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Rheological, mechanical and transport properties of blown films of high density polyethylene nanocomposites

Cybele Lotti a, Claudia S. Isaac a, Marcia C. Branciforti a, Rosa M.V. Alves b, Susana Liberman c, Rosario E.S. Bretas a,*

a Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Rod. Washington Luis, Km 235, C.P. 676, São Carlos, SP 13565-905, Brazil
b Centro de Pesquisa e Desenvolvimento de Embalagens (CETEA), Campinas, SP 13070-178, Brazil
c Braskem S.A., III Polo Petroquímico, Via Oeste, Passo Raso, Triunfo, RS, 95853-000, Brazil

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Abstract

In this work, high density polyethylene (HDPE) was mixed in a twin screw extruder with organophilic treated clay, Cloisite 20A, and a compatibility agent, a HDPE grafted with maleic anhydride (PEMA). The screw profile was changed from a less dispersive (Profile 1) to a high dispersive configuration (Profile 2). A masterbatch procedure was used to obtain a final organoclay concentration of 5 wt.%. Both profiles allowed the intercalation of the HDPE into the clay, increasing the clay’s gallery distance to 3.7 nm. However, the samples produced with Profile 2 (Nano 2 samples) were more elastic and had a more stable structure than the samples produced with Profile 1. Therefore, two kind of blown films of Nano 2 samples were made: FN1 and FN2. The last one was blown at a higher screw velocity than the FN1. Both films had an increase of 95% in the elastic modulus and a reduction of 60% and 45% in O2 and water vapor permeability rates, respectively, compared to the film of pure HDPE. However, the FN2 structure was more unstable than the FN1 structure. It was concluded that both screw profiles gave the same level of HDPE intercalation in the clay; however, the more dispersive profile produced more time-stable and elastic structures. The increase in the elongation rate during the film blowing process produced also more time-stable morphologies; however, this higher orientation created matrix/filler interfacial defects.

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Keywords: Nanocomposites; Blown films; HDPE; Rheological properties; Transport properties

1. Introduction

The packaging industry plays a significant role in a nation economic development; thus, its improve-

ment can help the economic growth by increasing the efficiency of food marketing and other products, and by adding value to exports, for example [1]. In this context, nanocomposites, a new class of materials, have a fundamental role in this improvement, because they have better mechanical, thermal and barrier properties than the pure polymer [2]. The nanocomposites are characterized by the use of a

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reinforcement agent with nano dimensions, which is added in small quantities compared to the traditional composites. When these materials are processed by film blowing, better properties are expected, besides the improvement in the ability to withstand the tensions during the blowing.

The ability of a polymer to be blown depends on its melt strength or an equivalent rheological property, like the elongational viscosity, the zero shear viscosity or the storage modulus. The higher these properties are, the higher the bubble stability is.

The rheological properties of a nanocomposite are dependent on molecular weight, molecular weight distribution, branches amount, nanofiller concentration and dispersion. During the mixing and film blowing processes, the polymer and the nanofiller are submitted to an intense thermo-mechanical history in order to intercalate/exfoliate and disperse the filler; however, this thermo-mechanical history can also degrade the polymer. Thus, the measurement of the rheological properties before and after the processing can give indication of the type and stability of the formed structures.

The literature shows few works which evaluate the influence of the film blowing process on the nanocomposites final morphology. Shah et al. [3] demonstrated that the increase of draw down ratio reduced the gas permeability of an ionomer-nanoclay film due to a higher biaxial orientation of the clay platelets in the plane of the film, but the variation of blow-up ratio did not interfere. The exfoliated film had an increase of 50% in tensile modulus, without any significant reduction in tear strength and film extensibility. In another work, Ranadea et al. [4] showed that polyethylene grafted with maleic anhydride improved the nanoclay dispersion in the polyethylene matrix, which resulted in improved tensile and creep properties of the nanocomposites films. Min et al. [5] also studied the influence of a polyethylene grafted with maleic anhydride on the development of intercalated/exfoliated morphologies of blown films of high density polyethylene nanocomposites. A high compatibility agent content (PEMA/organoclay 20/1 ratio) improved exfoliation and, consequently, the mechanical and thermal properties. A 70% increase in tensile strength was obtained, even with the reduction in crystallinity due to the high amounts of compatibility agent. Nevertheless, none of these studies evaluated the effect of the processing conditions of the film blowing process in the morphology and properties of the nanocomposites.

