelets that minimizes bending stresses to curtail breakage, despite their relatively high modulus (twice that of fiberglass).

The degree of dispersion of the reinforcement is critical for both modulus and strength development, in regard to the generation of aspect ratio and, in the latter case, for the elimination of stress concentrations. Nanoscale layered silicates, like their microscale counterparts, can be treated with agents that promote dispersion during normal mixing operations, while possibly also contributing to improved bonding to the matrix. In the case of smectic silicate nanocomposites, the dispersing agent is a surfactant coating pre-applied to the gallery walls.

The mechanism for this treatment lies in the natural inorganic cationic counterions adsorbed to the inner surfaces of the clay galleries to balance the negative charges resulting from isomorphic substitution of lower valence atoms in the clay lattice. These hydrated cations can be exchanged for functionalized onium cations that allow tailoring of the naturally high energy surface with ionic surfactants to enhance polymer intercalation, layer exfoliation, and effective interfacial bonding to the polymer matrix. It is usually desirable that the coating composition be compatible (presenting a strong interface) with, if not miscible (forming a homogeneous mixture) with, the final composite matrix polymer. The resulting strong interface or interfacial region enhances thermo/mechanical performance due to either more efficient stress transfer or

to the immobilization of the polymer molecules as they are effectively interfaced to the inorganic domain.

The preferred attributes of clays for polymer reinforcement include high purity and uniformity, large platelet size (or aspect ratio, since the layer thickness commonly runs around 1 nm), optimal exchange capacity (CEC) and degree of ion exchange (milliequivalent ratio, or MER), and proper cationic surfactant selection for good thermal stability, clay dispersibility, and nanocomposite property building.

Preparation of Nanocomposites by Dispersive Mixing

A major consideration in the preparation of polymer nanocomposites is the generation of a highly dispersed nanoscale hard phase within the polymer matrix. Different routes to this achievement may involve in situ generation of the inclusion (bottom up approach) or size reduction from macroscale powders (top down approach). The latter must begin with an agglomerated form of the reinforcement to allow satisfactory handling for feeding to a compounding device. These agglomerates must be easily comminuted to their component aggregates for reinforcement. In the parlance of layered silicate nanocomposites, the aggregated stacks of clay platelets referred to as tactoids must then be reduced to smaller stacks of swollen structures in which polymer molecules have infiltrated the galleries separating the clay layers. Ideally, these intercalated stacks will further disassociate upon additional processing to allow the delamination of the individual layers, which can then be distributed uniformly throughout the polymer medium to produce an exfoliated structure. The larger general literature on filler dispersion in polymer systems discusses the steps of agglomerate wetout followed by the generation of aggregates. The size and structure of the aggregates comprising the agglomerate as well as its friability are all important in generating the final aggregate distribution.¹²

The analogous process in nanocomposites takes a slightly different format. Unlike microscale reinforcements such as conventional carbon black and minerals like silica, the "aggregate" state of the dispersion process is of little value for nanocomposites, as the clay tactoids comprising that condition are of microscale dimensions and low aspect ratio. Rather, intercalated structures represent the important intermediary stage of dispersion, and the goal, unlike the case for carbon black, is in fact the achievement of a uniform separation of the primary particles, the nanometer-thick clay layers, as individual platelets.

A critical parameter in this dispersion process is the magnitude of the inter-particle forces relative to those operating between the particles and the suspending medium. When this ratio is high, dispersion is difficult and a highly structured morphology would result. On the other hand, when the forces with the dispersion medium predominate, indicating a high degree of interaction, not only will the dispersion to primary particles be easier, but the resulting nanocomposite will display a higher degree of reinforcement.

Exfoliated smectic silicate nanocomposites can be formed prior to melt processing either by solution blending or by in-situ during polymerization following intercalation with the monomer. The in-situ reactive approach, while specific to the particular nanoclay-polymer matrix pair selected for the nanocomposite, can be more effective at producing exfoliation of the clay structure due to the higher intercalation efficiency of lower molecular weight monomers or oligomers and the swelling of the interplatelet galleries that results from the growing size of the polymer molecule contained therein.

Some examples of reacting systems adaptable to the formation of nanocomposites include the polymerization of a polyamide thermoplastic from its monomers, the

crosslinking of a thermosetting epoxy and the vulcanization of rubber. A more direct and generally applicable procedure, however, utilizes intercalation of the polymer molecules from the melt, leading to exfoliation during the compounding process, which compares with traditional mixing operations for polymer microcomposites, such as fiberglass reinforced plastic, and may be accomplished in any of the conventional polymer mixing devices, though the mixer configurations and processing conditions would likely be different. Compounding conditions such as the design of mixing elements, throughput rate, and rotational speed, while not critical, may be optimized for each specific polymer-silicate pair. In general, a low temperature and high residence time with moderate mixing intensity are desirable. Concentrates for later letdown can be prepared in various carrier resins selected for their processibility, cost, or compatibility with both the surfactant-treated (organo-)clay and the final nanocomposite matrix polymer, by which they can serve as dispersion and/or coupling agents for later letdown.

The following steps apply to the introduction of a layered silicate (smectic) clay into a polymer for the preparation of a LSN:

1. Clay treatment: selected organic (onium) cations appropriate for the desired matrix polymer exchanged for the natural inorganic cation (Na^+) in the gallery.
2. Wetout of the clay aggregates with polymer or monomer species.
3. Thermodynamically driven intercalation of the polymer or monomer molecules into the modified galleries.
4. Polymerization (for in-situ synthesis).
5. Swelling of the galleries, possibly leading to exfoliation.
6. Dispersive mixing to break up swollen tactoids and distribute the resulting fragments uniformly in the matrix resin.

Polymer intercalation of the layered silicates directly from a polymer melt or the dispersion of pre-impregnated clays into the final nanocomposite composition can be accomplished in various types of polymer compounding equipment, including batch mixers and single- or twin-screw extruders, to provide both distributive and dispersive mixing. The single screw extruder has been found significantly less effective.^{13,14}

The effects of the dispersive mixing process on the final state of reinforcement size, or aspect ratio, and dispersion depend on the characteristics of both the reinforcement and the matrix, as well as the parameters of the mixing process. Pre-treatment of the clay tactoid by cationic surfactants (gallery wall decoration) or dispersing agents would enhance individual platelet wetout and gallery opening (layer separation, as measured by the crystalline d-spacing). In addition, the chemical nature and viscoelasticity of the coating or dispersant and its compatibility with the composite matrix are important material parameters. The viscoelasticity of the matrix polymer is also important in determining the magnitude of the stresses developed in the compounding process that will act to disperse the individual reinforcements. Matrix viscoelasticity depends on the matrix polymer selection, its formulation and the process temperature. The dispersive stress level depends not only on the matrix characteristics, but also on the strain rate of the mixing process, while the total strain generated during compounding, which governs the distribution of the dispersed fibers, increases with the speed and time of mixing. Finally, the deformations and deformation rates imparted during mixing, along with the mixer geometry, including the degree of fill of the chamber volume, determine the efficiency of the mixing process.

The factors affecting the dispersion of discontinuous reinforcements during compounding into a polymer matrix can thus be summarized as follows:

Degree of element agglomeration.

Wetout or degree of intercalation.

Coating or dispersant compatibility with the polymer matrix.

Coating or dispersant viscoelasticity (vs. that of the composite matrix).

Level of mixing stresses.

Matrix viscosity.

Polymer type

Composition/formulation.

Temperature.

Strain rate.

Total mixing strain.

Mixer efficiency.

Residence time or number of mixing stages.

Unlike glass fiber composites, which show decreased reinforcement with additional processing,¹⁵ nanocomposites reinforced with smectic silicates can actually become more highly reinforced due to increasing exfoliation with minimal additional breakage.¹⁶ Thus, the degree of dispersion of the nanoscale elements can increase on additional melt processing without significant aspect ratio reduction, while that of fiberglass reinforcements decreases. On this basis, the strength and modulus of nanocomposites can be expected to increase, while that of fiberglass composites decreases with mixing energy input. In both cases, additional compounding (in the absence of resin degradation) could be expected to increase the elongation, and perhaps the toughness.

The thermodynamic effects on the dispersion of smectic silicates are magnified at the nanoscale in comparison to microscale reinforcements like glass fiber, which require only conventional mixing actions for dispersion and distribution. The accommodation for the kinetics of thermodynamically driven polymer melt intercalation of the smectic silicate structure leads to an additional processing requirement for enhanced residence time to effect optimum tactoid exfoliation.

