Effect of Organoclay Mixture on the Rheological Properties of ABS-Clay Nanocomposites

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Summary: In this work, poly(acrylonitrile-butadiene-styrene) (ABS) and different organically modified montmorillonite clay nanocomposites were prepared by melt intercalation in a co-rotating twin screw extruder. The influence of the screw torque during processing and of the mixture of the modified organoclays in the intercalation/exfoliation of the clay in the polymeric matrix was evaluated through low angle X-ray diffraction range and capillary and parallel plate-plate rheometry.

Keywords: ABS; melt intercalation; montmorillonite; nanocomposites; rheology

Introduction

The use of polymer matrix nanocomposites, such as polymer/organically modified montmorillonite clay systems, has attracted interest from different industrial segments since these are low density materials with excellent mechanical properties. However, the benefits of this new class of materials are reached only when the nanometer inorganic filler are appropriately dispersed in the polymeric matrix leading to strong interphase interactions, which allow the use of low quantities of inorganic material.[1–3]

The preparation of clay filled polymer nanocomposites can be performed by the method of melt intercalation. This is usually the preferred method due to its versatility and compatibility with large scale industrial processes, such as twin-screw extrusion. Some parameters has significant effects in the structure of the nanocomposites such as the clay surface treatment, the processing conditions and the polymer matrix properties.[1–3]

The poly(acrylonitrile-butadiene-styrene) (ABS) is an engineering plastic of great commercial importance, since it presents superior mechanical properties such as high impact resistance, Young's modulus and mechanical strength with cost similar to the commodity plastics. Therefore, studies of nanocomposites of ABS/montmorillonite have been published in the literature.[4-7]

Since ABS is a terpolymer of distinct phases, one polar thermoplastic phase (poly(styrene-co-acrylonitrile)) and other non-polar elastomeric phase (butadiene), it should be expected that the ABS compatibility with organophilic clays might differ with the surfactant polarity in the clay surface treatment.

The objective of this work was to investigate the effects of a binary mixture of two different commercial organically modified montmorillonite (OMMT), Cloisite 30B and 20A, as well as the torque of the extrusion screw in the morphology and rheological properties of ABS/OMMT nanocomposites.

Experimental Part

Materials

The ABS used was the Terluran® GP 35 (BASF), which was gently donated from Positron. The two OMMT used were

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purchased from Southern Clay: Cloisite® 20A (C20A), modified with dimethyl di-(hydrogenated tallow) ammonium chloride; and Cloisite® 30B (C30B), with bis-(2-hydroxyethyl) methyl tallow ammonium chloride. The antioxidant (0.5 wt.%) used was the Irganox® 245 supplied by Ciba. The materials were dried at 80 °C for 4 hours before processing for humidity removal.

The composition of ABS is 44% of acrylonitrile, 42% of styrene and 14% of butadiene which was determined by Fourier Transform Infra-Red spectroscopy (FTIR) according to ASTM E168 using a Equinox 554 spectrometer from Bruker with Pike accessory, and resolution of 4 cm^{-1}.

Nanocomposites Preparation

Initially, two masterbatches containing 20 wt.% of clay content were prepared by melt intercalation using a co-rotating twin-screw extruder (Coperion ZSK 26Mc) with diameter (D) of 25 mm and L/D of 44 at 120 rpm. The screw mixing elements configuration and barrel temperature profile are shown in Figure 1. Afterwards, ABS/OMMT with 4 wt.% of clay were prepared by diluting the masterbatches in the ABS matrix through extrusion. Process conditions followed the previous one but with two feed rates (4 and 8 kg/h) in order to obtain two relative screw-torque levels (45 and 70%, respectively). Extruded spaghetti was immersed in water at room temperature to cool, following its granulation in a knife mill.

The experimental design (Table 1) was planned with two variables: type of clay and screw torque, at three and two levels, respectively. The type of clay was characterized through the Flory-Huggins interaction parameter (χ_{AB}), which was calculated from group contribution using the Hoy's table[8] and the methodology proposed by Lim et al.[5] The values obtained of χ_{AB} between ABS and the organoclays C30B, C20A and C20A + C30B mixture (1:1) were 0.64, 1.35 and 0.96, respectively.

Nanocomposites Characterization

The OMMT concentrations in the nanocomposites were obtained after burning it at 900 °C for 12 minutes in an oven with synthetic air atmosphere (two samples), following the methodology of Fornes *et al.* [9].

