Preparation of Polymer-Clay Nanocomposites by Melt Mixing in a Twin Screw Extruder: Using On-Line SAOS Rheometry to Assess the Level of Dispersion

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Abstract

A prototype on-line rotational rheometer was fixed between a twin screw extruder and a multi-rod die of an industrial pelletization line used for the manufacture of polymer-clay nanocomposites. After diverting the required amount of melt to the device, measurements were performed in small amplitude oscillatory shear and used to estimate the level of dispersion of the organoclay in the polypropylene matrix, by means of correlations that are commonly utilized. The aim is to determine whether changes in clay type, clay content, feed rate and screw speed cause detectable alterations in the rheological response and thus in the level of dispersion, with a view to practical process monitoring and control. The analysis of the data is supported by XRD and electron (scanning and transmission) microscopy observations.

Introduction

Academic and industrial research on the preparation, properties and applications of polymer-clay nanocomposites has been intense, as attested by the numerous reviews published in the last years (Utracki, 2004; Hussain et al., 2006; Okada and Usuki, 2006; Yu et al., 2006; Chen et al., 2008; Esfandiari et al., 2008; Zhang et al., 2008; Chen and Evans, 2009; Choudalakis and Gotsis, 2009; Mittal, 2009; Hua et al., 2010; Jancar et al., 2010; Jeon and Baek, 2010; Kiliaris and Papaspyrides, 2010; Li et al., 2010; Kato et al., 2011). Presently, considerably improved mechanical performance, thermal stability, barrier characteristics and fire retardation properties of a given polymer can be obtained at very low clay loadings. Increased biodegradability of biodegradable polymers has also been reported (Sinha Ray et al., 2002). Although different approaches have been utilized for the preparation of these materials, namely in situ template synthesis by sol-gel technology, in situ intercalative polymerization, solution intercalation, or melt mixing, the latter seems to be preferred method in practice. Particularly when using twin screw extruders, it is possible to generate the stresses and times required for diffusion of the polymer inside the confined spaces between clay lamella (intercalation), as well as the high levels of shearing necessary for exfoliation (Bousmina, 2006). Also, the process is continuous, environmentally benign, allows the use of polymers which are not suitable for the other preparation routes and can be adapted to the specificities of a given material or process due to the modular construction of twin screw extruders (Sinha Ray and Okamoto, 2003; Mittal, 2009; Kiliaris and Papaspyrides, 2010).

The performance of a polymer-clay nanocomposite is determined by the composition, properties of its ingredients, chemical affinity between polymer and organoclay and processing conditions (screw profile, operating conditions, feeding sequence), as most of these parameters will influence evolution of dispersion and its final level. The effect of processing conditions has been extensively investigated (Davis et al., 2002; Fasulo et al., 2004; Zhu and Xanthos, 2004; Modesti, 2005; Lertwimolnun and Vergnes, 2006; Peltola, 2006; Scatteia et al., 2006; Shah and Paul, 2006; Lertwimolnun and Vergnes, 2007; Treece et al., 2007; Domenech et al., 2012; Giraldi et al., 2008). This influence implies that during practical compounding stringent process control and periodic monitoring of the characteristics of the nanocomposite being manufactured are imperative.

On-line and in-line monitoring techniques are particularly attractive for this purpose. Optical and spectroscopic methods have been applied to assess the extent of exfoliation in poly-mer-clay nanocomposites. Optical transmission measurements showed that transmission increases with increasing extent of exfoliation, because light scattering due to the presence of clay aggregates reduces (Bur et al., 2005; Bertolino and Canevarolo, 2010). It was observed that the development of an exfoliated structure results in an intense increase of fluorescence (Maupin et al., 2004; Bur et al., 2007). However, the technique used required that the fluorescent tracer (Nile blue) was incorporated into the clay galleries before compounding. In-line near-infrared spectroscopy, together with appropriate chemometrics using off-line data, provided a good correlation with dispersion (Witschnigg et al., 2010; Barbas et al. 2013a). Online dielectric relaxation spectroscopy revealed that clay fillers impact on nearly all relaxation processes changing both the characteristic frequency and strength of the relaxation (Bur et al., 2005; Lee et al., 2005). Recently, Kracalik et al. (2011) subjected the nanocomposites emerging from the die to a Rheotens (Göttfert Ltd., Buchen, Germany) extensional experiment and demonstrated that the sensitivity of melt strength correlates well with dynamic rheological data measured by rotational rheometry.

Together with transmission electron microscopy (TEM) and X-ray diffraction (XRD), rotational rheometry (in small amplitude oscillatory shear, SAOS) is frequently used to assess dispersion in polymer-clay nanocomposites. In a storage modulus (G') versus frequency plot, an increase of G' at low frequency is usually interpreted as evidence of greater dispersion (Krishnamoorti and Giannelis, 1997; Vermogen et al., 2005; Lertwimolnun and Vergnes, 2006; Durmus et al., 2007; Xu et al., 2009; Domenech et al., 2012). The exponent of a power law fitted to the variation of complex viscosity (η^*) with frequency was shown to increase with dispersion (Vermogen et al., 2005; Durmus et al., 2007). The growth in melt yield stress (σ_0) was related to an intensification of clay exfoliation (Lertwimolnun and Vergnes, 2006; Lertwimolnun and Vergnes, 2007; Vergnes, 2011; Domenech et al., 2012).

Therefore, the use of on-line rotational rheometry to monitor the preparation of polymer-clay nanocomposites by melt mixing seems of significant practical interest. Although an isothermal frequency sweep in SAOS typically takes several minutes, the technique remains suited for process monitoring due to the richness of the information provided, at least during the initial process development and optimization stages. Such a rheometer was previously developed and experimentally validated (Covas et al., 2008), an improved version with automated operation having been recently made available (Mould et al., 2011). Since the device was designed to perform measurements at various locations along the barrel of the extruder, it was successfully used to provide data on the axial evolution of dispersion of polymer-clay nanocomposites (Mould et al., 2012). In the present work, the on-line rheometer is fixed between an industrial extruder and a multi-rod die and the capacity to discriminate the effects of changes in clay type and content, screw speed and feed rate are investigated, as a requirement for process monitoring ability. The analysis is supported by XRD and electron microscopy data.

Experimental

Materials

The materials used in this work, a general purpose commercial polypropylene homopolymer (PP), a compatibilizer (polypropylene grafted with maleic anhydride, PP-g-MA) and two commercial natural montmorillonite clays modified with a quaternary ammonium salt, are presented in Table 1. A stabilizer pack was also incorporated. The compositions of the nanocomposites prepared are identified Table 2.