A longer residence time, preferably at a reduced hydrodynamic stress level to minimize viscous dissipation, could be accommodated with a longer extruder, perhaps with a non-intermeshing configuration to enhance available melt volume. Such a counter-rotating twin screw extruder was found by Dennis et al.¹³ to be a preferred compounding device for layered silicate nanocomposites. Longer residence times would in general be generated by enhanced backflow, a lower throughput rate, and a lower screw speed in any type of extruder. As some degree of stress development in the melt is needed for dispersive mixing, the screw speed should not be too low, however. Long residence time combined with a moderate screw speed would be the most favorable conditions for the compounding of smectic silicates into a polymer melt. However, care must be taken to avoid polymer degradation by heat or chemical reaction (e.g., hydrolysis).

Temperature containment would be especially critical in compounding of ammonium-modified nanocomposites to prevent undesirable degradation of the surfactant leading to oxidative degradation of the matrix itself during such longer residence times.¹⁷ Thus, the barrel temperature should be kept close to the melting or softening point of the matrix resin.

Since physico-mechanical properties generally improve from the enhanced dispersion achieved by extending the mixing of smectic silicate nanocomposites, it is favorable to use multiple steps or passes through the compounding machine. The first could be to prepare a concentrate or masterbatch at high solids content (up to 20–25% maximum for montmorillonite) with a polymer intercalant or dispersant. The resistance of flexible nanoscale platelets to attrition and aspect ratio reduction during compounding operations would be especially advantageous versus brittle microscale reinforcements at the higher volume concentration in a masterbatch. The masterbatch could be based on a different molecular weight of the same polymer as the final matrix or alternatively a different polymer carrier more suited for silicate intercalation that is also compatible with the final nanocomposite matrix polymer. The latter route applies ideally to polyolefin nanocomposites, where maleic anhydride modification is a common route to enhanced polymer intercalation. A disadvantage of the masterbatch approach is the locally high viscosity exhibited by a high concentration of exfoliated nanoplatelets that could hamper their final homogeneous distribution. This effect can be somewhat counteracted by the high dispersal forces generated at low temperature during the melting of the masterbatch as it is being let down into the final matrix in a second compounding operation. By the same token, less potential breakage would be experienced due to compaction if the reinforcements are introduced downstream into a pre-melted polymer stream during the initial compounding operation. Dispersion counts and aspect ratio measurements that relate to property development must be made on silicate aggregates in the final nanocomposite through electron microscopy, due to their small size scale.¹³

Structural Characterization and Properties

Polymer intercalation of the clay galleries proceeds by a diffusional mechanism that is affected by interactions between the polymer and both the silica gallery wall and the pendant cationic surfactant groups decorating it. Strong polymer-surface forces can detrimentally retard the progress of the intercalation process, which has also been found dependent upon the inverse first power of the polymer molecular weight.¹⁸ Morphology typical of a layered silicate nanocomposite is shown in Fig. 1. Molecular models relate such a structure to the configurations of the cationic surfactant and intercalated polymer.¹⁸

The layer spacing in the clay assemblages (tactoids) serves as a measure of its degree of intercalation that can be measured by wide-angle x-ray scattering, although definitive verification of the dispersed clay morphology must be by transmission electron microscopy. Nanocomposite property development generally tracks the degree of clay exfoliation and dispersion as measured by these techniques.

As polymer systems deform more extensively at elevated temperature, melt rheology becomes a discriminating indicator of variations in the micro-/nanoscale morphology. Nanocomposites characterized by a state of high dispersion can be expected to show a rheology that is influenced by the proximity of constituents, with inter-constituent forces forming an effective network that generates a yield threshold to flow under conditions of low strain or strain rate. This effect, noticed in dynamic as well as flow situations, can be described by a form of the Kerner equation for idealized spherical inclusions.¹⁹ At larger deformations and higher rates the breakup of the network reduces the modulus in a manner related to the well-known Payne effect in carbon black reinforced rubber compounds.

Thus, the melt viscosity of layered silicate nanocomposites is generally higher than that of the neat polymer matrix at low deformation rate, where a high plateau in G' at

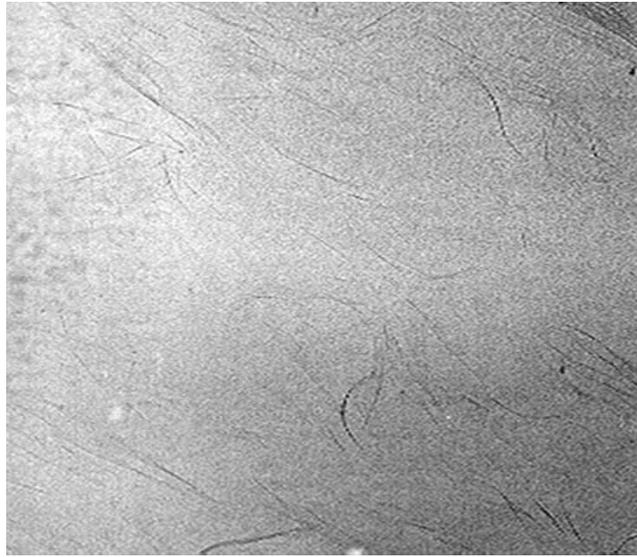


Figure 1. Morphology typical of a layered silicate nanocomposite.

elevated silicate concentrations indicates the presence of a network structure,²⁰ but falls rapidly to approach the base polymer level at the high rates that are characteristic of commercial processing operations. The plateau in G' can form at lower concentration levels as the degrees of exfoliation and matrix tethering increase.

The smaller size and plate-like geometry of smectic silicate nanocomposites make them less susceptible to orientation effects during processing and fabrication, though the converging flow into the reduced gauge section of an injection molded tensile bar still provides sufficient planar orientation for morphology characterization and standardized physical property measurement. (See, for example, the swelling measurements on molded nylon nanocomposites in Table 1.)

Table 1
Dimensional change in Nylon 66 nanocomposites on moisture exposure²¹

% Change	Wt.% Organo-montmorillonite		
	0	5.2	7.5
Length	0.11	.05	0.03
Width	0.30	0.10	0.04
Thickness	1.40	1.28	1.20
Volume	1.81	1.43	1.27
Weight	2.05	1.44	1.41

Conditions: 24-Hour exposure of injection molded specimens to 100% RH air at 38°C according to Society of Automotive Engineers specification SAE J2551-CB.

Significant enhancements in stiffness, dimensional stability, and heat resistance universally occur at low concentrations of the layered silicates. Ultimate mechanical properties, such as strength, toughness, and ductility, are relatively more attenuated and dependant on the complex behaviors specific to each composite system. As increasing the clay loading beyond a certain concentration representative of the percolation threshold (about 1% by volume) frequently results in deterioration of strength, low loadings of silicate mineral are preferred and should be capable of providing significant reinforcement when properly structured and bonded to the matrix polymer. Pertinent parameters for optimizing layered silicate exfoliation and dispersion include compositional variables affecting gallery conformation and thermodynamic or reactive compatibility along with the physical parameters of mixing intensity and strain.

Substantial improvements in permeation reduction and flame retardation derive from the platy structure of the clay nanocomposites. Barrier films and automotive fuel service applications also requiring low weight fit this combination of performance attributes particularly well. Other benefits for LSNs are their good processing and surface appearance, similar to those of the base polymer, non-abrasiveness to the processing equipment, low density (in comparison to more highly loaded microscale composites), low warpage, and reduced moisture sensitivity (due to the barrier effect). The nanoparticles can also act as nucleators in semi-crystalline plastics, while the restricted mobility of amorphous chains tethered to the silicate surfaces can be expected to increase the heat resistance of the polymer.

Multiaxial impact data generally validate the superior toughness of LSNs over fiberglass microcomposites. It should be noted that the high notched Izod impact strength developed by high concentrations of fiberglass that are not matched by LSNs can be attributed to the energy expended as the longer strands are pulled out of the matrix during fracture, rather than to meaningful damage tolerance. One reason for the better performance of LSNs in comparison to fiberglass composites in multiaxial impact could be the planar geometry of the reinforcing platelets, which are not subject to flow orientation in the plane of the test plaque during molding. Indeed, nearly isotropic tensile properties in the plane can be achieved.