X-ray diffraction (DRX) was performed using a Rigaku diffractometer DMAX

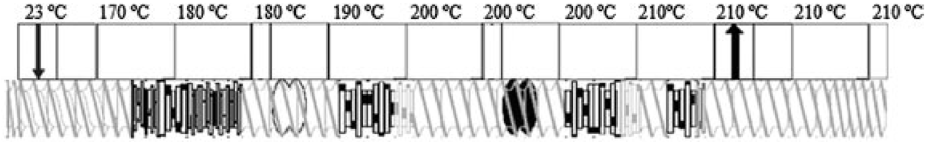

Figure 1.
Screw configuration and barrel temperature used in the co-rotating twin screw extruder.

Table 1.
Experimental design with sample code.

	−1	0	+1
Torque	45%	–	70%
χ_{AB}	0.64	0.96	1.35

Torque χ_{AB}	45 (%)	70 (%)
0.64	ABS/C30B-45%	ABS/C30B-70%
0.96	ABS/(C20A + C30B)-45%	ABS/(C20A + C30B)-70%
1.35	ABS/C20A-45%	ABS/C20A-70%

2200, in the interval of 2θ from 1.5° to 10°, operating at 30 mA and 40 kV in CuKα ($\lambda = 0.154$ nm) and 2θ/min = 3.

The rheological behavior of the nanocomposites at steady state high shear rates was measured using an Instron 447 capillary rheometer, with L/D = 33 and shear rates from 30 to 1500 s^{-1} at 210 °C. At steady state low shear rates (0.01 to 100 s^{-1}) and at small-amplitude oscillatory shear (SAOS) the rheological behavior were obtained using an ARES (Rheometric Scientific) rheometer at 210 °C, using parallel plate geometry, with 25mm diameter, 1mm gap in nitrogen atmosphere. SAOS material functions were obtained at strain amplitudes within the regime of linear viscoelasticity (0.1 to 0.25%).

Results and Discussion

Actual concentrations of OMMT (wt. %) are presented in Table 2, two measurements for each compound. It can be observed that the amount values obtained experimentally differ from nominal one (4 wt.%). The lowest value was of 3.2% and the highest one 6.4% obtained from ABS/C30B-70% and ABS/C20A-70%, respectively. However, taking into account overall value, the OMMT amounts are slightly higher than the nominal one except for the ABS/C20A-70% compound that resulted to have a more significant deviation. The observed dispersion on these results suggests interdependence between both variables (torque and χ_{AB}) and their levels. Besides, they can be a result of the clay homogeneity in the polymeric matrix.

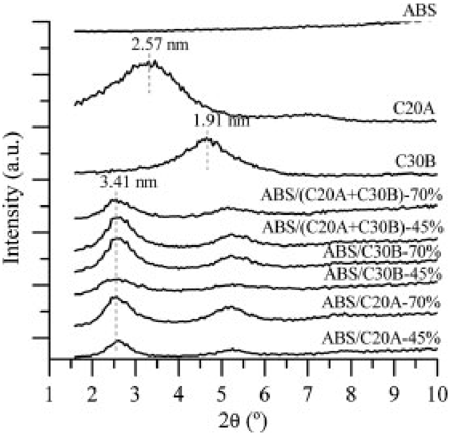

Figure 2.
DRX spectra including interlamelar distance in nm of ABS, OMMT and corresponding nanocomposites.

Figure 2 shows the XRD spectra of the OMMT (C20A and C30B) and of the ABS/OMMT nanocomposites. The interlamelar distance was calculated by Eq. 1, according to Bragg's law.[10] It can be observed that the basal distances significantly increased in all nanocomposites reaching a value of 3.41 nm. However, the highest increase is observed for the composites with C30B clay ($\Delta d_{001} = 1.50$ nm). Therefore, this kind of clay should have a higher affinity for the ABS matrix.

$$n.\lambda = 2.d.sen\theta \qquad (1)$$

Where n is an integer, λ is the wavelength (CuKα = 1,5458 cm^{-1}), d is the interlayer spacing between crystallographic planes of the sample, and θ is the angle

Table 2.
Actual OMMT concentrations, G', G'', tanδ and n_ω for ABS and its nanocomposites.

	OMMT (wt.%)	$G'_{\omega = 0.013\,s^{-1}}$ (Pa)	$G''_{\omega = 0.013\,s^{-1}}$ (Pa)	tan δ (G''/G')	$-n_\omega^*$
ABS	–	145	250	1.72	0.26
ABS/C20A-45%	3.7–4.8	3134	896	0.29	0.73
ABS/C20A-70%	5.0–6.4	5586	1326	0.24	0.79
ABS/C30B-45%	3.7–5.0	8547	2378	0.28	0.78
ABS/C30B-70%	3.2–4.5	4916	1679	0.34	0.69
ABS/(C20A + C30B)-45%	4.0–5.0	6163	1762	0.29	0.78
ABS/(C20A + C30B)-70%	3.3–4.6	3141	1068	0.34	0.71

*all curve fittings presented $r^2 > 0{,}996$.

between the incident ray and the scattering planes.

