Batch and Continuous Processing of Polymer Layered Organoclay Nanocomposites

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ABSTRACT: The generation of nanocomposites upon intercalation and exfoliation of clay tactoids using melt compounding is a difficult process. In this study various polymeric binders were melt compounded with organophilic clay particles using myriad methods, including sonication, batch mixing, and twin screw extrusion. The characterization of the compounded samples employing X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed that there is little intercalation and exfoliation when nonpolar poly(dimethyl siloxane) (PDMS) and poly(propylene) (PP) binders were used, resulting in no significant changes in the dynamic properties of the suspensions upon small-amplitude oscillatory shearing. On the other hand, when polar polymeric binders, i.e., silanol terminated poly(dimethyl siloxane) and maleic anhydride modified PP were used for compounding with organoclays, TEM and XRD revealed intercalation with some partial exfoliation, resulting in increases in the dynamic properties, along with sensitivity to the thermomechanical history during processing. These results reinforce earlier findings, which suggest that the interfacial properties between the organoclays and the polymeric binders need to be tailored properly to enable the generation of nanocomposites of organoclays using melt compounding technologies. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1391–1398, 2007

Key words: nanocomposites; nanoparticles; organoclay; melt compounding

INTRODUCTION

Since 1970s a number of processes are available to enable the formation of nanocomposites from various silicates.[1–3] Such nanocomposites offer improved mechanical properties,[4–6] reduced gas permeability,[4,7–9] decreased thermal expansion coefficient,[4] increased solvent resistance,[10,11] and enhanced ionic conductivity.[12]

There are myriad routes to the manufacture of layered polymer–silicate nanocomposites, which exhibit at least one dimension of the clay particles in the nanometer range.[13] These include, first, the use of solvents together with polymer or the prepolymer to allow the solvent to delaminate the silicate layers; second, *in situ* polymerization of the monomer with the silicates to enable the monomer to delaminate the silicates with the polymerization occurring in between the delaminated sheets of silicate; third, compounding of the silicates with compatible polymer melt binders to allow the binder to intercalate and sometimes exfoliate the silicate layers; and fourth, the template synthesis in which aqueous solutions containing the polymer and silicates are used to enable the polymer to control the crystallization of the silicates and to be trapped in between the growing crystals.[13]

The direct melt compounding of polymer and clay without using organic solvents is a popular method for the generation of nanocomposites.[5,14–20] This processing approach is very suitable for use in industrial and commercial applications, since the final compounded products can easily be further extruded or molded to a final "net shape," all without the use of solvents.[21,22] However, the surfaces of the silicates need to be modified (to organophilic) to allow the polymer melt to intercalate.

A number of polymeric binders can be used in the generation of clay-based nanocomposites. Poly(dimethyl siloxane) (PDMS) [$Si(CH_3)_2$–O–] exhibits various attractive properties such as low surface energy, low toxicity, high optical transparency, and good chemical and thermal stability. However, the mechanical properties of PDMS need to be improved upon being reinforced with inorganic fillers. The generation of nanocomposites using organophilic clays offers particular promise.[10,11,23]

The polyolefin-based nanocomposites offer various advantages for different applications because of their low cost, relatively high mechanical properties, and in general, the commercial potential of the market of various polyolefin products.[24–32] Earlier studies have indicated that the exfoliation and dispersion of clay

platelets can be achieved especially upon the introduction of polarity to nonpolar polyolefins, for example, by the use of maleic anhydride for poly(propylene) (PP).[24–28,30,31,33]

The issue of the effect of the molecular weight of the polymer melt on the kinetics of the intercalation and exfoliation process has been investigated by Giannelis and coworkers[15] and Paul and coworkers.[34–36] The conclusions of these two sets of studies are different; that is, Paul and coworkers have determined that the intercalation and exfoliation occur more readily with increasing molecular weight of nylon 6 under typical melt mixing conditions in extrusion. On the other hand, Giannelis and coworkers[15] have determined that the effect of increasing of the molecular weight for polystyrene binder is to render the intercalation and exfoliation more difficult to achieve. However, it should be noted that the studies of Giannelis and coworkers[15] have taken place under quiescent (static) conditions whereas the compounding of the clays with the polymeric binders has taken place in the confines of twin screw extrusion (TSE) processing (thus under relatively high shear rate conditions) in the experiments of Paul and coworkers.[34–36]

In the following paragraphs the melt compounding route to generation of nanocomposites is further elucidated by focusing on the processing of polar and nonpolar PDMS and PP resins compounded with organophilic clays using sonication, intensive batch mixing, and twin screw extrusion.

