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EFFECT OF EXTRUSION PROCESSING VARIABLES ON THE POLYETHYLENE/CLAY NANOCOMPOSITES RHEOLOGICAL PROPERTIES

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Abstract. In this work, high density polyethylene, HDPE, was compounded in a twin screw extruder with organophilic treated montmorillonite clay and a compatibilizer agent. The screws configuration was changed from distributive to highly dispersive [1], using four different profiles. The extrusion conditions were also changed. The exfoliation degree was evaluated by X-rays. The rheological measurements showed different behavior according to the processing adopted.

Keywords: twin screw extruder, clay, dispersion, nanocomposites, rheology.

1. Introduction

Nanocomposites constitute a class of materials in which the reinforcement agent has nano dimensions and it is used in small quantities compared to the traditional composites.

The melt intercalation method is frequently used for the layered silicate based nanocomposites. This method was first proposed by Vaia *et al.* [2, 3]. They showed that the intercalation of polymers chain into the galleries of clay could occur when layered silicate and polymer are compounded above the melting point. On the basis of this approach, the nanocomposite formation can be done using conventional polymer processing techniques. Several factors determining the state of dispersion have been reported, such as the organic modifier of clay [4-6], the properties of the polymer matrix [7-8], and the kind and concentration of compatibilizer used [9-10]. These factors determine whether the organoclay could be intercalated and/or exfoliated into the polymer matrix. Furthermore the state of exfoliation is strongly affected by the processing conditions and the extruder configuration [10-13].

The incorporation of the organoclay into the polymer matrix is usually conducted in a twin screw extruder [14-

15]. The co-rotating twin screw extruder (TSE) is a versatile device that can provide mixing ranging from intensive dispersive to laminar distributive depending on the screw configuration and operation conditions. In intermeshing TSE, mixing takes place mostly in the kneading section as a result of shear and elongation.

The preparation [16-21], structures [21-23] and thermal/mechanical properties [17, 18, 23] of polymer/clay nanocomposites have been extensively studied. Rheological properties of particulate systems are sensitive to the structure, particle size, shape, and surface characteristics of the dispersed phase and the rheology potentially offers a means to assess the state of dispersion of nanocomposites directly in the melt state. The rheology has been used to investigate the nanocomposites exfoliation degree due to HDPE/clay percolated network structure. This network increases the material elasticity (solid-like-behavior) and this effect may be observed in low frequencies (ω) or high relaxation time.

In this study, different screw configurations and operating conditions were employed to evaluate the extrusion processing influence on the dispersion for a HDPE/clay nanocomposite. The exfoliation occurrence was evaluated by rheological measurements.

2. Experimental

2.1. Materials

a) High Density Polyethylene (HDPE), commercial sample GM 9450F with MFI 0.36 g/10min (463 K/5 kg), from Petroquímica Ipiranga.

b) Montmorillonite Clay (MMT) chemically modified by ammonium quaternary salt, CLOISITE 20A, from BENTONIT UNIAO.

c) HDPE grafted with maleic anhydride compatibilizer (PEMA) containing 1 wt % of maleic anhydride (AM), POLYBOND 3009, from CHEMTURA Indústria Química do Brasil Ltda.

2.2. Equipment

A modular intermeshing co-rotating twin screw extruder TECK TRIL model DCT-20 was used to compound the composites.

2.3. Methodology

Screw set up: Four screw profiles were mounted and are schematically showed in Fig. 1. Screw elements used are listed at Table 1.

Process Parameters: Barrel temperature profile sectioned in nine zones from hopper to die: 423–483 K; feeding rate of 2.6 kg/h (minimum condition) and 5.9 kg/h (maximum condition). Rotation screw speeds were 300 rpm (minimum condition) and 600 rpm (maximum condition).

