

Estimation of Reinforcement in Compatibilized Polypropylene Nanocomposites by Extensional Rheology

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ABSTRACT: Structural characterization in polymer nanocomposites is usually performed using X-ray scattering and microscopic techniques, whereas the improvements in processing and mechanical properties are commonly investigated by rotational rheometry and tensile testing. However, all of these techniques are time consuming and require quite expensive scientific equipment. It has been shown that a fast and efficient way of estimating the level of reinforcement in polymer nanocomposites can be performed by melt extensional rheology, because it is possible to correlate the level of melt strength with mechanical properties, which reflect both

the 3D network formed by the clay platelets/polymer chains as well as final molecular structure in the filled system. The physical network made of silicate filler and polymer matrix has been evaluated by X-ray diffraction and transmission electron microscopy. Extensional rheometry and tensile testing have been used to measure efficiency of the compatibilizer amount in a polypropylene-nanoclay system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2253–2259, 2009

Key words: nanocomposites; melt compounding; melt strength

INTRODUCTION

Nanocomposites using different polymer matrices and layered silicates have been intensively investigated because of the improvements in their processing and use properties. Consequently, it is possible to prepare new, tailored, materials¹ or to use nanofillers in polymer recycling.^{2–4} The improvement in material properties due to nanoclay addition has usually been evaluated using a combination of transmission electron microscopy (TEM) and morphological (X-ray diffraction (XRD)), mechanical (tensile testing), and sometimes also rheological (rotational rheometry) analyses. However, these conventional methods require quite expensive scientific equipment and long sample preparation and characterization times. Generally, intercalated and delaminated (partially exfoliated) polymer nanocomposites reveal significant enhancements in their properties: higher elastic modulus, tensile strength, thermal resistivity,

lower gas and liquid permeability, reduced flammability,⁵ and improved rheological properties (e.g., higher melt strength) compared with the unfilled polymer matrix.¹ The high level of possible reinforcement due to the addition of the layered silicates results from their large active surface area (in the case of montmorillonite 700–800 m²/g).⁶ In the case of highly dispersed systems, a 3D physical network is achieved, formed by the silicate platelets and the polymer chains. This phenomenon can be investigated by analyzing the melt elasticity using rotational rheometry.^{1–4,6–22} A fast way to evaluate this network effect is using elongational rheometry,^{23–26} which provides information about the melt strength.

To disperse the clay in hydrophobic polypropylene (PP), a compatibilizer (mostly PP grafted with maleic acid anhydride (MA)) must be admixed. However, the molecular weight of the compatibilizer is usually lower than that of the PP matrix due to the grafting reaction and the presence of free MA molecules.²⁷

We have already presented^{23,24} that the effective level of reinforcement in PP nanocomposites cannot be based solely on an evaluation of the delamination level (increase in interlayer distance) determined by X-ray scattering. In the PP-PPMA-nanoclay system, the simple rule “higher delamination leads to an improvement in material properties” is not always

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TABLE I
Temperature profile in different extruder sections

Section	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	cool	160	180	190	200	200	200	200	200	200

valid because of the influences of the grafted PP on the material properties. With a higher compatibilizer addition, the final delamination increases but the average molecular weight decreases. This means that there is an optimal compatibilizer admixture at which physical reinforcement caused by silicate delamination is still higher than the deterioration in mechanical properties due to decreasing molecular weight and combination of the interfacial area able to be generated.

A fast and accurate method to find this optimal compatibilizer admixture in different PP nanocomposites is to compare the material reinforcement in the systems using extensional rheometry. A further advantage of elongational experiments is the use of primary granulates: no preparation of samples is necessary. To date, a few articles have dealt with the possibility of using extensional rheometry for the characterization of elongational viscosity in polymer nanocomposites.^{28,29} However, no correlation between the melt strength and the mechanical properties with respect to nano-structural details has yet been published. The goal of this article is to present a fast, qualitative method of reinforcement evaluation based on extensional rheology in polymer nanocomposites with a view to speed up the industrial application of the systems investigated.