Material	Designation	Supplier	Grade	MFR
Polypropylene	PP	LyondellBasell	Moplen HP500N	12 g/10 min (2.16 kg/ 230°C)
Polypropylene grafted with maleic anhydride	PP-g-MA	Crompton	Polybond 3200	Polybond 3200 (2.16 kg/ 190 °C)
Montmorillonite	D67G	Laviosa	Dellite 67G	-
	C20A	Southern Clay Products	Cloisite 20 A	-

Table 1. Materials used in this work

PP wt. %	PP-g-MA wt.%	Dellite 67 G wt. %	Cloisite 20 A wt.%	Stabilizer pack wt.%	Operating conditions
94.2	5.0	-	-	0.8	$300\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$
89.2	5.0	-	5.0	0.8	$300\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$
86.5	5.0	-	7.7	0.8	$300\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$
86.5	5.0	-	7.7	0.8	$230\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$
86.5	5.0	-	7.7	0.8	$150\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$
86.5	5.0	-	7.7	0.8	$300\ \mathrm{min}^{-1}, 40\ \mathrm{kg/h}$
85.4	5.0	8.8	-	0.8	$300\ \mathrm{min}^{-1}, 50\ \mathrm{kg/h}$

Table 2. Compositions and corresponding operating conditions

Experimental Setup

All materials were prepared in a Maris TM45 twin-screw extruder (screw diameter, $D = 45\ \mathrm{mm}$, length to diameter ratio, $L/D = 36$). The screws contained four mixing zones consisting of staggered kneading disks (proprietary design). Polymer and filler were fed separately by gravimetric feeders. The barrel and die set temperature were kept constant at $180^{\circ}\mathrm{C}$, while screw speed and feed rate were varied as shown in Table 2. During the experiments, melt temperature at the die ranged between 210 and $221^{\circ}\mathrm{C}$, melt pressure between 8.6 and 12 bar and motor amperage between 25 and 41 A .

On-line rheological measurements were performed between extruder and die, after diverting the required amount of melt to the device. The set-up has been validated elsewhere (Mould et al., 2011). The extrudate was cooled down in water and pelletized, samples being collected for off-line rheological, structural (XRD) and morphological (SEM and TEM) characterization. Figure 1 illustrates the experimental set-up.

Characterization

On-line Oscillatory Rheometry

As most rotational rheometers, the prototype can operate in various modes, but only SAOS experiments were performed. In order to make a measurement, the melt is diverted from the main stream (between extruder and die) by means of an adapter connecting it to the testing chamber of the rheometer. Once sufficient material sample has been collected, the incoming flow is interrupted by rotating a valve. The operation takes approximately 12 to 15 s and creates negligible shear rates, to prevent changes in morphology. As described in detail by Mould et al. (2011), an automatic sequence is then initiated, comprising squeezing the sample between the parallel plates (with a diameter of 20 mm) until the pre-defined gap (1 mm) is obtained, and wiping the excess material around the plates by sliding a cleaning ring. The rheological test starts when the sample reaches thermal equilibrium at the experiment set temperature (due to the difference between inlet melt temperature and set value of 200°C, equilibration time varied between 3 and 4 min). For each sample, frequency sweeps from 100 to 0.1rad/s were performed under a constant strain of 1%.

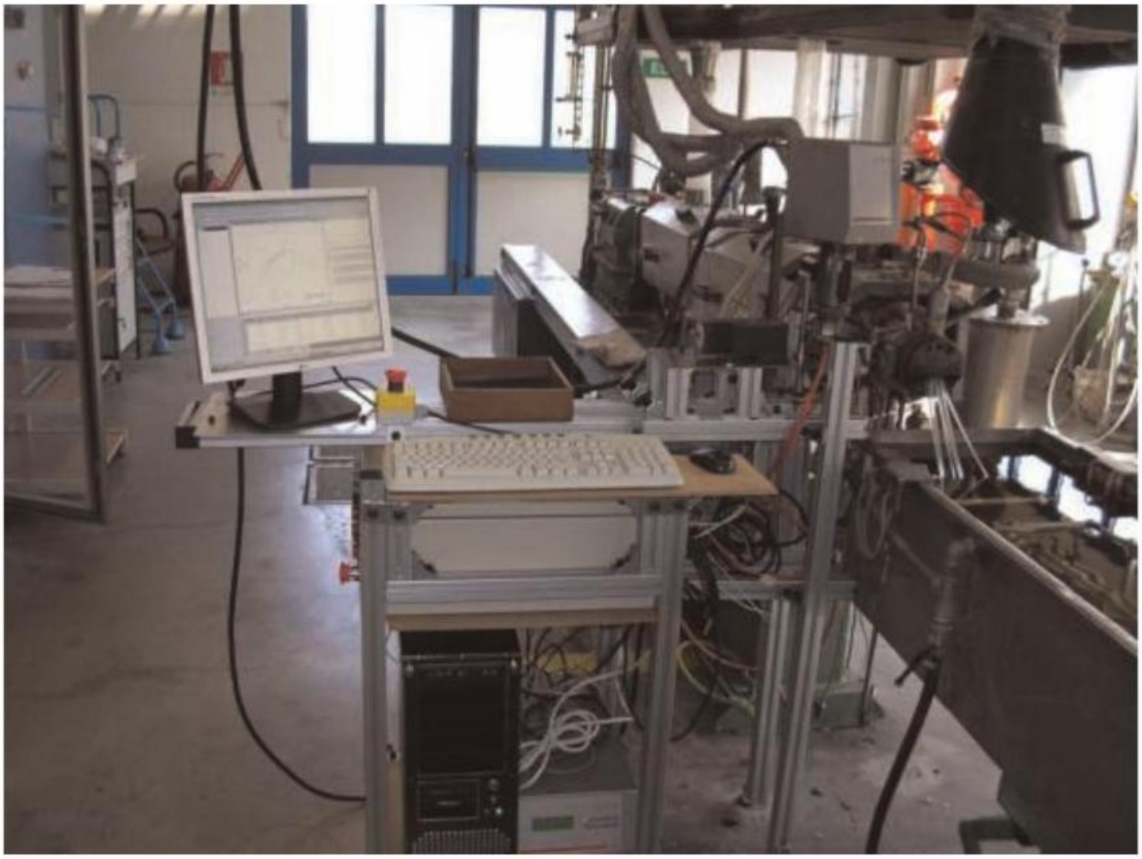


Fig. 1. Experimental set-up

Off-line Oscillatory Rheometry

Tests were performed in a strain controlled ARG2 (TA Instruments) using parallel plates with a diameter of 25 mm and a 1 mm gap. The discs were manufactured by compression molding at 200°C. In the same way of the on-line tests, isothermal at 200°C frequency sweeps from 100 to 0.1rad/s were performed for each sample under a constant strain of 1%.

X-ray Diffraction (XRD)

Diffraction patterns were obtained using a AXS Nanostar-D8 Discover diffractometer (from Bruker) equipped with a CuKα generator ($\lambda = 1.5404Å$) at 40 kV and 40 mA , in a 2θ range between 0.08 and 10°. The organoclays were analyzed directly, whereas the nanocomposite samples were previously compression molded into disks with a diameter of 20 mm and a thickness of 4 mm .

Electron Microscopy (SEM and TEM)

Samples for scanning electron microscopy (SEM) were beforehand embedded in a resin, subjected to a lapping procedure to obtain a flat surface, and coated with a gold thin film. The analysis of 3 mm^2 of each sample was performed in a Leica Cambridge S 360 microscope. Transmission electron microscopy (TEM) microphotographs were taken of samples with a thickness of 70 nm , cut using a diamond knife of a Leica ultramicrotome at −60°C. The cut sections were transferred onto copper grids and then examined without staining in a Philips CM120 TEM. The Equivalent Circle Diameter (ECD) was quantified on a 0.2 mm^2 area using an Image Analysis software interpolation. The Specific Tactoids Dispersion (STD) was determined as the number of clusters per unit area and per unit filler concentration; the error associated with the measurements is around 10%.