Partitioning of a nanoscale reinforcement between the phases of an inhomogeneous polymer blend or distributing it in relation to other reinforcements can enhance physical and mechanical performance, particularly in regard to failure properties such as strength, elongation and toughness. Stiffening tends to be more dependent on overall composition, although the local modulus of surrounding matrix can be influential.

Nanocomposites Formed from Polyamides Representing High Polarity/Engineering Thermoplastic Polymer Matrices

Amongst the engineering thermoplastic nanocomposites, those based on nylon 6 have experienced the most dramatic development due to their greater compatibility with the inorganic silicates and are today entering commercial markets. Early work with nylon polymers documented in the reviews and books cited above⁵⁻¹¹ involved montmorillonite clays modified with either an amino acid or a hydrocarbon functionality. The former was chemically reacted to nylon 6 polymer by serving as the catalyst for the ring opening polymerization of caprolactam. Various alkylorganoclays have been melt blended into nylon 6 and nylon 66. A review of nylon 66 nanocomposites has been presented by Goettler and Recktenwald.²¹ The high efficiency of layered silicate reinforcements in raising the stiffness of a nylon 66 nanocomposite is shown in Fig. 2. The flexural

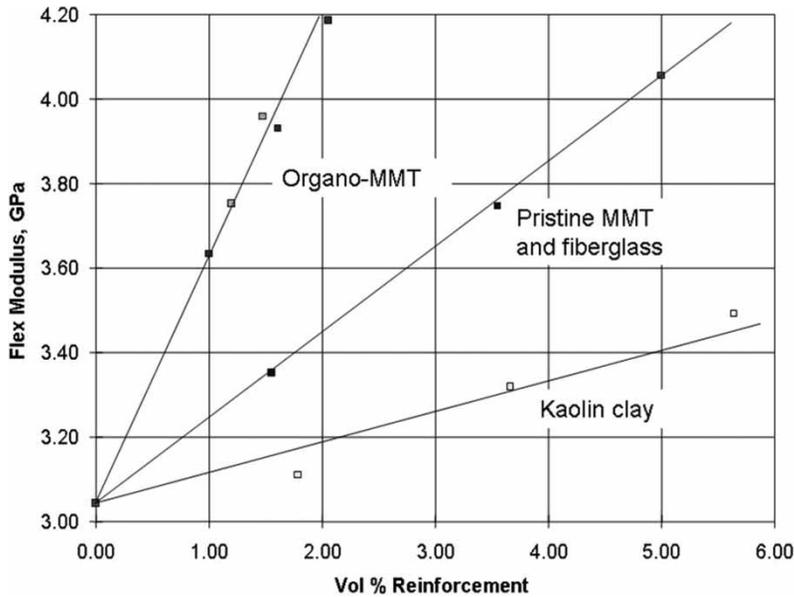


Figure 2. Modulus increase by layered silicate reinforcement of PA66.

modulus of the composites compounded from tallow-based nanoscale organoclay increases ten times more rapidly than that based on non-intercalating kaolin clay that acts like a particulate microscale filler, and almost three times more rapidly than compounded fiberglass or pristine montmorillonate microcomposites. Indeed, it is not clear whether the rule-of-mixtures prediction necessarily represents an upper bound on the modulus for these nanocomposites.

In fact, modulus was found to increase up to twice that of the nylon matrix in injection moldings and three times in blown film.²² A greatly reduced coefficient of linear thermal expansion can also be expected since thermal expansion inversely tracks the modulus.

Heat distortion temperature under load (DTUL) could be boosted to 170°C for nylon 6,6 nanocomposites at the 1.8 GPa stress condition vs. 80°C for the nylon matrix, though microscale fiberglass reinforcement can reach 250°C, perhaps because its larger length scale provides for more effective reduction of creep (ductility over long times at high temperature). A contributing morphological factor could be the reduced spherulite size in the nylon crystallites nucleated in the nanocomposites by the presence of the montmorillonite. The characteristic molding shrinkage of nylon 66 reduces from 18 mil/in to 5–6 mil/in by the incorporation of montmorillonite. Moldings are less anisotropic with smoother surfaces and less warpage than in fiberglass microcomposites. The planar alignment of the platelets is illustrated by the water swelling data reported in Table 1.²¹

Most importantly, tensile strength, ultimate elongation, and impact toughness are in good balance in these nanocomposites. Flat panels molded from nylon 66 nanocomposite have considerably higher multiaxial impact strength than microscale composites containing glass fibers, which are known to cause premature directional cracking under such loading.

A high molecular weight in the nylon matrix of nanocomposites is favorable for imparting ductility and toughness.²³ Due to chemical interactions, the smectic silicates

may reduce nylon molecular weight during the compounding or processing operation. The resulting loss of ductility and toughness could be reduced or reversed by melt processing such condensation polymers as nylon under dry conditions that build molecular weight while forming the final part. Alternately, the molecular weight of nylon nanocomposite pellets can be adjusted following compounding via solid state polymerization (SSP) by aging them in a hot, dry environment under the same conditions used to build molecular weight in the neat polymer.

Hybrid nanocomposites comprising combinations of reinforcements of different size scale and shape offer the opportunity for synergy in mechanical properties.²¹ The increase in modulus generated by the fiberglass component in a hybrid nanocomposite with a nanoscale layered silicate was found to be twice that achievable when the nanoclay is absent.

Nanocomposites Formed from Polyolefins Representing Low Polarity/Commodity Polymer Matrices

Polyolefin LSNs offer lower cost and easier processing, though at the expense of greater incompatibility between the polar inorganic and non-polar organic phases. Nanoscale reinforced olefinic thermoplastic vulcanizates are reviewed here as useful structures for exemplifying the basic concepts of polymer nanocomposites.

Thermoplastic vulcanizates (TPVs), vulcanized rubber/plastic blends made by dynamic vulcanization, in which the rubber phase is crosslinked while it is being compounded into a molten plastic phase, have become important materials of commerce because they exhibit rubber-like properties along with thermoplastic-like processibility.²⁴ Such materials comprise a distinct continuous thermoplastic phase and a dispersed phase in the form of cured micron-sized rubber particles. It has already been shown that polymer/clay nanocomposites can display a broad range of high performance properties by combining various polymer matrices and different types of organically treated layered silicates.²⁵ The combination of these two complementary technologies generates opportunities for synergistic performance enhancement beyond classical benchmarks.

Thermoplastic vulcanizate (TPV) nanocomposites are three-phase polymer systems in which nanoscale reinforcement can reside in either a continuous thermoplastic polymer phase or a discrete microscale crosslinked rubber phase. Their complex multiscale morphology simultaneously representing polymer blends and polymer composites allows them to serve as model systems for identifying, intensifying, and demonstrating the characteristic behaviors generally associated with melt blended polymer nanocomposites. The polypropylene-based TPV nanocomposites described in this review are distinguished by the phase location of the nanoscale layered silicate reinforcements, producing TPVs with reinforced plastic phase (TPV-RP) and TPVs with reinforced rubber phase (TPV-RR).

The tensile and rheological properties of TPV nanocomposites are dependent not only on the phase location of the silicate, but also on the type of silicate modification, silicate content, and the extent of the exfoliation/dispersion of the silicate layers. With increase of the organoclay loading, the tensile moduli of TPV nanocomposites generally increase, while the tensile strength tends to decrease due to the relatively weak interface between the nanoclay and polymer matrix, which becomes more critical as the contact area between the dispersed nanoclay and polymer matrix increases by tactoid impregnation.

This review begins with consideration of the polarity match between the polymeric matrix material and the organically treated nanoclay as a critical factor in determining

the properties of nanocomposites and then examines the reinforcement effects produced by isolation of the organoclay in TPV nanocomposites to either the continuous plastic phase or the dispersed rubber phase. The first case is accommodated by adding nanoclay to a commercial TPV, in which the dispersed rubber phase is already crosslinked and therefore solid, while nanocomposites of the second type were specially prepared.²⁶ In neither case is the nanoclay likely to migrate across the phase boundary during processing, thus distinguishing these PP/EPDM rubber TPVs from the more general PP/EPDM rubber blend nanocomposites described previously by Lee and Goettler.²⁷

Preparation

TPV-RP nanocomposites can be produced from commercially available pre-formed TPVs (for example, Santoprene[®] 101–80 thermoplastic elastomer comprising crosslinked ethylene-propylene diene rubber in PP (NTPV) and Geolast[®] 701–87 elastomeric alloy compatibilizing a polar nitrile-butadiene rubber with non-polar PP (PNTPV) from Advanced Elastomer Systems L. P.). The montmorillonite layered silicate is modified by ion exchange to alter its surface properties, for example with dimethyl dihydrogenated tallow ammonium ion (Cloisite[®] 20A organoclay from Southern Clay Products, Inc.) for organoclay suited to a NTPV or with an unsaturated methyl dihydroxyethyl tallow ammonium ion (Cloisite[®] 30B organoclay) suited for use in a PNTPV. Non-polar nanocomposites having a reinforced rubber phase (NTPV-RR) are derived by combining the nanoclay with rubber prior to its dynamic vulcanization in polypropylene.²⁸

Polarity Matching

Clay tactoid swelling in nanocomposites, as measured by the silicate layer separation, responds to the degree of interaction of the gallery walls (including both adsorbed cations and exposed silicate) with the surrounding matrix polymer. These effects are illustrated for both NTPV and PNTPV TPV-RP nanocomposites.

