Intercalated Polypropylene Nanocomposites

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INTRODUCTION

Polypropylene (PP) is a versatile material whose use has significantly penetrated numerous sectors of the manufacturing, medical, and packaging industries. Polymer clay nanocomposites are multiphase organic/inorganic hybrid materials pioneered by researchers at Toyota,[1–3] which may exhibit significantly improved mechanical, flammability, and permeability properties relative to the base polymer matrix at very low clay loading. Although first demonstrated for nylon, polymer clay nanocomposites have since been prepared for a range of thermoplastic and thermoset polymers. However, the development of PP clay nanocomposites poses special challenges because of polypropylene's hydrophobicity. Nevertheless, possible commercial applications have motivated substantial research into strategies for the dispersion of clays in this technologically important polymer. This article reviews recent progress in the synthesis, preparation, and characterization of polypropylene nanocomposites. The resulting clay intercalation structure receives particular attention because most polypropylene nanocomposites prepared to date have yielded significant structures of this kind. After reviewing the state-of-the-art in polypropylene nanocomposite synthesis, characterization of clay and polymer morphology, and measurement of rheological and mechanical properties, we identify future research challenges that should be addressed to continue improving the possibility for commercial applications of these materials.

OVERVIEW

Mixtures of clay platelets and polymer chains compose a colloidal system. Thus in the melt state, the propensity for the clay to be stably dispersed at the level of individual disks (an exfoliated clay dispersion) is dictated by clay, polymer, stabilizer, and compatibilizer potential interactions and the entropic effects of orientational disorder and confinement. Anisometric dimensions of clay platelets also have implications for stability because liquid crystalline phases may form. In addition, the very high melt viscosity of polypropylene and the colloidal size of clay imply slow particulate dynamics, thus equilibrium structures may be attained only very gradually. Agglomerated and networked clay structures may also lead to nonequilibrium behavior such as trapped states, aging, and glassy dynamics.

Clay structure in polymer nanocomposites can be characterized as a combination of exfoliated platelets and intercalated tactoids. Clays themselves are layered silicate minerals with charged surfaces neutralized by interlayer counterions. Unless a liquid crystalline order disorder transition occurs, the exfoliated structure is spatially and orientationally disordered and the clay is dispersed at the level of individual disks. Intercalated clay retains interlayer ordering, at least within a particular tactoid; however, intergallery spacing is increased relative to natural clay because stabilizing surfactants, compatibilizers, and/or matrix polymers are infiltrated within the clay galleries. In the extreme case of clay/polymer matrix immiscibility, intercalation spacing not much greater than the clay and its counterion indicates negligible penetration of polymeric or compatibilizing species between clay layers. Clay platelets or tactoids themselves comprise the mesoscale structure of nanocomposites. Possible structures include that of a dispersed suspension, a percolated network, or a liquid crystal with orientational order. The hierarchy of possible states is depicted in Fig. 1.

The reinforcement of polypropylene and other thermoplastics with inorganic particles such as talc and glass is a common method of material property enhancement. Polymer clay nanocomposites extend this strategy to the nanoscale. The anisometric shape and approximately 1 nm width of the clay platelets dramatically increase the amount of interfacial contact between the clay and the polymer matrix. Thus the clay surface can mediate changes in matrix polymer conformation, crystal structure, and crystal morphology through interfacial mechanisms that are absent in classical polymer composite materials.

For these reasons, it is believed that nanocomposite materials with the clay platelets dispersed as isolated, exfoliated platelets are optimal for end-use properties. For example, the high aspect ratio of the exfoliated disk and their nanoscale width provide the greatest potential for solid-state mechanical property enhancement. Furthermore, the probability of defects and inclusions that can compromise the impact strength of composite materials is reduced by homogeneous dispersion at the nanoscale.