Processing Methodology: A masterbatch of PEMA and MMT clay at 75/25 wt % was prepared. Nanocomposites were produced by diluting masterbatch into HDPE matrix at proportion of 20/80 wt %, in extrusion

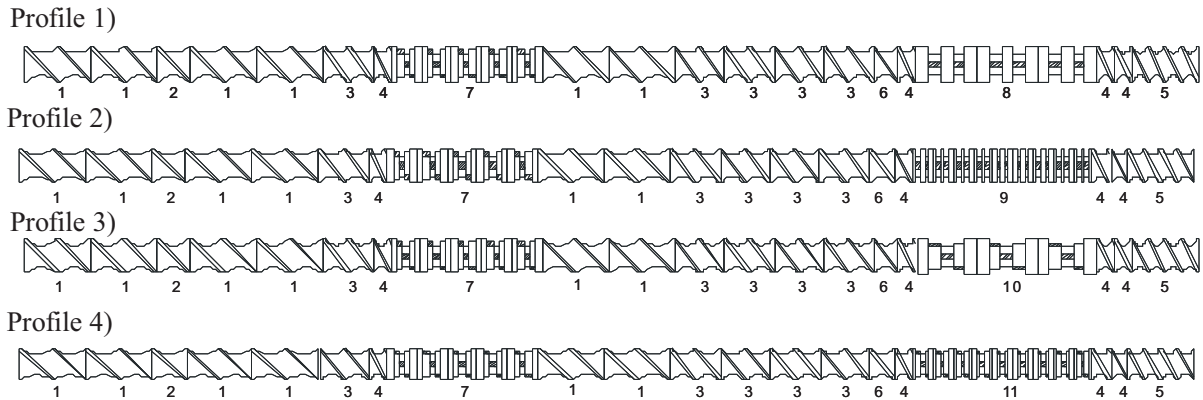


Fig. 1. Twin screw elements profiles employed in extrusion process

Table 1

Screw element types used in extrusion process

Number	Screw element type	Element specification
1	40/40	Forward conveying, 40 mm pitch, 40 mm length
2	40/20	Forward conveying, 40 mm pitch, 20 mm length
3	30/30	Forward conveying, 30 mm pitch, 30 mm length
4	20/20	Forward conveying, 20 mm pitch, 20 mm length
5	20/40	Forward conveying, 20 mm pitch, 40 mm length
6	30/15	Forward conveying, 30 mm pitch, 15mm length
7	KB 45/5/18	Forward kneading block, 45°, 5 disks, 18 mm length
8	KB 90/5/36	Neutral kneading block, 90°, 5 disks, 36 mm length
9	KB 90/5/12	Neutral kneading block, 90°, 5 disks, 12 mm length
10	KB 45/5/36	Forward kneading block, 45°, 5 disks, 36 mm length
11	KB 45/5/12	Forward kneading block, 45°, 5 disks, 12 mm length

Table 2

Nomenclature and operational conditions used in extrusion process

Experiment number	Feeding rate, kg/h	Screw speed, rpm	KB stagger angle, °	KB width, mm	Extrusion profile	Sample name
1	2.6	300	45	12	4	P1
2	5.9	600	45	12	4	P2
3	5.9	300	90	12	2	P3
4	2.6	600	90	12	2	P4
5	5.9	300	45	36	3	P5
6	2.6	600	45	36	3	P6
7	2.6	300	90	36	1	P7
8	5.9	600	90	36	1	P8

process. All samples were produced with the purpose to reach 5 wt % of Clay in the nanocomposites.

Extruder rotation speed, feeding rate, width and stagger angle of kneading screw elements were selected as variables. For each variable two levels were selected (maximum and minimum). Table 2 presents the levels for each variable, besides the nomenclature adopted for samples and screw profile employed in each extrusion.

2.4. Characterization

Rheology: Rheological characterization was performed at AR2000 TA Instruments Rheometer, with parallel plates geometry under nitrogen atmosphere. The tests were conducted under steady-state shear and oscillatory shear.

X-Ray: X-Ray Diffractograms were obtained at RIGAKU, MINIFLEX model, for 2θ range from 2 to 40° . Radiation ($\lambda = 1.5458 \text{ \AA}$) with 50kV and 30mA.