In this work, some parameters of the mixing and film blowing processes were changed in order to study their influence on the intercalation/exfoliation level of films of a HDPE/clay nanocomposite [6]. The influence of these parameters on the rheological, mechanical and transport properties of the films was also analyzed.

2. Experimental

2.1. Materials

A HDPE (film blowing grade), HF0150 from Braskem S.A., with melt flow index of 10 g/10 min (190 °C, 2.16 kg), weight average molecular weight, Mw, of 420,907 g/mol and molecular weight distribution of 20.89 was chosen as matrix. An antioxidant was added by the supplier to avoid extensive thermal degradation. A HDPE grafted with maleic anhydride (1%), PEMA, trade name Polybond 3009 from Chemtura, with melt flow index of 5 g/10 min (190 °C, 2.16 kg) and melting temperature of 127 °C was used as compatibility agent. The nanoclay was montmorillonite, MMT, trade name Cloisite 20A from Southern Clay, organically modified with a dimethyl-dihydrogenated tallow-ammonium chloride salt and with less than 2% of moisture. The heat stability of the clay was measured by high resolution thermo-gravimetrical analysis, TGA, using a Hi-Res TGA 2950 equipment from TA Instruments, at a heating rate of 20 °C/min, under nitrogen atmosphere.

2.2. Mixing

It is known [7] that during mixing of a polymer with powder filler, the higher the polymer viscosity is the higher the stresses and the higher the dispersive mixing. On the other hand, the lower the polymer viscosity is, the higher the distributive mixing is. Thus, it is expected that in order to exfoliate the clay the temperatures should be the lowest, but in order to distribute the clay, the temperatures should be raised. Following this assumption, masterbatches of PEMA and MMT (75/25 wt.%) were produced in a co-rotating twin screw extruder, from Werner & Pfleiderer, model ZSK30, with \( D = 30 \) mm and \( L = 1065 \) mm. Mixing temperatures between 160 and 230 °C were tested. However, at the lowest temperatures, no extrusion was done because of the extremely high torques developed by the extruder. The optimal temperature range (moderate to low
torques) was found to be between 215 and 225 °C, at a screw velocity of 120 rpm, with a mass flow rate of 2.5 kg/h, which resulted in an average residence time of approximately 100 s. Two different screw profiles were tested: one designed basically with transport and kneading block elements (Profile 1), less dispersive, and other with two additional turbine elements (Profile 2), highly dispersive. Schemes of the two profiles are shown in Fig. 1. The resultant masterbatches processed at those two set of conditions were named Master 1 and Master 2, respectively.

The range of extrusion temperatures recommended by the HDPE supplier was between 180 and 220 °C. Thus, the masterbatches were mixed with the HDPE matrix and extruded at the same processing conditions than the masterbatches, producing two set of nanocomposites samples, Nano 1 and Nano 2. The final concentration of MMT, PEMA and HDPE in the nanocomposites was 5, 15 and 80 wt.%, respectively.

Blends of HDPE and PEMA (85/15 wt.%) using both screw profiles and conditions were also produced and were named Matrix 1 and Matrix 2, respectively.

2.3. Wide angle X-ray diffraction characterization (WAXS)

The extent of clay intercalation/exfoliation was determined by WAXS using a Siemens model D5000 diffractometer with Cu Kα radiation (λ = 1.5458 Å) operating at 50 kV and 30 mA. Samples were scanned between 0.6 and 12.0° at a rate of 1°/min. Measurements were recorded at each 0.02°.

2.4. Rheological characterization

Both polymers, HDPE and PEMA will be processed three times (production of masterbatch, nanocomposite and blown film); thus, even if the set processing temperatures were optimized to avoid degradation, the viscous heating could increase these temperatures and degraded the polymers. To study the thermo-mechanical degradation of both polymers, rheological measurements were made at high shear rates. The rheometer used was an Instron capillary, model 4467, with L/D = 33, L = 2.54 cm at T = 225 °C. The procedure was the following: the polymer pellets were passed through the capillary
once; the extrudate was collected and passed through the capillary twice, at the same conditions.

The high resolution TGA curve of the nanoclay is given in Fig. 2. It is observed an initial loss mass at approximately 50 °C, which can be attributed to water loss, and a second and extensive loss mass, between 231.8 and 450 °C, which is attributed mainly to organic surfactant degradation [8]. That is, the quaternary ammonium salt will be stable up to approximately 231 °C, which is higher than the processing temperatures. It is also worthwhile to mention that the residence time for the preparation of the masterbatches was very small; thus, in this work, it was assumed that surfactant loss or polymer degradation were minimal during the processing.