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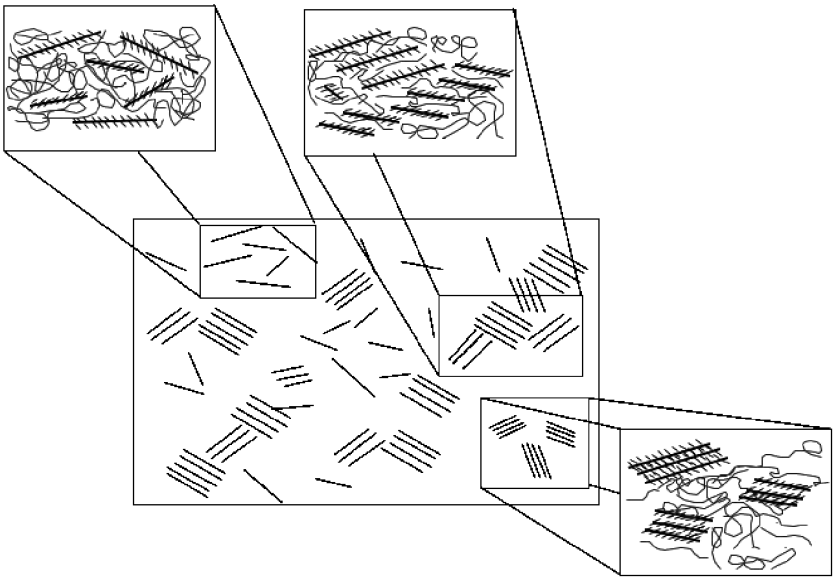

Fig. 1 Schematic of the hierarchy of clay structures in polypropylene nanocomposites of mixed morphology. Clay tactoids and exfoliated platelets comprise the mesoscale morphology. The internal intercalation structure of clay tactoids is determined by the compatibilizer and compounding conditions. (*View this art in color at www.dekker.com.*)

However, even intercalated clay nanocomposites yield valuable mechanical property enhancement and other useful end-use properties.

This review focuses on polypropylene–clay hybrid materials. Recent general reviews of polymer clay nanocomposites and their properties are available elsewhere.[4–6]

SYNTHESIS AND PREPARATION

Organophilic smectite clays can be introduced into a polymer matrix by methods involving in situ polymerization or melt mixing. Commonly used layered silicates of this kind include montmorillonite or synthetic sodium fluoromica. These clays typically have submicron disk radii and a width of about 1 nm. Before introducing them into the polymer host, the clays are rendered organophilic by the exchange of natural counterions for more hydrophobic species such as amine surfactants. The ion exchange treatment increases clay intergallery spacing because of the increased excluded volume of the hydrophobic surfactant. Amines with alkyl chain length in the range C_{12}–C_{18} are most effective in increasing the intercalation spacing of a fluoromica clay.[7] However, for polypropylene, these steps alone are insufficient to generate significant polypropylene intercalation or clay exfoliation.[8] The additional step of introducing a compatibilizer consisting of short-chain polypropylene with grafted maleic anhydride (PP-MA) functionality leads to enhanced intercalation and some exfoliation.[8–12] The blending has been accomplished by using a molecular diluent, such as toluene or trichlorobenzene, but this requires an additional step to remove the solvent.[13–15] Direct melt preparation by twin-screw extrusion or Braebender mixing is more consistent with potential commercial applications. Although the detailed mechanism of intercalation has yet to be elucidated, a qualitative explanation is that the polarity of the maleic anhydride yields more favorable interactions with organophilic clay. These interactions offset the entropic penalty for confinement of intercalated chains. There also exists the possibility of acid–base equilibrium reactions of the amine surfactant and maleic anhydride.

In efforts to manipulate the degree of dispersion and mechanical properties of polypropylene nanocomposites, researchers have varied clay surface treatment, compatibilizer molar mass, and compatibilizer acid content. The miscibility of the compatibilizer with neat polypropylene at melt temperatures,[10] higher compatibilizer acid content,[11] and larger compatibilizer loading[16] have been reported to be conducive to improved intercalation spacing and dispersion. However, the molar ratio of MA to PP-MA has also been proposed as an indicator of intercalation capability.[17] Kim et al.[18] found that maleic anhydride content above about 1.0% is undesirable because it leads to the reordering of clay layers. Other

intercalation and compatibilization agents, such as diethyl maleate graft polypropylene, semifluorinated alkyltrichlorosilane, and epoxypropyl methacrylate, have also been used to prepare polypropylene nanocomposites.[15,19,20] Recently, novel methods to promote dispersion by supercritical processing have been disclosed.[21]

The effect of melt compounding fluid dynamics on dispersion and end-use properties has, to date, received limited attention for the specific case of polypropylene nanocomposites. Lack of control of these parameters is likely a significant source of the substantial variation among literature reports of intercalation spacing and materials property characterization. A possible mechanism for the interaction of flow and clay dispersion has been provided by Fornes et al.[22] Their schematic, reproduced in Fig. 2, shows that when clay is dispersed by nonequilibrium mechanisms such as melt compounding, applied flow fields can act to rupture initially large clay aggregates, to refine tactoid dimensions, and to promote exfoliation by contacting the compatibilizer, clay, and matrix polymer.