MATERIALS AND EXPERIMENTAL

Materials

Two different grades of poly(dimethyl siloxane) (PDMS) and poly(propylene) (PP), were used. First PDMS used was a high-molecular-weight, nonpolar nature PDMS gum, SE 63, obtained from GE Silicones (Waterford, NY). The second PDMS used was a low-molecular-weight (M_w = 19,000 and M_w/M_n = 1.5), polar, i.e. silanol terminated, PDMS, PS 342.5, obtained from United Chemical Technologies (Bristol, PA). This PDMS was used in the melt compounding studies of Giannelis and coworkers.[10,11] For curing of low-molecular-weight PDMS tetraethylorthosilicate (TEOS from Sigma-Aldrich) was used as a crosslinking agent and tin (II) ethylhexanoate (from Gelest, Morrisville, PA) was used as a catalyst. For every gram of polymer, 30 μL of TEOS and 5 μL of tin (II) ethylhexanoate were used.[10,11]

The first PP used was not modified (Pro-fax 6331) and was procured from Basell Polyolefins (Elkton, MD). Its melt flow index (according to ASTM D 1238 method, at 230°C, load 2.16 kg) is 14 g/10 min, its solid density is 0.9 g/cm^3 (according to ASTM D 792 method, at 23°C), and its melting temperature is

167.4°C. The second PP-based binder was polar in nature and was a maleic anhydride functionalized PP copolymer, PPMA, obtained from Exxon-Mobil Chemical Company (Houston, TX), Exxelor PO1015. Its maleic anhydride level is typically in the range of 0.25–0.5% by weight [Exxelor PO1015 technical data sheet]. Its melt flow index is 150 g/10 min, (ASTM D 1238 method, at 230°C, load 2.16 kg). It has a solid density of 0.9 g/cm^3 (DIN 53479 method) and exhibits a melting temperature of 144.8°C.

Two organophilic clays, i.e., a dimethyldialkyl ammonium modified montmorillonite clay and an octadecylamine modified montmorillonite clay, were procured from Nanocor, Illinois (Nanomer-I.44P and Nanomer-I.30E respectively). The dimethyldialkyl ammonium modified montmorillonite clay contained 60–70 wt % montmorillonite clay and 30–40 wt % dimethyldialkyl ammonium and exhibited a specific gravity of 1.44. The octadecylamine modified montmorillonite clay contained 70–75 wt % montmorillonite clay and 25–30 wt % octadecylamine and exhibited a specific gravity of 1.7.

Batch mixing

A Haake 300-mL internal intensive batch mixer was used to compound the organoclay particles with the high-molecular-weight PDMS, PP, and PPMA binders to allow comparisons with the twin screw extrusion (TSE) process. The batch mixer was used with roller blade type agitators, which are typically used for high intensive mixing applications commonly utilized for compounding of thermoplastic and thermosetting resins with rigid fillers.

Ultrasonic mixing

Low-molecular-weight PDMS and organoclay were ultrasonically mixed at ambient temperature with an ultrasonic bath at a frequency of 48 kHz and at 50 W for various durations, followed by TSE.

Twin screw extrusion with a mini-twin screw extruder

A 7.5-mm co-rotating fully intermeshing twin screw extruder was used (ME7.5 obtained from Material Processing and Research Inc., Hackensack, NJ). This extruder is reported to be the smallest fully functional twin screw extruder of its kind and was designed and built specially to process nanoparticles. The screws were designed to offer three mixing and pressurization zones, as shown in Figure 1. The twin screw extruder was used in conjunction with various different types of loss-in-weight and volumetric solid feeders (Brabender and K-Tron), infusion pumps or a Bio-Chem fixed displacement diaphragm pump. An Infra-
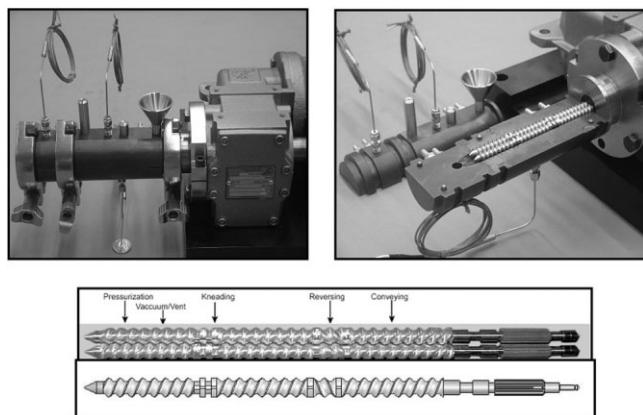
Figure 1 7.5 mm fully intermeshing co-rotating twin screw extruder used in the melt compounding.

metrics thermal imaging camera was used to monitor the temperature of the extruded strands. The twin screw extruder was mated with a rectangular slit die with dimensions of land length of 36.8 mm, slit gap of 1 mm, and slit width of 10 mm.

Structural characterization

X-Ray diffraction (XRD) patterns were obtained using a Rigaku Miniflex diffractometer equipped with Cu K_α source (1.5406 Å) operating at 30 kV and 15 mA. The diffraction patterns were collected in the Bragg angle, 2θ, range of 1–15° at a scanning rate of 0.5° min^{-1} and using a step size of 0.02°.

Transmission electron microscopy

The transmission electron microscopy (TEM) samples were cryosectioned at a thickness of 90 nm with a Leica UCT microtome between –120 and –138°C. The sections were stained with 2% OsO_2 for 20 min and then examined and photographed using a JEM 1200 EX II transmission electron microscope at 80–120 kV range.

