

# Nano/micro Ternary Composites Based on PP, Nanoclay, and CaCO<sub>3</sub>

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**ABSTRACT:** Nano-/microcomposites based on polypropylene/montmorillonite/calcium carbonate were prepared by melt mixing. Their structures and properties were characterized by small-angle X-ray diffraction, thermal analysis, and rheological measurements. The intercalation degree was found to be dependent on the compatibilizer content and the processing temperature. The addition of the organoclay slightly increased the melt crystallization temperature of polypropylene, acting as nucleating agents, and improved the degree of crystallinity. The rheological tests showed that nanocomposites increased the complex viscosity when compared with the microcomposites with the same filler content and exhibited a pronounced shear-

thinning behavior in the low frequency range. A Carreau-Yasuda model was used to model the rheological behavior of these materials. The nano-/microcomposites showed a significant improvement (about 50%) of the Young's modulus when compared with microcomposites with the same filler content due to the intercalation or exfoliation of the organoclay and the enhanced degree of crystallinity. Moreover, some formulations showed an enhancement of elongation at break and ultimate strength. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3360–3367, 2009

**Key words:** poly(propylene); nanocomposites; composites; thermoplastics; mechanical properties

## INTRODUCTION

The use of inorganic fillers is a common practice in the plastics industry to improve some properties of thermoplastics, such as heat distortion temperature, hardness, toughness, and stiffness. The effects of filler on the mechanical and other properties depend strongly on its nature, shape, particle size, aggregate size, surface characteristics, and degree of dispersion in the polymer. In general, the mechanical properties of the composites filled with micron-sized filler particles are lower than those filled with nanoparticles of the same filler content.<sup>1,2</sup>

Polypropylene (PP) as one of the most important commodity polymers is widely used in technical applications, because of its good processability, relatively high mechanical properties, great recyclability, and low cost.

Nanocomposites attract increasing interests because of their potential of providing novel performances. The tremendous interfacial area in a polymer nanocomposite helps to influence the composites properties to a great extent even at rather

low filler loading.<sup>3</sup> However, the homogeneous dispersion of nanoparticles is very difficult to achieve, because nanoparticles with high surface energy tend to easily agglomerate. To break up the agglomerates, studies have been carried out on the approaches of in situ polymerization of monomers in the presence of nanoparticles<sup>4–6</sup> and other intercalation polymerization techniques.<sup>7</sup>

Polymer-based nanocomposites are very difficult to produce by using conventional processing technologies like extrusion or melt blending. To overcome this limit, surface modification of nanoparticles or the use of compatibilizers become a key issue. In particular, in the case of PP it is frequently necessary to use a compatibilizer such as the maleic anhydride modified polypropylene (PPgMA).<sup>8</sup>

Lertwimolnun and Vergnes<sup>9</sup> showed that an improvement of the degree of dispersion is obtained for concentration of PPgMA higher than 10 wt %. No further improvement on the nanoparticle dispersion is observed for PPgMA content above 25 wt %. The state of intercalation is globally affected by processing parameters. Increasing shear stress, mixing time, and decreasing mixing temperature improve clay layer silicate intercalation or exfoliation.

Rheological measurements are an effective method to compare different level of intercalation or

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exfoliation.<sup>10</sup> Wang et al.<sup>11</sup> studied the intercalation capability of PPgMA. In addition to the polarity, the molecular weight, which determined the shear viscosity of PPgMA, also played a vital role in the effective breakup of clay agglomerates. PPgMAs with low molecular weight and higher melt flow index (MFI) needed to be compounded at low mixing temperature to generate a high shear viscosity and maintain a reasonable level of torque in the mixer. Rheological characterization by complex viscosity also demonstrated that PPgMA with a low molecular weight and a high MA content led to better interactions with the clay. However, the addition of lower molecular weight PPgMA affects the improvement in the mechanical and thermal properties of the PP/PPgMA/clay nanocomposites.

The aim of this work was to investigate the effect on the mechanical and rheological properties of the addition of nanoclays in nano-/microcomposites, prepared by direct melt intercalation method in an internal mixer, based on PP and calcium carbonate.

## EXPERIMENTAL

### Materials

PP (Moplen HP500J), supplied by Basel Polyolefins, was used as polymeric matrix (MFI 3.2 g/10 min;  $T_m = 166^\circ\text{C}$ ). PP *grafted* maleic anhydride (Polybond 3200), supplied by Crompton, was used as compatibilizer, containing 1 wt % of maleic anhydride (MFI 115 g/10 min;  $T_m = 162^\circ\text{C}$ ).

The organoclays used are Dellite 72T, that is a ditallow-dimethyl-ammonium ion modified natural montmorillonite (MMT), with a mean particle size of 8  $\mu\text{m}$  supplied by Laviosa Chimica Mineraria (Italy), and Nanofil 5 by Sud-Chemie (Germany) organic intercalated MMT with distearyl dimethylammonium chloride. The calcium carbonate (CaCO<sub>3</sub>), with a density of 2.93 g/ml, was supplied by Sigma Aldrich (product number 202,932).