Results and Discussion

On-Line vs. Off-Line Measurements

Figure 2 compares the on-line and off-line rheological data (complex viscosity, η^*, and storage modulus, G') obtained for the nanocomposite with Dellite 67G, i.e., PP + 5%PP-gMA + 7.7%D67G. The agreement seems good, similar differences having been obtained for the remaining samples. Earlier work (Covas et al., 2008; Mould et al., 2011) showed that the average deviation between the results obtained on-line and offline for various commercial polymer melts, polymer blends and polymer-clay nanocomposites varied between 3 and 13%. Frequently, in the case of polypropylene-based systems, the moduli measured on-line were a little higher than those measured offline. This was attributed to degradation of the samples measured off-line, as they are subjected to additional thermal cycles required for manufacturing discs and heating them up to the test temperature. Since the system used here was stabilized, the above feature is not present in Fig. 2. In the remaining of this work, only on-line rheological data will be presented.

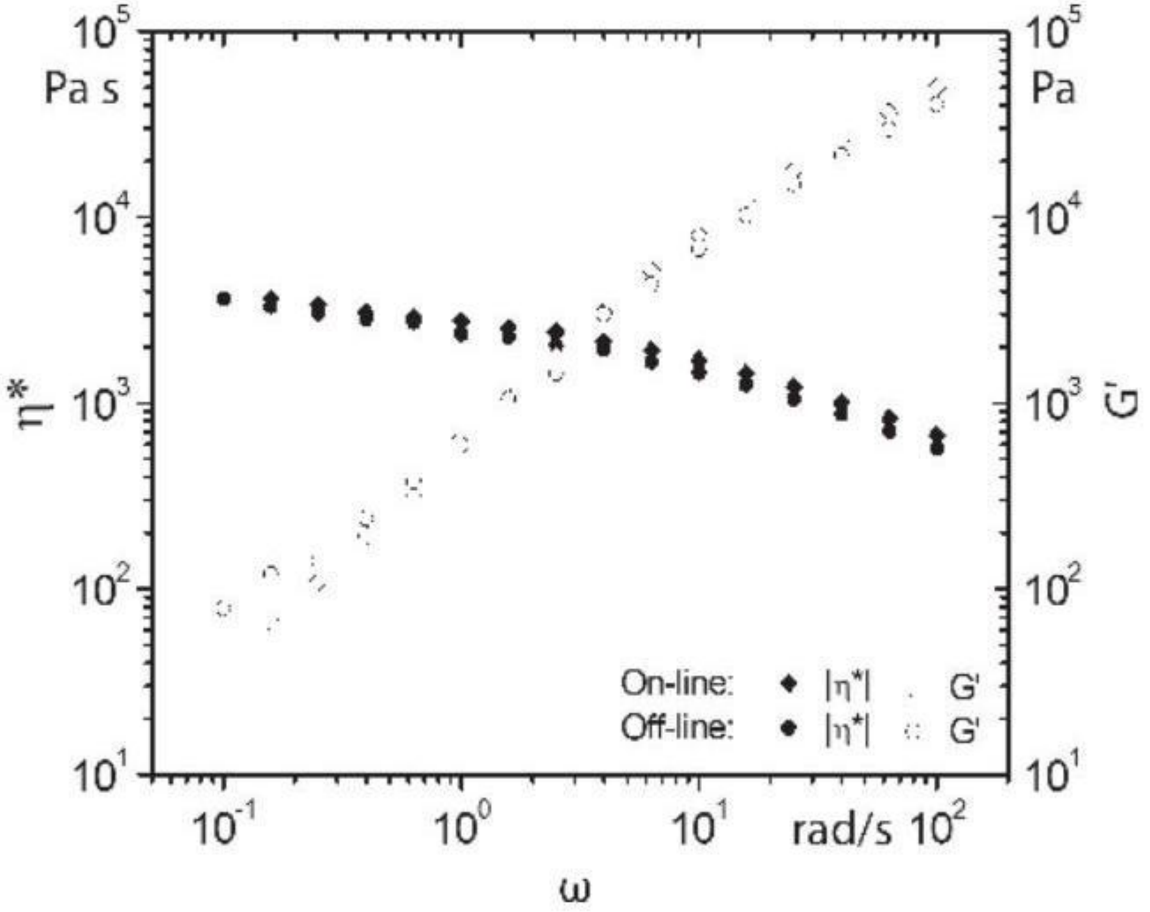


Fig. 2. On-line vs. off-line rheological data for PP + 5% PP-g-MA + 7.7%D67G

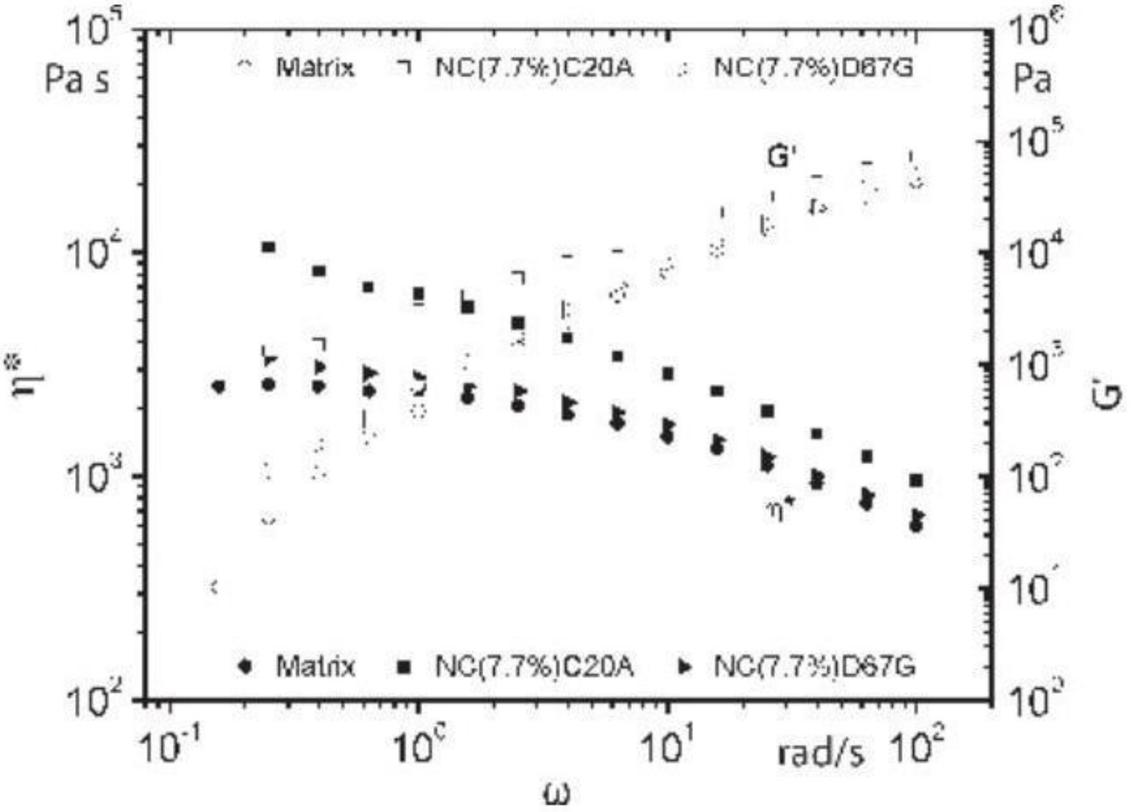


Fig. 3. On-line rheological data for PP + PP-g-MA (matrix), PP + 5%$PP-g-MA+$ 7.7%$D67G$ (NC(7.7%)D67G) and PP + 5%$PP-g\ MA+7.7\%C20A(NC(7.7\%)C20A)$

Effect of Clay Type

The effect of changing clay type on the measured rheological properties is depicted in Fig. 3. Both curves show an increase of G' at low frequencies, but Cloisite 20 A exhibits higher values than Dellite 67 G . This would indicate a priori that a better dispersion was achieved with the former.