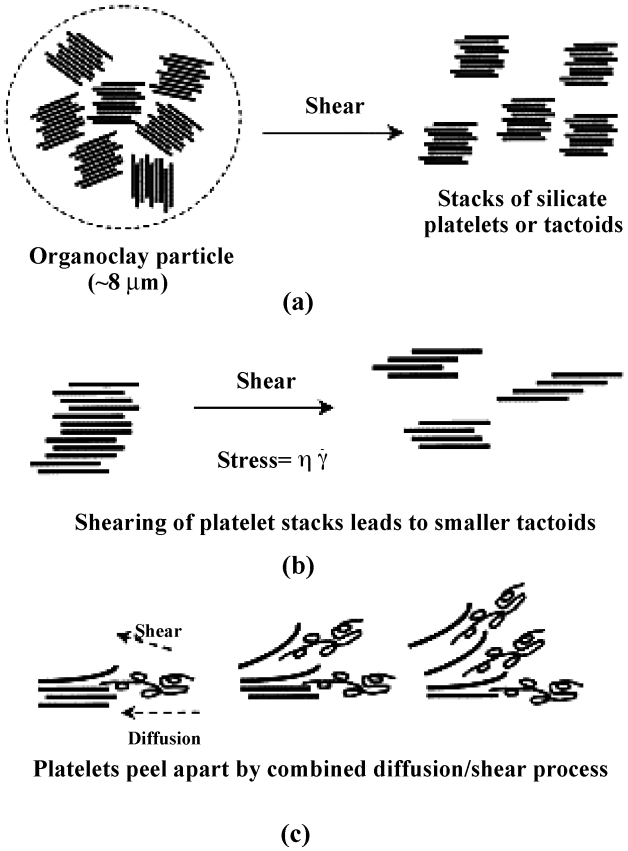

Fig. 2 The mechanisms by which the fluid dynamics of compounding may affect clay dispersion in polymer/clay nanocomposites. (From Ref. [22]. ©Elsevier Science Ltd., 2001.)

Although melt compounding is currently the principal method of polypropylene nanocomposite preparation, metallocene catalysis yields nanocomposites with high polymer isotacticity by in situ polymerization.[23] In situ polymerization to prepare polypropylene nanocomposites is potentially attractive because of the reduced need for compatibilizer treatments that are required in melt compounding. Although exfoliation and mechanical property enhancement are achieved by in situ polymerization, current reports indicate that the dispersion is not entirely homogeneous because micrometer-size, clay-rich particles persist after polymerization.[23]

CHARACTERIZATION OF CLAY INTERCALATION AND EXFOLIATION STRUCTURE

X-ray diffraction (XRD) and transmission electron microscopy (TEM) are principal methods for the interrogation of the intercalation structure of polymer clay nanocomposites. The ordered clay layers yield peaks in XRD intensity at scattering angles specified by the Bragg condition. For example, the spacing for naturally occurring Na-montmorillonite is about 1.1 nm. For one preparation,[24] when natural counterions were exchanged for stearylamine, the interlayer spacing increased to 2.1 nm, and melt compounding in polypropylene with a PP-MA compatibilizer further increased the intercalation spacing to 2.9 nm. In comparison, melt compounding of organophilic montmorillonite in neat polypropylene yields little increase in spacing,[10] thereby demonstrating the role of the PP-MA compatibilizer in promoting intercalation.

A major challenge in polymer nanocomposite characterization is to quantify dispersion in mixed systems comprised of both intercalated tactoids and exfoliated clay sheets, such as that depicted in Fig. 1. XRD alone offers little scope for such quantification;[25] however, quantitative analysis of sufficiently large regions of TEM micrographs is a promising way forward. Techniques for the quantification of the degree of exfoliation in polypropylene nanocomposites with mixed clay morphology have recently been discussed.[15,17] These methods should be more routinely employed to better permit the assessment of the relative performance of available synthetic and compounding strategies.