Rheological characterization

The linear viscoelastic properties of the compounded suspensions were characterized using small-amplitude oscillatory shear. The Advanced Rheological Extended System of Rheometric Scientific (currently TA Instruments) was used in conjunction with 25- and 50-mm parallel disk fixtures.

Nanocomposite preparation

Four different formulations were prepared. Formulation 1 consisted of 96% by weight of PDMS gum (SE63) and 4% by weight of dimethyldialkyl ammo-

nium modified montmorillonite clay (3.2% by volume of organoclay). It was processed using both intensive batch mixing and TSE. For batch mixing the binder was introduced first, followed by the clay particles, while the blades continued to rotate. The torque reached a steady level of about 4.7 N m within about 2–3 min (the duration corresponding to the achievement of steady state torque is referred to as "time equal to zero"). This premixed material was then subjected to additional melt compounding (up to 20 min) in the torque rheometer/batch mixer to generate series of specimens batch mixed under different specific energy input levels. The batch mixer was operated under ambient temperature at a degree of fill of 70% by volume and at 60 rpm. Formulation 1 was also subjected to TSE in the 7–15 g/h flow rate range (100 and 150 rpm screw rotational speeds).

Formulation 2 contained 90% by weight of silanol terminated PDMS and 10% by weight of dimethyldialkyl ammonium modified montmorillonite clay (7.2% by volume organoclay). This PDMS binder is a low-viscosity Newtonian binder (around 1 Pa s at 25°C). The low viscosity necessitated that the sedimentation of the particles be minimized upon the immediate curing of the PDMS extrudates at 120°C so that they could be handled for subsequent microscopy and XRD. The feeding into the twin screw extruder required the continuous sonication of the clay/PDMS suspension and the feeding of the suspension into the twin screw extruder using the fixed displacement diaphragm pump. Because of the relatively low shear viscosity of the binder the pressure drop through the die, the torque on the screws, and the temperature rise due to viscous energy dissipation were all relatively small.

Formulation 3 contained 95% by weight of nonfunctionalized PP and 5% by weight of octadecylamine modified montmorillonite clay (2.7% by volume organoclay). This formulation was processed only using intensive batch mixing. The batch mixer was operated at a degree of fill 70% by volume at 30 rpm at of 180°C. Under steady state the torque on the agitator blades reached 17.5 N m, which was maintained for an additional 10 min.

Formulation 4 contained 95% by weight of functionalized PPMA and 5% by weight of octadecylamine modified montmorillonite clay (2.7% by volume organoclay). It was compounded by using both intensive batch mixing and TSE. The batch mixing was carried out at a degree of fill of 70% by volume of the available mixer volume at 30 rpm at a temperature of 170°C. Upon reaching a steady state torque of 5.1 N m the suspension was mixed for additional durations of 2, 10, and 20 min, to generate samples prepared under differing specific energy input levels.

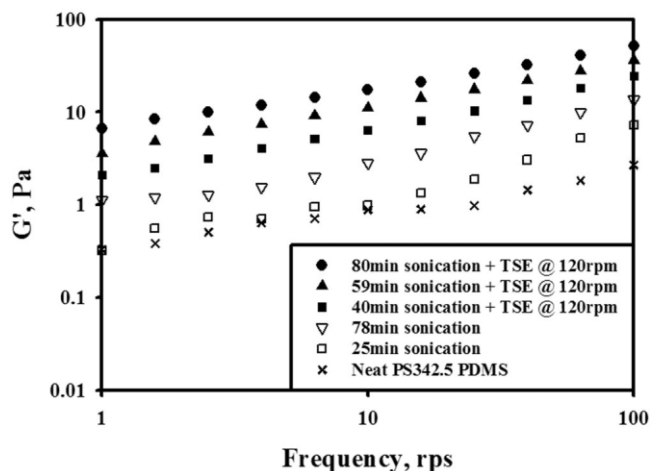Before feeding of PPMA pellets into the extruder, they needed to be ground (to less than 250 μm) to

Figure 2 Storage modulus, G', versus frequency for PDMS/organoclay compounds processed using different methodologies (Formulation 2), including twin screw extrusion (TSE).

allow feeding into the extruder. Both the PPMA and the clay powders were sieved and were dried overnight at 100°C. The generated pressure drop values at the die were between 35 and 60 psi.

RESULTS AND DISCUSSION

Rheological characterizations of formulations 1 and 2

The use of nonpolar PDMS with organoclays (Formulation 1) did not generate any significant increases in the dynamic properties of the suspensions in comparison with those of the neat PDMS. Overall, the incorporation of the clay particles slightly altered the magnitude of complex viscosity and the storage modulus of the suspension in comparison with those of the pure nonpolar PDMS binder. Furthermore, there was no sensitivity of the resulting rheological properties on the processing method used. The storage, G', and loss modulus, G'', and the magnitude of complex viscosity, η^*, values of the suspension samples prepared with the TSE process were similar to those of samples processed with the intensive batch processing method, in spite of the higher shear stress values experienced by the suspension in the confines of the twin screw extruder. The rheological characterization results thus suggested that the intercalation and the exfoliation-based generation of nanoparticles could not be achieved upon intensive batch mixing or TSE processes when the nonpolar PDMS was used.