Even though the two organoclays have the same surfactant (dimethy dihydrogenated tallow ammonium, 2 M 2 HT), Cloisite 20 A has lower particle size (its initial average particle size is 5μ m, while that of Dellite 67 G is approximately 9μ m (Utracki, 2004)). The XRD diffractograms of Fig. 4 indicate that the initial basal spacing of C20A is smaller than that of D67G (2.7 nm versus 3.7 nm , as estimated using Bragg's law (Lertwimolnun and Vergnes, 2007)). The net result of processing under identical conditions is also indicated in Fig. 4: while for C20A the clay interlayer spacing increased to 3.0 nm , thus indicating that some degree of intercalation was achieved, the value of 3.4 nm for D67G points towards little intercalation, or even collapse of the clay galleries. In any case, these results are coherent with the rheological data.

Morphological analysis by SEM (Fig. 5) and TEM (Fig. 6) corroborates these observations. The white zones in the SEM micrographs of Fig. 5 are clay agglomerates and the dark background is the PP/PP-g-MA matrix. Agglomerates are clearly

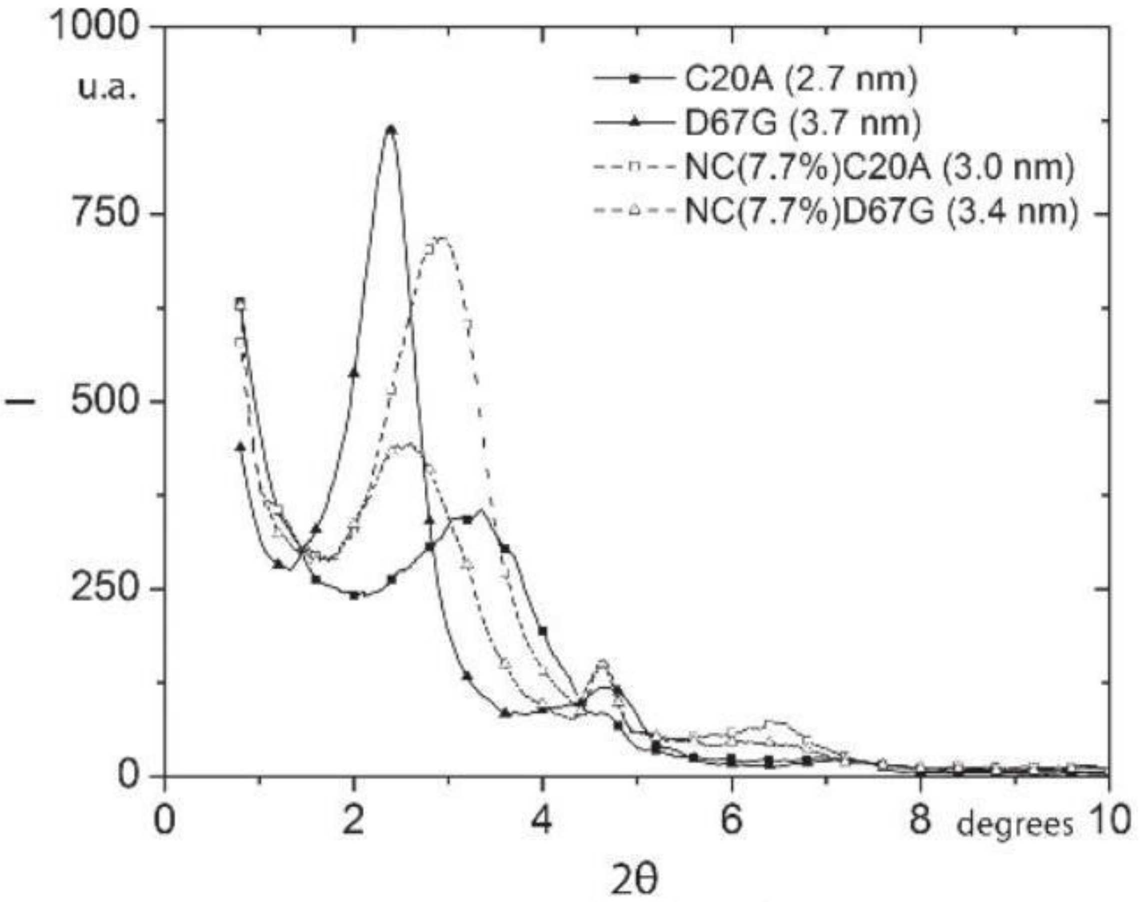
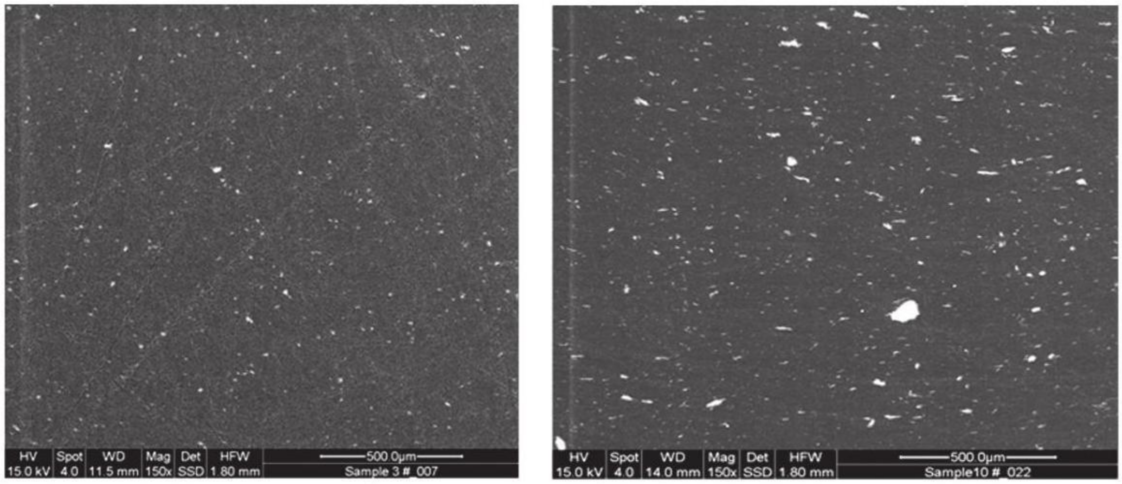