3. Results and Discussion

3.1. Rheology Characterization

Steady state shear: Viscosity and stress curves at low shear rate were obtained for each nanocomposite under study. Figs. 2 and 3 show the materials rheological behavior. It is possible to observe that polyethylene (HDPE) matrix presents a tendency to Newtonian near shear rate of 0.015s^{-1} while nanocomposites P1, P2, P3, P4, P5, P6, P7 and P8 presented a pseudo-plastic behavior at the same shear rate. From those same curves it is also possible to compare the nanocomposites viscosities obtained by different processing conditions used. Fig. 2 shows that nanocomposite P1 shows higher viscosity than nanocomposite P7 near shear rate of 0.015 s^{-1} . The same behavior can be observed for P2 and P8, P3 and P5 and P4 and P6 pairs. Stress measurements at low shear rate (Fig. 3) demonstrate an increase of stress near shear rate of 0.015 s^{-1} , as compared to HDPE matrix. Such behavior at this region is an indication of a higher interaction between the two phases, suggesting an intercalated and/or exfoliated system. Same comparative analysis among pairs of nanocomposites was done to verify behavior similarities for the processing conditions used. *Oscillatory:* Dynamic frequency sweeps of HDPE and HDPE/clay nanocomposites were performed on a controlled strain rate rheometer AR 2000 TA Instruments, with a parallel plates geometry using 25 mm diameter plate. All measurements were performed at 483 K. The gap was set at 1mm. Linear rheological measurements were performed at a frequency range of 0.01 to 628.3 rad/s.

To ensure the linear viscoelastic region, the strain was set to 300 Pa and then elastic modulus (or storage modulus) (G'), loss modulus (G''), and complex viscosity

(η^*) were obtained. G' represents the strain energy reversibly stored in the material, whereas G'' represents the amount of energy irreversibly given off by the material to its environment. The elastic modulus measurements (G') and complex viscosity (η^*) versus frequency, are presented in Figs. 4 and 5. These figures show that modulus G' curve for HDPE matrix remains with high slope and consequently with minor G'' value near 0.015s^{-1} . This behavior is normally found, by the fact that, when G' curve slope comes into zero at low frequencies it means an increasing of pseudo-solid-like behavior for the sample. Thus, when the clay platelets are well dispersed inside polymeric matrix, G' modulus value will be higher. In the same way, the more negative the slope of complex viscosity curve is (η^*) (close to -1), more stress effect is presented in nanocomposite, which is characteristic of a well dispersed and exfoliated system.

Fig. 6 presents nanocomposites and HDPE G' modulus and G'' modulus curves. Comparing nanocomposites G' and G'' curves it is possible to observe that for the majority of the samples, G' values keep superior to G'' values in all frequency range analyzed. Only for P3, P4 and P8 nanocomposites a trend for G' and G'' curves crossover when $\omega_c = 0.01 \text{ rad/s}$ was observed.

When crossing over and curves inversion occurs or when the material presents a G'' modulus superior to G' , this material has a predominantly viscous behavior; however when a certain frequency is obtained, inversion occurs and the G' values overcome the G'' values, indicating that the material assumed a pseudo-solid behavior. This fact can be seen for the HDPE matrix (Fig. 6) where the crossing over point is observed showing the viscoelastic behavior characteristic of polymers. Considering the nanocomposites, the fact that G' remains above G'' in the whole frequency range studied, it proved that the pseudo-solid behavior of the samples can be associated to the clay platelets in the polymer matrix. Besides, the difference between the nanocomposites samples G' modulus when compared in pairs, as it is shown in the curves, seems to be associated to the samples processing changes, reflecting higher or lower dispersion or exfoliation degree of the clay into the HDPE matrix. Table 3 presents the rheological properties η^* and G' obtained in the lower frequency analyzed (0.015rad/s) and crossing frequency point of G' and G'' (ω_c) observed on oscillatory rheological curves.

In Fig. 6, an increase of nanocomposites η^* and G' can be observed, as compared to HDPE matrix. It can also lead to the conclusion that the nanocomposite P1 presents G' and η^* values higher than P7. The feeding rate and extrusion velocity used in the P1 and P7 processing were the same but the screw extruder elements arrangement was different. These results suggest that P1 showed better dispersion and/or exfoliation than P7. It was indicative that using KB with smaller thickness (12 mm) and smaller stagger angle (45°), at that processing

