Effects of extrusion process, type and content of clays, and foaming process on the clay exfoliation in HMS PP composites

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ABSTRACT: The use of a high melt strength polypropylene (HMS PP) matrix reinforced with layered clays could be very useful to improve the properties of materials produced with processes involving melt stretching, like foaming. The control of the particles structure, that is, the degree of exfoliation and the clay distribution in the polymeric matrix, is the key to achieve the desired properties. In this study, the effects of the extrusion process, the clay type and content, and the foaming process on the morphology of different HMS PP based composites are studied. Both, natural and organomodified clays were used. The extrusion process has a negative effect in the composites containing natural clays as their interlayer distance decreases as the number of extrusion cycles increases. On the contrary, this process improves the intercalation of the organomodified clays. However, in both composites the interlayer spacing decreases when the clay content increases. While a percolated network is formed in the composites containing organomodified clays, no network is formed with the natural clays. Finally, the effect of the foaming process has also been analyzed. The Improved Compression Moulding (ICM) route was used to produce the foamed materials. This technique subjects the materials only to a temperature and a pressure gradient without applying any other external forces that could contribute to the clay exfoliation. In this way, only the effects of foaming and melt stretching are observed. In both composites, an increase in the interlayer distance is observed when the materials are foamed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42828.

INTRODUCTION

Common linear polypropylene (PP) has many desirable properties such as good temperature stability, good chemical resistance, high melting temperature, high tensile modulus, and the capability of static load bearing.[1] These beneficial properties have permitted to use polypropylene in different applications. However, its linear structure leads to poor processability in processes involving melt stretching, such as extrusion coating, film blowing, thermoforming and foaming.[2] A way to improve the polymer melt strength is to incorporate long chain branches (LCBs). The PPs with LCBs show a pronounced strain hardening and hence an improved melt strength.[3] Another way used to enhance the melt strength of linear PPs is to incorporate layered silicates. Several authors have proved that an increase in the melt strength is obtained by increasing the clay content.[4–6] Furthermore, the mechanical performance, the thermal stability and the flame retardancy of the polymeric matrix can also be improved by adding nanoparticles.[7–10] Nevertheless, all these properties are greatly affected by the degree of filler exfoliation

and dispersion achieved during the mixing process. A fully dispersed and stable state will lead to optimal properties whereas the presence of particles agglomerates or a low compatibility between the particles and the polymeric matrix lead to a poor material performance, which can be even lower than that of the unfilled polymeric matrix.[11] Consequently, one of the keys to achieve the desired properties is the control of the particles structure, that is, the degree of exfoliation and the clay distribution in the polymeric matrix.

Measuring the quality of exfoliation and dispersion in a composite is not trivial. This has been traditionally characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Nevertheless, these traditional techniques are limited in the sense that they only prove a small volume of the sample and therefore, they should be combined with other techniques such as melt rheology. Both, linear and non-linear rheological properties are very sensitive to changes in the nanoscale and mesoscale structure and therefore, rheology can be used as a powerful tool to evaluate the dispersion of the particles in the

melt state.[12–14] Moreover, one of the main advantages of rheology is that samples of macroscopic dimensions are used and hence, rheology offers an integrated picture of the composite material.

The degree of exfoliation has been widely investigated in composites produced with a common linear PP and montmorillonites. The effects of using non-organomodified and organomodified montmorillonites have been studied together with the effects of the initial interlayer spacing and the clay content.[4,5,15–20] The effects of the amount and kind of compatibilizer employed have also been thoroughly investigated.[5,16,18–23] Finally, the production parameters have also been modified in order to analyze the effect of the production process on the clay structure.[22–26]

From these studies, it can be concluded that a better intercalation between the clay and the polymer is obtained by using organomodified montmorillonites.[15] The use of a compatibilizer improves the intercalation between the montmorillonites and the linear PP.[16,18,23] Moreover, the interlayer spacing increases as the ratio of compatibilizer increases.[23] Clay exfoliation can only be achieved when a high compatibility between polymer and clays exists.[5] There seems to be an optimum range of initial interlayer distance for obtaining an effective intercalation.[16] The aggregation of small portions of layers is produced and the level of intercalation is reduced when the clay content increases.[17] The melt processing route, that is, the way in which the different raw materials are blended, also conditions the clay structure.[26] The processing temperature is also very important. When a low processing temperature is used the shear stress is higher and therefore, the clay exfoliation is promoted.[24]

While the clay structure of linear PP/montmorillonite layered composites has been extensively investigated, as far as the author knowledge, there are no many papers that study the degree of intercalation/exfoliation of layered composites produced with a HMS PP. In fact, only one paper has been found. Bhattacharya et al.[27] characterized their materials by using XRD and TEM. They obtained an increase in the interlayer spacing for the polymer nanocomposites relative to the pure organomodified clay. Moreover, they found that this distance decreased as the clay content increased. TEM results revealed that the clay particles were well dispersed within the polymeric matrix. However, there is one aspect that has not been reported in this paper. HMS PP is normally produced from reactive extrusion or electron beam irradiation processes, in which LCBs are added to a common linear PP.[28,29] As a consequence, this polymer could be degraded in processes in which it is subjected to high shear forces (like in the extrusion process) and hence, changes on their rheological properties would also occur, so that the rheological study of the effect of the extrusion process on the clay morphology could be very interesting.

On the other hand, from the point of view of foaming applications, the system HMS PP/montmorillonites is very interesting due to the synergistic properties which could be achieved with the combination of this polymer and the layered silicates. However, as these properties are conditioned by the final composite morphology, the effect of the foaming process on the clay morphology should be also carefully analyzed. Up to know there are no many works focused on studying this aspect. Zheng et al.[30] foamed linear PP/clay nanocomposites by extrusion using CO_2 as blowing agent. They reported that supercritical CO_2 is helpful for expanding further the interlayer spacing and for promoting the partial exfoliation of nanoparticles in PP/clay nanocomposites. Zhai et al.[31] foamed PP/silica nanocomposites by extrusion using CO_2 as blowing agent. They found that the multisilica aggregates could be dispersed during the foaming process. They explained this result considering that the biaxial stretching action during cell growth could be transferred onto the nanoparticles.

Taking these ideas into account, the goal of this work is to analyze the effects of the extrusion process, the clay content and the foaming process on the structure of HMS PP/layered clays composites. For this purpose, two completely different composites have been studied. The first material was produced using non organomodified (natural) clays and without a compatibilizer, while in the second material both organomodified clays and a compatibilizer were used. To analyze the effect of the extrusion process, the composites have been subjected up to three extrusion cycles. The effect of the extrusion process on the dynamic rheological properties of the pure HMS PP has also been investigated to determine if the polymer is being degraded during this process. Moreover, composites containing three different clay contents (2.5, 5, and 7.5 wt %) were generated in order to analyze the effect of the clay content. Finally, cellular materials were produced by the Improved Compression Moulding (ICM) route in order to analyze the effect of the foaming process.[32–35] ICM was selected because in this foaming process the material is only subjected to temperature and pressure and hence, there are no other forces associated to the foaming process which could contribute to the clay exfoliation (such as shear forces in extrusion foaming).