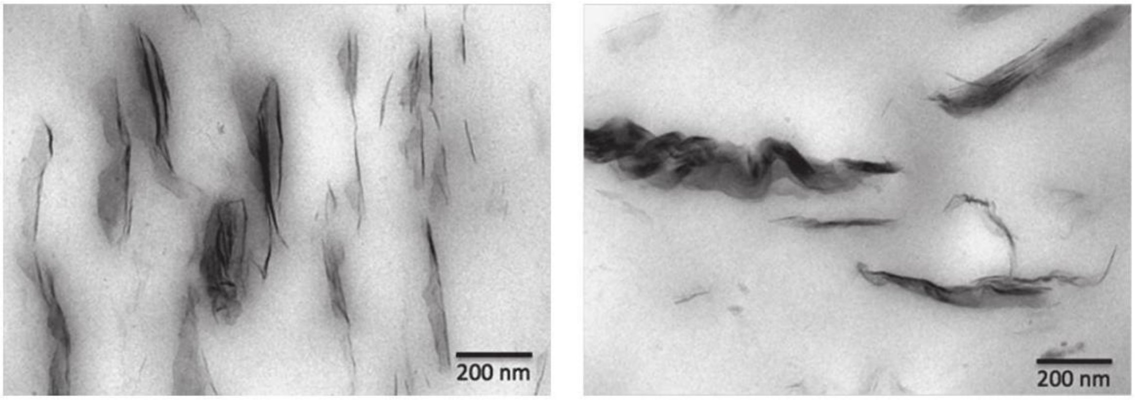
Fig. 4. XRD diffractograms of C20A, D67G, PP + 5%PP-g-MA + $7.7\% C20A (NC(7.7\%) C20A)$ and $PP + 5\% PP - g - MA + 7.7\% D67G$ (NC(7.7%)D67G)



A)

B)

Fig. 5. SEM micrographs of (A) $PP + 5\%PP - g - MA + 7.7\%C20A$ and (B) $PP + 5\%PP - g - MA + 7.7\%D67G$



A) B)

Fig. 6. TEM micrographs of (A) PP + $5\%PP - g - MA + 7.7\%C20A$ and (B) $PP + 5\%PP - g - MA + 7.7\%D67G$

smaller and more homogeneous in the system prepared with C20A. Figure 6A (composite containing C20A) shows that the stacked layer structures are thinner than in Fig. 6B. For C20A, the number of tactoids per unit area is 90 and the specific tactoids dispersion (STD) is 12, whilst for D67G the corresponding values are 152 and 17, respectively.

Effect of Clay Content

Figure 7 depicts the effect of altering clay content from 5 to 7.7wt. % on complex viscosity and storage modulus of the nanocomposites. As expected, not only the global values of the rheological parameters increase, but the plateau of G' at low frequency seems more prolonged. These changes could result directly from differences in organoclay loading, but alterations in the extent of dispersion could also make a contribution. After correcting the hydrodynamic effect due to the filler amount (vertical shift of the complex viscosity curves), the values of the apparent melt yield stress were determined as 477 and 1257 Pa for the samples with 5wt. % and 7.7wt. %, respectively, i.e., a better dispersion seems to be achieved with 7.7wt. %.

Opposite results were obtained with other techniques. As seen in Fig. 8, the lamellar distance of the nanocomposite prepared with 5wt. % of C20A is somewhat higher than that having 7.7wt. %(3.4 nm versus 3.0 nm). From TEM micrographs, the corresponding number of tactoids per unit area is 44 and 90 , respectively, and STD is 9 and 12. These values being smaller

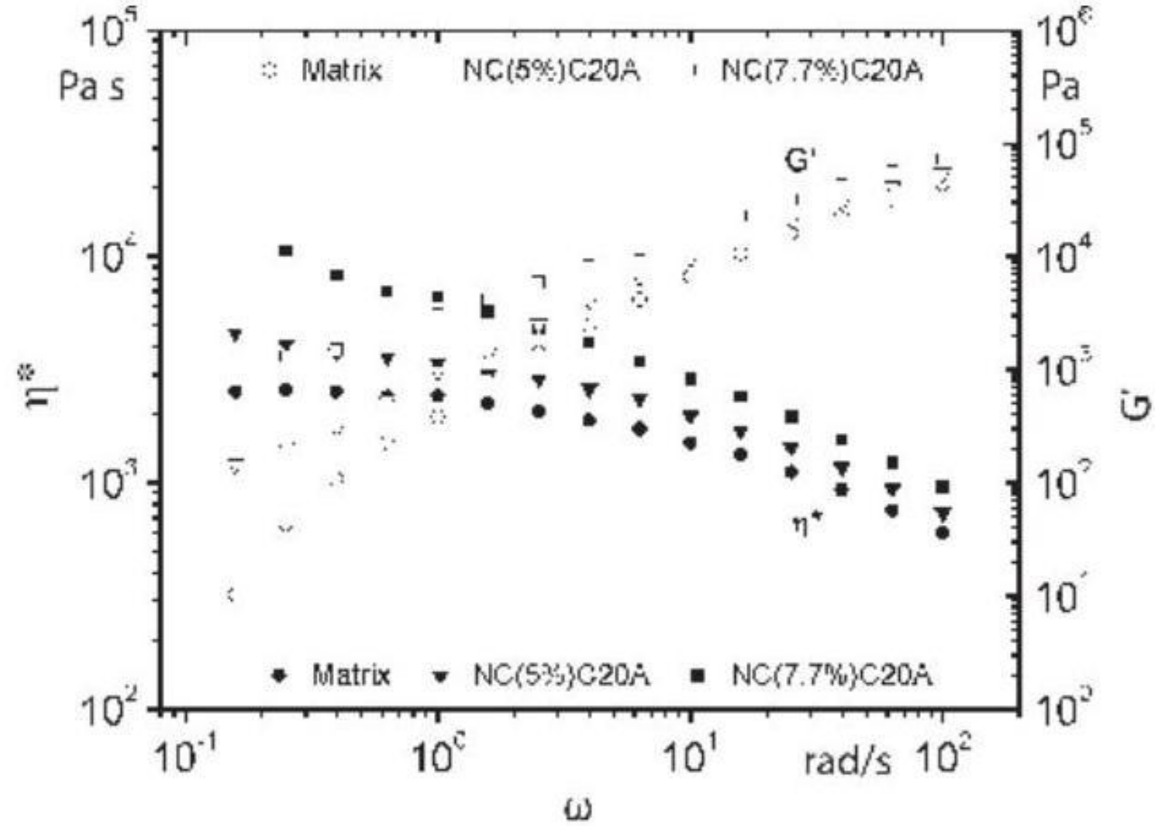


Fig. 7. On-line rheological data of PP clay-nanocomposites containing different clay content (5 and 7.7% C20A)

for the nanocomposite prepared with less clay, they also indicate better dispersion. While XRD and TEM analyze the extent of dispersion in a small area of the sample (the former in terms of intercalation, the latter detecting both intercalation and exfoliation), rheology is sensitive both to dispersion and filler content, which could explain the different conclusions.