The typical dynamic properties of the twin screw extruded and/or sonicated specimens of the polar PDMS melt compounded with organoclays, i.e., Formulation 2, are shown in Figures 2 and 3. With increasing sonication time the storage modulus, G', val-

ues (which are indicative of the energy stored as elastic energy during a cycle of deformation), the loss modulus values (which are indicative of the energy dissipated as heat during a cycle of deformation), and the magnitude of complex viscosity, η^*, values (which approach the steady shear viscosity of the suspension as the shear rate and the frequency are reduced to 0) were found to increase upon the incorporation of the organoclays. Furthermore, the dynamic properties are observed to be sensitive to the mixing method and conditions used. This sensitivity of the dynamic properties to the mixing conditions is interesting and is different from the nature of the sensitivity observed for noncolloidal suspensions. For noncolloidal suspensions (particles are greater than 1 μm) the shear viscosity and the elasticity generally decrease with increasing mixing time/intensity.[37] This is associated with a better coating of the noncolloidal particles with the binder and the resulting reduction in the yield stress and the shear viscosity of the suspension. However, the dynamic properties shown in Figures 2 and 3 suggest that the elasticity and the shear viscosity of the suspension samples increase with increasing mixing time and mixing intensity, contrary to the general results obtained with noncolloidal suspensions.

The key to the understanding of the differences in sensitivity to compounding conditions should lie in the ability to generate nanoparticles. With the generation of nanocomposites, surface area of the resulting nanoparticles is orders of magnitude greater than the surface area of the aggregates, which gave rise to the platelets that were separated from each other. The increase in the surface to volume ratio of the filler particles would increase the elasticity and the shear viscosity of the suspension. Thus, these results suggest
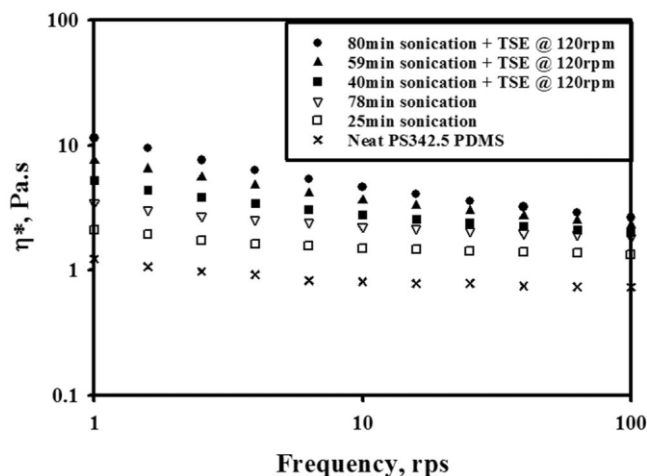

Figure 3 Magnitude of complex viscosity versus frequency for PDMS/organoclay compounds processed using different methodologies (Formulation 2), including twin screw extrusion (TSE).
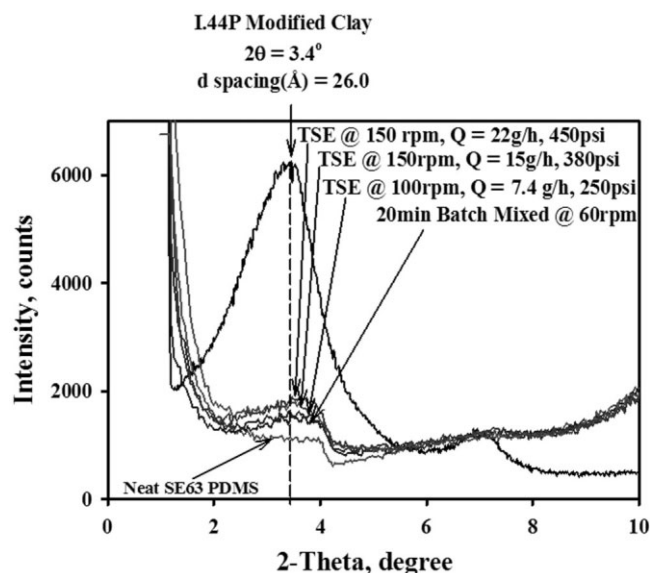
Figure 4 Typical XRD pattern of specimens of Formulation 1 melt compounded using twin screw extrusion (TSE) and batch mixing.

that the organoclay-based nanocomposites could be formed with Formulation 2, a hypothesis to be tested with XRD and TEM.

In comparison with sonication, the TSE process significantly reduces the time necessary for various levels of elasticity and viscosity to be achieved, as shown in Figures 2 and 3. The TSE process, especially with the screw configuration selected as shown in Figure 1, has the ability to impart significant dispersive mixing wherein the suspension is repeatedly subjected to the high shear stress values associated with the intermeshing of the kneading discs of the two screws with each other or at the barrel/kneading disk clearances.