EXPERIMENTAL

Materials

A branched high melt strength PP (HMS PP) supplied by Borealis (PP Daploy WB 135 HMS) with a MFI of 2.4 g/10 min (230°C/2.16 kg) was used in this study. The HMS PP density at room temperature is 0.905 g/cm³. Two kind of commercial clays were also used. A non organomodified montmorillonite, Cloisite® Na+ supplied by Southern Clay Products with a density of 2.86 g/cm³, from now called "Na+" and an organomodified montmorillonite with quaternary ammonium salt, Cloisite® 20A also supplied by Southern Clay Products, with a density of 1.77 g/cm³, from now called "C20A." A maleic anhydride modified homopolymer polypropylene (PP-MA), Polybond 3200, supplied by Chemtura with a MFI of 115 g/10 min (190°C/2.16 kg), was used as a chemical compatibilizer with the organomodified clays C20A.

Antioxidants Irgafos 168 and Irganox 1010 (from Ciba) were also employed in order to reduce the thermal degradation of the polymers. The foaming was performed using a chemical blowing agent, azodicarbonamide (ADC) Lanxess Porofor M-C1 with an average particle size of 3.9 ± 0.6 µm. All the raw materials were vacuum dried at 50°C for 12 h before use.

Table I. Summary of the Formulations Produced with the Clays Na+

Sample name	HMS PP (wt %)	PP-MA (wt %)	Antioxidants (wt %)	Na+ (wt %)	ADC (wt %)	Number of extrusions
2.5Na+-1	97.4	0	0.1	2.5	0	1
2.5Na+-2	97.4	0	0.1	2.5	0	2
2.5Na+-3	97.4	0	0.1	2.5	0	3
Foam-2.5Na+-3	95.4	0	0.1	2.5	2	3
5Na+-1	94.9	0	0.1	5	0	1
5Na+-2	94.9	0	0.1	5	0	2
5Na+-3	94.9	0	0.1	5	0	3
Foam-5Na+-3	93.0	0	0.1	4.9	2	3
7.5Na+-1	92.4	0	0.1	7.5	0	1
7.5Na+-2	92.4	0	0.1	7.5	0	2
7.5Na+-2	92.1	0	0.1	7.5	0	3
Foam-7.5Na+-3	90.5	0	0.1	7.4	2	3

Composite Preparation

Composites with Na+ Clays. In the first step the natural clays (Na+), the antioxidants (a total amount of 0.1 wt % containing Irgafos 168 in a proportion of 0.08% and Irganox 1010 in a proportion of 0.02% by weight) and the HMS PP were melt-extruded using a co-rotating twin screw extruder Collin ZK 25T with L/D of 24. The rotational speed used was 50 rpm and the melt temperature was 200°C (Extrusion 1). Three composites containing three different contents of clays were produced (2.5 wt %, 5 wt %, and 7.5 wt %). Then, a second extrusion (Extrusion 2) was performed with the same twin screw extruder. In this case the rotational speed used was 120 rpm and the melt temperature was 155°C. Finally, a third extrusion (Extrusion 3) of these materials was done with the same extrusion parameters. The solid materials produced are summarized in Table I.

The pellets containing the blowing agent, for foaming, were prepared by mixing the composites obtained after the first extrusion with 2 wt % of the blowing agent (ADC). A rotational speed of 120 rpm was used and the melt temperature was 155°C. A second extrusion of the composite containing the blowing agent was performed, under the same conditions, in order to obtain a more homogenous material and in order to reach a total of three extrusions. To denote the solid composites containing the blowing agent, which were subsequently foamed, the word "Foam" has been added at the beginning of the corresponding nomenclatures (Table I).

Composites with C20A Clays. In the first step, a masterbatch containing the organomodified clays (C20A) and the compatibilizer PP-MA in the same proportion (1 : 1) was produced. The extruder described above was also used, with a rotational speed of 50 rpm and with a melt temperature of 200°C. Composites with the desired clay contents (2.5 wt %, 5 wt %, and 7.5 wt %) were prepared by diluting, under the same extrusion conditions, the previous masterbatch in the HMS PP. During this dilution process, the antioxidants were also added. This extrusion cycle, in which the masterbatch is diluted in the HMS PP, is called Extrusion 1 as it is the first time that the composite

HMS PP/C20A is extruded. Then, the composites containing the C20A were subjected to two additional extrusion cycles under the same conditions as the Na+ composites (120 rpm, 155°C).

Using the same procedure previously described for the Na+ samples, the composites obtained after the first extrusion were also blended with the blowing agent. The solid materials produced are summarized in Table II. The material containing 7.5 wt % of C20A (for foaming) does not appear in Table II because it was not possible to produce a foamed material with the same density as the other cellular materials using this composite.

The same processing route used with the polymer containing the Na+ was also employed with the pure HMS PP, with the aim of using this last material as a reference. The solid materials produced from the pure HMS PP are summarized in Table III. No cellular materials were manufactured with this polymer.

Foaming Process

The cellular materials were prepared via the Improved Compression Moulding (ICM) route. In this process the pellets containing the blowing agent are placed in a mold. Then the mold is situated in a hot-plate press. An initial pressure is applied to the system (41.5 bars) while it is heated until the foaming temperature (200°C), which is higher than the decomposition temperature of the blowing agent. After a certain time, (approximately 15 min) when the blowing agent is fully decomposed the pressure of the press is released allowing the polymer to expand until the desired ratio. Finally, the mold is introduced in cold water to cool-down the sample and hence stabilizing the cellular structure as fast as possible.[36] The peculiarity of this foaming system is that the mold used is a self-expandable mold that allows controlling the material density by mechanical means and therefore the foam density does not depend on the formulation used. Foams with a density of 0.18 g/cm^3 were produced. These foams are discs with a diameter of 180 mm and a height of 10 mm. A more detailed description of the ICM technique can be found elsewhere.[32–35]

Table II. Summary of the Formulations Produced with the Clays C20A

Sample name	HMS PP (wt %)	PP-MA (wt %)	Antioxidants (wt %)	C20A (wt %)	ADC (wt %)	Number of extrusions
2.5C20A-1	94.9	2.5	0.1	2.5	0	1
2.5C20A-2	94.9	2.5	0.1	2.5	0	2
2.5C20A-3	94.9	2.5	0.1	2.5	0	3
Foam-2.5C20A-3	92.9	2.5	0.1	2.5	2	3
5C20A-1	89.9	5	0.1	5	0	1
5C20A-2	89.9	5	0.1	5	0	2
5C20A-3	89.9	5	0.1	5	0	3
Foam-5C20A-3	88.1	4.9	0.1	4.9	2	3
7.5C20A-1	84.9	7.5	0.1	7.5	0	1
7.5C20A-2	84.9	7.5	0.1	7.5	0	2
7.5C20A-3	84.9	7.5	0.1	7.5	0	3

SAMPLES CHARACTERIZATION

X-ray Diffraction (XRD)

X-ray diffraction (XRD) was performed with a Bruker D8 Discover A25 diffractometer with Cu-Kα radiation of wavelength 0.154 nm to determine the structure of the layered clays. The diffraction spectrum was obtained over a 2θ range of 0–30°.

Solid precursors with a thickness of 0.5 mm produced by compression molding at a temperature of 220°C and with a pressure of 21.8 bars were used to conduct the XRD measurements of the non-foamed materials. Also the foamed materials were analyzed with this technique. These foamed materials were grinded in liquid nitrogen and the XRD experiments were performed in the powder of the foam.