CRYSTALLIZATION STRUCTURE AND KINETICS

The mechanical properties of semicrystalline isotactic polypropylene materials that are formed by injection

molding are inferior to theoretical upper limits based on the polypropylene unit cell. Processing modifications designed to enhance the orientation of PP, such as low injection temperature or dynamic packing operation, can generate modest improvements in tensile modulus, even without the addition of conventional or nanoscopic filler. However, the traditional avenue to manipulate polypropylene properties is to reinforce the polymer with anisometric, high-modulus inorganic particles, such as talc. Another more promising possibility is to tailor the filler so as to induce morphological changes in the crystalline structure of polypropylene itself. These morphological changes will in turn have implications for mechanical properties such as modulus, strength, and toughness. In this scenario, the nanoscopic scale of the filler becomes relevant because smaller fillers, with their larger surface area-to-volume ratio, reside in close proximity to a greater percentage of the bulk PP than conventional fillers. There are a number of ways in which nanoscopic fillers, such as exfoliated or intercalated layered silicate, may influence the crystalline morphology of PP.

First, the crystalline unit cell may change. This effect has been observed in, for example, nylon 6 nanocomposites where addition of clay induces a change from α to γ crystalline form.[26] Three crystalline lattices for isotactic PP are known and there is evidence for preferential formation of the γ-phase in PP nanocomposites.[27,28]

Second, the crystalline morphology may be affected. For example, a transformation from spherulitic to oriented structure may occur. When crystallized at high shear rates, PP forms oriented structures that can hypothetically be modified by the presence of dispersed clay.[29] Fibrous crystalline morphology has also been reported in PP nanocomposites.[30]

Third, the degree of crystallization may change. As quantified by differential scanning calorimetry, it has been reported that the crystallinity of PP nanocomposites decreases modestly with increased clay content.[31]

Fourth, the characteristic size of crystalline morphology may be affected. Svoboda et al.[31] found that for nanocomposites with spherulitic structure, the average crystallite size decreases significantly with increasing clay content, possibly because of a role of clay in nucleation. Time-resolved light scattering and optical microscopy at the early stages of crystallization have also identified differences in the number of point nuclei in PP and PP nanocomposites.[32]

Fifth, the kinetics of crystallization may be modified. Time-resolved light scattering and differential scanning calorimetry studies have found that added intercalated clay can either increase or decrease characteristic crystallization times for polypropylene.[30–34] Interactions between an initially present nucleating agent, a PP-MA compatibilizer, and the dispersed clay generate complex crystallization kinetics, even in isothermal crystallization studies.[32] The data suggest that nanocomposite crystallization is dominated by the presence of a compatibilizer because nanocomposite data overlay PP/PP-MA blend measurements and crystallization times are not significantly affected by changes in clay loading.[32]

Interestingly, there have been preliminary reports of segregation of clay particles at the spherulitic boundary of maleated PP nanocomposites.[34] The possibility of polymer crystallization-induced changes in mesoscale clay morphology warrants further investigation because of the implications of such segregation for nanocomposite mechanical properties.

RHEOLOGY

The flow properties of polypropylene nanocomposites are relevant to processing operations such as injection molding. In addition, the viscoelastic response to linear and nonlinear deformation is a sensitive indicator of clay dispersion and interaction. Thus rheology can be used to evaluate the performance of various strategies for synthesizing and compounding polypropylene nanocomposites.

The compounding of organophilic clay and compatibilizer with polypropylene dramatically changes the linear viscoelastic response to shear deformation as quantified by the storage modulus G' and the loss modulus G''. Fig. 3 compares the G' and G'' of polypropylene and an intercalated nanocomposite with 4.8% inorganic clay. The

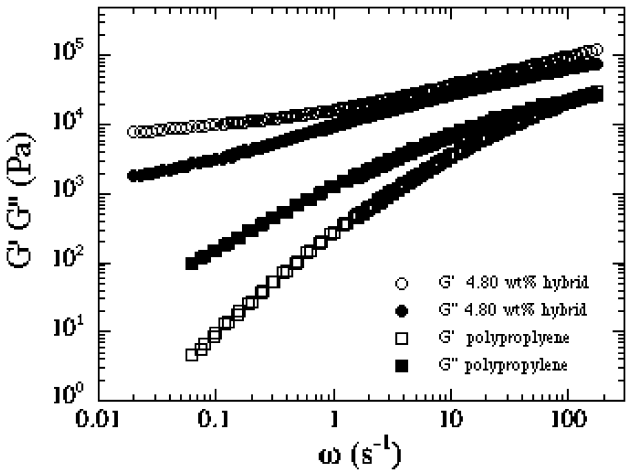

Fig. 3 The melt state linear viscoelastic moduli of 4.8 wt.% intercalated polypropylene nanocomposites. (From Ref. [24]. ©American Chemical Society, 2001.)