X-ray analysis of PDMS-based formulation, i.e., formulations 1 and 2

The typical X-ray diffraction data of the suspension samples of Formulation 1 processed using either intensive batch mixing or using TSE under differing dispersion conditions are shown in Figure 4, along with the diffraction data for the pure organophilic clay. The diffraction peak of this organically modified clay appears at $2\theta = 3.4°$ and its corresponding d-spacing is 26.0 Å. The d-spacing is calculated from Bragg's Law, i.e. $n\lambda = 2d\sin\theta$, where n is an integer, λ is the wavelength, θ is the glancing angle of incidence beam, and d is the interplanar spacing of the clay layers.

With Formulation 1, the XRD data suggest that the location of the clay peak has not changed at all upon the melt compounding process. Thus, Figure 4 strongly suggests that the nonpolar PDMS/organo-

clay mixture, i.e. Formulation 1, did not give rise to the intercalation and exfoliation of the clay platelets, consistent with the rheological behavior of the suspension.

The typical XRD data of the polar PDMS/organoclay formulation, i.e. Formulation 2, are shown in Figure 5. The peak location of the typical twin screw extruded sample occurs at $2\theta = 2.7°$ and its corresponding d-spacing is 33.0 Å. Thus, the basal spacing of the clay platelets increases upon melt compounding of the suspension. This confirms the findings from the rheological analysis and indicates that the polar nature of the PDMS allows the binder to penetrate the gallery space to intercalate, to alter the d-spacing and increasing the elasticity and the viscosity of the resulting suspension.

TEM of formulation 2

In addition to the X-ray data and rheological analysis, TEM images of the sonicated and twin screw extruded sample were obtained. Typical micrographs are shown in Figure 6. These TEM results indicate that some of the clay particles are intercalated and delaminated to separate from each other. The conversion into nanoparticles thus gives rise to the changes in the X-ray signature and the rheological material functions. However, the conversion is not complete and there are locations at which the tactoids remain intact. Thus, one is confronted with a degree of structure transformation problem with the associated statistics of distributive and dispersive mixing of the tactoids and spatial distributions and orientations of exfoliated
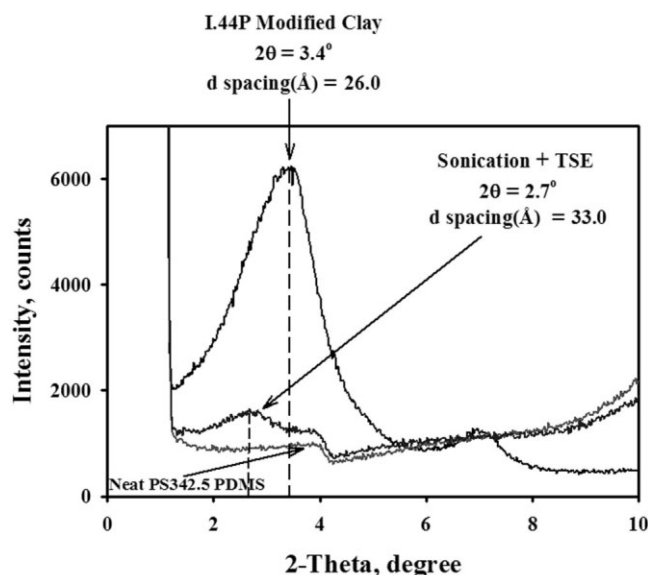

Figure 5 Typical XRD pattern of specimens of Formulation 2 melt compounded using sonication and TSE.
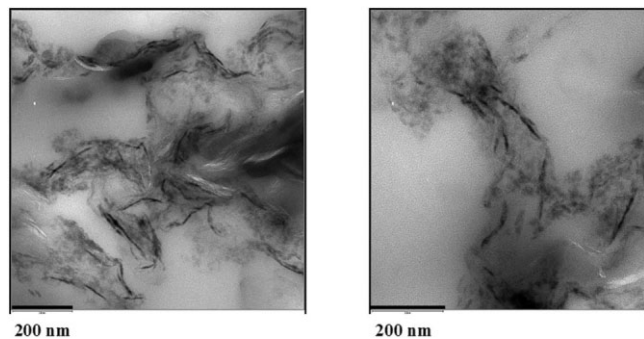
Figure 6   Typical TEM micrograph of Formulation 2.

Figure 7   Storage modulus, G', versus frequency for PPMA/organoclay compounds processed using different methodologies (Formulation 4) at 170°C, including twin screw extrusion (TSE).

platelets. Such an exhaustive study was not pursued here.

Rheological characterizations of formulations 3 and 4

Typical small-amplitude oscillatory shear behavior of the nonpolar PP binder melt compounded with the organoclay particles did not give rise to significant changes from the behavior of the neat PP. With this nonpolar PP binder the generation of nanostructures was not expected, that is, the clay platelets were expected to remain as tactoids. The storage modulus and the magnitude of complex viscosity values of this suspension indeed were very close to those of neat nonpolar PP and thus confirmed this expectation. Overall, the incorporation of the clay particles only slightly increased the shear viscosity and the elasticity of the suspension in comparison with those of the pure binder, PP (similar to the behavior of nonpolar PDMS). The rheological characterization results thus suggested that the intercalation and the exfoliation-based generation of nanoparticles could not be achieved when the nonpolar PP was used. Similar to the nonpolar PDMS/organoclay mixture there was sensitivity to the processing method or conditions.