Dynamic Shear Measurements

A stress controlled rheometer AR 2000 EX from TA Instruments was used to perform the tests. Dynamic shear measurements were conducted at a temperature of 250°C under a nitrogen atmosphere with 25 mm diameter parallel plates. A fixed gap of 1 mm was used to perform the rheological measurements.

Cylindrical samples with a thickness of 1.5 mm and a diameter of 22 mm were prepared in a hot-plate press at a temperature of 220°C and with a pressure of 70 bars. When the sample is loaded the particles network is partially deformed. The initial state could be recovered again waiting a certain time. In order to define a well-controlled starting point for all the rheological experiments a time sweep was previously performed at a frequency of 1 rad/s. This time sweep was conducted during 900 s.

After the initial time sweep a frequency sweep was carried out at the same strain, which was selected in order to be within the linear viscoelastic response of the material. The dynamic-mechanical experiments were performed over an angular frequency range of $0.01 < \omega < 100$ rad/s. From these measurements three parameters were analyzed, the dynamic shear viscosity (η^*), the storage modulus (G'), and the loss modulus (G'').

RESULTS

Effect of the Extrusion Process

Effect of the Extrusion Process on the Rheological Behavior of the Pure HMS PP. The effect of the extrusion process is first analyzed in the pure HMS PP. Figure 1 shows the complex viscosity (η^*), the storage modulus (G'), and the loss modulus (G'') as a function of frequency for the pure HMS PP as received and after one, two, and three extrusions.

The complex viscosity [Figure 1(a)] of the pure HMS PP at low frequency decreases as the number of extrusions increases and the transition from the Newtonian-plateau to the shear thinning regime was shifted to higher frequencies, which means that the Newtonian zone becomes broader. Moreover, the HMS PP that has not been extruded (HMS PP-0) is the material that exhibits the highest shear thinning behavior. The zero shear viscosity (η_0) in dynamic measurement has been obtained from the Eq 1 and the values are shown in Table IV.[37]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{1}$$

It is possible to detect a decrease in the zero shear viscosity when the number of extrusions increases. As the complex

Table III. Summary of the Formulations Produced with the Pure HMS PP

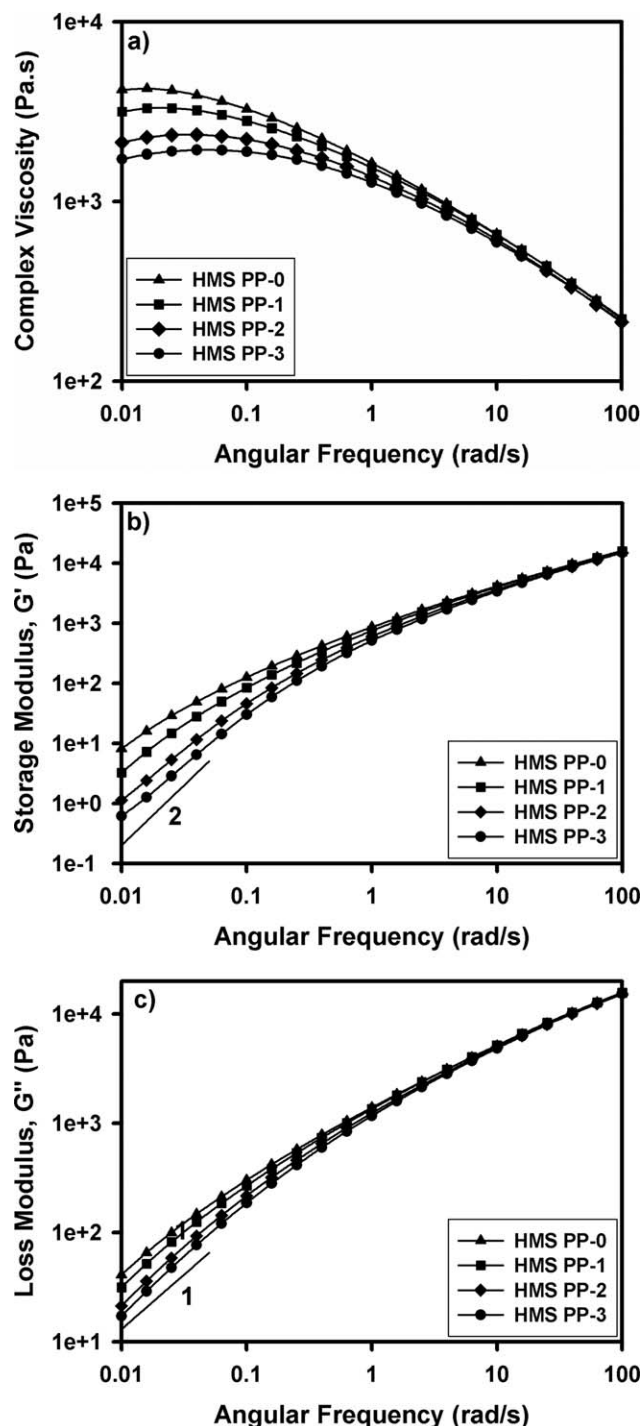| Sample name	HMS PP (wt %)	PP-MA (wt %)	Antioxidants (wt %)	Na+ (wt %)	C20A (wt %)	ADC (wt %)	Number of extrusions
HMS PP-1	99.9	0	0.1	0	0	0	1
HMS PP-2	99.9	0	0.1	0	0	0	2
HMS PP-3	99.9	0	0.1	0	0	0	3

Figure 1. Linear viscoelastic properties of the pure HMS PP after being subjected to different extrusions. (a) Complex viscosity as a function of frequency. (b) Storage modulus vs. angular frequency. (c) Loss modulus vs. angular frequency. The slope of both the storage modulus and the loss modulus in the terminal region is also shown in this figure.

viscosity, the storage modulus is also affected by the extrusion process [Figure 1(b)]. Indeed, the storage modulus is very sensitive to changes in molecular structure. At low frequencies, in the terminal region where only the longest relaxation times contribute to the viscoelastic behavior, it is well known that the

storage modulus is proportional to the square of the frequency, $G' \propto \omega^2$. This frequency dependency is not obtained with the HMS PP as received, since the branches add additional longer relaxations modes.[3,38] The slope of G' in the terminal region has been calculated and the values are shown in Table IV. As the number of extrusions increases, the slope of G' approaches 2. The effect of the extrusion process on the loss modulus (G'') is also shown in Figure 1(c). In the same way that $G' \propto \omega^2$ in the terminal region, the loss modulus is proportional to the frequency, $G'' \propto \omega$. The terminal slopes of G'' have also been calculated and the values are shown in Table IV. While both, the storage modulus and the complex viscosity are strongly affected by the extrusion process, no important changes are obtained in the loss modulus of the different materials. The crossover frequency (ω_x) is also shown in Table IV. This is the frequency at which G' and G'' intersect. In the materials, in which the crossover frequency is outside the measuring range, that is, ω_x is higher than 100 rad/s, this value has been calculated by extrapolating the G' and G'' curves at higher frequencies. The results show that when the number of extrusions increases the crossover point is shifted to higher frequencies.

In general, an increase in the molecular weight, molecular weight distribution or branching leads to a smaller Newtonian limit, a deviation from the terminal slopes and an increased shear thinning behavior.[38,39] Therefore, it can be concluded that some degradation of the polymer occurs during extrusion, either by a reduction in the number of branches or in the length of the chains.