### Methods

#### Nano-/microcomposite

All the components were dried at 100°C for 18 h before processing. The mixing process was carried out in a Haake Rheomix 600 internal mixer. The mixing temperature was set to 170°C and the rotor speed was 70 RPM. The nano- and nano/microcomposites were prepared by melt blending the PP, PPgMA, and nanoclays for 3 min, after which CaCO<sub>3</sub> microparticles were added to the mixing chamber. The total mixing time was 10 min.

The notation used for the nano/microcomposites was PP/X/Y/Z, where X is the weight percentage of PPgMA with respect to PP, Y is the weight per-

TABLE I  
Composition Used in this Work

Blend	PPgMA (wt %)	Clay (wt %)	CaCO <sub>3</sub> (wt %)
PP/0/0/0	0	0	0
PP/10/0/0	10	0	0
PP/15/0/0	15	0	0
PP/25/0/0	25	0	0
PP/0/1/0	0	1	0
PP/0/3/0	0	3	0
PP/0/5/0	0	5	0
PP/10/1/0	10	1	0
PP/10/3/0	10	3	0
PP/10/5/0	10	5	0
PP/15/1/0	15	1	0
PP/15/3/0	15	3	0
PP/15/5/0	15	5	0
PP/25/1/0	25	1	0
PP/25/3/0	25	3	0
PP/25/5/0	25	5	0
PP/15/7/0	15	7	0
PP/15/0/15	15	0	15
PP/15/0/18	15	0	18
PP/15/0/20	15	0	20
PP/15/0/22	15	0	22
PP/15/3/15	15	3	15
PP/15/5/15	15	5	15
PP/15/7/15	15	7	15

centage of nanoclay with respect to the overall polymer content (PP + PPgMA), and Z is the weight percentage of CaCO<sub>3</sub> with respect to the nanocomposite (PP + PPgMA + Nanoclay) (Table I).

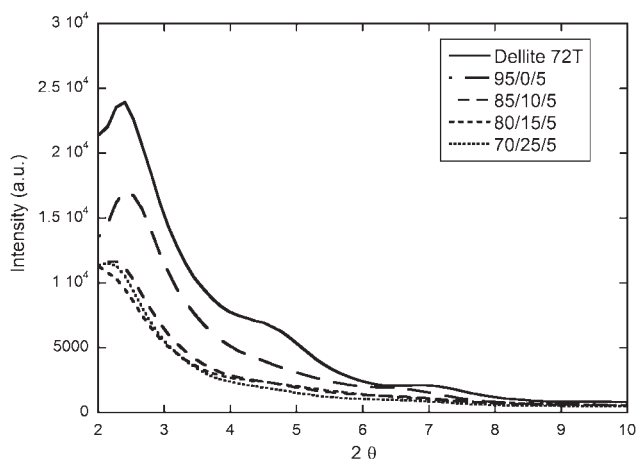
#### Evaluation of intercalation or exfoliation

The degree of intercalation or exfoliation of nanocomposites was evaluated by using a wide-angle X-ray Scattering and rheometric techniques. The wide angle X-ray diffraction analysis was performed at room temperature by using a Philips X-ray generator and a Philips diffractometer, type PW1710. The X-ray beam was nickel-filtered CuK $\alpha$  radiation of wavelength 1.54 Å operated at the generator voltage of 40 kV and current of 20 mA. The diffraction intensity data were collected automatically at a scanning rate of 0.6°/min with 0.01°/s steps. The WAXS analysis was performed on discs of 25 mm diameter and 1 mm thickness.

The rheological analysis was performed by using a parallel plate rheometer (ARES Rheometric Inc.), using discs of 25 mm diameter and 0.1 mm thickness. The complex viscosity was measured over a frequency range of 0.01–10 Hz at 200°C in a nitrogen environment.

#### Measurement of crystallinity and thermal stability

A differential scanning calorimeter (TA Instruments DSC 2920) was used to evaluate the effect of nanoparticles on the polymer crystallinity. The specimens



**Figure 1** Effect of PPgMA content on the X-ray patterns of the nanocomposites.

cyclically heated and cooled from  $-30$  to  $210^{\circ}\text{C}$ , using a heating/cooling rate of  $5^{\circ}\text{C}/\text{min}$ . To estimate the degree of crystallinity, the following equation<sup>12</sup> was used:

$$X = \frac{\Delta H}{\Delta H_{100}} \cdot 100 \quad (1)$$

where  $\Delta H$  is the heat of crystallization of the sample analyzed ( $\text{J}/\text{g}$ ) and  $\Delta H_{100}$  is a reference value that represents the heat of crystallization for a 100% crystalline polymer. For PP  $\Delta H_{100}$  is  $209 \text{ J}/\text{g}$ .<sup>13</sup> The heat of crystallization of the samples was measured after melting of the specimen to delete the thermal and mechanical history.

The thermal stability of layered nanocomposites was investigated by using a thermogravimetric analyzer (TGA) (TA Instruments, TGA 2950) by using a heating rate of  $10^{\circ}\text{C}/\text{min}$  from room temperature to  $600^{\circ}\text{C}$  in inert (nitrogen) atmosphere.