Structure. According to wide angle x-ray diffraction (WAXD), the gallery height in the 20A organoclay increases by 1.2 nm during the melt compounding of NTPV nanocomposites. The more polar hydroxyethyl surfactant of the 30B organoclay produces less attenuation of the inherently hydrophilic nature of pristine montmorillonite, generating lower enthalpic interactions between the organoclay and the polymeric matrix. The resulting lower gallery swell combined with degradation (see further discussion below) results in a gallery collapse of about that same magnitude to form a collapsed structure of greater disorganization. The TEM micrograph in Fig. 3 shows a swollen and partially exfoliated 20A nanoclay in the NTPV nanocomposite, in contrast to the highly aggregated structure of the 30B clay shown in Fig. 4 that results from the polarity mismatch between the surfactant on the clay and the polymer matrix. Type 20A organoclay in a PNTPV nanocomposite swells a little more than in the NTPV during melt compounding, showing a slight advantage of the (somewhat more polar) compatibilized matrix in promoting partial exfoliation, because the 20A gallery retains some hydrophilic character from the partially exposed silicate while the 30B organoclay swells about the same amount as in the NTPV case. The reduction of its gallery spacing in both the NTPV and PNTPV nanocomposites is attributed to the more severe degradation and elimination of its hydroxyethyl ammonium cation during melt processing above 150°C, as shown by TGA weight loss measurements.

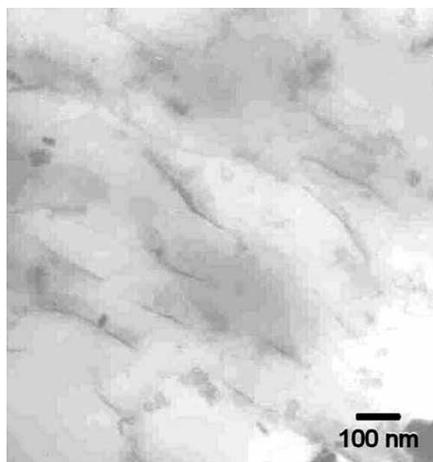


Figure 3. TEM micrograph of swollen and partially exfoliated 20A nanoclay in an NTPV nanocomposite.

Despite a reasonable match of polarity between a polyolefinic matrix and the surfactant on 20A organoclay, it is still impossible to obtain a complete exfoliation of the clay. The attractive forces in non-polar systems are relatively small. Furthermore, the organic modifier does not decorate the entire silicate surface comprising the walls of the galleries, thus allowing the nanoclay to maintain some hydrophilic character. However, even with these shortcomings, a respectable dispersion of nanoclay can still be accomplished under the action of the shearing forces generated during melt compounding.

Because of their residual hydrophilic nature, it is reasonable that large portions of both types of organoclay would migrate toward the polar nitrile rubber phase in PNTPV nanocomposites during melt mixing, even though the organoclay can not penetrate into the rubber phase because it is crosslinked and exists in a solid state.

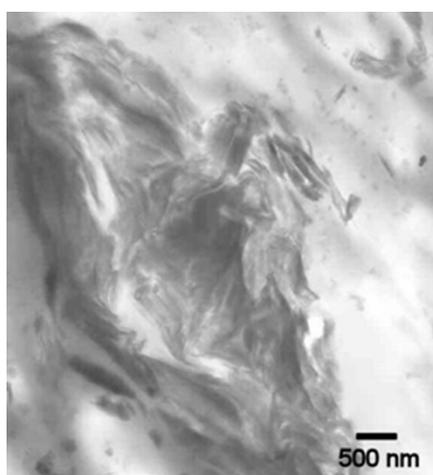


Figure 4. TEM micrograph of highly aggregated type 30B nanoclay in an NTPV nanocomposite.

The black specks in the TEM images of this effect shown in Fig. 5 represent particles of carbon black also present in the TPV.

Tensile Properties. The stress-strain curves of neither the neat TPVs nor their composites display the classical yield or necking behaviors that characterize semi-crystalline plastics. As the organoclay loading increases in NTPV nanocomposites, whose stress-strain curves are shown in Figs. 6a and 6b with nanoclay types 20A and 30B, respectively, the initial slope (Young's Modulus) increases significantly by up to 170% at 8 wt.% organoclay (2.0 vol.% silicate mineral) for the favorable 20A-NTPV combination but only slightly for the ill-matched 30B-NTPV, while strength and elongation decrease in both nanocomposites. Thus, less reinforcement prevails under the poorer interactions reflected in the reduced opening of the 30B nanoclay structure in the NTPV nanocomposite.

PNTPV nanocomposites increase in tensile modulus by up to 77% as the concentration of organoclay comprising either a non-polar or polar type surfactant increases to 8 wt.% loading, while both tensile strength and elongation at break gradually decrease. Surprisingly, the Young's Modulus of the PNTPV nanocomposite containing type 20A nanoclay still slightly exceeds that with type 30B nanoclay, reflecting the residual polar character of the organoclay even when it contains a non-polar surfactant. The graphs in Figs. 7a and 7b represent the stress-strain curves for the PNTPV nanocomposites, similarly to those in Figs. 6a and 6b for the NTPV nanocomposites.

It is noteworthy that the addition of 30B organoclay to the NTPV-RP nanocomposite is less detrimental to tensile strength than 20A organoclay. The poor compatibility leading to a weak interface between the organoclay and the PP matrix explains the lack of strengthening in either case. However, the poorly intercalated and dispersed state of the 30B nanoclay minimizes the extent of this weak interfacial area, resulting in less strength attenuation than produced by the better dispersed 20A organoclay, as shown in Figs. 8a and 8b. Although in the case of the PNTPV-RP nanocomposites the tensile strength still decreases as clay is added, the smaller decrease with the 30B vs. 20A organoclay, while greater than in the NTPV because of its better dispersion, can here also be attributed to its better interaction with the modified PP matrix.

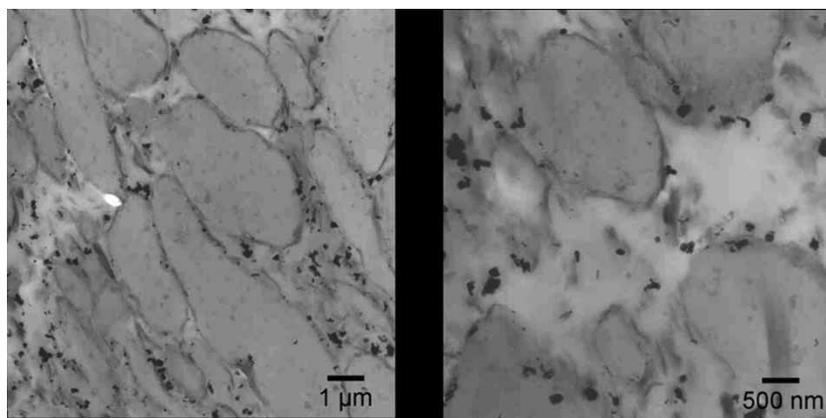


Figure 5. TEMs at two magnifications showing migration of organoclay toward the phase boundary in a PNTPV nanocomposite.