Effect of the Extrusion Process on the Clay Exfoliation

XRD spectra patterns have been obtained for both, the pure clays and the polymeric composites. Clays show a characteristic diffraction peak corresponding to the (001) plane. From this peak the interlayer spacing (d) was calculated using the Bragg's equation:

$$\lambda = 2d \sin(\theta) \tag{2}$$

where λ is the wavelength and 2θ is the diffraction angle.

When this peak is shifted to lower angles means that an intercalated structure is obtained. The polymer chains penetrate the stacks of the silicate layer and swell the galleries of the silicate layers to a higher value without destroying the stacking of layers. On the other hand, it can also occur that such peak does not appear. The absence of the diffraction peak is normally attributed to an exfoliated structure. In the exfoliated or

Table IV. Linear Viscoelastic Properties of the HMS PP After Being Subjected to Different Extrusion Cycles

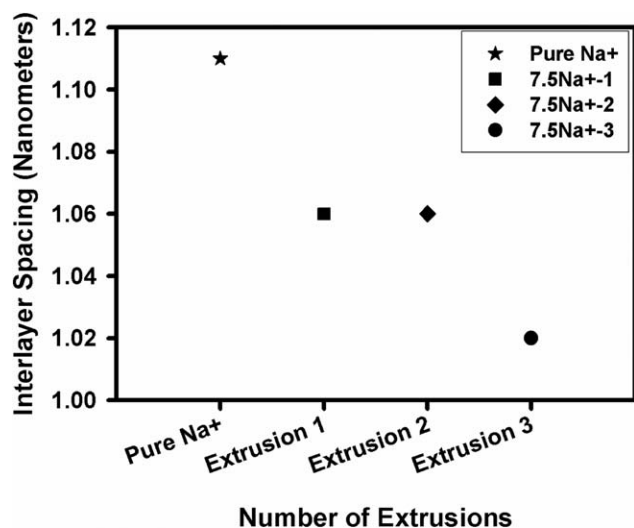| Sample name	Slope G' (Pa.s)	Slope G'' (Pa.s)	η_0 (Pa.s)	ω_x (rad/s)
HMS PP-0	1.38	0.97	4096	79
HMS PP-1	1.65	1.04	3140	95
HMS PP-2	1.73	1.06	2127	122
HMS PP-3	1.78	1.08	1716	134

Figure 2. Interlayer spacing of the pure Na+ together with that of the Na+ composites (containing 7.5 wt % of clays) after each extrusion cycle.

delaminated system the individual silicate layers are dispersed in the polymeric matrix.

The effect that the number of extrusions has on the Na+ exfoliation is analyzed in Figure 2. Only the HMS PP composite containing 7.5 wt % of Na+ is shown in the figure because a similar behavior is obtained for the other two composites produced with 2.5 wt % and 5 wt % of Na+.

First, d of the pure natural clays Na+ as received has been measured. These particles were not organomodified and therefore the initial d is already very small (1.11 nm) which hinders the exfoliation and dispersion of the clays in the polymeric matrix. Then the effect of the extrusion process is studied. After the first extrusion a decrease in the interlayer distance occurs. Then the composite undergoes a second and a third extrusion in which again a slight decrease in d is observed. XRD results indicate that in these HMS PP/Na+ composites when the number of extrusions increases the clay platelets are closer, although the differences found in d are very small. Therefore, in this material, in which the clay exfoliation is hampered by the fact of having non organomodified clays and absence of a compatibilizer, the extrusion process has a negative effect.

The effect of the extrusion process on the complex viscosity [Figure 3(a)] is also analyzed in the polymeric composites containing the highest amount of natural clays (7.5 wt % of Na+). The same conclusions that were obtained with the pure HMS PP are obtained with the composite produced with the natural clays. When the number of extrusions increases, the viscosity decreases, the Newtonian zone becomes broader and the shear thinning behavior also decreases. Consequently, the changes obtained are mainly due to modifications in the polymeric matrix and not to the fact of adding particles. Again the zero shear viscosity is calculated using Equation 1 and the results are shown in Table V. Although no important differences are found in the complex viscosity behavior, significant changes are obtained in the absolute values of the complex viscosity by the fact of adding natural clays to the polymeric matrix.

Independently on the number of extrusions, the zero shear viscosity of the polymeric composites is always 1.4 times greater than that of the pure HMS PP (Table IV). The effect of the extrusion process on the storage modulus of this composite is represented in Figure 3(b). As with the HMS PP, the main differences between the materials are found at low frequencies.
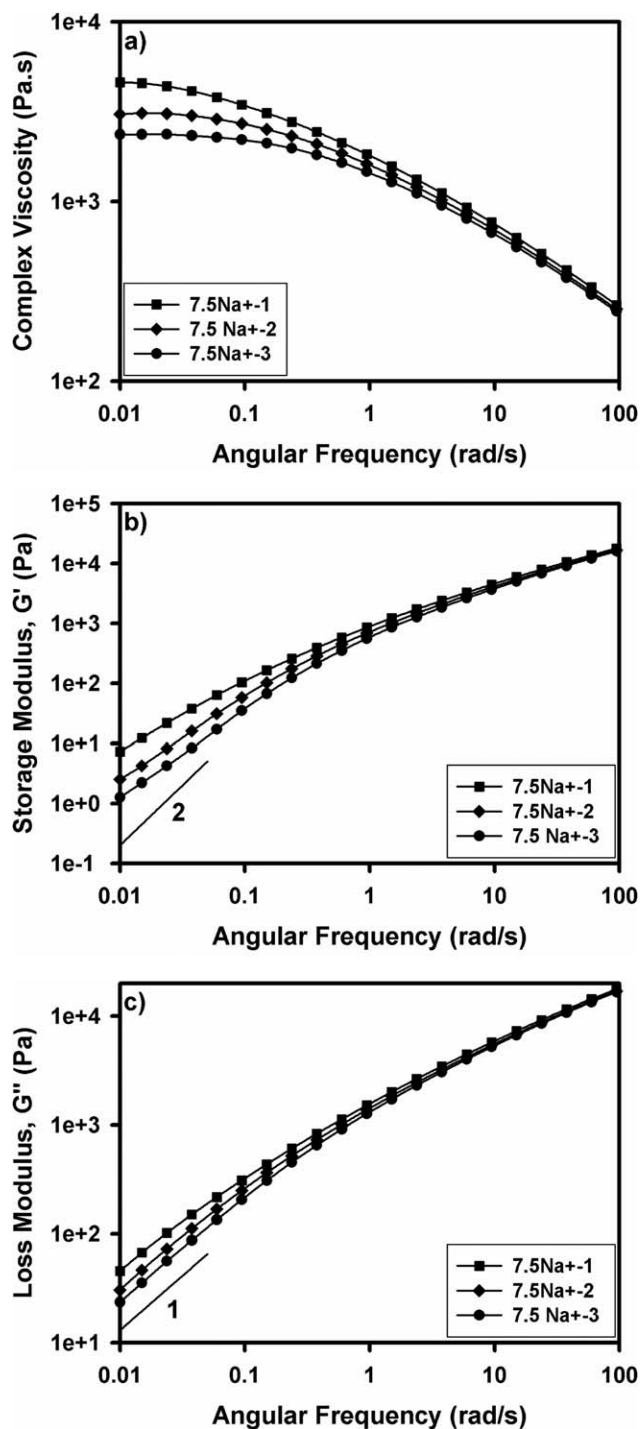

Figure 3. Linear viscoelastic properties of the composite containing 7.5 wt % of Na+ after being subjected to different extrusions. (a) Complex viscosity as a function of frequency. (b) Storage modulus vs. angular frequency. (c) Loss modulus vs. angular frequency.