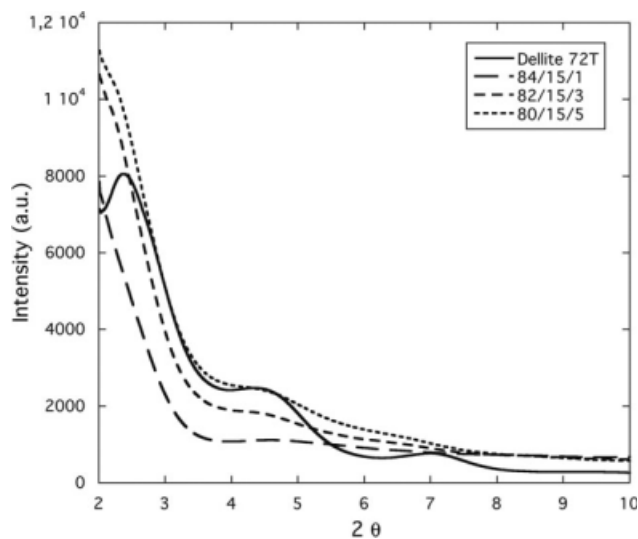
### Mechanical properties

The effect of composition on mechanical properties was carried out on a dynamometer (Instron 4204) at a crosshead speed of  $10 \text{ mm}/\text{min}$ . The samples were prepared according to ASTM D638 by compression molding at  $200^{\circ}\text{C}$ . Five specimens of each sample were tested and the mean values and standard deviations were calculated. A hot press was used to produce thick plates of PP microcomposite and nano/microcomposite; from thick plates dog bone samples were obtained for mechanical tests.

## RESULT AND DISCUSSION

### Degree of intercalation or exfoliation

Some preliminary results showed that the use of compatibilizer was necessary to obtain intercalation

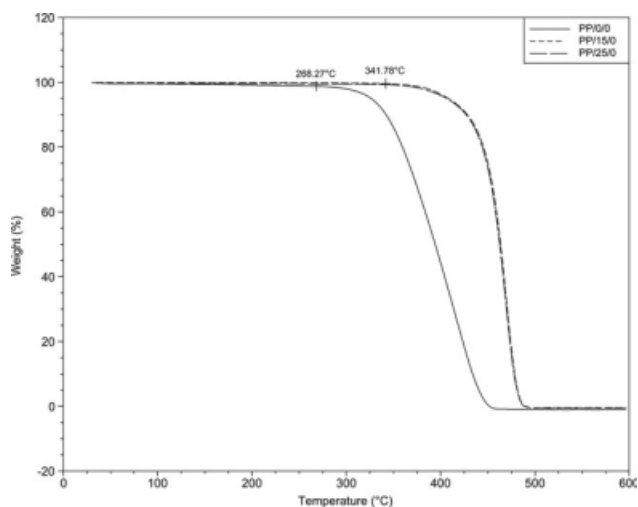


**Figure 2** Effect of nanoclay content on the X-ray patterns of the nanocomposites.

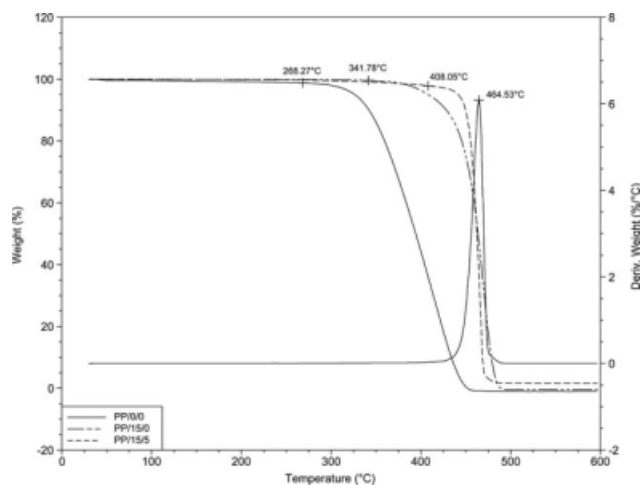
of the nanoclay in the PP, as confirmed by previous works.<sup>8</sup> In Figures 1 and 2, the X-ray patterns of the blends obtained by changing the compatibilizer and nanoparticles content are shown. In both cases, a shift of the clay peaks toward lower values of  $2\theta$  is evident. This means that a possible increase in the interlayer spacing due to intercalation of the polymer in the layered silicate platelets took place.

### Crystallization and thermal stability

The thermogravimetric analysis was used to monitor the weight loss of samples as a function of time or temperature. This technique is widely used to evaluate the effect of nanoparticles in nanocomposites degradation and/or oxidation processes, in which intercalated/exfoliated nanoparticles induce a strong increase in the thermal stability.<sup>14</sup> In Figure 3, the