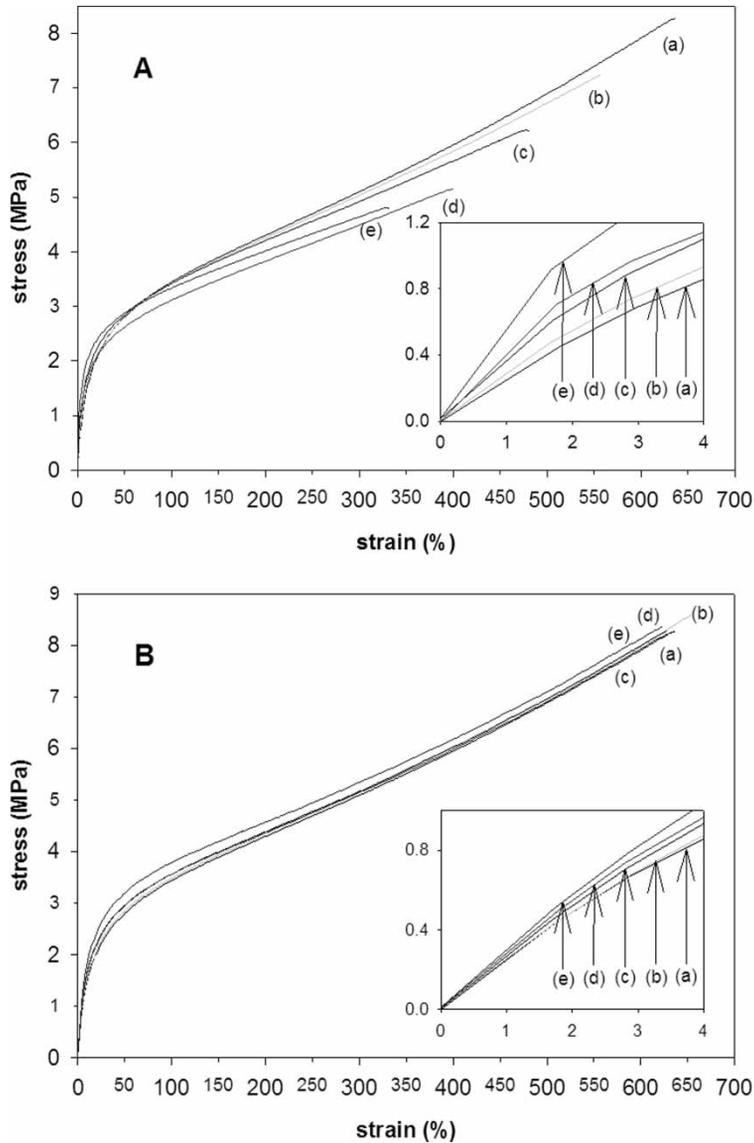


Figure 6. Tensile stress-strain curves of NTPV nanocomposites containing A: type 20A nanoclay, and B: type 30B nanoclay. Clay concentrations increase in increments of 2 wt.% treated clay from zero for curve (a) to 8 wt.% for curve (e).

Nanoclay Partitioning

In TPVs, the nanoscale reinforcements can be isolated in one of the phases. Since the deformation properties of the matrices in each phase will be different, the nanoscale reinforcement network will experience different stresses and strains depending on its location. In TPVs, the rubber phase will be the harder phase during the compounding or the processing of the nanocomposite, when the polypropylene is molten, while it represents the softer phase when the polypropylene solidifies after forming. Thus, strain

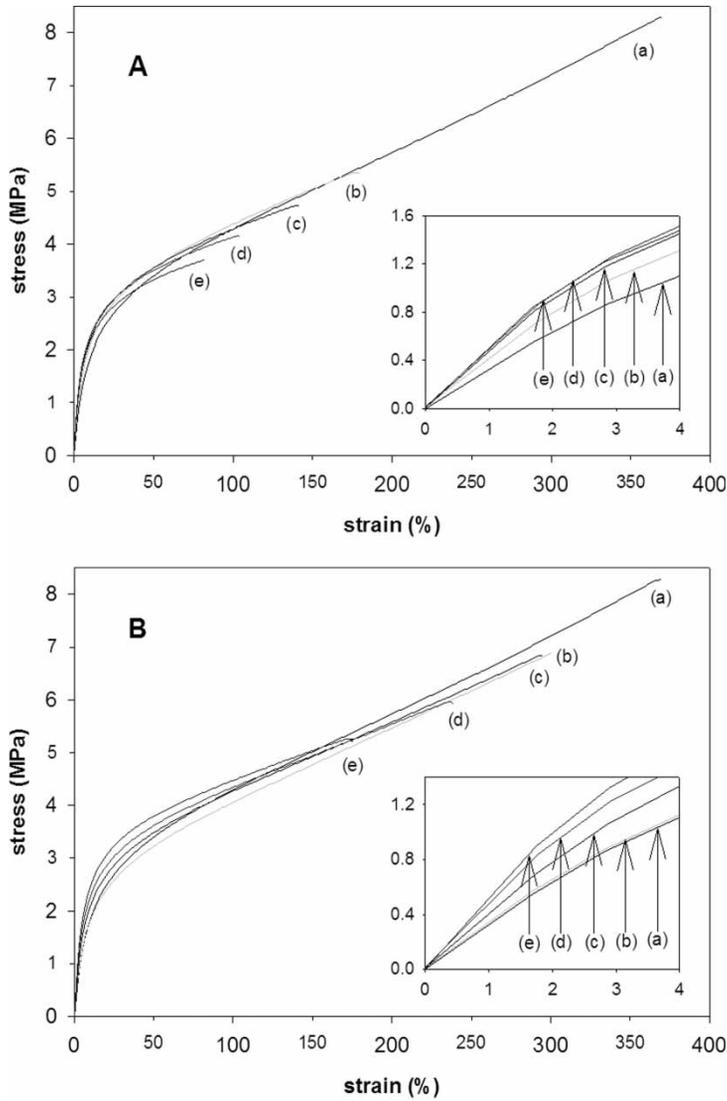


Figure 7. Tensile stress-strain curves of PNTPV nanocomposites containing A: type 20A nanoclay, and B: type 30B nanoclay. Clay concentrations increase in increments of 2 wt.% treated clay from zero for curve (a) to 8 wt.% for curve (e).

will be amplified in the continuous polypropylene phase during melt flow, but stress will be amplified in that phase under mechanical loading.

Melt Viscoelasticity. The dynamic viscosity of NTPV-RP nanocomposites, wherein the nanoclay is constrained to lie only in the continuous PP matrix, shows significant differences from the corresponding NTPV-RR nanocomposites, in which the nanoclay is dispersed only in the cured rubber phase, as shown in Fig. 9.²⁶ The origin of these

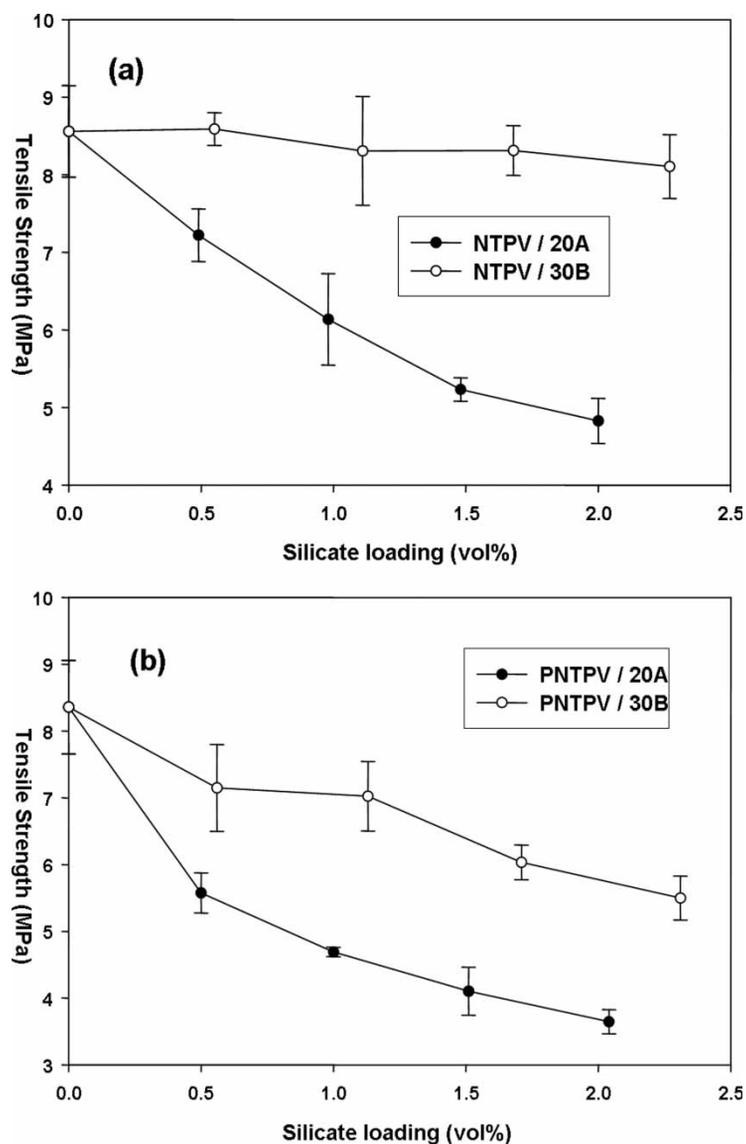


Figure 8. Tensile strength variations with nanoclay content in a: NTPV and b: PNTPV nanocomposites for nanoclay types 20A and 30B.

differences derives from strain amplification in the continuous polypropylene melt phase of greater deformability (lower viscosity) than the crosslinked rubber, which cannot flow.