Table V. Linear Viscoelastic Properties of Both the HMS PP and the Composite Containing 7.5 wt % of Na+ after Being Subjected to Different Number of Extrusions

Sample name	Slope G′ (Pa.s)	Slope G″ (Pa.s)	η_0 (Pa.s)	ω_x (rad/s)
HMS PP-3	1.78	1.08	1716	134
7.5Na+-1	1.28	0.93	4548	88
7.5Na+-2	1.35	1.00	3046	111
7.5Na+-3	1.39	0.99	2356	128

The slope of the curves in this terminal region is even lower than that of the pure HMS PP as both, Figure 3(b) and Table V indicate. Independently on the number of extrusions the slope of the PP composites is 1.2 times lower than that of the pure HMS PP. As the XRD results show that the particles are neither exfoliated nor intercalated, this decrease in the slope of the storage modulus is just a consequence of the large amount of natural clays used in this material (7.5 wt %). Finally, the loss modulus is also represented in Figure 3(c). No important changes are obtained in the loss modulus by adding the particles. As with the HMS PP the slope of G'' of the different PP composites is always 1 and the crossover frequency increases with the number of extrusions. From the analysis of the rheological results it can be concluded that when the clays are mainly agglomerated no important changes are detected in the rheological behavior of the composites in comparison with that of the unfilled polymeric matrix, apart from modifications of the absolute value of the viscosity.

The same analysis was performed with the organomodified clays, C20A. Figure 4 shows the XRD patterns of the pure C20A together with those of the composites after each extrusion. As with the HMS PP/Na+ composites only the interlayer distance of the composites containing 7.5 wt % of C20A is represented, as similar trends are obtained with the other clay contents.

XRD results show that the initial interlayer distance of the organomodified clays, C20A, as received, is 2.4 times larger than that of the natural clays, Na+. In this material the effect of the extrusion process is completely opposite to that obtained with the HMS PP/Na+ composites. The extrusion process has a positive effect and the interlayer spacing increases with the number of extrusions. Although this distance is higher, which means that the peak corresponding to the (001) plane has been shifted to lower angles, this peak still appears in the XRD results. Therefore, an intercalated structure is obtained and this intercalation is better as the number of extrusions increases, although a completely exfoliated structure is not achieved. During the melt extrusion process the clay agglomerates are under external forces from the polymer. Moreover, during this extrusion process, the polymer macromolecules are able to diffuse into the clay gaps. Both, the applied force on the clays and the diffusion of macromolecules would be affected by the extrusion conditions. During the melt extrusion process the polymer is able to separate the clay sheets due to two main reasons. First, the larger initial d that the C20A clays show favors the penetration of the polymer into the clay gallery. Second, the use of both

organomodified particles and a compatibilizer (PP-MA) makes more favorable the compatibilization between the clays and the polymer and consequently, the forces that the polymer exerts on the clay agglomerates are greater.[40–43]

The effect that the number of extrusions has on the dynamic linear rheological behavior of the HMS PP composite containing the highest amount of organomodified clays (7.5 wt % of C20A+) is also analyzed. Figure 5(a) shows that the complex viscosity increases with the number of extrusions. This behavior is completely opposite to that obtained either with the pure HMS PP or with the composite containing natural clays. In this kind of composites in which organomodified clays have been used, the extrusion process has an important effect on the clay exfoliation or, as in this case, in the clay intercalation. In these materials the low frequency Newtonian viscosity is not detected. This behavior is replaced by a non-Newtonian power law behavior. Due to both, the large amount of particles used and the increase in the interlayer spacing, the presence of a space-filling network caused by attractive forces between the clay particles is favored by increasing the number of extrusions. The clay platelet network that emerges behaves as a solid-like material and therefore, the complex viscosity increases with the number of extrusions. In these materials it is not possible to determine the zero shear viscosity using Equation 1, because this equation is only valid in the terminal region, and this region has not been achieved with the C20A clays. The storage and loss modulus are shown in Figure 5(b,c), respectively. Both moduli show a plateau at low frequencies which is characteristic of solid-like materials. Moreover, when the number of extrusions increases this plateau is broader. For a constant content of clays, an important increase in both moduli is obtained by increasing the number of extrusions. This is again indicating that the particles are being intercalated and that the formation of a particle network is being favored because the intercalated particles are more likely to touch each other. Furthermore, G' and G'' do not show a crossover frequency which once again indicates a
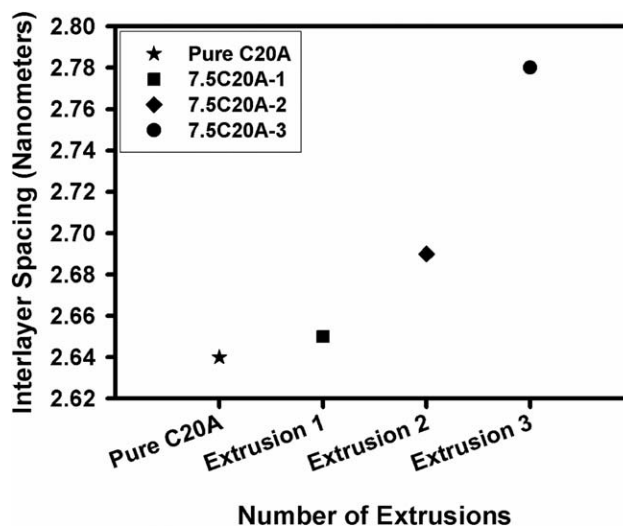
Figure 4. Interlayer spacing of the pure C20A together with that of the C20A composites (containing 7.5 wt % of clays) after each extrusion.
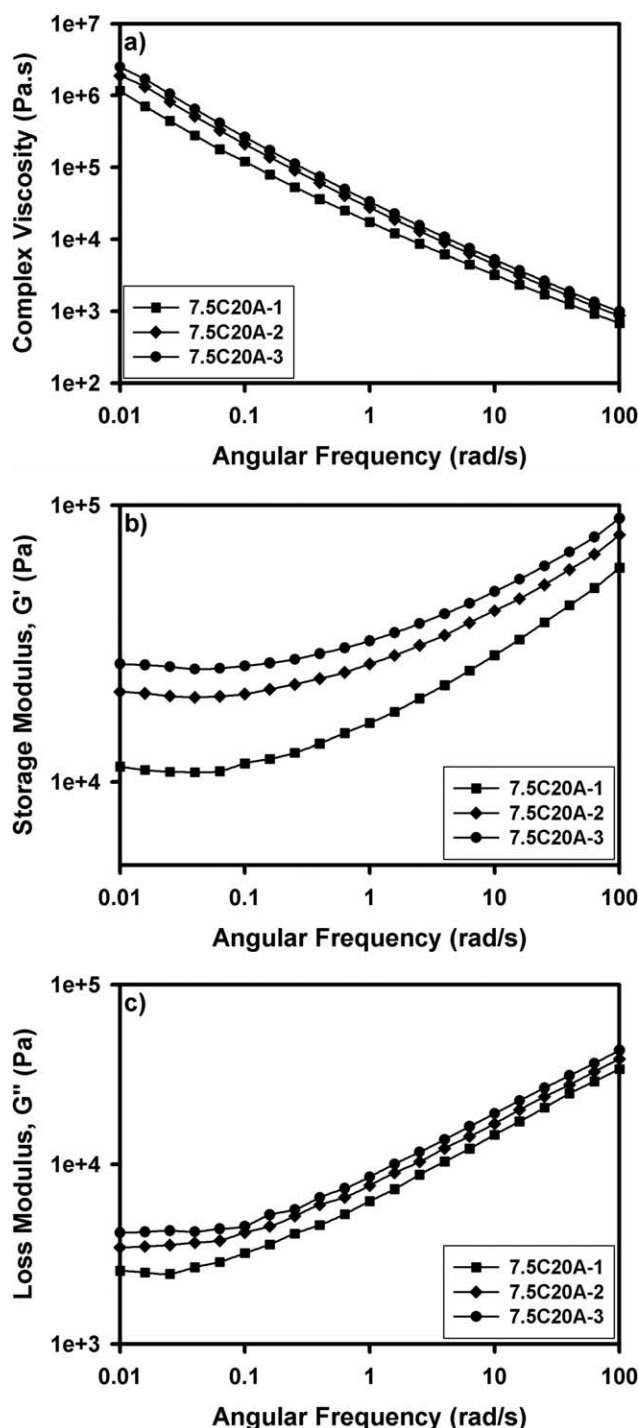
Figure 5. Linear viscoelastic properties of the composite containing 7.5 wt % of C20A after being subjected to different extrusions. (a) Complex viscosity as a function of frequency. (b) Storage modulus vs. angular frequency. (c) Loss modulus vs. angular frequency.