EXPERIMENTAL

Materials

The isotactic PP homopolymer HC600TF (MFI 2.8 g/10 min; 230°C/2.16 kg) was supplied by Borealis, Inc., Linz, Austria. Used nanofiller (montmorillonite intercalated with dimethyl distearyl ammonium chloride) with commercial indication Nanofil 5 was supplied by Süd-Chemie Inc., Munich, Germany. The compatibilizer (Scona TPPP 2112 FA, MFI 14.8 g/10 min) was supplied by Kometra, Ltd., Schkopau, Germany.

TABLE II
Press profile

Temperature (°C)	200	200	200	200	50
Pressure (bar)	1	20	1	100	150
Time (min)	20	5	5	7	7

Preparation of nanocomposites

For the compounding process, an intermeshing, corotating twin screw extruder Theysohn TSK30/40D (Theysohn Holding Ltd, Vienna, Austria) with a string die was used. The feed rate was set at 20 and 7 kg/h, with a screw speed of 200 rpm. The temperature profile is described in Table I. The compatibilizer admixture content relative to the organoclay content (5 wt %) was chosen at ratios (clay : compatibilizer) from 1 : 0 to 1 : 3.

For the Rheotens measurements, the primary granulate obtained from the extrusion process was used. For structural (X-ray diffraction, transmission electron microscopy) and mechanical characterization, plates with a thickness of 2 mm and standard dog-bone shaped specimens (150 mm length, 20 mm width, 4 mm thickness), respectively, were prepared using the hydraulic vacuum press machine (Collin 200 PV, Dr. Collin Ltd., Ebersberg, Germany). The press profile is given in Table II.

Extensional melt rheology

As stated in the introduction, two methods of reinforcement assessment can be used in the molten state in polymer nanocomposites: analysis of the melt elasticity using rotational rheometry or melt strength evaluation, e.g., using Rheotens equipment. The advantage of Rheotens measurements consists in their simplicity without the need for expensive scientific equipment and additional time for sample preparation. The principle of Rheotens measurements can be seen in Figure 1. It is based on the

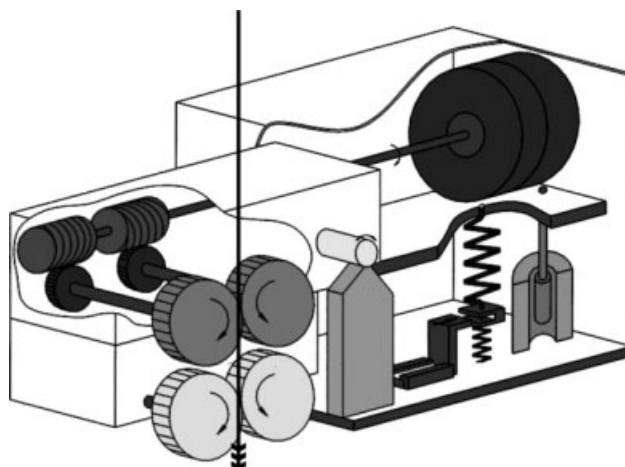


Figure 1 Principle of Rheotens measurement.³⁰

TABLE III
Capillary rheometer testing specification

Cylinder diameter	12 mm
Die (length/diameter)	30/2 mm
Temperature	210°C
Piston speed	1.9 mm/s
Shear rate	273.6 s ⁻¹

elongation of an extruded string by two or four rotating wheels connected with a force transducer. The rotation speed is linearly increased until the molten string breaks. The tensile force applied to the wheels and the draw rate at break allows the calculation of the melt strength (stress at break)³¹:

$$\sigma_b = F_b v_b / A_0 v_0,$$

σ_b —stress at break (Pa),

F_b —tensile force at break (N),

v_b —draw rate at break (mm s⁻¹),

A_0 —initial cross section of molten string (at the die outlet) (m²),

v_0 —extrusion speed of molten string (piston speed) (mm s⁻¹).