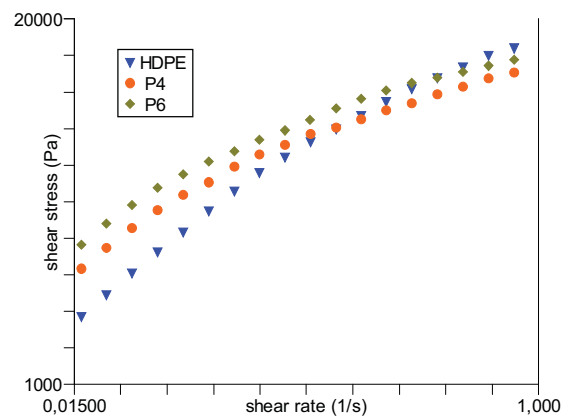
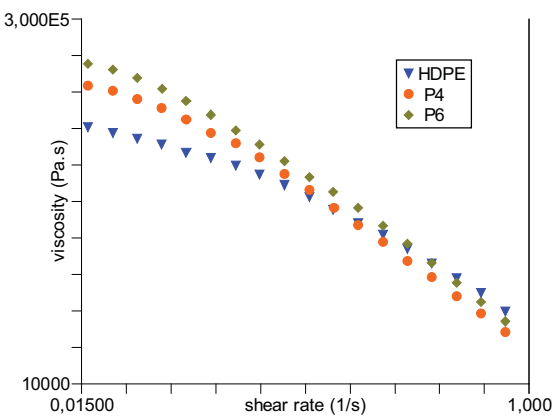
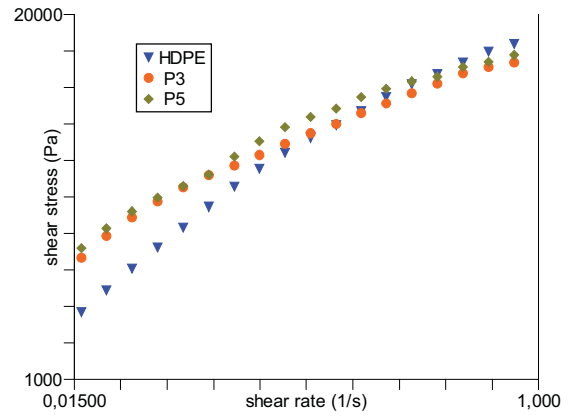
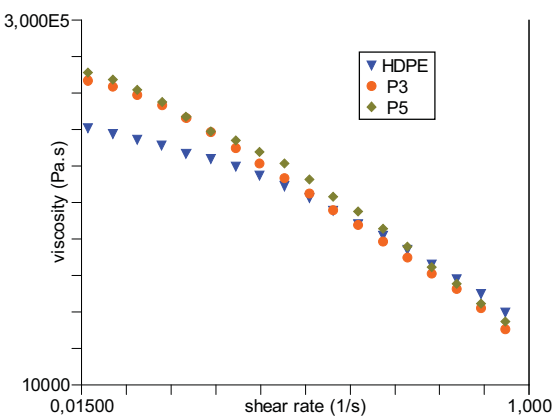
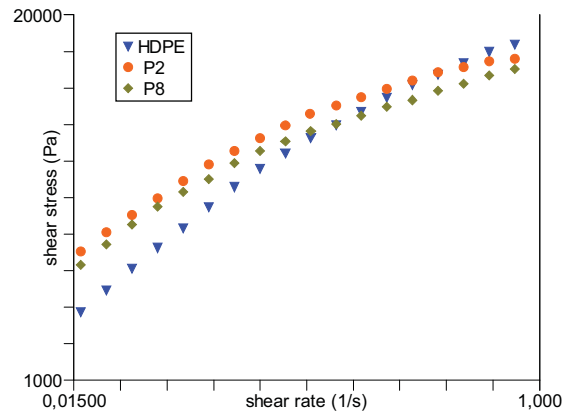
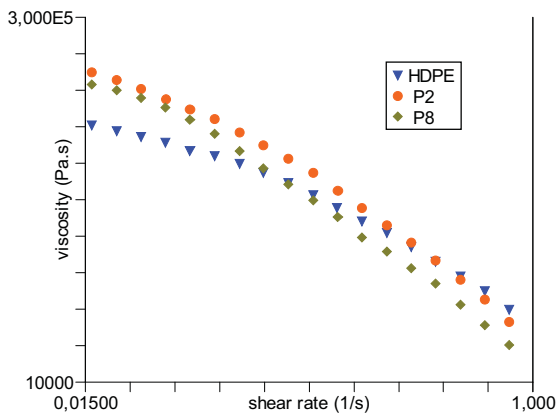
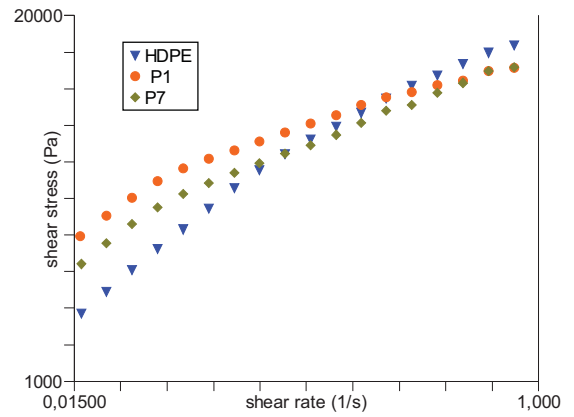
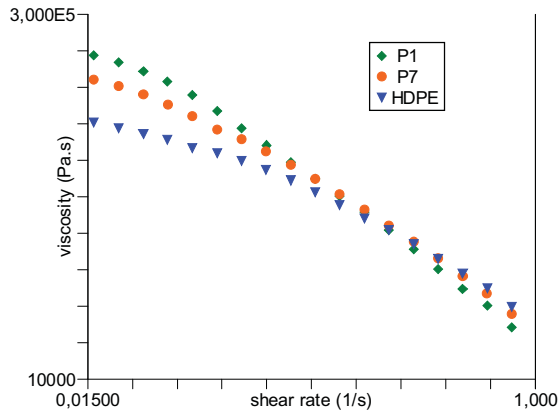