On the other hand, the theological behavior of the polar, copolymer i.e., maleic anhydride functionalized, theological PPMA and organoclay formulation (Formulation 4) was different. The typical dynamic properties of the twin screw extruded and intensive batch mixed specimens of Formulation 4 are shown in Figures 7 and 8. The dynamic properties are observed to increase upon the melt compounding of the organoclays into the PPMA. Furthermore, there is some slight sensitivity to the processing method and conditions. From the frequency-sweep experiments it is seen that with increasing mixing time (increasing specific energy input) the viscosity and the elasticity of Formulation 4 increase, presumably because of intercalation by the polar binder and exfoliation of the silicate platelets. This formulation is expected to form nanocompos-
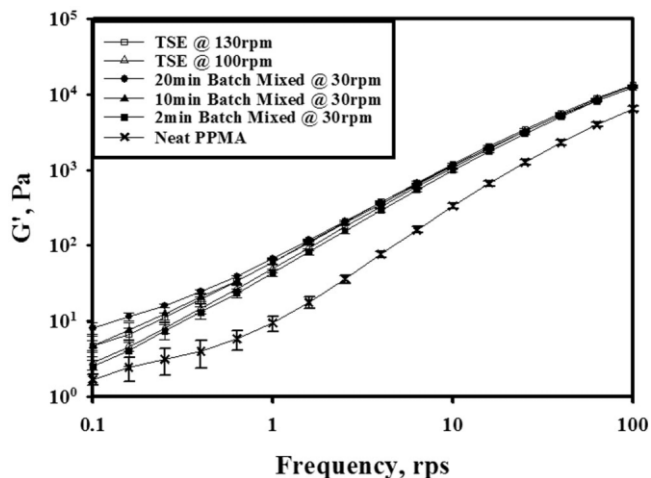
ites on the basis of its polar nature associated with the copolymerization with maleic anhydride.[24–28,30,31,33]

However, had we been able to truly exfoliate the clay platelets, the resulting surface area of the nanoparticles would have been orders of magnitude greater than the surface area of the tactoids (with typical thickness of nanoclay platelets upon separation around 1 nm). The surface to volume ratio of the filler particles would have increased more significantly than that anticipated from the typical 275% increase of the magnitude of complex viscosity at 0.1 rps noted in Figure 8. Thus, similar to the polar PDMS case, the observed increases in the elasticity and the shear viscosity of the suspension suggest intercalation and possibly some exfoliation but not a fully exfoliated suspension.
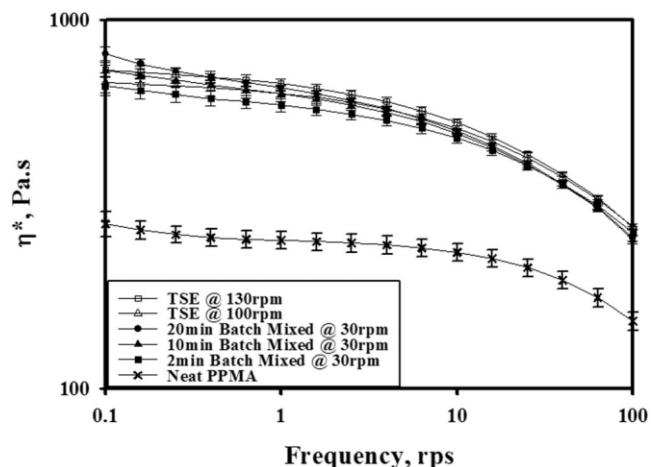

Figure 8   Magnitude of complex viscosity versus frequency for PPMA/organoclay compounds processed using different methodologies (Formulation 4) at 170°C, including twin screw extrusion (TSE).
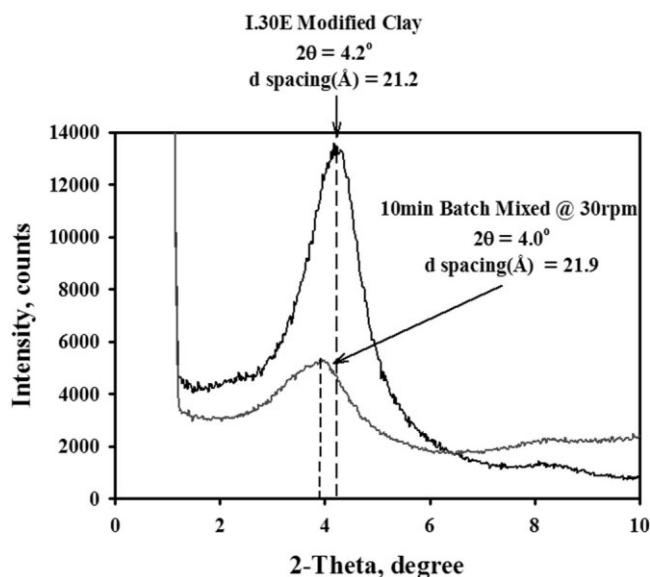
Figure 9 Typical XRD pattern of specimens of Formulation 3 melt compounded using intensive batch mixing.