Linear viscoelastic behavior obtains below 10% strain in both the TPV-RP and TPV-RR nanocomposite melts, but a drop in the complex viscosity for the TPV-RP at higher strain levels indicates network disintegration due to strain amplification in the mobile PP phase between the less deformable rubber domains. Furthermore, the dispersed nanoclay and associated polymer molecules can align into the shear plane under the amplified strain in the continuous molten matrix phase, thus reducing the resistance to deformation and flow. In fact, the viscosity of the TPV-RP nanocomposites containing

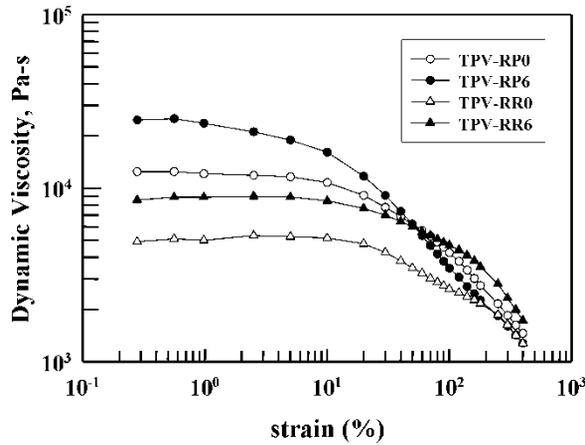


Figure 9. Comparison of the dynamic melt viscosities of NTPV nanocomposites containing the nanoclay of type 20A in either the continuous polypropylene or discrete rubber phase.

6% organoclay reverses position with that of the unreinforced matrix as the shear strain increases. In contrast, the complex viscosity of the TPV-RR nanocomposite remains larger than that of the neat TPV-RR at about the same multiple in all strain regions. Any nanoclay pre-dispersed in the cured rubber domains experiences a lower level of strain and affects the TPV rheology only through the microscale interaction of the rubber domains with the PP deformation and flow. It is further constrained by the cross-linked rubber network structure against any major deformations that could result in re-orientation.

The complex viscosities of both non-polar TPVs and their NTPV-RP and NTPV-RR nanocomposites exhibit Power Law viscosity behavior in the linear viscoelastic strain region over a wide range of frequency, as shown in Fig. 10.²⁶ The two types of nanocomposites exhibit about equal percentage increases in viscosity at all frequencies.

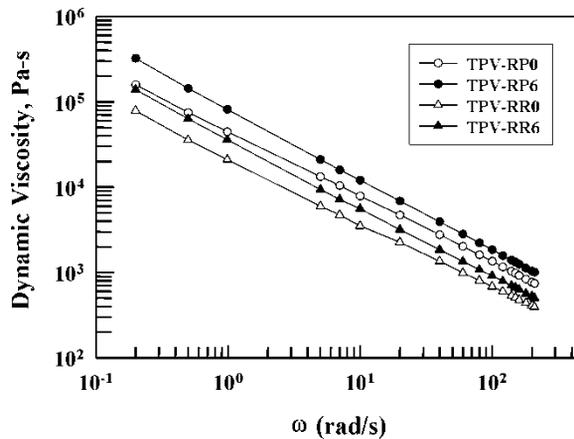


Figure 10. Power law viscosity behavior of both NTPV-RP and NTPV-RR nanocomposites containing type 20A nanoclay.

While both the TPV-RP and the TPV-RR nanocomposites display less fluidity than the corresponding neat TPV, as evidenced by their higher viscosity, the presence of nanoclay inclusions in the continuous PP matrix renders the TPV-RP nanocomposite melts more dissipative due to interfacial slippage at the high deformations generated in the continuous plastic phase. On the other hand, the presence of nanoclay in the cured rubber phase makes the melt more elastic by stiffening the solid rubber that acts like a filler at processing temperatures (Fig. 11).

It is interesting that the same changes to the dynamic viscosity of the TPV by adding nanoclay to the dispersed rubber phase can be duplicated by instead increasing the concentration levels of the curatives used to crosslink the rubber network. These effects are apparently tied to the size of the dispersed rubber phase, which develops while it is crosslinking during the compounding process. As the rubber becomes less deformable, due, for example, to the development of high crosslink density, it fractures into smaller domains, which can interact more strongly to restrict the deformation of the continuous polypropylene phase in which they are dispersed during flow.²⁸ Similar results, as shown in Fig. 12 obtain with nanoscale reinforcement of the dispersed rubber phase due to the nanoscale network developed between dispersed silicate layers.

In both cases, this effect adds to the greater flow resistance induced by the dispersed rubber phase being less deformable due to its higher modulus. Whether via restrictions on the rubber phase deformability or via refinement of the rubber phase domain size, the inclusion of nanoscale silicate platelets mimics the generation of a crosslinked molecular network in imparting similar characteristics to a heterogeneous blend of a discontinuous rubber phase in a continuous thermoplastic matrix.²⁹

In continuous flow, as compared with dynamic deformation, the TPV melt displays a lower viscosity even when the nanoclay is present in the rubber phase.³⁰ This behavior is attributed to microscale network breakdown under such high continuous strain. The effect is similar to that shown previously in Fig. 9 for the more sensitive nanoscale network breakdown at high dynamic strain when the nanoclay resides in the plastic phase. A

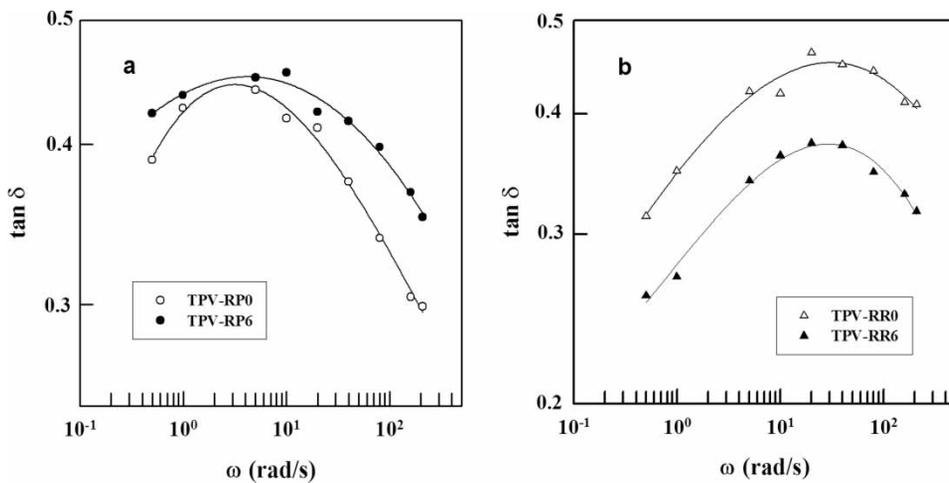


Figure 11. Melt viscoelasticity of a: type NTPV-RP and b: type NTPV-RR nanocomposites containing type 20A nanoclay.