All the rheological measurements at low shear rates and low frequencies were made in a controlled strain rheometer ARES from Rheometric Scientific, using 25 mm plate-plate geometry, temperature of 225 °C, gap of 1 mm and nitrogen atmosphere. Measurements of steady state shear viscosity \( \eta(\gamma) \) were made between 0.01 and 100 s\(^{-1}\); delay before measurement input was determined from stress-overshoot experiments. Measurements of the storage modulus \( G' \), the loss modulus \( G'' \) and the complex viscosity \( \eta^* \) as a function of frequency and time were also done. The strain was set at 1%. The time sweep test was done at 1 rad/s during 4000 s. Stress growth experiments were made at a shear rate of 0.01 s\(^{-1}\) during 450 s; the shear rate was withdrawn and the relaxation tensions were measured during another 450 s.

The steady state shear viscosity at high shear rates was measured in an Instron Capillary rheometer, with \( L/D = 33 \) also at \( T = 225 \) °C.

### 2.5. Films blowing

The films blowing of the nanocomposites was made in a film blowing machine with annular matrix, from Collin, model ECS30, with screw length \( L = 500 \) mm and \( L/D = 25 \). The temperature range was set between 190 and 235 °C. After stable processing conditions were obtained for HDPE (FHDPE), the nanocomposite was processed at the same conditions (FN1) and at a higher screw velocity (FN2) than the FHDPE film. The films thickness varied between 39 and 55 \( \mu \)m. Table 1 shows the set conditions used for the film blowing, while Table 2 shows the nomenclature and description of the samples developed in this study.

### 2.6. Films mechanical characterization

Tensile tests of the blown films were made in an Instron Tensile Testing Machine model 5569 at room temperature, following ASTM-889, at machine direction. The elastic modulus was determined at 25 mm/min crosshead speed, while all other tensile characteristics were measured at 500 mm/min. At least five measurements for each sample were done.

### 2.7. Films permeability rates

The water vapor permeability rate (WPTR) was measured following ASTM F1249-016 standard test

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Set conditions for the nanocomposites film blowing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set conditions</td>
<td>FHDPE</td>
</tr>
<tr>
<td>( T_1 ) (°C) (Temperature of extruder screw zone 1)</td>
<td>190</td>
</tr>
<tr>
<td>( T_2 ) (°C) (Temperature of extruder screw zone 2)</td>
<td>210</td>
</tr>
<tr>
<td>( T_3 ) (°C) (Temperature of extruder screw zone 3)</td>
<td>209–210</td>
</tr>
<tr>
<td>( T_4 ) (°C) (Temperature of extruder screw zone 4)</td>
<td>220</td>
</tr>
<tr>
<td>( T_5 ) (°C) (Temperature of extruder screw zone 5)</td>
<td>220</td>
</tr>
<tr>
<td>( T_6 ) (°C) (Temperature of extruder screw zone 6)</td>
<td>220</td>
</tr>
<tr>
<td>( T_7 ) (°C) (Temperature of extruder die zone 1)</td>
<td>230</td>
</tr>
<tr>
<td>( T_8 ) (°C) (Temperature of extruder die zone 2)</td>
<td>235</td>
</tr>
<tr>
<td>( N_1 ) (rpm) (Extruder screw velocity)</td>
<td>62</td>
</tr>
<tr>
<td>( N_2 ) (m/min) (Nip rolls velocity)</td>
<td>2.1</td>
</tr>
<tr>
<td>( P_1 ) (bar) (Die pressure)</td>
<td>379</td>
</tr>
<tr>
<td>( E_1 ) (°C) (Bulk mass temperature)</td>
<td>210</td>
</tr>
</tbody>
</table>

Fig. 2. Thermogravimetric analysis of MMT (Cloisite 20A).
on Permatran equipment, model W3/31 with infra-red sensor, from MOCON at 38°C and relative humidity of 90%. The oxygen permeability rate (OTR) was measured following ASTM D3985-06 standard test using the coulometric method, in Oxtran equipment, model ST, from MOCON, with pure oxygen, at 23°C and pressure of 1 atm. For these tests the films thickness was measured with a micrometer of planar nib, model 732, from STAR-RETT, with resolution of 0.001 mm. Each test was performed on three samples.