curves differ significantly, particularly at low frequencies. The apparent plateau in the nanocomposite data at low frequencies is consistent either with the response of a viscoelastic solid, or a viscoelastic liquid with a long relaxation time. The abrupt transition from liquidlike to solidlike linear viscoelasticity as clay loading is increased is suggestive of the generation of a gel or a network structure at a critical clay volume fraction. Because it is thought that such clay clustering is not likely to lead to optimal end-use properties such as modulus and toughness, measurement of melt state linear viscoelasticity is a useful tool to indirectly characterize the nanocomposite clay structure. Toward this end, qualitative effects of alkyl amine clay treatment and PP-MA compatibilizer acid content on clay structure have been assessed by rheological characterization.[17,24] Intercalation kinetics has also been estimated.[35] Koo et al.[36] generated maleated polypropylene nanocomposites with different intercalated and exfoliated clay morphologies by varying the matrix polymer molecular weight and found that the linear viscoelastic modulus G' was sensitive to morphological changes.

Nonlinear rheological characterization is predictive of nanocomposite behavior in typical processing operations such as injection molding. The presence of intercalated clay even at a clay loading of less than 5.0 wt.% can increase the viscosity by many orders of magnitude at low shear rates; however, at higher shear rates, which are more characteristic of processing conditions, viscosity enhancement is much more modest. This strong shear thinning behavior may have two origins: 1) anisometric particles such as rods and disks display shear thinning even at low concentrations because flow preferentially orients the particles in the flow direction; and 2) deformation applied to a gel cluster network can induce rupture of mechanical contacts and, consequently, shear thinning.[24]

Furthermore, nonlinear rheological measurements indicate that intercalated polypropylene nanocomposites possess fragile structures that are easily manipulated by flow. For example, the onset of strain dependence of the storage modulus occurs at an applied strain $\gamma_0 \sim 0.3$ for neat polypropylene; however, the transition for a 4.8 wt.% nanocomposite occurs at $\gamma_0 \sim 0.007$.[24] The startup of steady shear experiments after samples were presheared and then allowed to rest quiescently demonstrates that structures deformed during flow reestablish themselves on time scales longer than hundreds of seconds.[24] Linear viscoelasticity and XRD of intercalated polypropylene nanocomposites annealed for various periods provide additional evidence that structural evolution persists even longer—at least for many hours.[37,38] This evolution in linear and nonlinear rheology is likely related to strong attractive interactions, aging, and glassy dynamics in polymer nanocomposites that are not stably dispersed.[24,39,40]

Although shear rheology has been the focus of most studies to date, a report on the effect of uniaxial elongational flow on maleic anhydride-modified polypropylene nanocomposites has recently appeared.[41] Post facto TEM images indicate that at an elongational rate of 1.0 sec^{-1} and a Hencky strain of 1.3, clay platelets align perpendicular to the flow direction. Because flow in injection molding is comprised of a significant extensional component, these results point to the possibility of direction-dependent material properties in components molded by this method.

MECHANICAL PROPERTIES

Modulus, yield stress, toughness, and heat deflection temperature (HDT) are measures that characterize the potential for improved end-use performance of a polymer nanocomposite relative to the neat polymer or a traditional composite. Dispersed clay can affect the mechanical properties of a semicrystalline thermoplastic such as polypropylene in a number of ways. First, the high-modulus clay inclusions of anisotropic shape can reinforce the thermoplastic. This mechanism differs little from the classical picture of composite reinforcement. Thus in this view, the anisotropic shape of the discotic clay is important to mechanical property enhancement; however, the nanoscopic dimension of the clay plays no direct role. Second, inhomogeneous dispersion that results when even a small amount of micron-scale clay aggregates is present can seriously compromise the material's impact strength. Thus homogeneous dispersion at the submicron scale is desirable for successful practical application of polymer nanocomposites. Third, the nanoscale dimension of the clay filler leads to a large interfacial region at the clay surface. Thus even small amounts of clay can possibly mediate large changes in polymer matrix conformation, crystal structure, or crystal morphology. There is indirect evidence for a role of each of these conditions in mediating polypropylene nanocomposite mechanical properties.