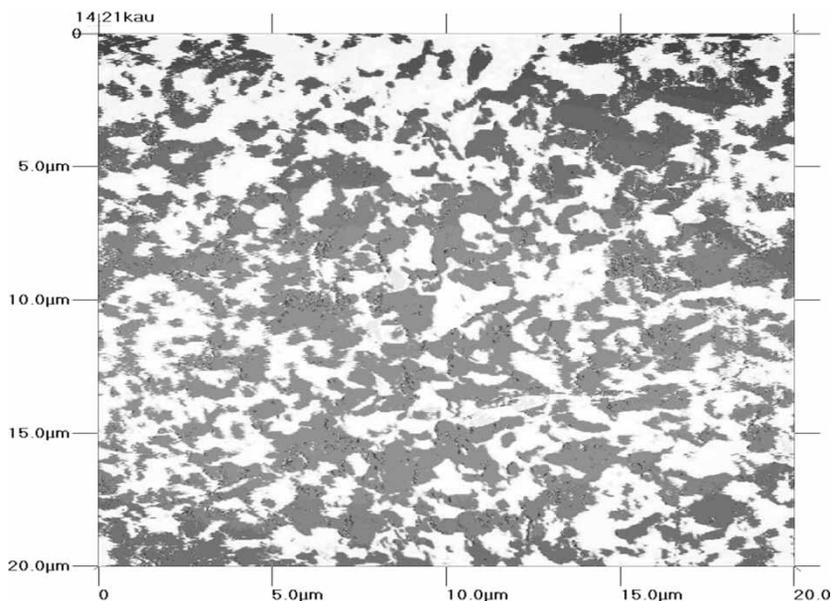


Figure 12. Atomic force microscopy (AFM) of NTPV-RR nanocomposite showing small white rubber domains.

complicating factor is that the presence of excess or fugitive waxy surfactant from the organic treatment of the clay could be acting as a flow lubricant.

Mechanical Properties. As the organoclay concentration increases, the Young's Modulus of the TPV-RP nanocomposite substantially increases by 100% vs. only 30% for the TPV-RR type, as shown in Fig. 13a. Since the discontinuous cured rubber domains are of lower modulus, deformation of TPV-RP nanocomposite generates stress amplification in the continuous PP matrix. The increase in stiffness of the TPV-RP nanocomposites is greater than in the TPV-RR nanocomposites because the platelets reinforce more efficiently against the stress buildup that occurs in the continuous plastic matrix of higher modulus at room temperature.

On the contrary, however, the TPV-RR nanocomposites more effectively maintain tensile strength (Fig. 13b) and elongation (Fig. 13c) as the clay content and the stiffness increase, while these ultimate properties decrease in the TPV-RP nanocomposites with increasing organoclay loading. The tensile strength and ultimate elongation are less in the TPV-RP nanocomposite than in the TPV-RR because of the same stress amplification in the reinforced continuous plastic phase, which causes it to prematurely rupture, fracturing the reinforced composite. Therefore, the TPV-RP nanocomposites stiffen efficiently but tend to fail prematurely as the silicate loading increases, leading to reductions in the ultimate strength and elongation, in comparison to the TPV-RR nanocomposites.

Thermal Stability

The thermal stability of organically modified smectic clays³¹ depends on the chemistry of the cationic surfactant. If it decomposes during processing, the surfactant can escape

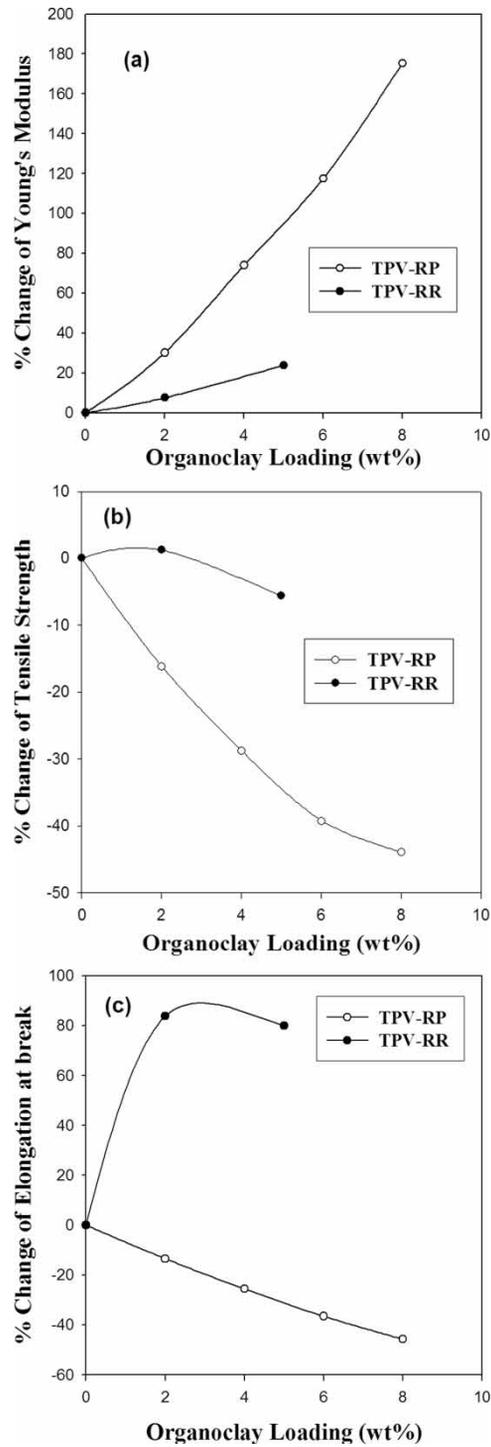


Figure 13. Comparison of reinforcing effects on tensile properties of NTPV nanocomposites with the nanoclay located in either the continuous polypropylene or the discrete rubber phase. a: Young's Modulus; b: tensile strength; c: ultimate elongation.

from the gallery, reducing gallery height in the compounded nanocomposite. But, any thermodynamic interaction between the polymer and the organoclay sufficiently strong to attract polymer chains into the gallery could compensate for the egress of the surfactants, resulting in constant or even increased platelet spacing as shown in Fig. 14. Increased mixing temperature, time, and speed are seen to result in only small changes to d_{001} spacing in PNTPV nanocomposites containing 6 wt% 30B organoclay. The change from a broad shoulder to a better defined peak at melt temperatures

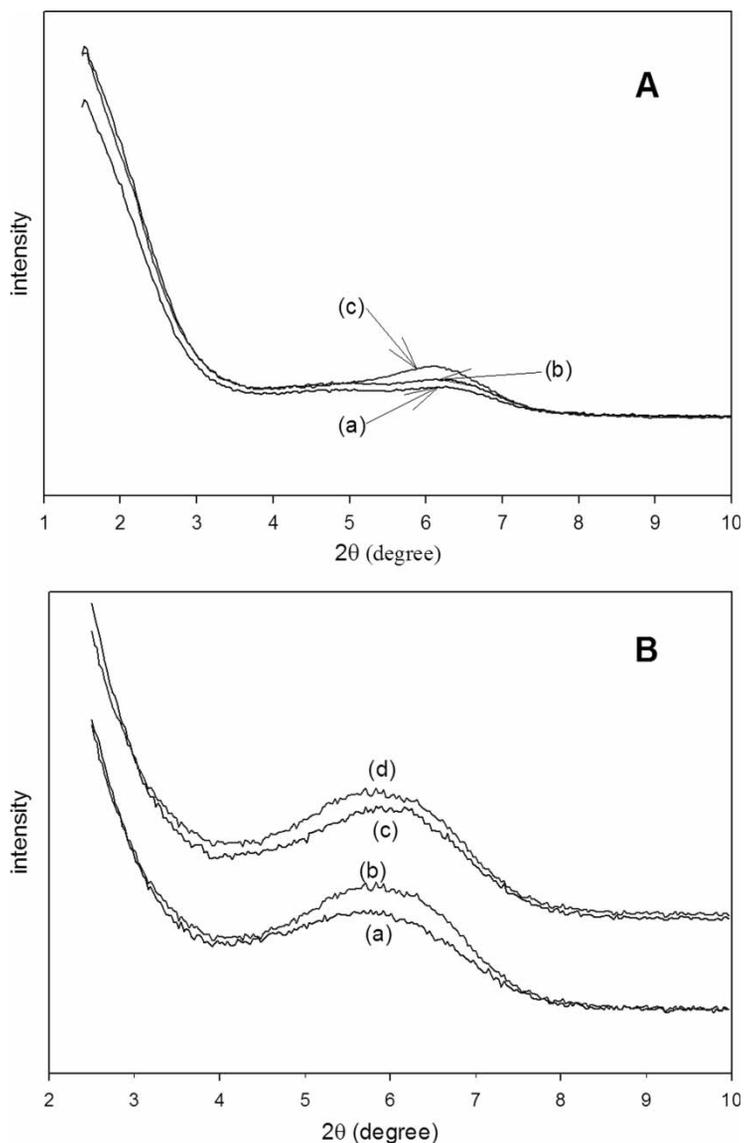


Figure 14. WAXD patterns of PNTPV nanocomposites with 6 wt% 30B clay identified as follows: A: formulation mixed at 60 rpm for 10 min at temperatures (a) 170°C (b) 190°C (c) 230°C; (B): formulation mixed at 230°C under regimens (a) 140 rpm for 10 min (b) 140 rpm for 20 min (c) 60 rpm for 20 min (d) 140 rpm for 20 min.

about 200° indicates that the organoclay forms larger and more well-defined tactoids as the processing temperature increases. It should be noted that a longer duration of mixing and higher rotational speed of the mixing blade produce greater aggregation of the platelets rather than dispersion.