2.8. Films surface characterization

To analyze the films roughness, their surface was analyzed by Atomic Force Microscopy (AFM), using a NanoScope IIIa equipment from VEECO Instruments, with head of 100 μm, in the contact mode. The mean surface roughness of the films $R_a$ was determined in a 50 μm x 50 μm area using the following equation [9]:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} |f(x,y)|dx\,dy$$  \hspace{1cm} (1)

where $f(x,y)$ = surface relative to a center plane, which is a flat surface parallel to the mean plane (the volume enclosed by the image surface above and below the center plane are equal) and $L_x$, $L_y$ = dimensions of the surface.

The standard deviation $R_q$ of the measured $Z$ values within the given area is calculated by [9]

$$R_q = \sqrt{\frac{\sum(Z_i - Z_{ave})^2}{N}}$$  \hspace{1cm} (2)

where $Z_{ave}$ = average of the $Z$ values within the given area, $Z_i$ = current $Z$ value and $N$ = number of points within the given area.

2.9. Films clay distribution

To analyze qualitatively the clay distribution, the mapping of some of the clay chemical elements (Si, Al, Mg and Fe) was done using a scanning electron microscope Philips model XL30, equipped with energy-dispersive X-ray spectroscopy (EDS), from Oxford Instruments, model 6650. It must be pointed out that the EDS mapping will not differentiate between clay aggregates, tactoids or lamellae, but it will map the clay distribution within the matrix. This is important to assure that after the film blowing, the clay is not accumulated in a preferential region.

3. Results and discussion

3.1. Pure polymers thermo-mechanical degradation

Fig. 3 shows the steady state shear viscosity $\eta(\dot{\gamma})$ at high shear rates of the pure polymers. It is observed that even after three runs, the HDPE viscosity did not change; thus, it is expected that this polymer will not suffer extensive thermo-mechanical degradation after continuous processing. On the other hand, the PEMA showed a slight increase in its shear viscosity after the second running. This increase might be credited [10] to the formation of a reversible physical network due to intermolecular dipole–dipole and/or hydrogen bonding interactions between the pendant maleic acid functional groups. The formation of the reversible network can be triggered by tension and/or temperature.

Table 2: Nomenclature and description of the samples developed in this study

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>Pure high density polyethylene</td>
<td></td>
</tr>
<tr>
<td>PEMA</td>
<td>HDPE grafted with 1% of maleic anhydride</td>
<td></td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite clay modified with a quaternary ammonium salt (Cloisite 20A)</td>
<td></td>
</tr>
<tr>
<td>Matrix 1</td>
<td>Blends of HDPE and PEMA (85/15 wt.%)</td>
<td>Extruded with Profile 1</td>
</tr>
<tr>
<td>Matrix 2</td>
<td>Blends of HDPE and PEMA (85/15 wt.%)</td>
<td>Extruded with Profile 2</td>
</tr>
<tr>
<td>Master 1</td>
<td>Masterbatches of PEMA and MMT (75/25 wt.%)</td>
<td>Extruded with Profile 1</td>
</tr>
<tr>
<td>Master 2</td>
<td>Masterbatches of PEMA and MMT (75/25 wt. %)</td>
<td>Extruded with Profile 2</td>
</tr>
<tr>
<td>Nano 1</td>
<td>Nanocomposite of HDPE, PEMA and MMT (80/15/5 wt.%)</td>
<td>Extruded with Profile 1</td>
</tr>
<tr>
<td>Nano 2</td>
<td>Nanocomposite of HDPE, PEMA and MMT (80/15/5 wt.%)</td>
<td>Extruded with Profile 2</td>
</tr>
<tr>
<td>FHDPE</td>
<td>Pure high density polyethylene</td>
<td>Blown film</td>
</tr>
<tr>
<td>FN1</td>
<td>Nano 2</td>
<td>Blown film processed at the same conditions than FHDPE</td>
</tr>
<tr>
<td>FN2</td>
<td>Nano 2</td>
<td>Blown film processed at a higher screw velocity than the FN1</td>
</tr>
</tbody>
</table>
3.2. Characterization of the mixtures

3.2.1. Wide angle X-ray diffraction

Fig. 4 shows the diffraction pattern of the MMT and the nanocomposites. The MMT displayed two main peaks, at 3.5° and 7°, which corresponds to the diffraction of its (001) planes and to a gallery distance of 2.5 nm. It can be observed that in the Nano 1 and Nano 2 samples, the MMT main peak at 3.5° dislocated to 2.4°, that is, both twin screw profiles allowed the intercalation of the HDPE into the MMT, increasing the clay gallery distance to 3.7 nm.