**Figure 3** TGA of PP/PPgMA systems.



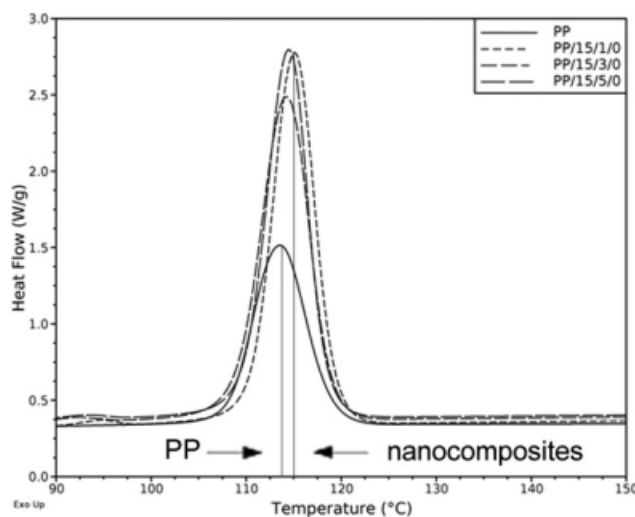
**Figure 4** Comparison of TGA of nanocomposites with bulk PP.

thermal stability curves of unfilled PP and PP/PPgMA blends are shown. As evident, the PP/PPgMA system with 15 wt % of MA has a better thermal stability when compared with the PP behavior (onset temperature of about 340°C), but an increase in compatibilizer content (PP with 25 wt % of MA), does not affect this parameter. The addition of 5 wt % of clay (Dellite 72T) induce a further increase in the onset temperature (about 410°C) (Fig. 4).

This behavior has been attributed to the enhancement of the platelets dispersion in the polymer matrix and to the formation of a carbonaceous-silicate char, builds up on the surface, that insulates the underlying material and slows the escape of volatile products generated during decomposition.<sup>15</sup> The residue at 600°C is slightly higher for nanocomposites because of the higher inorganic content in filled materials.

The intercalation process affected the crystallization behavior occurring during the controlled cooling of the samples, as shown in Figure 5. The analysis of the crystallization peaks of Dellite nanocomposites evidenced an increase in the degree of crystallization and a shift of the melt crystallization temperature to higher  $T_c$ . This has been attributed to the presence of nanoclay platelets dispersed in the matrix that promoted the heterogeneous nucleation and consequently increased the crystallization rate.

The calculated values of crystallinity are shown in Table II. The presence of calcium carbonate induced an increase in the crystallinity due to the nucleating effect of the microparticles, whereas nanofillers exhibited an opposite effect. This behavior is probably to be addressed to the hindering effect of the platelets on the macromolecular mobility and is still present in the micro/nano mixtures that show a crystallinity higher than the pristine PP but lower



**Figure 5** Effect of clay content on the melt crystallization temperature of nanocomposites.

than the microcomposites with the same overall filler content.

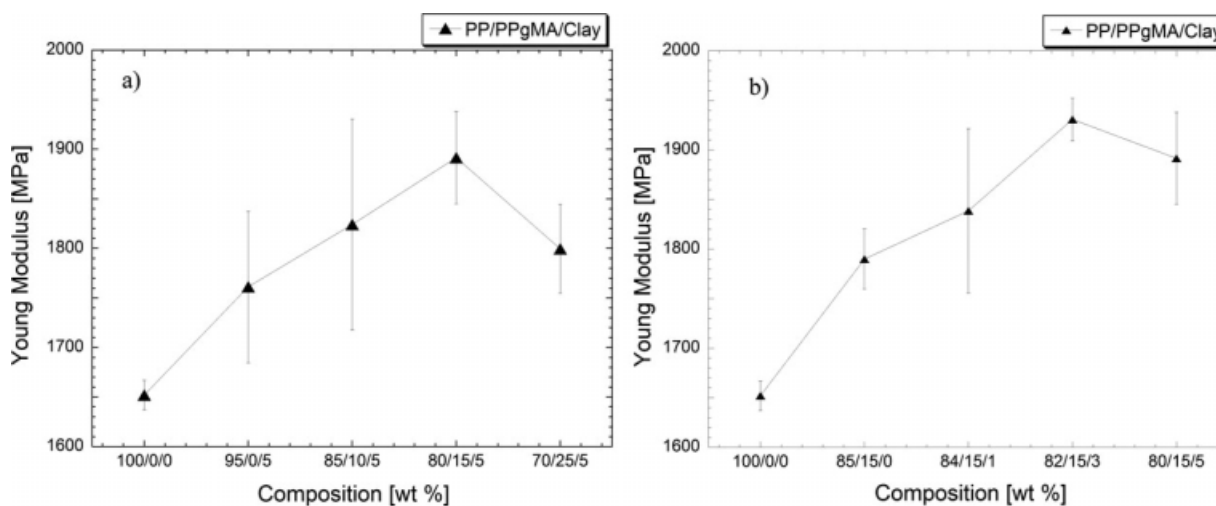
This trend was consistent with Lee et al.<sup>16</sup> who analyzed this effect at different cooling rate, but it disagreed with Modesti et al.<sup>17</sup> who showed a higher rise of crystallinity.