solid-like behavior in which the storage modulus lies well above the loss modulus in all the frequency range.

Effect of the Clay Content on the Clay Exfoliation

First, the composites containing natural clays, Na+, are studied. Figure 6 shows XRD results of the composites produced using

three different clay contents, 2.5, 5, and 7.5 wt %. Now, the number of extrusions has been maintained constant. Only the results of the materials after a total of three extrusions are shown, as similar behaviors are obtained with the other two extrusion cycles.

Independently on the clay content, the interlayer distance of the natural clays as received is always higher than that of the clays when they are blended with the polymer. As it was previously shown (Figure 2) the extrusion process has a negative effect in these composites. In addition, the fact of increasing the clay content also has a negative effect in the clay intercalation as the interlayer distance decreases as the clay content increases. From the analysis of the different results it can be concluded that the extrusion process is not effective in the exfoliation of natural clays, not even for low clay contents.

The linear dynamic rheological behavior of these materials has also been analyzed. The results of the composites together with those of the pure HMS PP are shown in Figure 7. When the amount of particles increases a slight increase in the complex viscosity is also obtained [Figure 7(a)]. However, no important differences are found between the different materials, as the values of the zero shear viscosity indicate (Table VI). In connection with the storage modulus [Figure 7(b)] its slope in the terminal region decreases; although, the values of this slope are always higher than one. The fact of increasing the clay content could favor the formation of a network structure and the behavior of the system could become similar to that of a solid one. However, in this case the complex viscosity shows a Newtonian plateau in the terminal region, the slopes of both moduli in this region are close to one and both, the storage and loss modulus intersect at a certain frequency (Table VI). These results indicate that in these materials a network structure has not been formed. A solid-like behavior is obtained when $G' > G''$ throughout the whole frequency range and G', G'' $\propto \omega^0$ in the terminal region.[12] With the amount of particles used the percolation threshold is not achieved. The formation
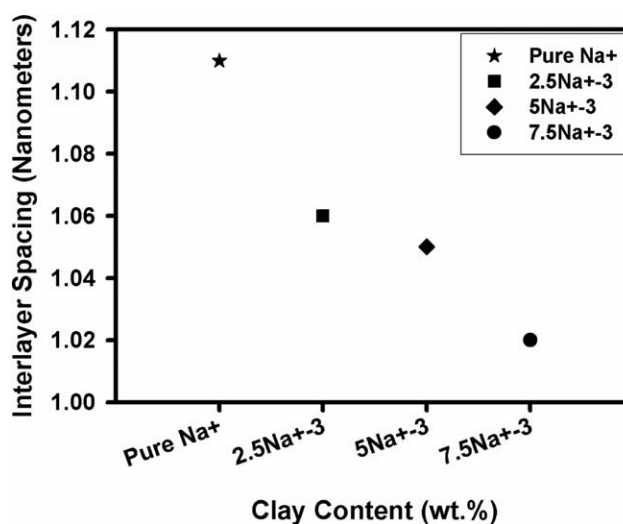

Figure 6. Interlayer spacing of the pure Na+ together with that of the Na+ composites produced with different clay contents, after three extrusions.
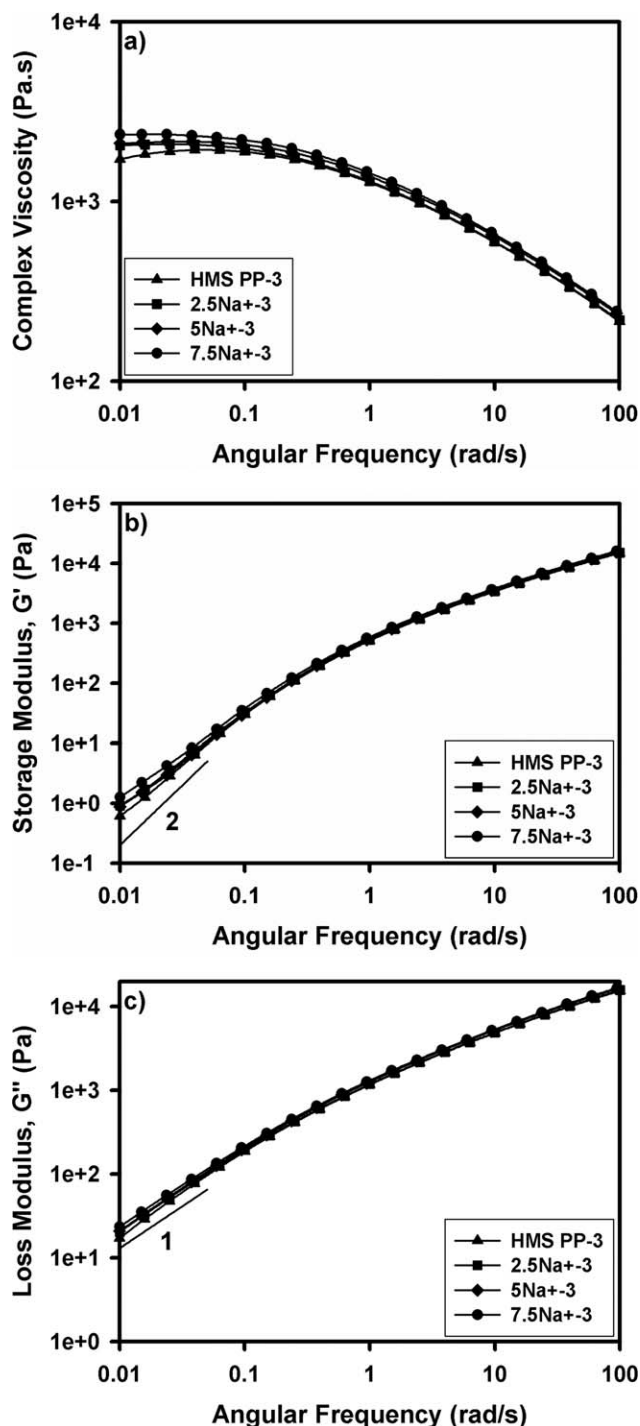
Figure 7. Linear viscoelastic properties of the pure HMS PP together with those of the composites containing different amounts of clays Na+ after being subjected to three extrusions. (a) Complex viscosity as a function of frequency. (b) Storage modulus vs. angular frequency. (c) Loss modulus vs. angular frequency.