3.2.2. Rheological characterization

The results of the steady state shear viscosity \( \eta(\gamma) \) of the mixtures are shown in Fig. 5a. It is observed, at low shear rates, that none of the samples, including the HDPE, displayed a Newtonian plateau; at

the measured shear rates range, they behave as Bingham fluids (with an apparent yield stress). A Bingham fluid behavior is characteristic of highly filled polymers in which a percolated structure or a pseudo-solid behavior is observed. Also, highly linear polymers with high molecular weights in
which the amount of entanglements is elevated, as the HDPE used in this work, can behave as Bingham fluids at low shear rates, attaining the Newtonian plateau at extremely low rates. Therefore, the slope of the $\eta(\gamma)$ curve at low shear rates can be an indicative of clay dispersion/exfoliation [11,12]. A purely viscous fluid has a Newtonian viscosity (the slope of the $\eta(\gamma)$ curve will be zero, corresponding to 180°); a purely elastic solid has infinite viscosity (the slope tends to infinity, corresponding to 90°). The closer the slope is to −1 (corresponding to 135°) the higher the apparent yield stress will be and more solid-like behavior the material will have.

It can be observed that the slope increased from $-0.38$ (HDPE and blends) to $-0.62$ (nanocomposites). Thus, the nanocomposites had a higher yield stress and were more solid-like than the HDPE and the blends due to the presence of the nanoclay. However, no difference in viscosity between the Nano 1 and Nano 2 samples was observed; thus, from these results nothing can be inferred about the effectiveness of the different screw profiles in the clay dispersion.

<table>
<thead>
<tr>
<th>NANO1</th>
<th>MATRIX1</th>
<th>MATRIX2</th>
<th>NANO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0.38</td>
<td>0.42</td>
<td>0.62</td>
</tr>
</tbody>
</table>

At high shear rates all the mixtures were highly pseudoplastic, with a Power law index $n = 0.42$; all had lower viscosity than the pure HDPE, that is, both the PEMA and the MMT plasticized the HDPE at high shear rates.

The dynamic rheological properties of the mixtures can provide useful information for the films blowing process. Fig. 5b shows these properties for the samples. It is observed at low frequencies that Nano 2 was the more elastic of the samples while Matrix 2 was the least one; at high frequencies, Nano 1 was the more elastic of the samples, while Matrix 2 still was the least one. That is, the MMT increased the polymer matrix elasticity at all frequencies. This result is important for the film blowing process, because it is known that the higher the $G'$, the more stable the inflated bubble of the process will be [13,14]. Thus, it is expected that composition Nano 2 will present the more stable bubble during blowing if the extrusion velocities are low, while Nano 1 will present the more stable bubble if the extrusion velocities are high.

The slope of the $G'$ vs. $\omega$ curves, at low frequencies, can also give an indication of the state of dispersion (or miscibility) of the samples. For molten homopolymers, this slope is 2.0 ($G' \sim \omega^2$), while for solid homopolymers, this slope is 0 ($G' \sim \omega^0$) [15]. The curves of the Matrix 1 and Matrix 2 samples have a slope of 0.70 ($G' \sim \omega^{0.70}$); therefore, this behavior can be an indication of immiscibility between HDPE and PEMA. On the other hand, the curves of the Nano 1 and Nano 2 samples have a slope of 0.58, which can be an indication of the formation of a disperse pseudo-solid structure.

Therefore, from the WAXS and the steady state and dynamic rheological tests, it was concluded that both screw profiles produced similar clay intercalation and dispersion.

To test the time stability of both structures, the complex viscosity $\eta^*$ was measured as a function of time, at $\omega = 1$ rad/s and at 225 °C. Fig. 6 shows this parameter for the mixtures. The HDPE had almost no change in viscosity with time; both, Matrix 2 and Nano 2 samples had a very small increase in their viscosities with time (9% and 4% increase, respectively). However, Matrix 1 and Nano 1 samples had a high increase (30% and 85%, respectively) indicating that reactions or interactions were taken place during the rheological test. Therefore, the structures formed with Profile 1 were highly instable; in the case of Matrix 1, the screw profile probably allowed the formation of a reversible physical network within the PEMA [10], while Profile 2 disrupted the formation of this physical network due to the presence of the turbine elements. In the case of Nano 1, the screw profile did not allow that all the interactions and reactions between the clay, the PEMA and the HDPE would take place.