Fig. 2. Steady state viscosity at low shear rate of nanocomposites and HDPE

Fig. 3. Steady state stress at low shear rate of nanocomposites and HDPE

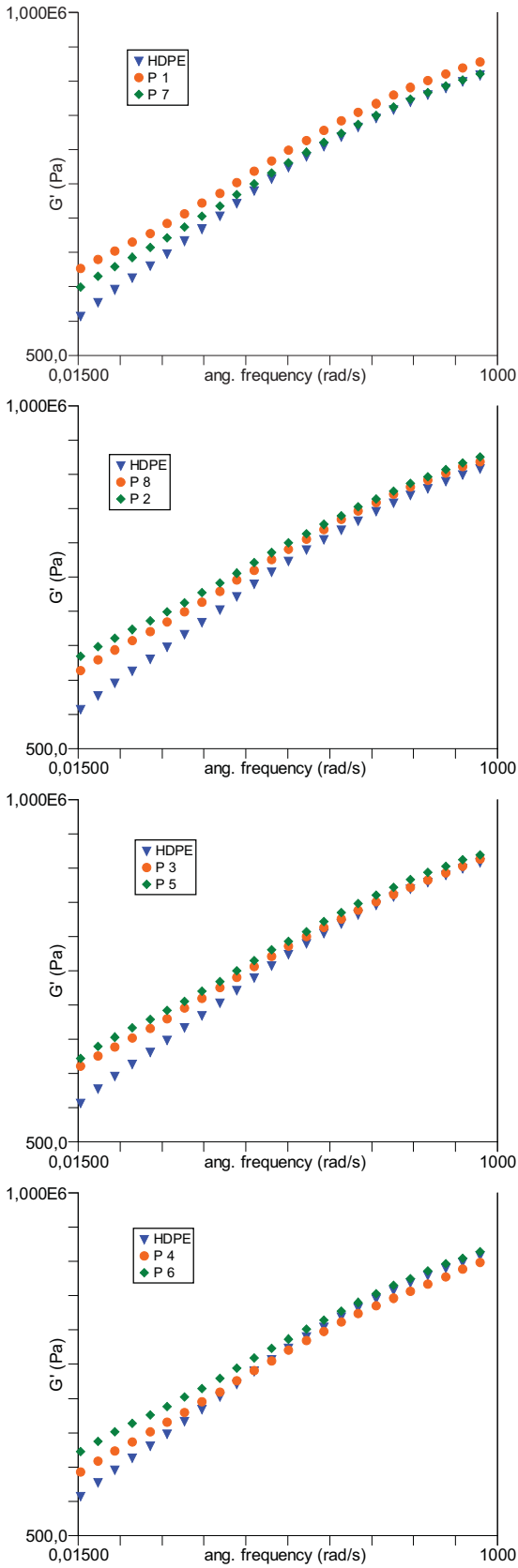


Fig. 4. G' at low frequency of nanocomposites and HDPE

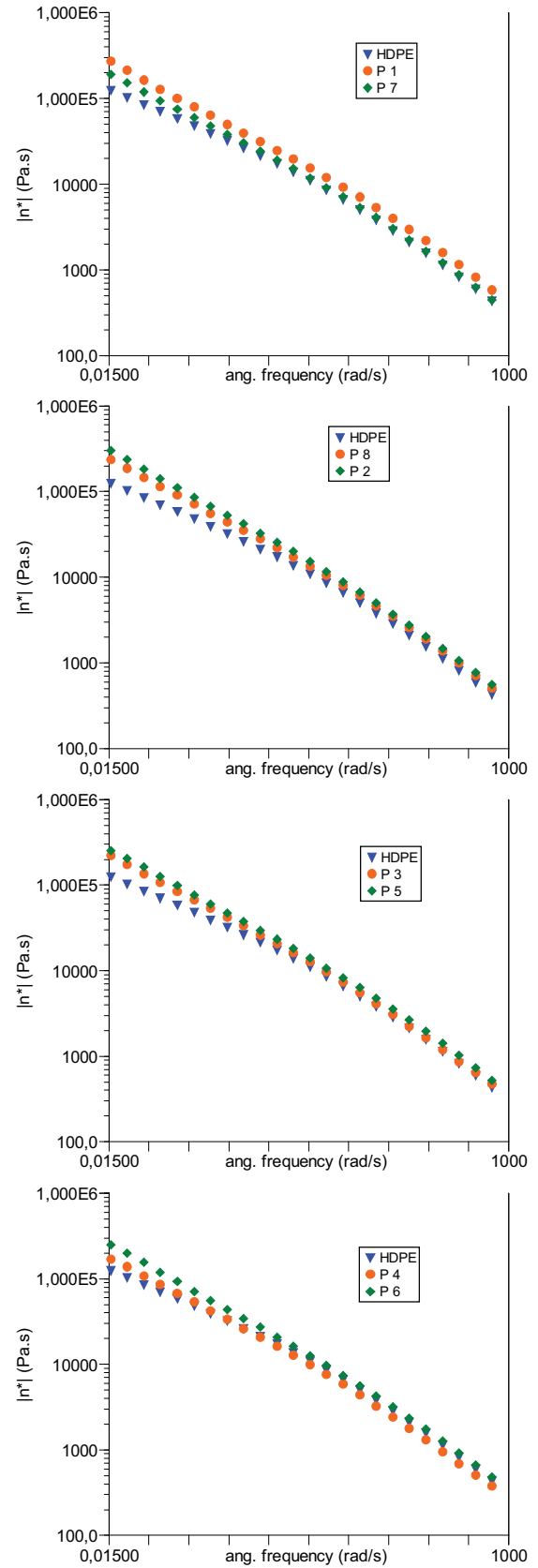


Fig. 5. η^* at low frequency of nanocomposites and HDPE

condition, referring to profile 4, it would contribute more strongly to mixing efficiency than P7 that used 36 mm thickness and 90° stagger angle KB in the screw mixing zone (profile 1). The same behavior was observed for P2 and P8 samples. These nanocomposites were obtained by using the same operation conditions (different from the P1 and P7) and it was observed again that samples prepared using KB with 45° stagger angle and 12 mm thickness demonstrated better clay dispersion efficiency into HDPE polymer. Table 3 presents η^* and G' values of P2 and P8 samples where P2 has higher η^* and G' values than P8.

The P5 and P3 samples were processed by using the same operation condition. The results show P5 η^* and G' values higher than P3, which leads us to conclude that

the profile 3 employed to P5 processing produced better clay dispersion into HDPE matrix than P3 (profile 2), at those conditions. The same conclusions can be made about P4 and P6 nanocomposites where it was verified that P6 presents higher η^* and G' values than P4, emphasizing the better performance of profile 3.

3.2. X-Ray Characterization

X-Ray analyses were done using 2θ angle ranging from 2 to 40° to investigate the HDPE, Cloisite 20A clay and PEMA peaks. The curves obtained are presented in Fig. 7.