In the absence of degradation, shearing of the residual tactoids can either reduce their thickness (number of layers) by peeling or just slide the constituent platelets relative to each other to generate a thinner bundle of higher aspect ratio. Under such shear and compressive stresses, the gallery could collapse with or without any loss of the surfactant as the long chains align and compact more closely at a smaller angle to the plane of the silicate layers, counteracting the dispersive action of the mixing.

While none of the ammonium cations are thermally stable, the totally hydrocarbon ammonium surfactant on type 20A organoclay remains intact in the range of compounding temperatures around 190°C. Phosphonium cationic surfactants, while known to be more thermally stable than the more common ammonium types used here, are of more limited utility because of their higher cost.

Selected Applications

Nanocomposites bring to the molded goods market significant increases in stiffness along with moderate improvements in tensile strength and heat distortion temperature at low mineral concentration that restricts density and helps maintain the excellent processing and surface appearance characteristics typical of unreinforced plastics. The low loading also minimizes abrasion during processing, thus reducing machine wear compared to other reinforcement systems. Molded LSNs typically exhibit near-isotropic planar properties and dimensional stability, thus reducing post-mold warpage.

Automotive (Mechanical Aspects)

The plastics content of automobiles has been increasing consistently since 1977 to 286 lb (7.3% of light vehicle weight) in 2000 and to 335 lb (8.3%) in 2004.³² Nanocomposites can bring enhancements in properties and performance along with savings in processing and fuel usage, due to weight reduction of more than 50% in selected parts. The largest volume today is in the substitution of layered silicate reinforced polypropylene for steel (large opportunity) or aluminum (lower advantage) in vehicle body panels.³² Potentially higher current cost could be reduced by new developments in clay treatment during refining and should also be offset by reduced energy and environmental impact.³³

Weight reduction is the primary driving factor, although tooling costs may also be lower than those for metal forming. The percentage in fuel savings is estimated to be half of the percentage weight reduction, and the corporate average fuel standards for pickup trucks, minivans, and SUV's is expected to increase from the current 21.6 to 24 mpg. Carbon fiber composites can lower structural part weights by as much as 60% while maintaining equivalent performance.³⁶ Although cost is still an issue, carbon nanotubes will eventually be able to bring about even greater weight reductions because of their higher mechanical properties. Particular applications are reduced battery weight in the hybrid cars of the future and nanoscale reinforced thermoplastic body panels. The key to acceptable performance of the latter lies in reducing their coefficient of thermal expansion along with the concomitant increases in modulus in order to insure acceptable fits to the metal parts which expand much less than the typical plastic. Plastics can also be used as glass replacements once nanoscale mineral coatings

become cost effective for hardening the plastic glazing to impart the necessary scratch resistance. The overall advantage of polymeric replacements for metal parts is the design freedom they bring through their easier formability, along with the integration of parts. Of course, there will always be some assembly required, even of plastics to each other, or to metals and glass.³²

In order to achieve the high levels of heat resistance required for automotive applications, the combination of nanoclay with fiberglass in a hybrid composite may be required. Such multiscale reinforcement offers an opportunity for synergy in mechanical and thermal properties.

Packaging (Permeation Barrier)

LSN's made from nylon MXD6, 6 or 6,6 are candidates for packaging film applications, where higher tensile strength, toughness, and improved barrier properties are important. Two- to six-fold reductions are possible in food packages through the incorporation of layered silicate nanoplatelets that increase the path tortuosity for permeating small molecules and/or modify the molecular morphology of the matrix polymer.⁵ The extent of the permeation resistance depends critically on the degree of exfoliation of the clay tactoids that determines the aspect ratio of the dispersed clay laminae. More modest reductions in water permeation have also been achieved. Nylon nanoclay compounds find application as permeation barriers in small-engine fuel tanks, cutting transmission rates by 75–80%.³⁴

Flame Retardancy

The barrier geometry of delaminated clays reduces the burn rate of nanocomposites,³⁵ but this advantage may be compromised by the presence of excessive organic treatment on the silicates. While positively reducing the rate of heat evolution, the dispersed nanoparticles at the same time may negatively impact UL burn test characteristics. One effect, that can be either positive or negative depending on the polymer matrix type and product application, is the reduced dripping resulting from the higher low shear rate viscosity of the nanocomposites.

Summary

While some mechanical properties of monolithic LSNs are typical of those available from conventionally reinforced materials, the balance of properties they can impart over a wide spectrum, combined with low weight and ease of processing, makes them viable in many markets. Automotive applications requiring high stiffness where appearance, moldability, dimensional conformance, or low weight is paramount would particularly benefit from these materials. While progress has been made, a better understanding of the mechanisms and conditions for optimizing mechanical performance is still needed to fully define the cost/performance advantage for polymer-based nanocomposites.

Controlling the enthalpic interaction between the polymer and the nanoclay is of utmost importance, and the structure of the resulting nanocomposite appears to depend strongly on achieving a polarity match. While polar-polar combinations involving dipole or hydrogen-based intermolecular bonding are most effective for clay delamination, an intercalated structure can even be achieved for a non-polar matrix with a non-

polar treated (Type 20A) organoclay under the application of shear during compounding. Nevertheless, a more highly swollen intercalation structure results from clay incorporation into a modified PP matrix, as in the case of the more polar PNTPV, due to the residual hydrophilicity of the organoclays. Thermodynamic interactions can be so strong as to drive migration of nanoclay to or across phase boundaries in inhomogeneous polymer blends.

When the nanoscale reinforcement is located in the continuous phase of an inhomogeneous polymer blend, it will be broken up by the high strains occurring there, as under high amplitude dynamic testing, continuous flow, or even high tensile deformations in the solid state. Thus, TPV-RP nanocomposites display reduction in ultimate elongation (and consequently strength) in tensile deformations while they at the same time demonstrate high degrees of stiffening in low strain deformations because of the stress amplification.

Encapsulation of the nanoscale reinforcement by the dispersed phase will maintain its reinforcing potential, producing increased viscosity and viscoelastic melt modulus under flow or high strain dynamic conditions, particularly when it is the harder phase and therefore experiences amplified stress rather than strain, as for example the crosslinked rubber in a molten TPV. When solid, such a blend with reinforcement in the now softer dispersed phase exhibits little stiffness or strength enhancement due to the low stress state in the surrounding matrix, but strength and elongation do not diminish because the rupture of the nanoscale network in the discontinuous soft phase does not result in a catastrophic fracture of the blend.

Consequently, nanoscale reinforcement of two-phase blends such as TPVs can be expected to usually generate poor ultimate tensile properties (strength and elongation), while the modulus can be greatly enhanced. In fact, when the interface between the organoclay and the polymer matrix is particularly weak, the tensile strength of TPV-RP nanocomposites can even vary inversely with the clay concentration or extent of dispersion (i.e., the amount of interface generated).

Viscosity is increased by nanoscale reinforcement in all cases, but melts behave more dissipatively when high deformation is imposed on the nanostructure, such as occurs in the continuous plastic phase of TPV-PR nanocomposites, while blends with a reinforced dispersed phase, such as the TPV-RR, behave more elastically due to reinforcement of the less deformed and perhaps stiffer dispersed phase. Nevertheless, viscosity is elevated more when reinforcement is contained in the rubber phase of a TPV, by restricting its deformation under flow, while any nanoscale network in the continuous phase would rupture under the high strain generated there, unless the deformation is dynamic and of suitably low amplitude.

LSNs find primary application in automotive body parts for mechanical performance at reduced weight that can translate into economic and environment advantage, in barrier films especially for food packaging, and in electrical components as environmentally friendly flammability retardants.

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