Thus, it was concluded that even if both screw profiles produced the same clay intercalation level and dispersion, the samples produced with Profile 2 (Nano 2 samples) were more elastic (at low extrusion rates) and had more time-stable structures; thus this composition was chosen to produce the blown films.

![Complex viscosity $\eta^*$ as a function of time for the mixtures at $T = 225$ °C and $\omega = 1$ rad/s.](image-url)
3.3. Film blowing and characterization

Two kind of blown films of the Nano 2 sample were produced, at the conditions described in Table 1. The FN2 film was blown at a 17% higher flow rate. Because the freeze line height was the same for both conditions, the elongation rate during blowing of the FN1 film was higher than of the FN2 [16,17]. The clay intercalation was analyzed by WAXS, as shown in Fig. 7. It is observed that both films had the same MMT gallery distance than the nanocomposite, showing that the film blowing process did not increase this distance.

In order to analyze the stability of the nanocomposites structure, measurements of the complex viscosity as a function of time of the blown films were made. The results are shown in Fig. 8.

The FN1 film had no change in complex viscosity with time; however, its viscosity was lower than of the Nano 2 mixture, probably because of the higher orientation promoted by the higher elongation rate; on the other hand, the FN2 had a slightly higher viscosity than the Nano 2 mixture and an increase of approximately 24% in the complex viscosity with time, showing that its structure was instable. That is, the FN2 extruder residence time was not enough to disrupt the formation of the reversible physical network of the PEMA and consequently additional interactions between the clay, the PEMA and the HDPE took place during the rheological test.

In order to evaluate this time/temperature effect on the morphology of the FN2 films, samples were collected at the end of the complex viscosity vs. time test and were analyzed by WAXS. The results are shown in Fig. 9. It can be observed that after 3600 s of rheological test, the clay’s diffraction peak of the FN2 sample disappeared, indicating the formation of an exfoliated morphology. That is, an additional frequency (or shear rate) of 1 s\(^{-1}\) at \(T = 225^\circ C\) during 3600 s was necessary to obtain an exfoliated morphology. This behavior shows that instable morphologies were formed during the FN2 extrusion; however, if the extruder residence time were highly increased, even at low shear rates, this formulation could exfoliate.

Fig. 10 shows the transient rheological properties of the blown films. The FN2 blown film displayed a stress-overshoot, not shown by the FN1 or the FHDPE blown films. The emersion of a stress-overshoot in a filled polymer can be interpreted as a consequence of higher polymer/filler interfacial interactions or to stress accumulation. That is, the FN2 film had either stronger (or without defects) polymer/filler interactions or accumulated stresses due to its unstable morphology.
Fig. 10. Stress-overshoot and relaxation after stop of shearing of the blown films at $T = 225^\circ C$, shear rate $= 0.01 s^{-1}$.

3.4. Films mechanical properties

The elastic modulus of the HDPE blown film and the nanocomposites films FN1 and FN2 and other tensile properties are shown in Fig. 11. There was an increase of about 95% of the Young modulus

![Graph showing elastic modulus and tensile properties](image)

Fig. 11. (a) Young modulus and (b) tensile properties of the blown films.

![Atomic force micrographs of blown films surface](image)

Fig. 12. Atomic force micrographs of the blown films surface: (a) FHDPE, (b) FN1 and (c) FN2.

**Table 3**

<table>
<thead>
<tr>
<th>Blown film</th>
<th>WPTR (g water/m² day/μm)</th>
<th>OTR (mL/m² day/μm)</th>
<th>$R_a$ (nm)</th>
<th>$R_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHDPE</td>
<td>0.127 ± 0.018</td>
<td>67.25 ± 1.50</td>
<td>390.4 ±10.1</td>
<td></td>
</tr>
<tr>
<td>FN1</td>
<td>0.053 ± 0.005</td>
<td>23.92 ± 2.63</td>
<td>270.8 ±7.5</td>
<td></td>
</tr>
<tr>
<td>FN2</td>
<td>0.072 ± 0.005</td>
<td>23.54 ± 2.88</td>
<td>268.3 ±6.3</td>
<td></td>
</tr>
</tbody>
</table>
of the nanocomposites films in comparison with the pure HDPE film. The ultimate strain and the yield stress were also slightly higher in the nanocomposites films. On the other hand, the ultimate stress was slightly lower in the nanocomposites films, and the yield strain decreased approximately 50% in comparison with the pure HDPE blown film. Comparing both nanocomposites films, it is observed that the FN1 film had higher elastic modulus, similar yield stress but lower yield strain, ultimate tensile stress and ultimate strain than the FN2 film.