Effect of Feed Rate

Shifting the feed rate from 40 to 50 kg/h does not seem to produce meaningful differences in the linear viscoelastic response of the material (Fig. 9). This apparent insensitivity is con-

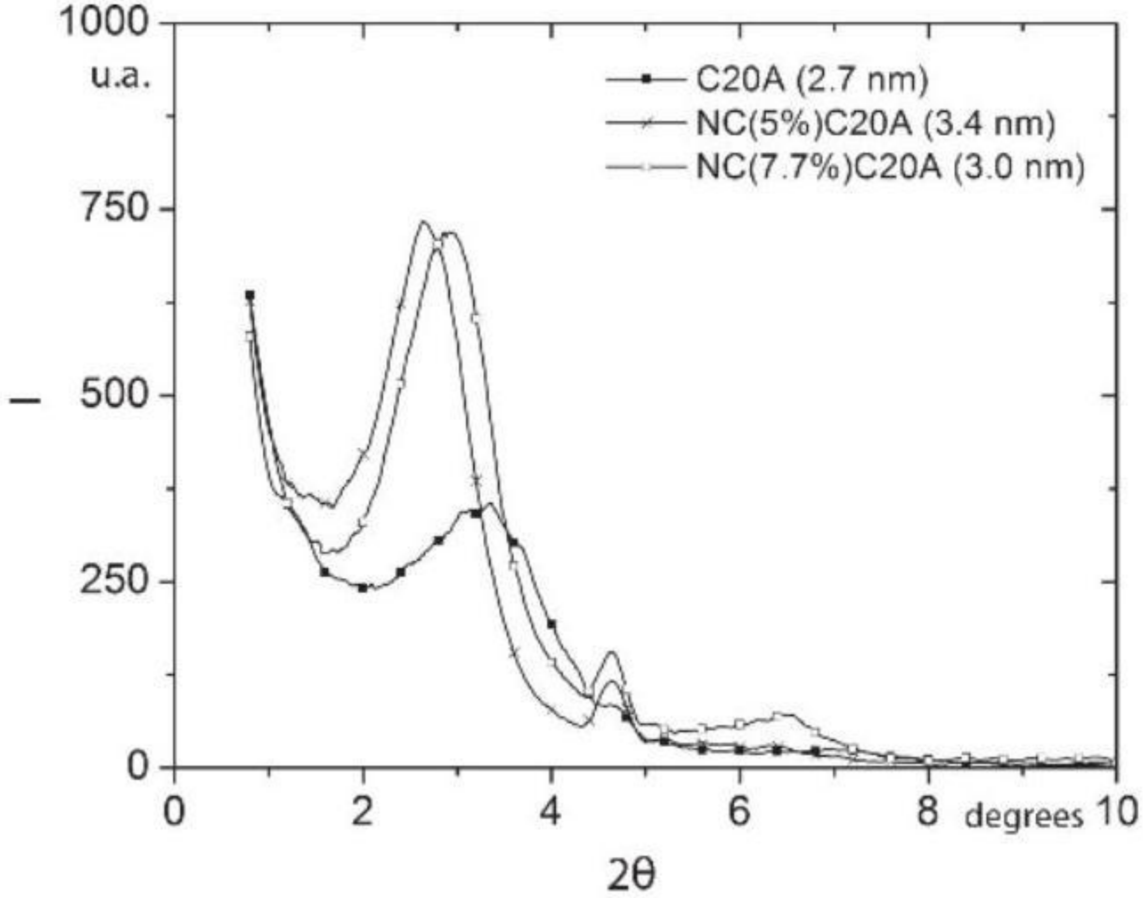


Fig. 8. XRD diffractograms of PP-clay nanocomposites containing different clay content (5 and 7.7% C20A)

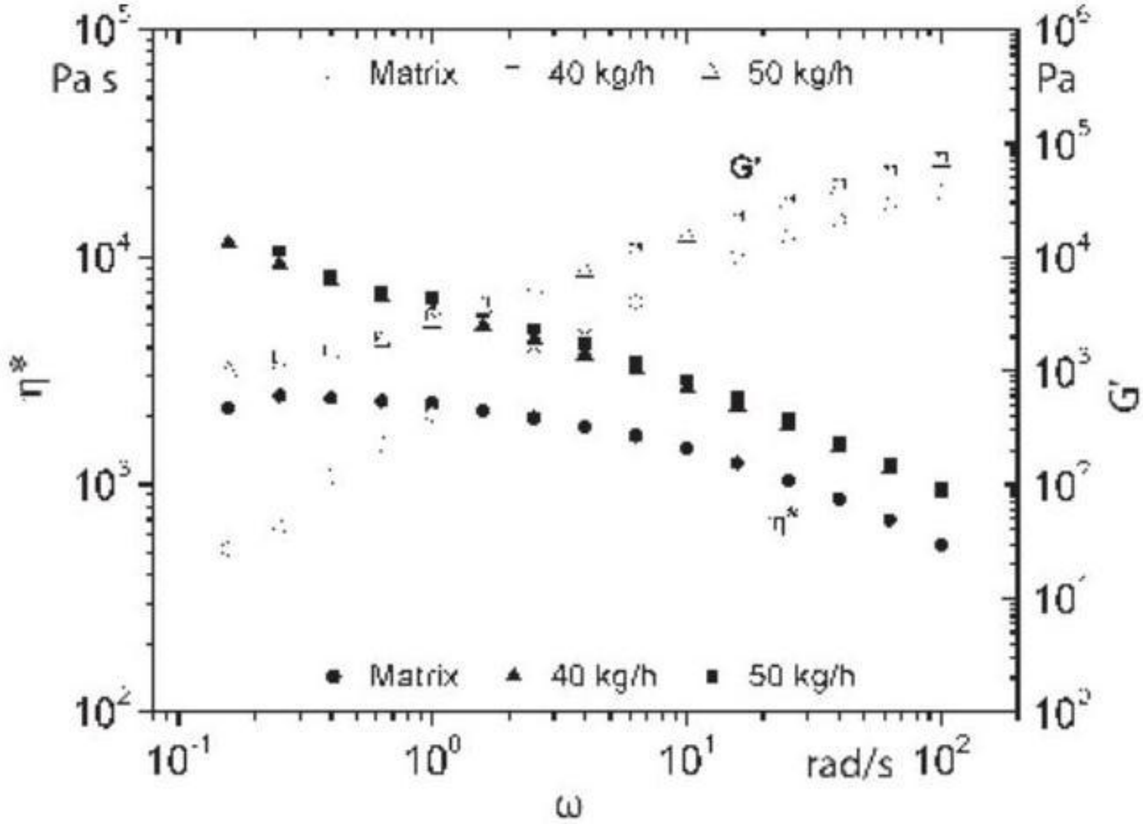


Fig. 9. On-line rheological data of PP clay-nanocomposites prepared using different feed rates

firmed by XRD (Fig. 10), which points to comparable lamellar distances for the two nanocomposites (2.9 nm for the one produced at 40 kg/h, 3.0 nm for that manufactured at 50 kg/h). Similarly, SEM micrographs (Fig. 11) exhibit equivalent morphologies. TEM analysis indicated that the nanocomposite prepared at 40 kg/h presented a lower number of tactoids per area and a lower STD (60 and 8, respectively for the sample produced at 40 kg/h, as opposed to 90 and 12, respectively, at 50 kg/h). This effect is in line with most previous studies, which report that lower feed rate values improve exfoliation levels because of the corresponding increase of residence time (Dennis et al., 2001; Lertwimolnun and Vergnes, 2006; Lertwimolnun and Vergnes, 2007; Domenech et al., 2012).