Figure 3 shows curves of shear viscosity as a function of shear rate for ABS and corresponding nanocomposites. It can be observed the presence of a Newtonian plateau for pristine ABS at low shear rates, whereas this is not the case with nanocomposites. This result highlights the pseudo-solid behavior of the nanocomposites, which is different from the plastic behavior of ABS. At low shear rates, an increase in the values of viscosity is observed for the nanocomposites, which is associated with the hydrodynamic interactions between clay particles and polymer-clay phases.[11] At this range of shear rate, the highest viscosity is observed for the ABS/C30B-45% suggesting a higher clay-polymer interaction. On the other hand, at high shear rate region ($> 100\,s^{-1}$) both nanocomposites and pristine ABS presented a power-law shear thinning behavior. Comparing the power law index (n) values (Figure 3) of the nanocomposites with that of pristine ABS, it can be verified a small decrease. Probably this result is due to clay lamellae orientation under high shear rates. The more accentuated decrease between nanocomposites power law index values was for ABS/C30B-45% compound ($n = 0.33$, corresponding to a decreasing of ca. 17%). This difference is probably associated to the higher affinity of the C30B clay with the polymeric matrix owing to the hydroxyethyl group, which is favored by the higher residence time when processed at 45% of torque.

Figure 4a shows curves of the storage modulus (G') versus angular frequency (ω) for pristine ABS and ABS/OMMT nanocomposites. ABS compound presented terminal behavior typical of thermoplastics where G' has a strong frequency dependency. For the nanocomposites it can be observed that at low frequencies the values of G' are considerably higher than the ABS and that the slope of the curve tends to zero. This characterizes a pseudo-solid behavior and has been attributed to the interaction between polymer chains with clay nanolayers.[12]

Table 2 shows that storage modulus (G') is higher than loss modulus (G'') at low frequency for all nanocomposites, whereas the contrary is observed for ABS. The ratio G''/G' is expressed as tan δ, where δ is the phase angle or the relative angular displacement of the shear stress and shear strain of viscoelastics materials. Tan δ is

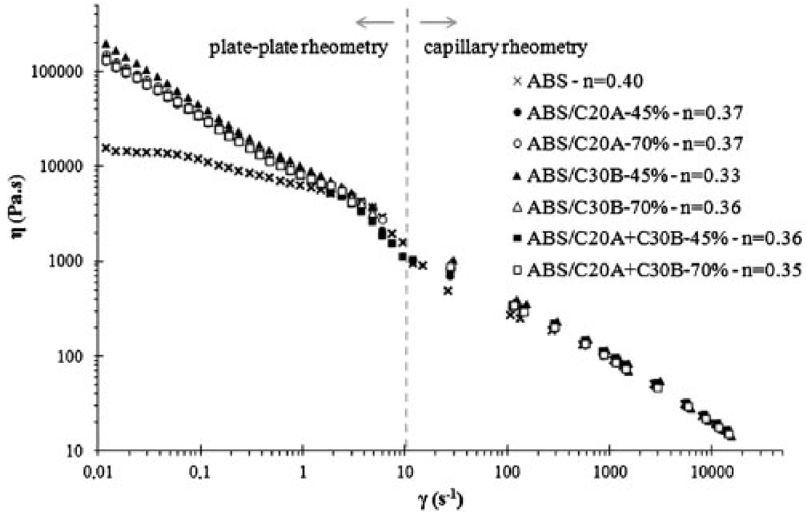

Figure 3.
Shear viscosity versus shear rate obtained by capillary and plate-plate rheometry.

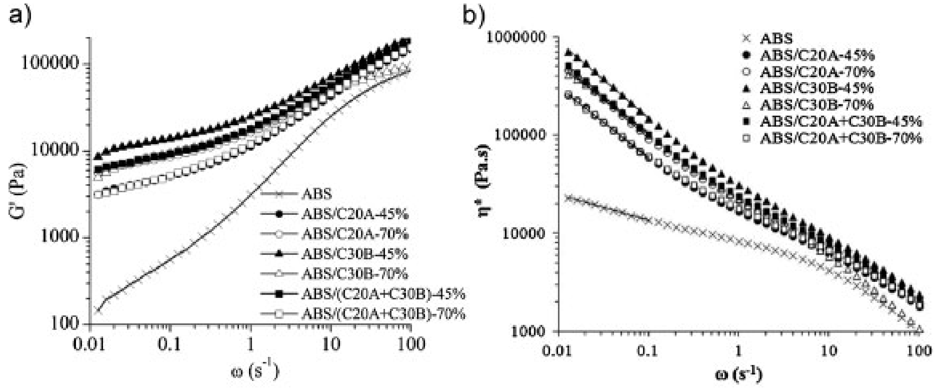

Figure 4.
(a) Storage modulus (Ǵ) and (b) complex viscosity (η^*) of ABS and ABS/OMMT.

lower than 1 for the nanocomposites and higher than 1 for pristine ABS, showing the predominance of the elastic character in the nanocomposites.