X-ray analysis of formulations 3 and 4

The typical XRD data of the melt-compounded samples of Formulation 3 are shown in Figure 9, along with the diffraction data for the neat organophilic clay. The major peak of the clay is found at a Bragg angle of about 4.2° and the corresponding d-spacing is 21.2 Å. The XRD data of the mixture suggest that the location of the clay peak has changed only slightly (with a corresponding d-spacing of the clay at 21.9 Å) upon the processing of the clay with the unmodified PP binder upon melt compounding. Thus, Figure 9, consistent with the rheological characterization results, again suggests that the melt compounding of the nonpolar PP with organoclays (Formulation 3) did not lead to the formation of nanocomposites, presumably on the basis of the inability of the nonpolar PP to penetrate the gallery space in between the clay platelets.

On the other hand, the use of the polar PPMA binder for melt compounding with the organoclays (Formulation 4) gives rise to a shift of the clay peak to a lower Bragg angle in conjunction with significant broadening of the clay peak. This typical behavior upon melt compounding is shown in Figure 10. It appears that the clay particles have indeed been intercalated by the polar binder, in conjunction with some degree of exfoliation. Furthermore, increase of the specific energy input increases the d-spacing of the clay (i.e., for 2 min additional intensive batch mixing the specific energy input value is 1581 J/kg and the corresponding d-spacing of the clay is 25.5 Å, for 10 min additional batch mixing the specific energy input value is 8172 J/kg and the corresponding d-spacing of the clay is 27.4 Å, and finally for 20 min additional

intensive batch mixing the specific energy input value is 16,940 J/kg and the corresponding d-spacing of the clay is 27.7 Å).

It is also observed that even at relatively short durations of mixing and relatively small specific energy input, evidence of the intercalation is found, indicating that if the interfacial properties between the organoclay and the polymer binder are favorable, the intercalation occurs relatively fast, thus confirming the findings of Vaia et al.[15] The highest d-spacings of clay were observed with TSE. The d-spacing of the intercalated clay for TSE was determined to be about 30.2 Å, consistent with the relatively higher ability of the TSE process to impart dispersive mixing on the clay tactoids, provided a correct screw configuration is selected.

TEM of formulation 4

The typical TEM micrographs corresponding to Formulation 4 samples, which were melt compounded using TSE, are shown in Figure 11. These micrographs indicate that significant degree of intercalation of the clay platelets by the polar binder and some degree of exfoliation of the clay platelets upon delamination, reorientation, and separation from each other occurred. Consistent with the findings of the rheological characterization results and the XRD findings, TEM results suggest that at least some part of the clay could be converted into nanoparticles to give rise to the indicated changes in the X-ray signature and the rheological material functions of the melt compounded specimens of Formulation 4.
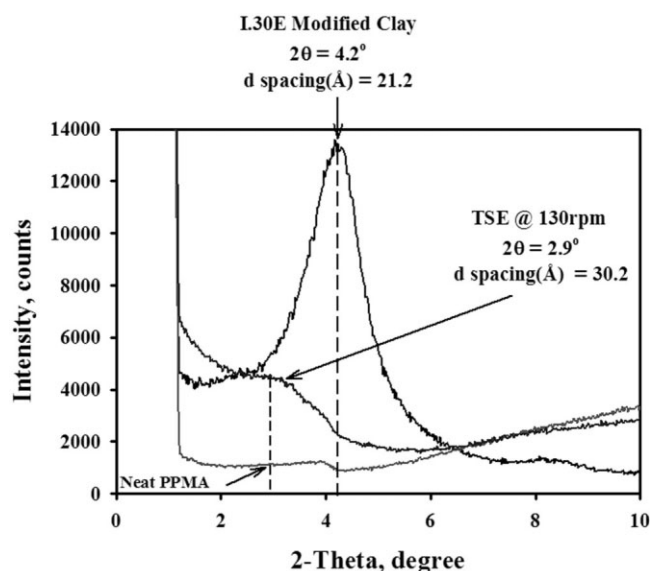

Figure 10 Typical XRD pattern of specimens of Formulation 4 melt compounded using twin screw extrusion (TSE).
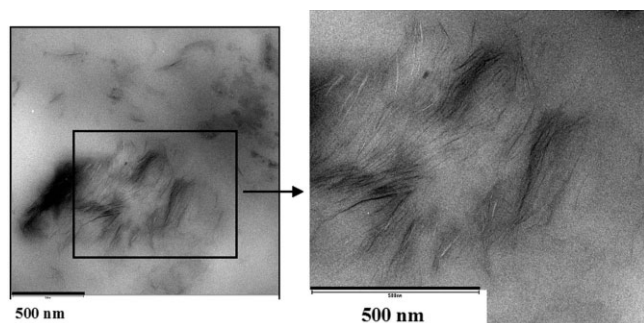
Figure 11 Typical TEM micrograph of Formulation 4 upon melt compounding using twin screw extrusion.