We used the Rheotens 71.97 (Göttfert Ltd., Buchen, Germany) in a combination with a capillary rheometer. The measuring conditions for capillary rheometer are listed in Table III. The rheotens equipment has been set applying wheel acceleration of 60 mm/s² and gap between wheels of 0.6 mm. To compare the melt strength level of different nanocomposite systems (revealing different magnitudes of v_b), the tensile force at a draw rate of 320 mm/s was chosen for comparison (Fig. 2).

The silicate platelets form different levels of 3D physical network in the polymer matrix depending on their level of delamination.¹⁻⁴ Higher delamination results in a higher extent of physical network (higher material reinforcement) and, therefore, in an increase in melt strength. Different particle–particle and polymer–particle physical interactions result in variations in viscoelastic response. Therefore, Rheotens measurements are used to identify changes in the melt elongational behavior. Individual silicate platelets form nanoscale network (cardhouse structure)²¹ and raise the melt strength of the composite. Depending on the degree of delamination, this transformation is obvious compared with the unfilled polymer.

Small angle X-ray scattering

X-ray measurements were performed using Bruker NanoSTAR (Bruker AXS, Karlsruhe, Germany) small angle X-ray scattering (SAXS) equipment. This sys-

tem was equipped with a two-dimensional X-ray detector. A wavelength of 0.154 nm (CuK α) was used. The samples were measured in transmission.

To avoid the influence of texture, all scattering measurements were performed on plate samples. The gallery period¹ of the nanofiller was determined on a powder sample. To avoid statistical effects, the scattering curves recorded at three different positions on the samples were averaged. To determine the gallery period, scattering curves were corrected for background scatter and the Lorenz correction was applied.³² The Lorenz correction was performed by multiplying the scattered intensity ($I(q)$) by q^2 , q being the magnitude of the scattering vector. The position of the gallery peak was then determined by fitting with a Lorenz function.

Transmission electron microscopy

The TEM experiments were performed using a Zeiss LEO 912 Omega transmission electron microscope (Carl Zeiss Inc., Jena, Germany) using an acceleration voltage of 120 kV. The samples were prepared using a Leica Ultracut UCT ultramicrotome (Leica Microsystems Ltd, Wetzlar, Germany) equipped with a cryo chamber. Thin sections of about 50 nm were cut with a Diatome diamond knife at -120°C.

Mechanical properties

A universal tensile testing machine (Type: Z010, Zwick Ltd and Co. KG, Ulm, Germany) was used to carry out the tensile tests according to ISO 527-1. All tests were carried out under standardized conditions (23 \pm 2°C/50 \pm 5% r.H.). The data was evaluated using the testXpert II software (ZWICK, Ulm, Germany).

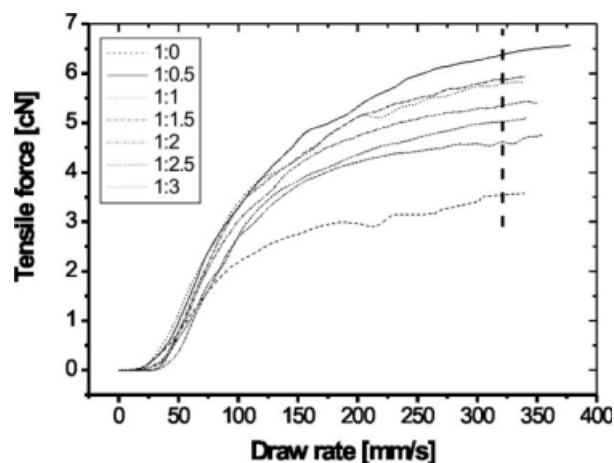


Figure 2 Melt strength level comparison.