This change in the rheological behavior associated with the dispersion of the clay nanolayers is also observed in the curve of the complex viscosity η^* at low frequency shown in Figure 4b. The parameter n_ω shown in Table 2 correspond to the curve fitting at low frequency (0.01 to $0.1\,s^{-1}$) of the log(η^*) versus log(ω) curve shown in Figure 4b, using the following power law model:

$$\eta* = k.\omega^{n_\omega} \tag{2}$$

This parameter n_ω is a semi-quantitative measure of clay dispersion in the polymeric matrix, where the values obtained for the nanocomposites indicates a dispersed percolated system.[11] Two of the highest n_ω were obtained for ABS/C30B e ABS/(C20A + C30B) compounds, which were processed at 45% of torque. This apparent trend can be explained as an increase in the dispersion level of the clay in the ABS matrix when processed at lower torque level or higher extruder residence time. However, the compound ABS/C20A-70% presented also an n_ω value at the same level of previous compounds. In this case, the increase in the absolute value of n_ω might be associated to the clay concentration, that is higher than the nominal in the composite processed at 70% of torque (Table 2).

Previous results suggest a greater affinity of Cloisite 30B with ABS, which might be due to the fact of the high content of styrene-acrylonitrile (SAN) in ABS. It is likely that clay dispersion/intercalation could occur preferably in the SAN phase, as suggested by Stretz et al.[7]. The authors have studied the dispersion of clay particles in ABS and SAN nanocomposites with Cloisite 30B. They found by morphological analyses using transmission electron microscopy that clay particles in ABS nanocomposites were dispersed in the SAN matrix phase and presented some accumulation at the rubber particle surfaces. Besides, it is important to highlight another study from our group, which the ABS/C30B nanocomposite processed with 45% of torque presented significant higher tensile modulus.[13]

Conclusion

From XRD results it was possible to conclude that nanocomposites of intercalated structure, with significant increase in the basal distance, were obtained for all cases studied. The small-amplitude oscillatory shear rheological behavior of the nanocomposites presented a pseudo-solid behavior whereas the ABS presented a plastic behavior, indicating polymer-clay interactions with evidence of a percolated structure. The polymer-particle interaction was also verified in steady state shear where the nanocomposites viscosities were significantly higher than of the ABS at low shear rates. The decrease in the power law index of the nanocomposites might be due to shear-induced clay lamellar orientation. Based on the rheological behavior it can be concluded that the nanocomposites prepared with Cloisite 30B at 45% of torque promotes the formation of percolated structure. This might be associated with the higher chemical affinity of this clay with the SAN phase of ABS and to the highest residence time in the extruder.

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[1] M. Okamoto, *Encycl. Nanosci. Nanotechnol.* **2004**, *8*, 791.

[2] H. F. Mark, *Encycl. Polym. Sci. Technol*, (3rd ed.), J. Wiley & Sons, N. York **2003**, v.1, p.174 and v.3, p. 336.

[3] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, D. R. Paul, *Polymer* **2001**, *42*, 9513.

[4] E.–K. Karahaliou, P. A. Tarantili, *J. Appl. Polym. Sci.* **2009**, *113*, 2271.

[5] S.-K. Lim, E.-P. Hong, Y.-H. Song, B. J. Park, H. J. Choi, I.-J. Chin, *Polym. Eng. Sci.* **2010**, 504.

[6] M. Modesti, S. Besco, A. Lorenzetti, V. Causin, C. Marega, J. W. Gilmar, D. M. Fox, P. C. Trulove, H. C. De Long, M. Zammarano, *Polym. Degrad. Stab.* **2007**, *92*, 2206.

[7] H. A. Stretz, D. R. Paul, P. E. Cassidy, *Polymer* **2005**, *46*, 3818.

[8] D. W. Van Krevelen, *Properties of Polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*, (3rd ed.) Elsevier, Amsterdam **1992**, p. 189.

[9] T. D. Fornes, P. J. Yoon, H. Keskkula, D. R. Paul, *Polymer* **2001**, *42*, 9929.

[10] B. D. Cullity, *Elements of X-ray diffraction* (Ed., Addison-Wesley, Massachusetts **1978**.

[11] R. Wagener, T. J. G. Reisinger, *Polymer* **2003**, *44*, 7518.

[12] Ph. Cassagnau, *Polymer* **2008**, *49*, 2183.

[13] D. Galvan, J. R. Bartoli, F. Massucato, M. A. d'Ávila, E. G. Fernandes, *11st CBPol*, **2011**, 1946.