### Mechanical properties

The effect of compositions on Young's modulus is summarized in Figure 6. Figure 6(a) shows that the Young's modulus increases with the PPgMA content and reached a maximum at 15%, whereas the concentration of clay is kept constant at 5%. These results suggested that, by increasing the concentration of PPgMA, a higher degree of intercalation or exfoliation occurred and the rigidity of the nanocomposites was improved. However, higher concentration of PPgMA did not result in a further increase in the Young's modulus, evidencing an optimum concentration value of compatibilizer that maximized the rigidity of these nanocomposites, as reported by

**TABLE II**  
Crystallinity Values

	$\Delta H_c$ (J/g)	$X_c$
PP/0/0/0	97.49	46.64
PP/15/0/0	102.6	49.09
PP/15/1/0	96.27	46.52
PP/15/3/0	94.12	46.42
PP/15/5/0	87.15	43.89
PP/15/0/15	89.61	50.44
PP/15/0/18	91.54	53.41
PP/15/0/20	91.33	54.62
PP/15/0/22	84.78	52.00
PP/15/3/15	88.34	51.54
PP/15/5/15	87.7	52.45
PP/15/7/15	84.34	51.73



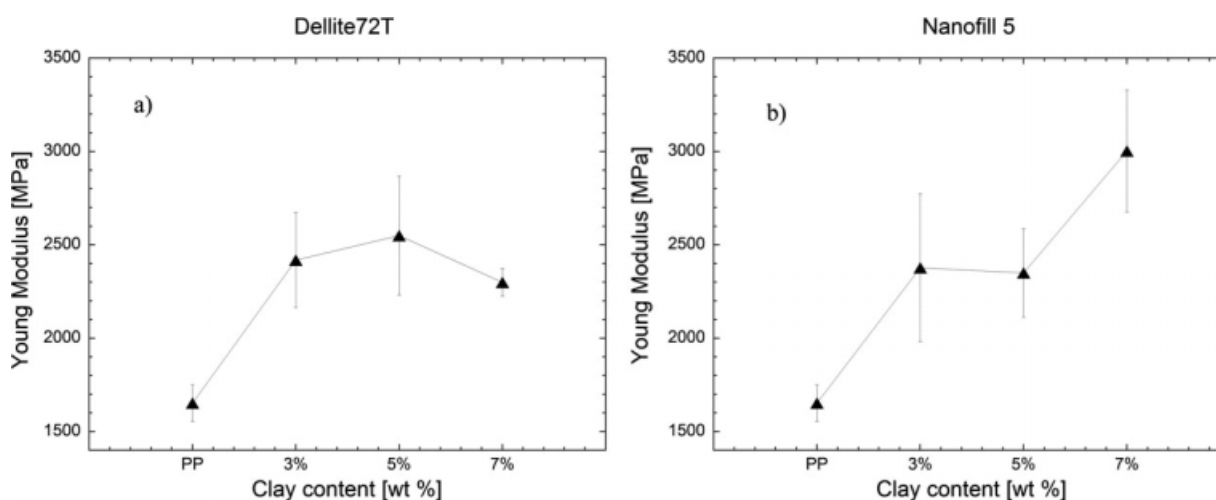
**Figure 6** Young's modulus of composites as function of (a) compatibilizer and (b) nanofiller contents (Dellite 72T).

Lertwimolnun and Vergnes.<sup>9</sup> On the basis of these results, a concentration of PPgMA equal to 15% was been set for the following studies. The effect of clay content, at constant concentration of PPgMA (15%) is reported in Figure 6(b), where the increase in the tensile modulus with the nanofiller content is shown. It is interesting to observe that for the prepared nanocomposites the maximum value of Young's modulus was obtained at concentration of clay equal to 3%. No further improvements were observed when the clay concentration was increased to 5%.

The X-ray and DSC analysis showed that nano-/microcomposites evidenced the same behavior when compared with the corresponding nanocomposites. Therefore, both the exfoliation or intercalation mechanism and the crystallization mechanisms were not significantly affected by the addition of CaCO<sub>3</sub> particles used for the preparation of the nano-/microcomposites.

The Young's modulus of nano-/microcomposites as a function of clay type (Dellite and Nanofil) and content are reported in Figure 7. All the nano-/microcomposites contained 15% of CaCO<sub>3</sub> and 15% of PPgMA. For both nanocomposites, an increase of about 50% (from 1652 to 2418 MPa for the Dellite system and from 1652 to 2377 MPa for the Nanofil system) was obtained with a concentration of clay equal to 3%, whereas negligible increase was observed when the concentration of clay raised to 5%. Only for nanocomposites prepared with Nanofil a further increase of Young's modulus was obtained by raising the nanoclay concentration up to 7%. The Young's modulus increase from 1652 to 3002 MPa could be explained by the higher ability to be intercalated of Nanofil clay with respect to Dellite, but more work should be done to better explain this behavior.

The ultimate mechanical properties of the two nanoclays evidenced a mixed behavior (Fig. 8). The