The clay diffraction peaks occurring at 2θ equal to 3.7°, 7° and 20°. The 3.7° peak is the most intense and is considered the main peak. HDPE and PEMA samples showed very similar diffraction peaks because both have the same unitary cell

The nanocomposites were also characterized by X-Ray. Fig. 8 shows the P1, P7 and clay diffractograms. The 2θ range used was up to 10° because relevant peaks of clay in higher angles were not observed.

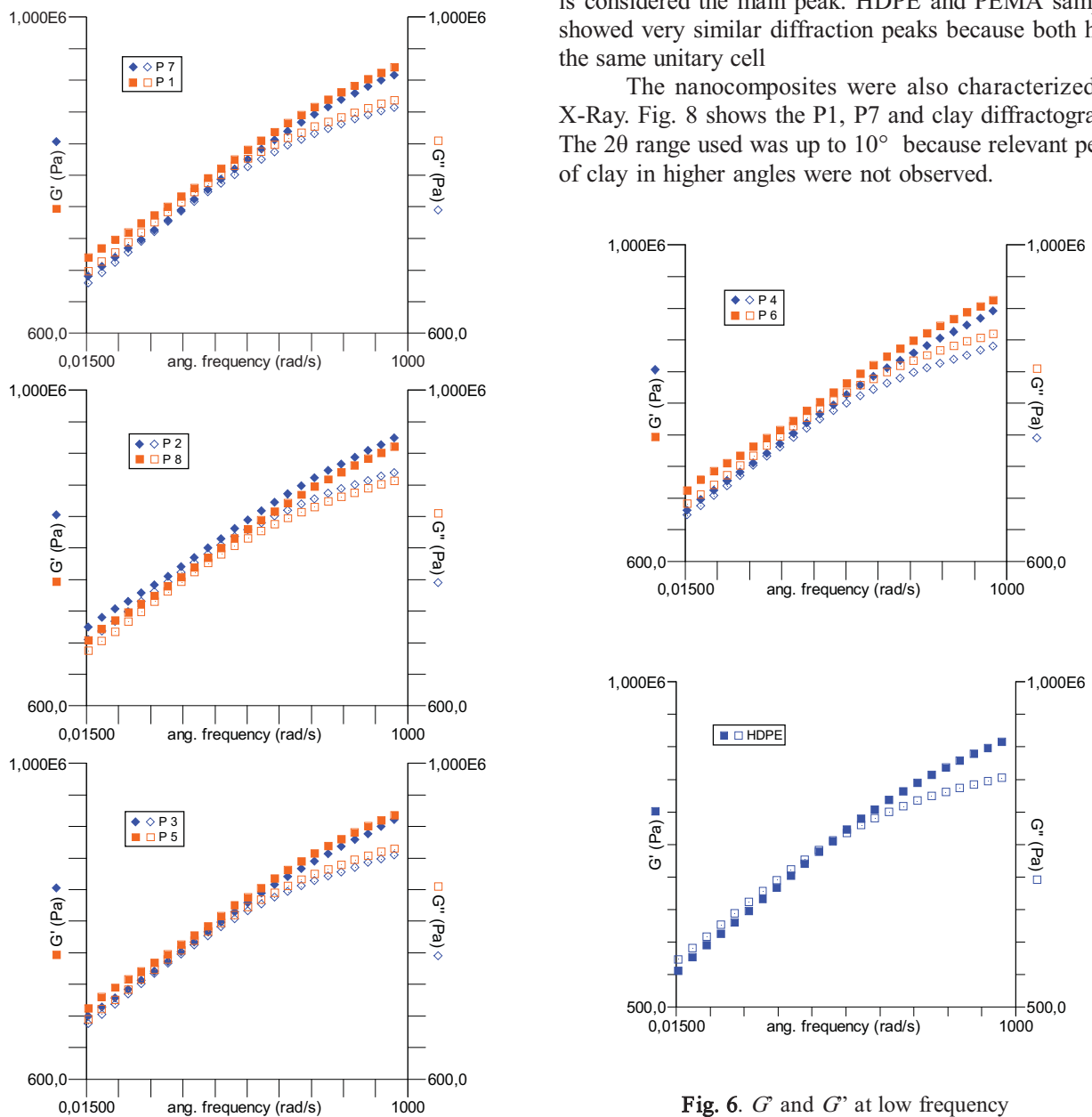


Fig. 6. G' and G'' at low frequency of nanocomposites and HDPE

η^* , G' and ω_c values

Table 3

Sample	η^* , Pa·s·10 ⁵	G' , Pa	ω_c
HDPE	1.339	750	2.5
P1	3.167	2366	-
P2	3.441	2599	-
P3	2.512	1813	0.01
P4	1.886	1329	0.01
P5	2.896	2139	-
P6	2.823	2125	-
P7	2.255	1653	-
P8	2.514	1821	0.01