RESULTS AND DISCUSSION

Extensional melt rheology

The elongational behavior of nanocomposite masterbatches prepared using different compatibilizer admixtures at two throughput rates is shown in Figure 3. It is obvious that the compatibilizer content as well as the effect of the feed rate on material properties can be analyzed by evaluating the melt strength. As stated in the Introduction section, determination of the optimum compatibilizer admixture in polyolefine nanocomposites is essential to reach the maximal reinforcement using layered silicates. We have shown^{23,24} that the MFI difference in PP matrices results in different optimum compatibilizer admixtures. The lower the MFI, the lower the compatibilizer content needed. The high molecular weight of the HC600TF matrix leads to high shear forces in the compounder and, therefore, facilitates delamination of silicate platelets. A lower quantity of compatibilizer is, therefore, required. Using the HC600TF matrix led to higher level of material reinforcement due to requiring two to four times less compatibilizer compared with other lower molecular weight PP matrices.^{23,24} It is obvious that the exact determination of the optimum compatibilizer admixture is a key factor in both maximizing the level of polymer reinforcement and minimizing compatibilizer costs. For the effect of the feed rate (at a constant screw speed) on the optimum compatibilizer content, an opposite trend was found to that for MFI. A lower throughput rate leads to a higher need for compatibilizer, which is explained by the lower fill factor in the screw segments. A higher feed rate leads to a higher fill factor and, subsequently, to higher shear forces applied on silicate tactoids to be delaminated. Therefore, it is necessary to evaluate the optimum compatibilizer admixture for PP matrices with different molecular structures or by varying the process-

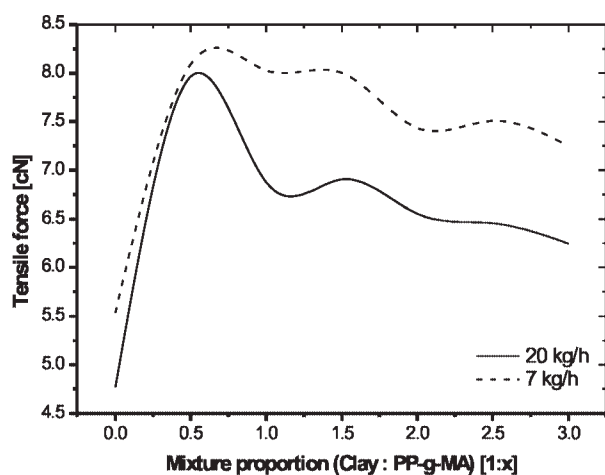


Figure 3 Melt strength level of nanocomposites.

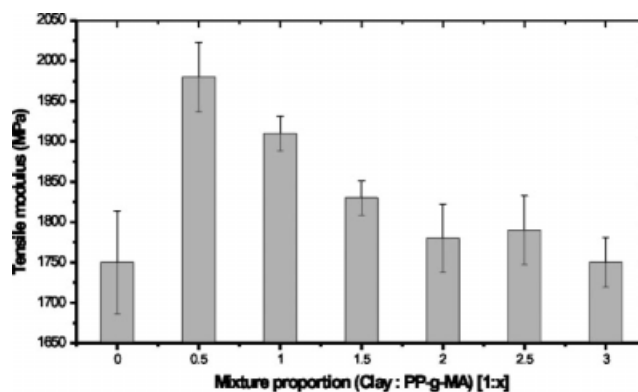


Figure 4 Tensile modulus in nanocomposites with different compatibilizer admixture.

ing conditions such as throughput rate. To our knowledge, this important aspect in the preparation of PP-organoclay nanocomposites has not been discussed in depth so far.

Mechanical properties

The results of mechanical testing in the solid state reflect those in the melt state. In Figure 4, the Young's modulus is plotted for the nanocomposites with differing compatibilizer admixtures. The same trend can be observed as for the extensional behavior. The highest increase in stiffness was found in the system filled with 2.5 wt % of compatibilizer. A further increase in the compatibilizer admixture leads to a decline in the tensile modulus. At 15 wt % compatibilizer the mean value of modulus reaches approximately the same value as for the mixture without compatibilizer. This result is in agreement with that published by Paul et al.,³³ where the mechanical properties of PP nanocomposites with different compatibilizer admixtures (1 : 0 to 1 : 2 PP-g-MA to organoclay ratio) were investigated. However, supposedly due to the high melt flow index of the matrix used (37 g/10 min, 230°C), an increase in