Table VI. Linear Viscoelastic Properties of Both, the HMS PP and the PP Composites Containing Different Amounts of Na+ after Being Subjected to Three Extrusions

Sample name	Slope G′ (Pa.s)	Slope G″ (Pa.s)	η_0 (Pa.s)	ω_x (rad/s)
HMS PP-3	1.78	1.08	1716	134
2.5Na+-3	1.47	1.03	2030	148
5Na+-3	1.40	1.03	2088	137
7.5Na+-3	1.39	0.99	2356	128

results for the materials after three extrusions are shown in Figure 8. Due to the positive effect that the extrusion process has on the exfoliation/intercalation of organomodified clays, the interlayer spacing of the clays in the composite is always higher than that of the clays as received, independently on the clay content used. However, as with the natural clays, Na+, d decreases when the amount of particles increases because when large amounts of particles are used it is more difficult to exfoliate them. Although the best structure is obtained with the lowest amount of particles, this structure is still an intercalated one. With the most favorable conditions used in this work, a complete clay exfoliation has not been reached.

Furthermore, the linear dynamic viscoelastic behavior of these composites is also analyzed. The results of these measurements are shown in Figure 9. The viscoelastic properties of the melts change with the variations in the clay content. Figure 9(a) shows how the low frequency Newtonian plateau is progressively replaced by a non-Newtonian power law when the clay content increases. The slope in the terminal region of the storage modulus is zero for all the composites studied [Figure 9(b) and Table VII]. However, the slope of the loss modulus decreases progressively when an increase in the clay content is produced [Figure 9(c) and Table VII]. Finally, another
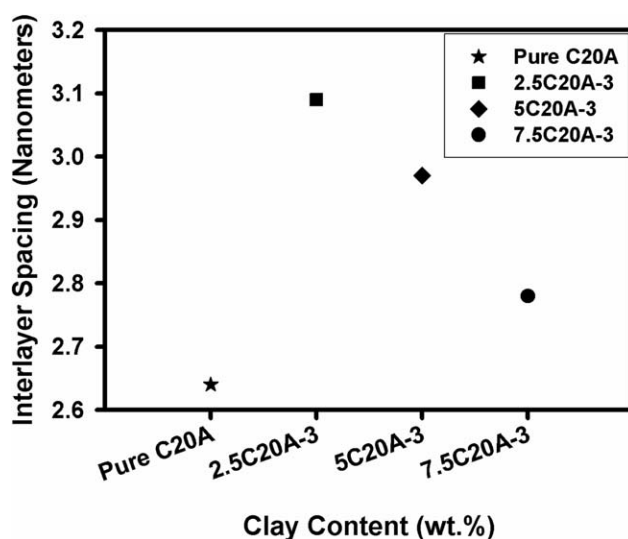

Figure 8. Interlayer spacing of the pure C20A together with that of the C20A composites produced with different clay contents after three extrusions.

of this percolated network is hampered by the fact of the poor intercalation achieved.

The effect of the clay content in the clay exfoliation of organo-modified clays (C20A) is also analyzed in this study. The XRD
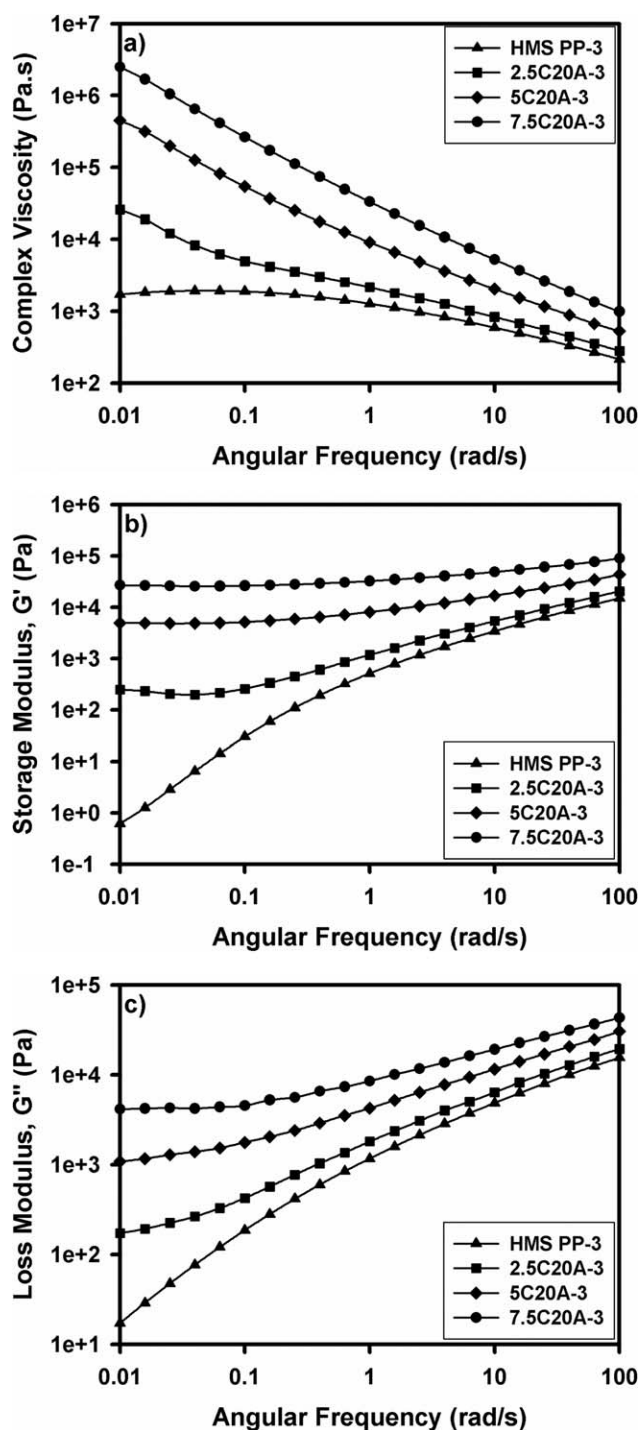
Figure 9. Linear viscoelastic properties of the pure HMS PP together with those of the composites containing different amounts of clays C20A after being subjected to three extrusions. (a) Complex viscosity as a function of frequency. (b) Storage modulus vs. angular frequency. (c) Loss modulus vs. angular frequency.

close to the percolation threshold. On the other hand, the rheological response obtained with the other two materials (5C20A-3 and 7.5C20A-3), which is more a solid like behavior, indicates that this clay contents are far above the percolation threshold.[12]

The percolation threshold (Φ_{per}) has been quantified. To determine this parameter, the Equation 3 has been used.[14]

$$G' = C\left(\Phi - \Phi_{per}\right)^{n} \qquad (3)$$

where C is a constant, n is a power law exponent, Φ is the clay volume fraction, Φ_{per} is the percolation threshold volume fraction and G' is the value of the storage modulus at low frequencies. Φ_{per} is obtained by fitting to a linear regression the curve $\log G'$ versus $\log\left(\Phi - \Phi_{per}\right)$. This was done for different values of Φ_{per}. The value of Φ_{per} for which the best fit is obtained is the percolation threshold of the composite. In this system, a value of the percolation threshold of 1 wt % was obtained. This result indicates that, in the case of the organomodified clays, all the clay contents employed all above the percolation threshold.