Effect of Screw Speed

According with the rheological data plotted in Fig. 12, the nanocomposite prepared at the medium screw speed (230 $\min^{-1}$) appears to be better dispersed than the remaining (150 and 300 $\min^{-1}$), which present a similar response (the apparent yield stresses for 150, 230 and 300 $\min^{-1}$ are 1259, 1710 and 1386 Pa , respectively). The rheological measurements seem to be more sensitive than XRD (Fig. 13), which indicates equivalent lamellar distance regardless of the screw speed. Similarly,

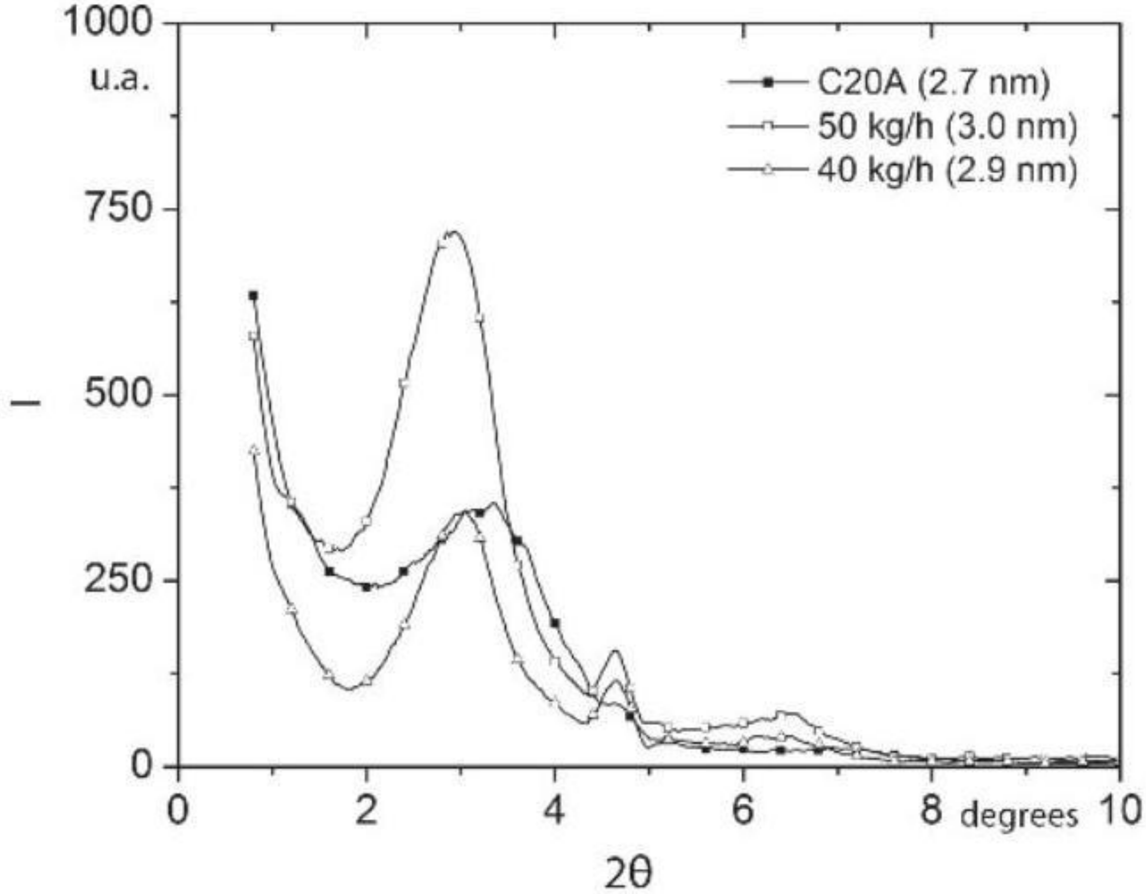


Fig. 10. XRD diffractograms of PP clay-nanocomposites prepared using different feed rates

SEM micrographs (not shown) indicated equivalent dispersion for all samples. However, from TEM observations the number of tactoids per unit area and STD for the samples prepared at 150 and 300 min^{-1}, were calculated as 98 and 90 , and 13 and 12, respectively, i.e., within experimental accuracy, the nanocomposites show comparable dispersion levels.

Screw speed is usually reported to promote dispersion (Dennis et al., 2001; Fasulo et al., 2004; Modesti et al., 2005; Lertwimolnun and Vergnes, 2006; Peltola ert al, 2006; Lertwimolnun and Vergnes, 2007; Treece et al., 2007; Domenech et al.,

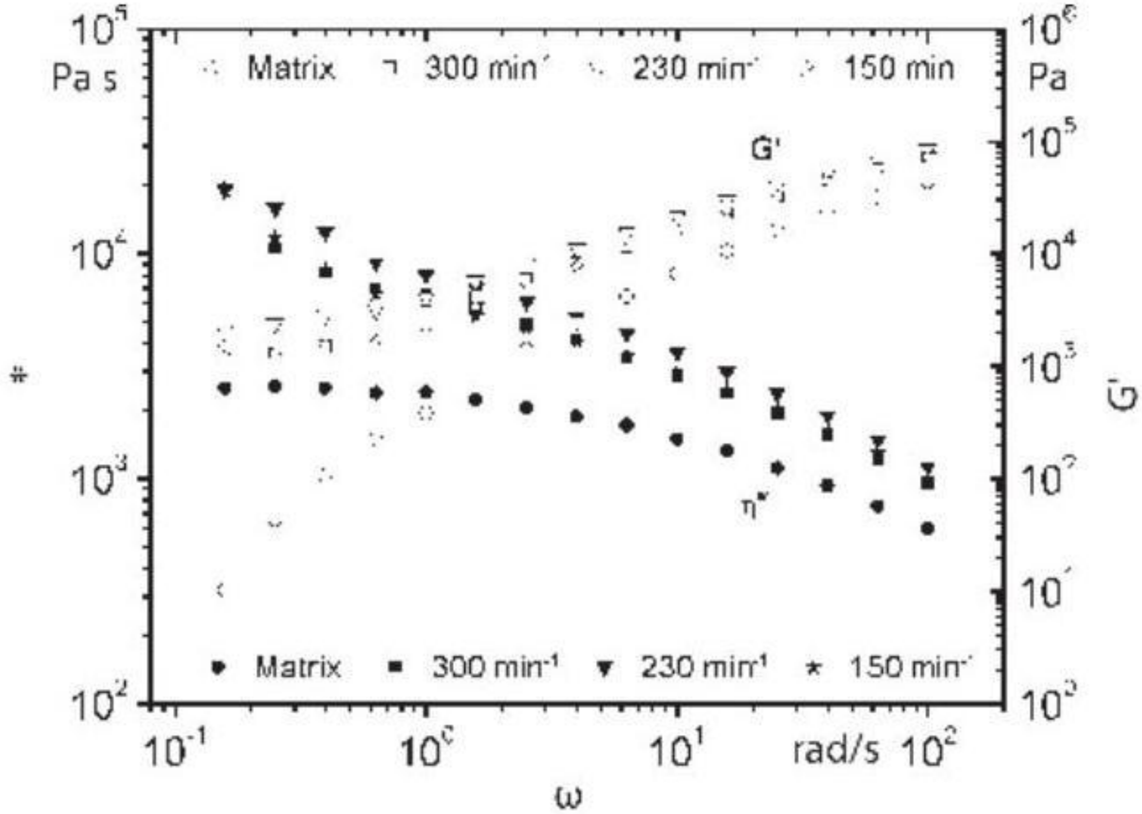


Fig. 12. On-line rheological data of PP clay-nanocomposites prepared using different screw speeds