The first reports of the successful preparation of polypropylene nanocomposites showed that the materials demonstrated only modest mechanical property enhancement relative to neat polypropylene or blends of polypropylene and PP-MA. At 7.2 wt.% inorganic clay content, 29% enhancement in tensile modulus was observed for the highest concentration of PP-MA studied.[12] Later work has generated improved tensile modulus enhancement. By varying the amine surfactant treatment and anhydride

content of the compatibilizer, Reichert et al.[7] generated an increase in tensile modulus at 5 wt.% organophilic clay loading, which was as large as 74%. If nanocomposites are prepared in a matrix of pure PP-MA, the relative material property enhancement is slightly greater. For example, at approximately 5 wt.% inorganic clay content, the tensile modulus increased by 86% relative to PP-MA; however, the nanocomposite modulus is still inferior to that typical of neat polypropylene.[42] Polypropylene nanocomposites prepared by in situ polymerization using metallocene catalysis have generated a >100% enhancement in tensile modulus at 10.5 wt.% clay loading.[23] A similar performance has been obtained for in situ polymerized PP synthesized by the Ziegler–Natta catalysis.[43] These improvements exceed results for other anisometric fillers, such as talc, which are not nanoscopic. For example, Walter et al.[44] found that more than 30 wt.% talc was required to yield modulus enhancement comparable to clay nanocomposites with less than 7 wt.% inorganic content.

Although significant progress in enhancing polypropylene nanocomposite tensile moduli has been achieved, this improvement is offset by the reduced elongation at break and impact strength of these materials. Elongation at break, which is a determinant of toughness, has been reported to fall by more than an order of magnitude relative to neat PP on melt mixing with organophilic clays and compatibilizers.[7,12] The changes have a number of possible origins: 1) the reduced toughness of PP-MA relative to PP because of its low molar mass; 2) the improved adhesion between the polymer matrix and the intercalated clay induced by the compatibilizer, which contributes to yielding a more brittle material; and 3) immiscible aggregates of clay acting as defects and stress concentrators, which contribute to failure even if they are present only at low concentrations.

A limitation to the penetration of polypropylene into various component and market categories is its low upper use temperature. One measure of this property is the HDT. At 8 wt.% clay, the HDT of polypropylene nanocomposites synthesized by in situ Ziegler–Natta catalysis is 40°C greater than for pure PP.[43]

CONCLUSION

Recent research has generated advances in polypropylene nanocomposites that are sufficient to motivate new technological applications. For example, PP-based nanocomposites have been developed for application as exterior automotive components.[45] Cone calorimetry measurements of peak heat release rate from maleated PP nanocomposites with 4% loading are reduced by 75% relative to the pure polymer.[46] These improvements are relevant to applications requiring reduced flammability.

Yet, relative to other thermoplastic nanocomposites, such as nylon 6, the improvement in end-use properties for polypropylene nanocomposites has been modest. Thus research in the areas of synthesis and, especially, compounding, which are aimed at closing this performance gap, is necessary. Alternatively, improved fundamental understanding of the detailed interactions and chemistry between clays, amine surfactants, and maleic anhydride compatibilizers can help elucidate the complex thermodynamics of clay dispersion. In addition, noting that many synthesized PP nanocomposites are likely to exist as nonequilibrium structures, research into the aging and rejuvenation of these mesoscale structures is warranted. Furthermore, better methods to characterize the full distribution and hierarchy of structural states present in PP nanocomposites are required because, for example, rare aggregates can seriously compromise nonlinear mechanical properties such as toughness, yield stress, and elongation at break. Finally, the interaction between clay platelets and polymer crystallization requires further attention because these interactions are likely a significant determinant of the end-use properties of polypropylene nanocomposites.

REFERENCES

1. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Mechanical properties of nylon 6–clay hybrid. J. Mater. Res. **1993**, *8* (5), 1185–1189.
2. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. Swelling behavior of montmorillonite cation exchanged for ω-amino acids by ε-caprolactam. J. Mater. Sci. **1993**, *8* (5), 1174–1178.
3. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Synthesis of nylon 6–clay hybrid. J. Mater. Res. **1993**, *8* (5), 1179–1184.
4. Vaia, R.; Giannelis, E.P. Polymer nanocomposites: Status and opportunities. MRS Bull. **2001**, *26* (5), 394–401.
5. Alexandre, M.; Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. Mater. Sci. Eng., R Rep. **2000**, *28* (1–2), 1–63.
6. Krishnamoorti, R.; Yurekli, K. Rheology of polymer layered silicate nanocomposites. Curr. Opin. Colloid Interface Sci. **2001**, *6* (5–6), 464–470.
7. Reichert, P.; Nitz, H.; Klinke, S.; Brandsch, R.;