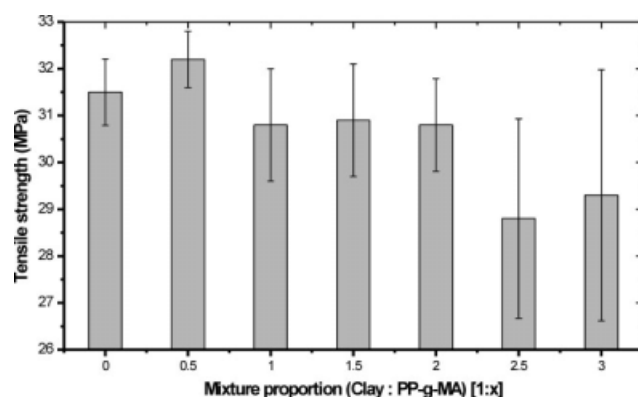


Figure 5 Tensile strength in nanocomposites with different compatibilizer admixture.

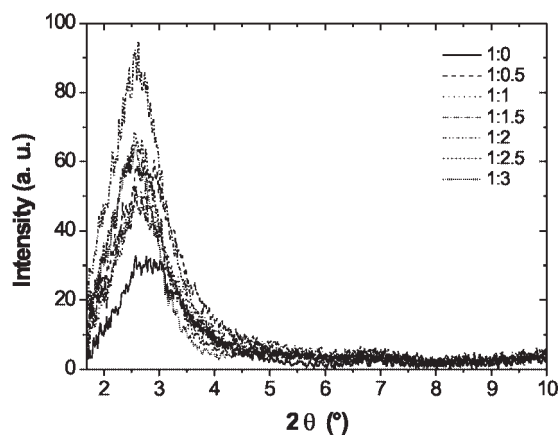


Figure 6 X-ray diffraction patterns of nanocomposites.

the compatibilizer content (1 : 0.5 up to 1 : 2 PP-g-MA to organoclay ratio) reported by Paul et al. did not result in a significant decrease in tensile modulus. As we already reported,^{23,24} molecular structure (in particular molecular weight) of PP matrix has significant influence on the optimum compatibilizer admixture and compatibilizing efficiency. The polymer matrix with the highest molecular weight possible to process with other composite components is favored to ensure maximal shear forces during compounding. Results for tensile strength (Fig. 5) reveal a similar trend as for melt strength and tensile modulus. The highest mean value of tensile strength was reached at a compatibilizer admixture of 2.5 wt %, while higher amounts resulted in a decline in tensile strength. The highest level of polymer-filler interfacial shear strength in the system, using 2.5 wt % of compatibilizer, is reflected in the high magnitudes of both melt and tensile strength. Therefore, it is possible to correlate the reinforcement level in the melt state with that in the solid state. In this way, extensional rheology can be used in terms of estimating the prior routes in the development of nanocompo-

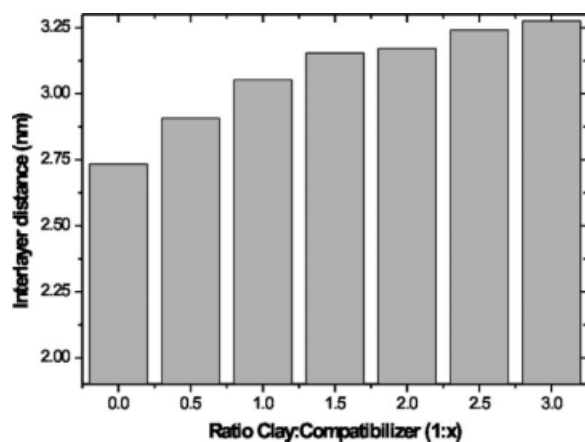


Figure 7 Gallery periodicity as a function of compatibilizer content.