**Figure 7** Effect of clay content and type on the tensile modulus of nano-/microcomposites.

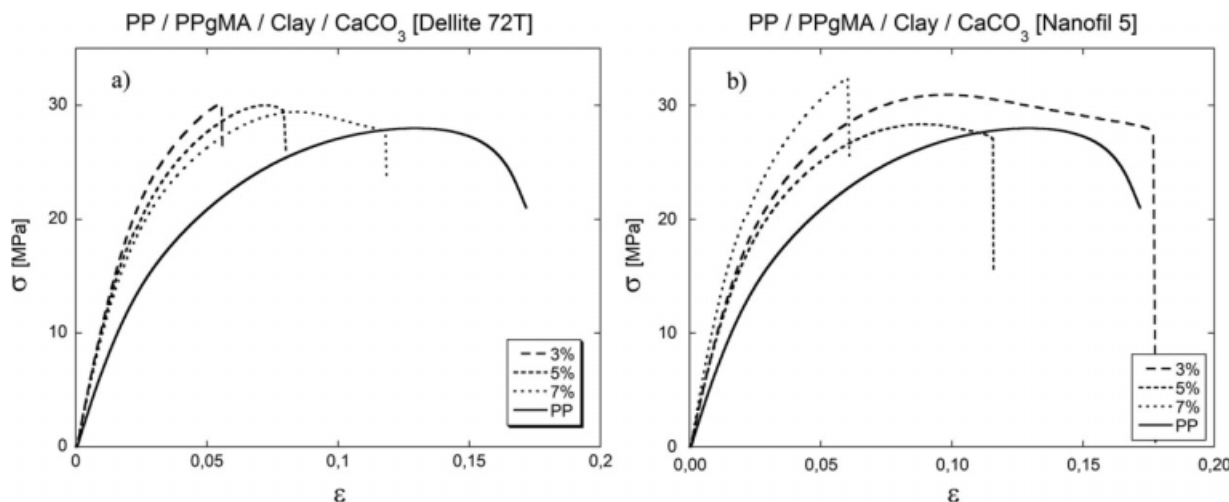


Figure 8 Comparison of stress-strain curves for (a) Dellite 72T e (b) Nanofil 5 nano-/microcomposites.

nano-/microcomposites based on the Dellite 72T exhibited an ultimate strain that grew with the clay content, whereas the yield stress was almost independent of the clay content. On the other hand, the nano-/microcomposites based on the Nanofil 5 showed a decreasing ultimate strain and a growing yield stress.

To show the mechanical contributions of the clays in these composites a comparison of the tensile modulus of nano-/microcomposites and microcomposites containing the same weight percentage of inorganic filler is represented in Figure 9. The composites containing only calcium carbonate have a Young's modulus approximately from 20% to 30% lower than the nano-/microcomposites containing the same total amount of inorganic components.

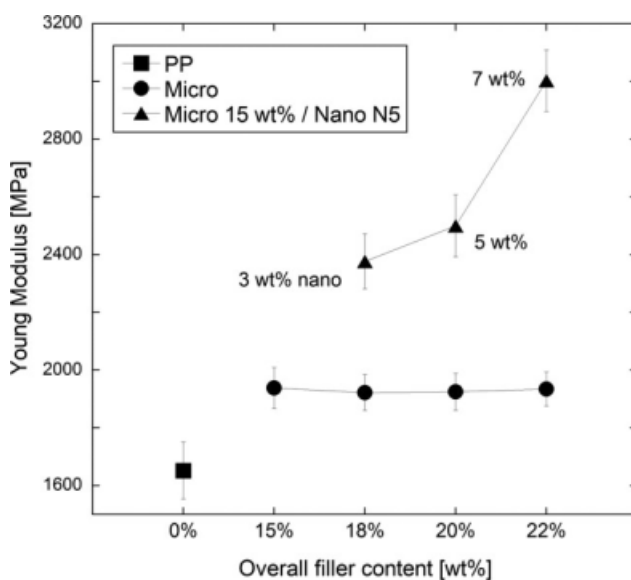


Figure 9 Young's modulus comparison between nano-/microcomposites and microcomposites containing the same wt % of inorganic filler.

This results is a proof that the nanoclay effectively contributes to the enhancement of the mechanical properties, at least for the compositions investigated.

### Rheological behavior and Carreau-Yasuda model

A rheological characterization was performed to analyze the influence of the composition on the flow behavior of the nano-/microcomposites. The rheological behavior was described in terms of the Carreau-Yasuda model without the yield stress parameter,<sup>18</sup> as reported in eq. (2).

$$\eta^*(\omega) = \eta_0 [1 + (\lambda\omega)^a]^{(n-1)/a} \quad (2)$$

where  $\eta_0$  is the zero shear viscosity,  $\lambda$  is the time constant, and inverse the  $1/\lambda$  is the critical value of shear rate at which the viscosity begins to decrease. The slope in the power law region is given from  $(n - 1)$ , while  $a$  is the Yasuda parameter and represents the amplitude of the region of transition between  $\eta_0$  and the power law region (shear thinning) (Fig. 10).

All parameters obtained by fitting rheological data are listed in Table III. The superposition between the

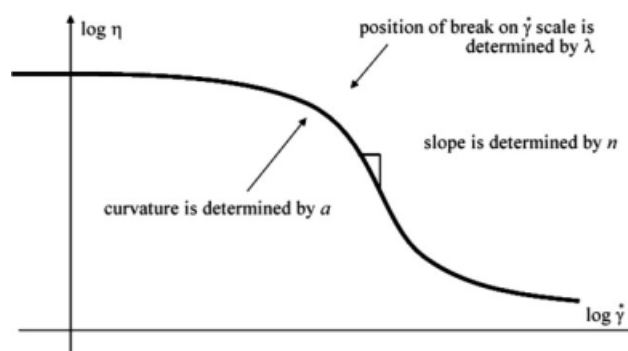


Figure 10 Theoretical rheological behavior of a nano-composite.