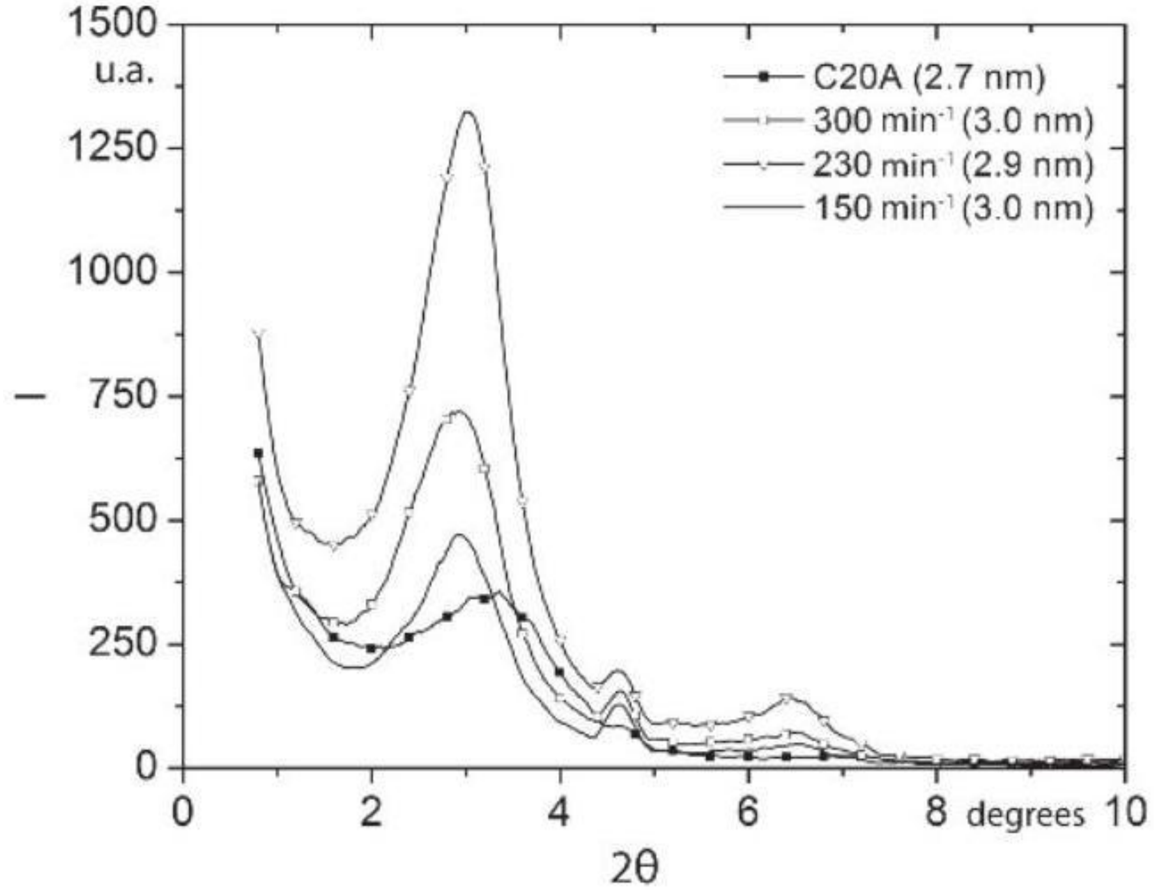
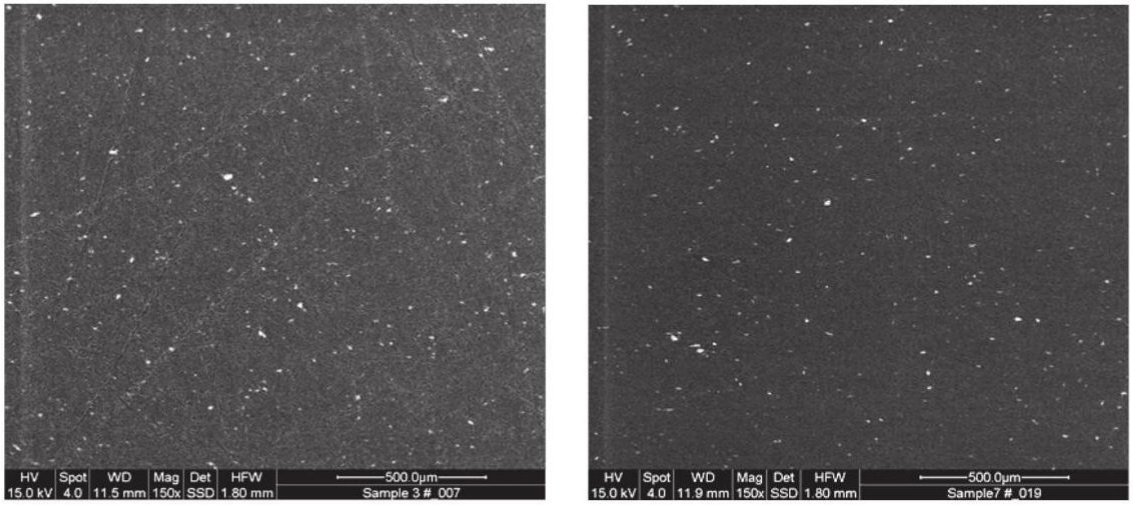


Fig. 13. XRD diffractograms of PP clay-nanocomposites prepared using different screw speeds



A) B)

Fig. 11. SEM micrographs of PP clay-nanocomposites prepared with different feed rates, A: $40\ \mathrm{kg/h}, B: 50\ \mathrm{kg/h}$)

2012) due to the greater intensity of the hydrodynamic stresses created by the higher shear rates, that should particularly promote exfoliation. This would explain why XRD diffractograms, being mostly sensitive to intercalation, remained similar. However, high screw speeds could eventually promote degradation of the surfactant and, eventually, of the polymer, causing a decrease of the viscosity (Shah and Paul, 2006; Barbas et al., 2013b). In fact, as seen in Fig. 12, the complex viscosity for the nanocomposite prepared at 300 min^{-1} is lower than the remaining.

Conclusions

The linear viscoelastic response of a polymer-clay nanocomposite is frequently utilized to estimate the extent of dispersion of the clay in the matrix. Therefore, on-line rotational rheometry seems interesting to monitor the preparation of polymerclay nanocomposites, with a view to process development and/or monitoring. This work investigated whether the technique would be sensitive to a change of clay type and to moderate changes in clay content, feed rate and screw speed.

First, it was shown that equivalent on-line and off-line rheological data showed good agreement. Rheology exhibited at least the same sensitivity of the other well-known characterization methods utilized to assess dispersion, electron microscopy (SEM and TEM) and X-ray diffraction, with obvious practical advantages. The trends observed by the various techniques were generally identical, particularly between rheology and TEM, given the sensitivity of the two techniques to both interaction and exfoliation.

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