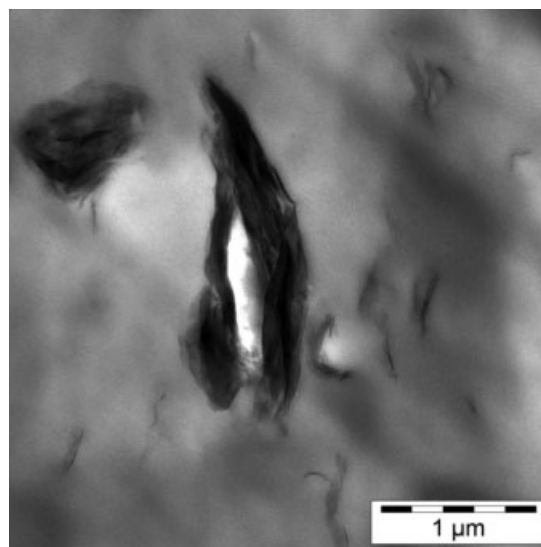


Figure 8 TEM of nanocomposite with 1 : 0 compatibilizer ratio.

sites and, presumably, any other filled systems based on polymer matrix.

Delamination of organoclay in polypropylene

The morphological analysis revealed a clear trend in delamination and homogeneity of silicate platelets in PP nanocomposites. In Figure 6, X-ray diffraction patterns of all investigated systems can be observed. The highest intensity peak was revealed in the system filled with 10 wt % of compatibilizer. On the other hand, the lowest peak can be seen in nanocomposite without compatibilizer. Calculated interlayer distance of organoclay is plotted in Figure 7 (relative to pure organoclay). It is obvious that the increase in

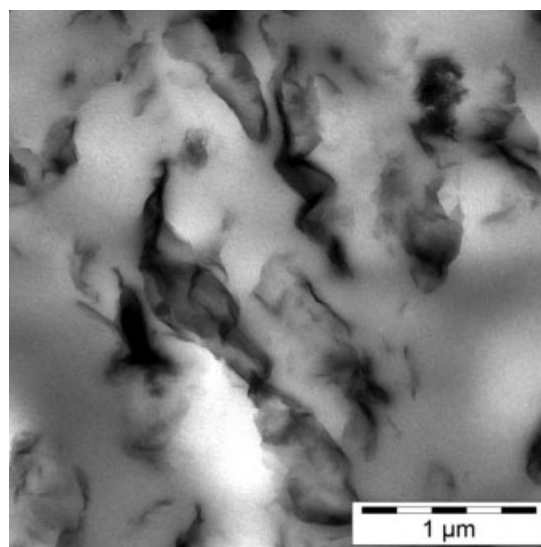


Figure 9 TEM of nanocomposite with 1 : 0.5 compatibilizer ratio.

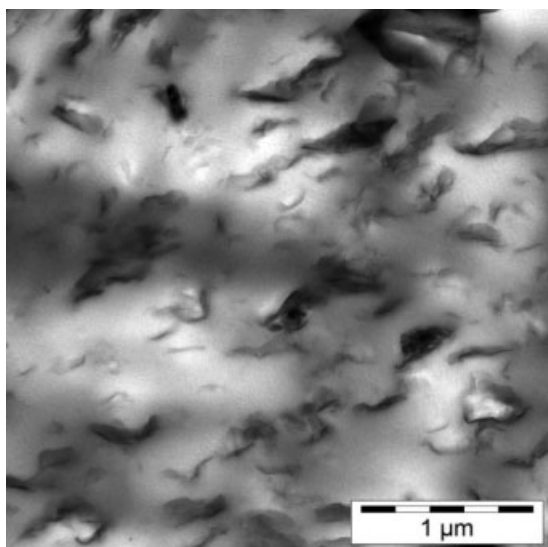


Figure 10 TEM of nanocomposite with 1 : 1 compatibilizer ratio.