Effect of the Foaming Process on the Clay Exfoliation

The third objective of this work is to determine the effect of the foaming process on the clay exfoliation. XRD results are shown in Figure 10 for both, the composites produced with the natural clays and the composites produced with the organomodified clays.

In the two composites, an increase in the interlayer distance is produced when the materials are foamed. Figure 10(a) shows that the interlayer distance of the foamed composites HMS PP/Na+ is even higher than that of the pure Na+. While the extrusion process had a negative effect in the clay exfoliation the foaming process helps in getting a better clay structure. In the foamed material the interlayer distance decreases when the clay content increases just as it happened in the solid composites. The interlayer distance has increased about 1.2 times compared to the solid material. The same behavior is obtained with the organomodified clays [Figure 10(b)]. Nevertheless, in this case the increase in the interlayer distance is slightly higher (1.4 times) than that obtained in the natural clays. The larger interlayer spacing of organomodified clays and the use of a compatibilizer make the foaming process to be more effective in these composites. However, the clays are not completely exfoliated, not even after the foaming process since the diffraction peak corresponding to the (001) plane still appears in the diffractograms. As there are no external forces (like shear) associated to the foaming process that help the polymer macromolecules

noteworthy fact is that while the composite containing 2.5 wt % of C20A shows two crossover frequencies, as Table VII indicates, for the other two higher contents G' is greater than G'' in the whole frequency range. The rheological response of the material 2.5C20A-3 indicates that this amount of particles is

Table VII. Linear Viscoelastic Properties of Both, the HMS PP and the PP Composites Containing Different Amounts of C20A after Being Subjected to Three Extrusions

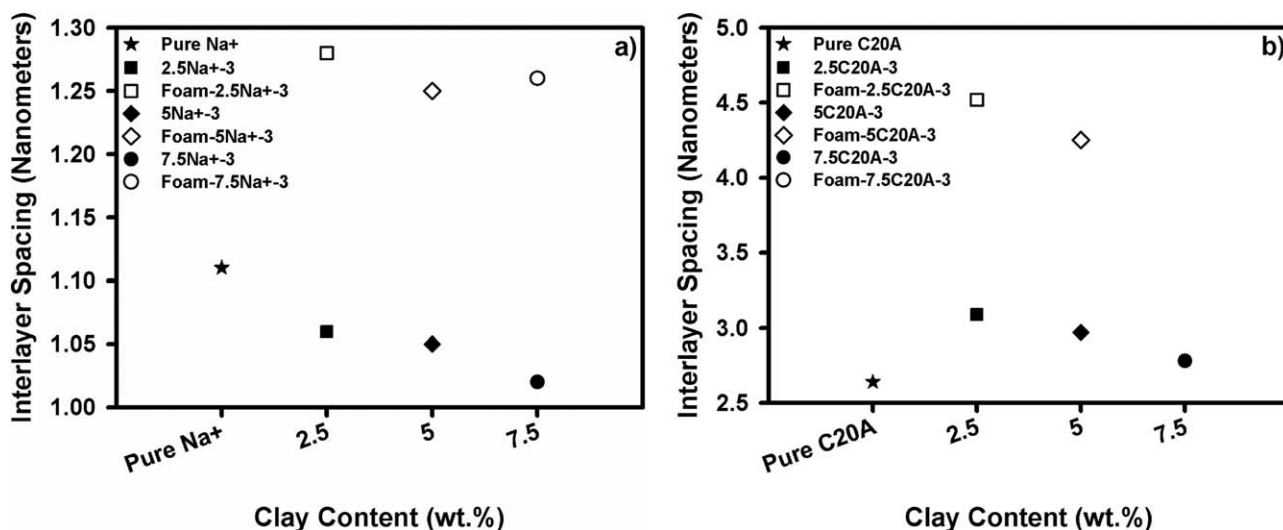| Sample name	Slope G' (Pa.s)	Slope G'' (Pa.s)	ω_{x1} (rad/s)	ω_{x2} (rad/s)
HMS PP-3	1.78	1.08	–	134
2.5C20A-3	−0.17	0.29	0.02	67
5C20A-3	−0.02	0.19	–	–
7.5C20A-3	−0.03	0.03	–	–

Figure 10. XRD results of the foamed materials. (a) Interlayer spacing of the pure Na+ together with that of the solid and foamed Na+ composites. (b) Interlayer spacing of the pure C20A together with that of the solid and foamed C20A composites.

to diffuse into the clay gaps, the increase in the interlayer distance is due to the expansion that the composite suffers during the foaming process. This expansion produces a physical separation of the particles and consequently their interlayer spacing increases.

CONCLUSIONS

The effects that the extrusion process, clay content and foaming process have on the morphology of two different HMS PP/clay composites have been widely analyzed in this work. For this purpose two different composites have been produced. The first composite was produced using only natural clays (Na+) and the second composite contains organomodified clays (C20A) and a compatibilizer (PP-MA).

XRD results show that while in the HMS PP/Na+ composites the extrusion process has a negative effect decreasing the clays interlayer spacing, in the HMS PP/C20A composites the extrusion process improves the clays intercalation. During this process the polymer is able to separate the clay sheets due to two reasons. First, the larger interlayer distance that the C20A clays show favors the penetration of the polymer into the clay gallery. Second, as a consequence of the greater compatibilization between the clays and the polymer, the forces that the polymer exerts on the clay agglomerates are greater, which helps to separate the clay layers. The linear dynamic rheological behavior of the pure HMS PP and the two composites was also studied. These results show that the HMS PP structure is affected by the extrusion process. During this process the polymer degrades. A reduction either in the content of branched components or in the length of the branched chain is taking place. The rheological behavior of the HMS PP/Na+ composites is affected by the extrusion process in the same way as the pure HMS PP. When the clays are not exfoliated no important changes are detected in the rheological behavior of the composites with regard to that of the unfilled polymeric matrix. Nevertheless, the rheological behavior of the HMS PP/C20A

composites is completely opposite to that obtained either with the pure HMS PP or with the other composite. Results indicate that the extrusion process favors the presence of a space-filling network caused by attractive forces between the clay platelets.

The effect of the clay content on the clay exfoliation is also studied. In both composites the interlayer spacing decreases when the clay content increases. As the interaction between the particles increases due to an increase in the particle content, it is more difficult to separate them. Rheological results indicate that in the HMS PP/Na+ composites a network structure has not been formed, with the clay contents used. However, in the composites produced with the C20A clays a value of the percolation threshold of 1 wt % has been obtained indicating that all the clay contents used in this work are above the percolation threshold.

Finally, the effect of the foaming process on the clay exfoliation has also been analyzed. In the two composites, an increase in the interlayer distance is produced when the materials are foamed. The expansion that the composite suffers during the foaming process produces a physical separation of the particles and consequently their interlayer spacing increases.

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