Thomann, R.; Mulhaupt, R. Poly(propylene)/organoclay nanocomposite formation: Influence of compatibilizer functionality and organoclay modification. Macromol. Mater. Eng. **2000**, *275*, 8–17.
8. Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Kato, M.; Tsukigase, A.; Usuki, A. Polyolefin–clay hybrids based on modified polyolefins and organophilic clay. Macromol. Mater. Eng. **2000**, *280* (7–8), 76–79.
9. Usuki, A.; Kato, M.; Okada, A.; Kurauchi, T. Synthesis of polypropylene–clay hybrid. J. Appl. Polym. Sci. **1997**, *63* (1), 137–139.
10. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. Preparation and mechanical properties of polypropylene–clay hybrids. Macromolecules **1997**, *30* (20), 6333–6338.
11. Kato, M.; Usuki, A.; Okada, A. Synthesis of polypropylene oligomer–clay intercalation compounds. J. Appl. Polym. Sci. **1997**, *66* (9), 1781–1785.
12. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. Preparation and mechanical properties of polypropylene–clay hybrids using a maleic anhydride-modified polypropylene oligomer. J. Appl. Polym. Sci. **1998**, *67* (1), 87–92.
13. Kurokawa, Y.; Yasuda, H.; Oya, A. Preparation of a nanocomposite of polypropylene and smectite. J. Mater. Sci. Lett. **1996**, *15* (17), 1481–1483.
14. Kurokawa, Y.; Yasuda, H.; Kashiwagi, M.; Oyo, A. Structure and properties of a montmorillonite/polypropylene nanocomposite. J. Mater. Sci. Lett. **1997**, *16* (20), 1670–1672.
15. Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T.C. Polypropylene/montmorillonite nanocomposites. Review of the synthetic routes and materials properties. Chem. Mater. **2001**, *13* (10), 3516–3523.
16. Xu, W.B.; Liang, G.D.; Wang, W.; Tang, S.P.; He, P.S.; Pan, W.P. PP-PP-g-MA-Org-MMT nanocomposites: 1. Intercalation behavior and microstructure. J. Appl. Polym. Sci. **2003**, *88* (14), 3225–3231.
17. Marchant, D.; Jayaraman, K. Strategies for optimizing polypropylene–clay nanocomposite structure. Ind. Eng. Chem. Res. **2002**, *41* (25), 6402–6408.
18. Kim, K.N.; Kim, H.; Lee, J.W. Effect of interlayer structure, matrix viscosity and composition of a functionalized polymer on the phase structure of polypropylene–montmorillonite nanocomposites. Polym. Eng. Sci. **2001**, *41* (11), 1963–1969.
19. Garcia-Lopez, D.; Picazo, O.; Merino, J.C.; Pastor, J.M. Polypropylene–clay nanocomposites: Effect of compatibilizing agents on clay dispersion. Eur. Polym. J. **2003**, *39* (5), 945–950.
20. Liu, X.H.; Wu, Q.J. PP/clay nanocomposites prepared by grafting–melt intercalation. Polymer **2001**, *42* (25), 10013–10019.
21. Manke, C.W.; Gulari, E.; Mielewski, D.F.; Lee, E.C. System and Method of Delaminating a Layered Silicate Material by Supercritical Fluid Treatment. US Patent 6,469,073, October 22, 2002.
22. Fornes, T.D.; Yoon, P.J.; Keskkula, H.; Paul, D.R. Nylon 6 nanocomposites: The effect of matrix molecular weight. Polymer **2001**, *42*, 9929–9940.
23. Sun, T.; Garces, J.M. High-performance polypropylene–clay nanocomposites by in-situ polymerization with metallocene/clay catalysts. Adv. Mater. **2002**, *14* (2), 128+.
24. Solomon, M.J.; Almusallam, A.S.; Seefeldt, K.F.; Somwangthanaroj, A.; Varadan, P. Rheology of polypropylene/clay hybrid materials. Macromolecules **2001**, *34* (6), 1864–1872.
25. Morgan, A.B.; Gilman, J.W. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study. J. Appl. Polym. Sci. **2003**, *87* (8), 1329–1338.
26. Lincoln, D.M.; Vaia, R.A.; Wang, Z.-G.; Hsiao, B.S.; Krishnamoorti, R. Temperature dependence of polymer crystalline morphology in nylon 6/montmorillonite nanocomposites. Polymer **2001**, *42*, 9975–9985.
27. Maiti, P.; Nam, P.H.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. The effect of crystallization on the structure and morphology of polypropylene/clay nanocomposites. Polym. Eng. Sci. **2002**, *42* (9), 1864–1871.
28. Nam, P.H.; Maiti, P.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites. Polymer **2001**, *42* (23), 9633–9640.
29. Liedauer, S.; Eder, G.; Janeschitz-Kriegl, H. On the limitations of shear induced crystallization in polypropylene melts. Int. Polym. Process. **1995**, *X*, 243–250.
30. Hambir, S.; Bulakh, N.; Kodgire, P.; Kalgaonkar, R.; Jog, J.P. PP/clay nanocomposites: A study of crystallization and dynamic mechanical behavior. J. Polym. Sci. B Polym. Phys. **2001**, *39* (4), 446–450.
31. Svoboda, P.; Zeng, C.; Wang, H.; Lee, J.; Tomasko, D.L. Morphology and mechanical properties of polypropylene/organoclay nanocomposites. J. Appl. Polym. Sci. **2002**, *85*, 1562–1570.
32. Somwangthanaroj, A.; Lee, E.C.; Solomon, M.J. Early stage quiescent and flow-induced crystallization of intercalated polypropylene nanocomposites