compatibilizer admixture leads to a higher interlayer distance of montmorillonite in the nanocomposite system. The same trend was observed concerning the homogeneity of the prepared systems, as can be seen in Figure 8–12. The nanocomposite without compatibilizer revealed a stacking of silicate platelets rather than delamination behavior. On the other hand, a significantly higher level of homogeneity occurs in the 2.5 wt % compatibilizer admixture (Fig. 9), with a maximum at 15 wt % compatibilizer (Fig. 12). It can be clearly seen that results of structural measurements revealed completely other trend when compared with the mechanical and rheological testing. Therefore, grade of delamination in compatibilized PP nanocomposites cannot possess informa-

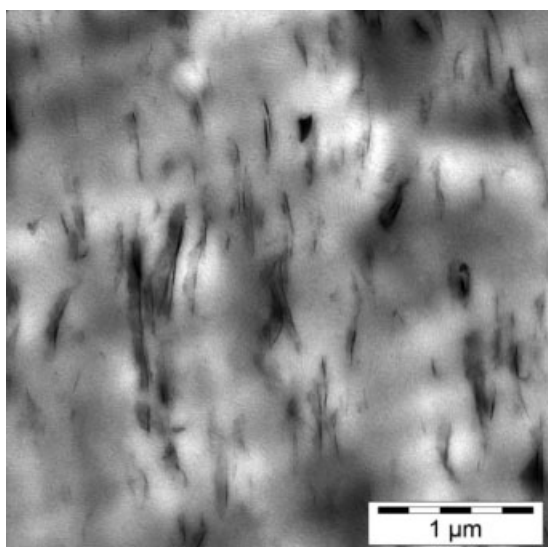


Figure 11 TEM of nanocomposite with 1 : 2.5 compatibilizer ratio.

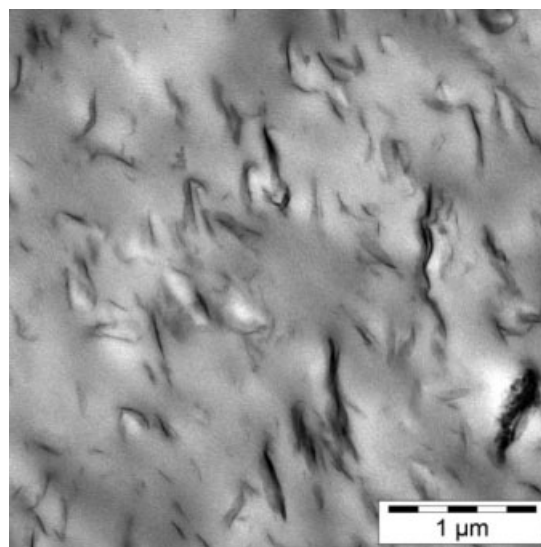


Figure 12 TEM of nanocomposite with 1 : 3 compatibilizer ratio.

tion on the level of polymer reinforcement, as in the case of systems without compatibilizers.^{2–4} Nevertheless, extensional rheology cannot replace conventional measuring techniques and is introduced in this paper only as a possibility of fast reinforcement estimation in the filled polymer systems.

CONCLUSIONS

The PP-PPMA-nanoclay system was investigated to find the optimum amount of compatibilizer. Although X-ray scattering and TEM revealed an increase in silicate dispersion with an increase in compatibilizer content, the mechanical and rheological properties of the material reached an optimum at significantly lower amounts of compatibilizer. Therefore, the effective reinforcement in PP-layered silicate nanocomposites cannot be evaluated successfully using only structural characterization methods. It was shown that the results of melt extensional rheometry can be correlated with those of tensile tests in a solid state. In this context, the method could be used as a fast, accurate, and cheap way to estimate the reinforcement in polymer nanocomposites. From industrial point of view, extensional rheometry could be employed on-line in the processing line and, subsequently, control and dose composite components in the adequate proportion directly during compounding. In the case of PP nanocomposites, an optimum compatibilizer content can also be assessed by this technique. However, it is necessary to measure this optimum each time by variation in PP, compatibilizer or filler type.

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