TABLE III  
Carreau-Yasuda Parameters Obtained From Fitting

	$\eta_0$ (Pa s)	$\lambda$ (s)	$a$	$n$
PP/15/0/0	2301	0.14	0.42	0.20
PP/15/0/15	5408	0.70	0.43	0.25
PP/15/0/18	7485	1.57	0.43	0.29
PP/15/0/20	7660	0.54	0.34	0.18
PP/15/0/22	10420	0.58	0.31	0.18
PP/15/3/15	12091	2.20	0.42	0.29
PP/15/5/15	11788	1.70	0.33	0.31
PP/15/7/15	12015	1.10	0.32	0.27

experimental data and the fit curve of complex viscosity was excellent. For the nanocomposites,  $\beta$  and  $a$  decreased as the clay content increased, exhibiting a not-Newtonian behavior. The complex viscosity of PP microcomposites (Fig. 11) increases as a function of filler content at low frequencies. The viscosity of PP nano-/microcomposites (Fig. 12) increases much more with increasing silicate content compared with the microcomposites. This is related to the volume fraction of the platelets or aggregates, which are more hindered in their rotations and movements of polymer chains.

The confinement of polymer chains within the MMT layers give rise to an higher energetic barrier for segmented motions in the confined space leading to a structure that can cause pseudo-solid behavior. Such behavior can be attributed to the formation of mesoscopic structures in the nanocomposite constituted by layers of silicates and polymer chains sequences bound by physical, chemical, and electrostatic interactions.

These results show a strong reinforcing effect of the silicates, giving rise to an improved thermomechanical stability of the matrix at elevated temperatures. For example, a 20 wt % of calcium carbonate sample

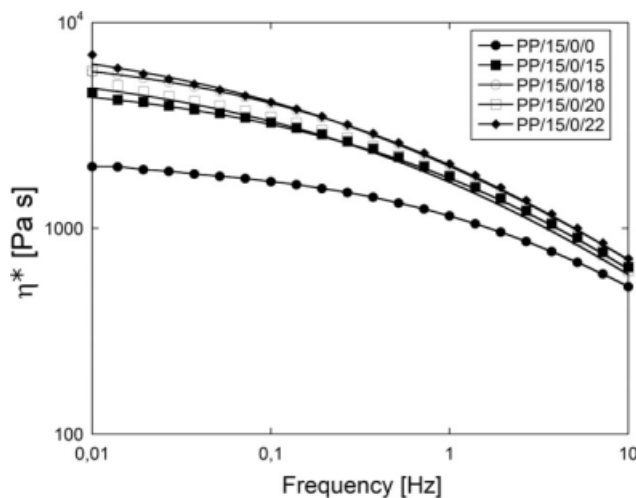


Figure 11 Effect of microfillers on the rheological properties of composites.

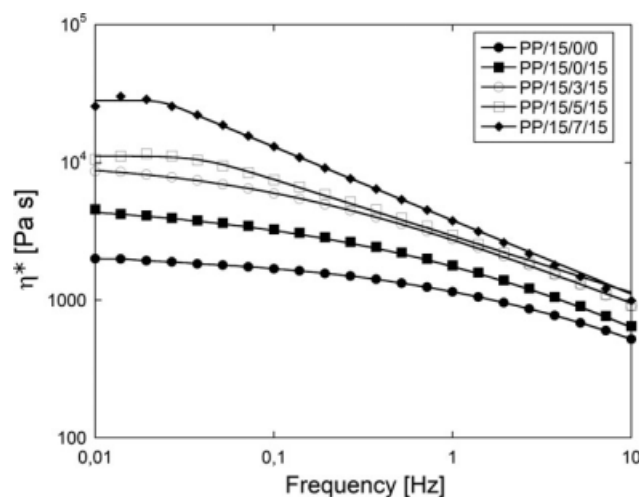
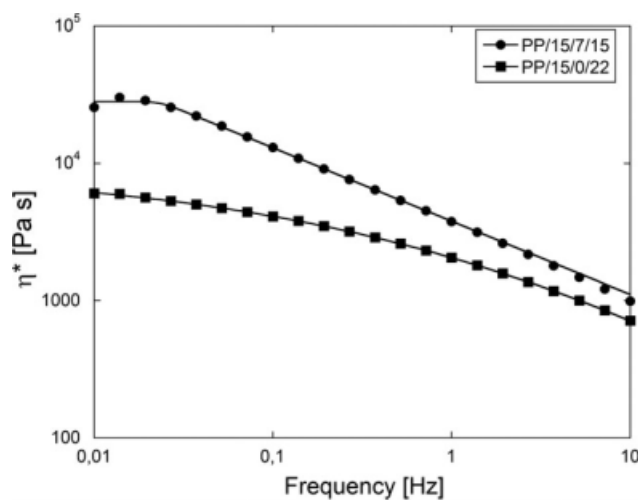


Figure 12 Effect of nanofillers on the rheological properties of composites.

exhibited a smaller  $\lambda$  value when compared with nano-/microcomposites with the same inorganic filler content, while the  $n$  values indicate a more pronounced shear-thinning behavior for nanocomposites.