by time-resolved light scattering. Macromolecules **2003**, *36* (7), 2333–2342.
33. Ma, J.; Zhang, S.; Qi, A.; Li, G.; Hu, Y. Crystallization behaviors of polypropylene/montmorillonite nanocomposites. J. Appl. Polym. Sci. **2002**, *83*, 1978–1985.
34. Maiti, P.; Nam, P.H.; Okamoto, M.; Hasegawa, N.; Usuki, A. Influence of crystallization on intercalation, morphology, and mechanical properties of polypropylene/clay nanocomposites. Macromolecules **2002**, *35* (6), 2042–2049.
35. Li, J.; Zhou, C.X.; Wang, G.; Zhao, D.L. Study on kinetics of polymer melt intercalation by a rheological approach. J. Appl. Polym. Sci. **2003**, *89* (2), 318–323.
36. Koo, C.M.; Kim, M.J.; Choi, M.H.; Kim, S.O.; Chung, I.J. Mechanical and rheological properties of the maleated polypropylene-layered silicate nanocomposites with different morphology. J. Appl. Polym. Sci. **2003**, *88* (6), 1526–1535.
37. Galgali, G.; Ramesh, C.; Lele, A. A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites. Macromolecules **2001**, *34* (4), 852–858.
38. Lele, A.; Mackley, M.; Galgali, G.; Ramesh, C. In situ rheo-x-ray investigation of flow-induced orientation in layered silicate-syndiotactic polypropylene nanocomposite melt. J. Rheol. **2002**, *46* (5), 1091–1110.
39. Fielding, S.M.; Sollich, P.; Cates, M.E. Aging and rheology in soft materials. J. Rheol. **2000**, *44* (2), 323–369.
40. Ren, J.; Casanueva, B.; Mitchell, C.; Krishnamoorti, R. Disorientation kinetics of aligned polymer layered silicate nanocomposites. Macromolecules **2003**, *36* (11), 4188–4194.
41. Okamoto, M.; Nam, P.H.; Maiti, P.; Kotaka, T.; Hasegawa, N.; Usuki, A. A house of cards structure in polypropylene/clay nanocomposites under elongational flow. Nano Lett. **2001**, *1* (6), 295–298.
42. Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A. Preparation and mechanical properties of polypropylene–clay hybrids based on modified polypropylene and organophilic clay. J. Appl. Polym. Sci. **2000**, *78* (11), 1918–1922.
43. Ma, J.S.; Qi, Z.N.; Hu, Y.L. Synthesis and characterization of polypropylene/clay nanocomposites. J. Appl. Polym. Sci. **2001**, *82* (14), 3611–3617.
44. Walter, P.; Mader, D.; Reichert, P.; Mulhaupt, R. Novel polypropylene materials. J. Macromol. Sci., Pure Appl. Chem., A **1999**, *36* (11), 1613–1639.
45. Sherman, L.M. Nanocomposites: A little goes a long way. Plast. Technol. **1999**, *45* (6), 52–57.
46. Gilman, J.W.; Jackson, C.L.; Morgan, A.B.; Harris, R.; Manias, E.; Giannelis, E.P.; Wuthenow, M.; Hilton, D.; Phillips, S.H. Flammability properties of polymer–Layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chem. Mater. **2000**, *12* (7), 1866–1873.

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