Jordan et al. in their excellent review about nanocomposites [18] concluded that the elastic modulus in nanocomposites seems not to be dependent of the interactions between the filler and the polymer. However, the yield stress, yield strain, ultimate stress and ultimate strain have a different trend than the elastic modulus; the addition of nanoparticles with poor interaction with the matrix causes the yield stress, the yield strain and the ultimate stress to decrease, compared to the neat matrix. That is, both nanocomposites films had good filler/matrix interactions; however, the interactions in the FN1 film were slightly worse than in the FN2 film, probably due to the formation of interfacial defects during the blowing promoted by the higher elongation rate.

3.5. Films gas permeability rates, surface characterization and clay distribution

The average water vapor (WPTR) and oxygen (OTR) permeability rates of the films (normalized to the film thickness) are shown in Table 3. The van der Waals volumes of oxygen and water are similar [19,20]; however, the transport mechanisms of both penetrants in a flexible polymer are different, mainly because of their different polarity (which allows the formation of water clusters, for example). It can be observed that both nanocomposites films had a significant decrease of WPTR and OTR permeability rates in comparison to the pure HDPE film. The FN1 film had a slightly lower WPTR than
the FN2 film. This behavior can be attributed to a higher orientation of the nanoclay’s tactoids in the FN1 film, which would form a more tortuous path for water diffusion than in the FN2 film. Due to the formation of water clusters (which increase the penetrant volume) the main transport controlling mechanism could be the diffusion thru the polymer. On the other hand, the FN1 and FN2 films had similar OTR. In this case, considering absence of oxygen clusters, the penetrant volume is smaller than the water clusters and the main transport controlling mechanism could be thru the polymer/clay interfaces; thus, the FN1 film had more defects in the polymer/clay interfaces (weaker interface) than the FN2 film, confirming the stress overshooting and tensile properties tests.

The surface films texture and roughness of the blown films were also analyzed by AFM: Fig. 12 shows AFM micrographs of the surface films while Table 3 shows the roughness as calculated from the micrographs. The surface morphology of the FHDPE film was composed of larger structures than the surface of the nanocomposites films; however, the roughness of the FHDPE is higher than of the nanocomposites films. The lower roughness of the nanocomposites will affect the surface opacity of the films, as verified in other works of our lab [14,21]: the higher the roughness is, the higher the surface opacity is. Therefore it is expected that the nanocomposites films will be less opaque than the pure HDPE film.

Figs. 13 and 14 show SEM/EDS micrographs of the films surface, with the mapping of some of the clay elements. EDS mapping analysis was carried out at the same magnification than the SEM images. From the elemental Si and Al mappings it can be observed that the clay is well distributed within the HDPE matrix in both films. Elemental mapping reveals that the various elements are distributed fairly evenly throughout the samples. Typical EDS spectra of MMT are shown in Figs. 13b and 14b. It must be pointed out that EDS results should be analyzed

![Fig. 14. SEM micrographs with EDS mapping of the FN2 nanocomposite blown film: (a) Micrograph, (b) EDS spectra, (c) Si mapping and (d) Al mapping.](image-url)
4. Conclusions

Two nanocomposites were produced by varying the profile of a twin screw extruder: Nano 1 (less dispersive profile) and Nano 2 (more dispersive profile). By WAXS measurements, both compositions showed that intercalation of the HDPE into the clay occurred; however, by measuring the dynamic rheological properties as a function of time it was observed that the Nano 1 composition was not time-stable. It was also found that the Nano 1 composition was less elastic than the Nano 2 composition at low frequencies. Thus, blown films of Nano 2 composition were produced: FN1 and FN2. The FN1 film was blown at a higher elongation rate than the FN2 film. It was observed that the FN2 blown film had also an instable morphology and displayed a high stress overshooting. Both blown films, however, had an increase of 95% in the Young modulus, and a decrease on water vapor and oxygen permeability rates of 45% and 60%, respectively, compared to the pure HDPE film. Both films also had lower roughness than the pure HDPE film, which will influence their surface opacity.

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