By increasing the filler content the viscosity increases considerably in intercalated/exfoliated nanocomposites, especially at low shear rates or low frequencies.<sup>15</sup> Usually unfilled polymers have a constant viscosity over a large frequency range with shear-thinning behavior at higher frequencies or shear rates. Nanocomposites with filler content above a few percent show shear thinning over the entire range of frequencies.<sup>19,20</sup> The unlimited increase in the viscosity when the shear rate goes to zero is caused by the presence of a network structure in the melt that leads to a yield stress. This can be caused by the dispersed particles, which can touch or connect to each other to form a continuous structure. The formation of a network does not require a physical connection between the particles. It is sufficient that the particles feel each others presence and are able to transfer stresses.<sup>19</sup> The probability that particles form a network depends on the interactions between the particles, on their shape (aspect ratio) and on their interparticle distance. A reduction of the distance between particles or an increase of the aspect ratio at constant volume fraction increases the probability that the particles connect. Because of their large aspect ratio, the space needed by the intercalated/exfoliated silicate layers to freely rotate in the melt is much larger than the volume they occupy. Therefore, the percolation threshold of exfoliated layered silicates is very low.<sup>19</sup>

A comparison of the complex viscosities of a micro- and nano-/microcomposite for the 22 wt % filler content is shown in Figure 13. In every condition, the complex viscosity of the nano-/



**Figure 13** Comparison of complex viscosities of a micro- and nano-/microcomposite with the same inorganic filler content.

microcomposites is higher when compared with that of microcomposites with the same inorganic filler content.

## CONCLUSIONS

The preparation and characterization of nano-/microcomposites, based on PP, and their comparison with corresponding microcomposites with the same content of inorganic filler has been discussed.

The samples were prepared by using two different organic-modified MMTs and/or a micrometric calcium carbonate. They were characterized by using X-ray diffraction, TGA, DSC, and mechanical properties. Compositions with effective intercalation of the nanoclay were found and remarkable increments of the Young's modulus was measured. In fact, the tensile modulus of the nanocomposite increased for all clay concentrations (from 1 to 7 wt % with respect to PP) being more than 30% higher than that of the neat PP. In some cases an increment was found for the ultimate tensile strength and strain.

A rheological analysis was used to investigate the effect of intercalation of nanoparticles in the nano- and nano-/microcomposites. The Carreau-Yasuda model was used to fit the rheological data and to describe the effects of platelets and microfillers on

the rheological behavior. Both micro- and nanocomposites exhibited enhanced rheological properties when compared with neat material, but nano-/microcomposites showed higher viscosity and elastic modulus with respect to the corresponding microcomposite with the same inorganic filler content, as confirmed by the parameter of the Carreau-Yasuda analysis.

The comparison of mechanical properties between micro-, nano-, and nano-/microcomposites showed that the replacement of a small amount of microfiller with the corresponding amount of nanofiller induce a strong increase in the Young's modulus.

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## References

- Sumita, M.; Tsukurmo, T.; Miyasaka, K.; Ishikawa, K. *J Macromol Sci Phys* 1983, 22, 601.
- Sumita, M.; Tsukurmo, T.; Miyasaka, K.; Ishikawa, K. *J Mater Sci* 1983, 18, 1758.
- Dagani, R. *Chem Eng News* 1999, 77, 25.
- Akelah, A. *J Mater Sci* 1996, 13, 3589.
- Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1996, 61, 1117.
- Gray, H. *Adv Mater* 1997, 9, 731.
- Rong, M.; Zhang, M.; Zhang, Y. *J Mater Sci Lett* 2000, 19, 1159.
- Fornes, T. D.; Yoon, P. J.; Hunter, D. L.; Keskkula, H.; Paul, D. R. *Polymer* 2002, 43, 5915.
- Lertwimolnun, W.; Vergnes, B. *Polymer* 2005, 46, 3462.
- Lertwimolnun, W.; Vergnes, B. *Polym Eng Sci* 2006, 46, 314.
- Wang, Y.; Chen, F. B.; Wu, K. C. *J Appl Polym Sci* 2005, 97, 1667.
- Ozawa, T. *Polymer* 1971, 12, 150.
- Van Krevelen, D. W. *Properties of Polymers*, Elsevier: Amsterdam, 1990;
- Bellucci, F.; Camino, G.; Frache, A.; Ristori, V.; Sorrentino, L.; Iannace, S.; Bian, X.; Guardatole, M.; Vaccaio, S. *e-Polymers* 2006, 014.
- Zanetti, M.; Camino, G.; Reichert, P.; Mulhaupt, R. *Macromol Rapid Commun* 2001, 22, 176.
- Lee, J. W.; Kim, M. H.; Choi, W. M.; Park, O. *J Appl Polym Sci* 2006, 99, 1752.
- Modesti, M.; Lorenzetti, A.; Bon, D.; Besco, S. *Polym Degrad Stabil* 2006, 91, 672.
- Berzin, F.; Vergnes, B.; Delamare, L. *J Appl Polym Sci* 2001, 80, 1243.
- Krishnamoorti, R.; Yurekli, K. *Curr Opin Colloid Interface Sci* 2001, 6, 464.
- Solomon, M. J. *Macromolecules* 2001, 34, 1864.