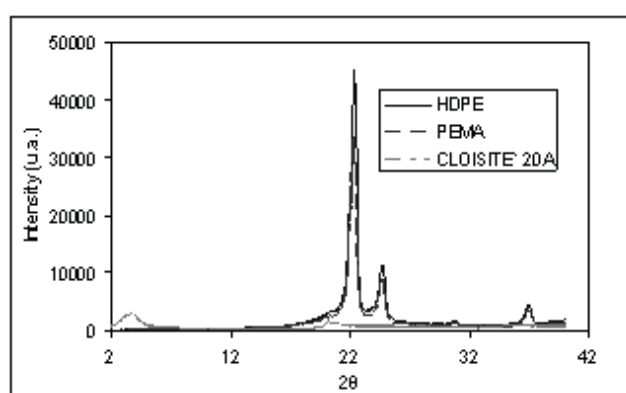


Fig. 7. X-Ray – pure samples

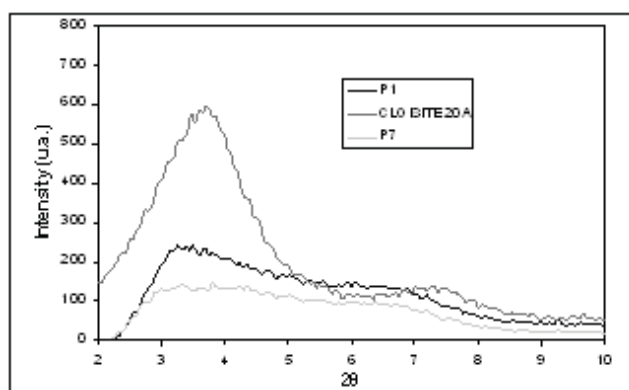


Fig. 8. X-Ray – P1 and P7 nanocomposites

The objective to use X-Ray was to investigate the nanocomposite structure. The polymer chain intercalation into clay silicates layers increases the inter-layers spacing. This effect shifts the peak position relative to the characteristic clay peak. In addition, the peak intensity decrease suggests that the silicate layers are more distorted and their structures are more irregular, as occurs in an exfoliated system.

Fig. 8 shows that P1 presented the characteristic clay peak but it has lower intensity and was shifted to 2θ angle smaller than 3.7° , which suggests occurrence of chain polymer intercalation into clay layers. The P7 nanocomposite showed less intensity peak beyond shifted position to 2θ angle smaller than 3.7° , also indicating intercalation occurrence. The other nanocomposites presented the same behavior.

4. Conclusions

The steady state and oscillatory rheological behavior of HDPE/clay nanocomposites were investigated by an AR 2000 rheometer.

The screw profile in a twin screw extruder presented an important influence in order to obtain dispersive/exfoliated nanocomposites. It was observed that the stagger angle and thickness of KB screw element associated with operation conditions proved to be a very important dispersion factor. Rheological results showed that the screw elements arrangement used in profiles 3 and 4, for its operation condition, presented better dispersion/exfoliation of clay into the HDPE matrix.

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ВПЛИВ ЧИННИКІВ ПРОЦЕСУ ЕКСТРУЗІЇ НА РЕОЛОГІЧНІ ВЛАСТИВОСТІ НАНОКОМПОЗИТІВ ПОЛІЕТИЛЕН/ГЛИНА

Анотація. Розглянута можливість компаундування поліетилену високої густини у подвійному черв'ячному екструдері органіфільною глиною, обробленою монтморилонітом та компатибілізатором. Запропоновано чотири різні профілі конфігурації черв'яка від розпрідільного до високодисперсного, а також різні умови проведення процесу в екструдері. З використанням рентген-аналізу визначено ступінь ексfolіації. Реологічні вимірювання показали різну поведінку нанокмпозиту у відповідності до умов процесу.

Ключові слова: подвійний черв'ячний екструдер, глина, дисперсія, нанокмпозити, реологія.