CONCLUSIONS

These results point to the difficulty of the generation of nanocomposites using melt compounding when the interfacial properties between the polymer melt binder and the organoclay are not favorable. The intercalation and the exfoliation occur only when the polymer and the organoclay coupling is appropriate. The dynamic properties upon melt compounding provide accurate signatures of the state of the intercalation and exfoliation. Sensitivity to the processing method and conditions (especially the specific energy input condition) occurs when the organoclay could be intercalated by the binder. The relationship between the elasticity and the shear viscosity of the nanocomposites versus the specific energy input differs completely from the specific energy input versus the elasticity and the shear viscosity of the noncolloidal suspensions. With nanocomposites formation the elasticity and the shear viscosity increase with increasing specific energy input whereas the reverse is encountered with noncolloidal suspensions.

The complete intercalation and the exfoliation of the clay particles could not be achieved in this study. The microstructures were characterized by a complex distribution of degrees of intercalation and exfoliation as a function of location in the melt compounded samples, all dependent on the thermomechanical history associated with the melt compounding process.

References

1. Fujiwara, S.; Sakamoto, T. Jpn. Kokai Pat. Appl. 109998 (1976).
2. Kawasumi, M.; Kohzaki, M.; Kojima, Y.; Okada, A.; Kamigaito, O. U.S. Pat. 4,810,734 (1989).
3. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
4. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 2493.
5. Giannelis, E. P. Adv Mater 1996, 8, 29.
6. Giannelis, E. P.; Krishnamoorti, R.; Manias, E. Adv Polym Sci 1999, 138, 107.
7. Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1185.
8. Messersmith, P. B.; Giannelis, E. P. J Polym Sci Part A: Polym Chem 1995, 33, 1047.
9. Bharadwaj, R. K. Macromolecules 2001, 34, 1989.
10. Burnside, S. D.; Giannelis, E. P. Chem Mater 1995, 7, 1597.
11. Burnside, S. D.; Giannelis, E. P. J Polym Sci Part B: Polym Phys 2000, 38, 1595.
12. Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, L. G.; Giannelis, E. P. Adv Mater 1995, 7, 154.
13. Alexandre, M.; Dubois, P. Mater Sci Eng 2000, 28, 1.
14. Vaia, R. A.; Ishii, H.; Giannelis, E. P. Chem Mater 1993, 5, 1694.
15. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. Macromolecules 1995, 28, 8080.
16. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. Chem Mater 1996, 8, 2628.
17. Tanoue, S.; Utracki, L. A.; Garcia-Rejon, A.; Sammut, P.; Ton-That, M.; Pesneau, I.; Kamal, M. R.; Jorgensen, J. L. Polym Eng Sci 2004, 44, 1046.
18. Mehrabzahed, M.; Kamal, M. R. Polym Eng Sci 2004, 44, 1152.
19. Artzi, N.; Narkis, M.; Siegmann, A. Polym Eng Sci 2004, 44, 1019.
20. Nassar, N.; Utracki, L. A.; Kamal, M. R. Int Polym Process 2005, 4, 423.
21. Dennis, H. R.; Hunter, D. L.; Cho, J. W.; Paul, D. R.; Chang, D.; Kim, S.; White, J. L. Polymer 2001, 42, 9513.
22. Cho, J. W.; Paul, D. R. Polymer 2001, 42, 1083.
23. Erman, B.; Mark, J. E. Structures and Properties of Rubberlike Networks; Oxford University Press: New York, 1997.
24. Kato, M.; Usuki, A.; Okada, A. J Appl Polym Sci 1997, 66, 1781.
25. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. J Appl Polym Sci 1998, 67, 87.
26. Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A. J Appl Polym Sci 2000, 78, 1918.
27. Nam, P. H.; Maiti, P.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. Polymer 2001, 42, 9633.
28. Maiti, P.; Nam, P. H.; Okamoto, M.; Hasegawa, N.; Usuki, A. Polym Eng Sci 2002, 42, 1864.
29. Gopakumar, T. G.; Lee, J. A.; Kontopoulou, M.; Parent, J. S. Polymer 2002, 43, 5483.
30. Hasegawa, N.; Usuki, A. J Appl Polym Sci 2004, 93, 464.
31. Kato, M.; Matsushita, M.; Fukumori, K. Polym Eng Sci 2004, 44, 1205.
32. Hotta, S.; Paul, D. R. Polymer 2004, 45, 7639.
33. Ton-That, M. D.; Perrin-Sarazin, F.; Cole, K. C.; Bureau, M. N.; Denault, J. Polym Eng Sci 2004, 44, 1212.
34. Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R. Polymer 2001, 42, 9929.
35. Fornes, T. D.; Yoon, P. J.; Hunter, D. L.; Keskkula, H.; Paul, D. R. Polymer 2002, 43, 5915.
36. Shah, R. K.; Paul, D. R. Polymer 2004, 45, 2991.
37. Kalyon, D.; Dalwadi, D.; Erol, M.; Birinci, E.; Tsenoglu, C. Rheol Acta 2006, 45, 641.