Monitoring the Production of Polymer Nanocomposites by Melt Compounding with On-line Rheometry

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Abstract

Polymer nanocomposites are often prepared by melt compounding due to the suitability of the latter to industrial scale production. Even though monitoring the production process for quality control and/or optimization purposes is generally done off-line, the possibility of using on-line oscillatory rheometry has many inherent advantages. This work illustrates the use of a prototype rheometer to monitor the production of polymer nanocomposites by making measurements at specific locations along the extruder axis. The device is presented and its operation is explained. Examples of its use to characterize polypropylene and polyamide matrix nanocomposites with organoclays and carbon nanotubes are discussed, thus demonstrating the usefulness of the device.

Introduction

Since it was reported that the addition of a small percentage of an organoclay or of carbon nanotubes (CNT) to a polymer matrix could result in final excellent mechanical and physical properties, nanocomposites gained a wide interest for both academia and industry (Giannelis, 1998; Alexandre and Dubois, 1998; Fischer, 2003; Ray and Okamoto, 2003; Breuer and Sundararaj, 2004; Hussain et al., 2006; Thostenson et al., 2005; Coleman et al., 2006; Lau, 2006; Ma, 2008, Paul and Robeson, 2008; Paiva et al., 2008; Pavlidoua and Papaspyrides, 2008; Spitalsky et al., 2010; Jancar et al., 2010; McNally and Pötschke, 2011).

These materials are often prepared using melt compounding techniques that are readily available in industry (and thus allow companies of quite different sizes and working in a variety of application fields to explore their benefits), provide good production yields and automatic operation, are environmentally friendly and capable to generate the hydrodynamic stresses required to achieve sufficiently good dispersion. Intermeshing co-rotating twin screw extruders are particularly popular for this purpose.

Generally, high filler dispersion levels are required to take full advantage of their characteristics. In the case of organoclays, intercalation and exfoliation into the polymer matrix is mandatory (Dong and Bhattacharyya, 2008; Yoo and Paul, 2008), whereas for CNT full dispersion is important for mechanical reinforcement, but the presence of some aggregates might be favourable for electrical conductivity (Takase et al., 2002; McNally and Pötschke, 2011). Dispersion is influenced by material and processing parameters. For layered silicatebased clays, the former encompass the organic modifier, the properties of the polymer matrix and the type and concentration of the compatibilizer (Lertwimolnun and Vergnes, 2006); for CNTs agglomerate size, structure and cohesion, surface energy and purity are dominant (Kasaliwal et al., 2010). In turn, the processing parameters determine the velocity fields, stress levels and residence times, which are obviously conditioned by the type of mixing equipment (Haggenmueller, 2000; Dennis et al., 2001; Dolgovskij et al., 2003; McNally and Pötschke, 2011). The geometry of the equipment and the operating conditions control the mixing rate and the final dispersion level. However, and despite the significant number of studies on the topic, clear correlations between processing parameters and state of dispersion are still lacking, with contradictory results being reported. Information on the morphological evolution along the screws is scarcer (Wang et al., 2001; Lertwimolnun and Vergnes, 2006; 2007; Covas et al., 2011), although it would contribute to assess the influence of screw geometry and to better understand the underlying mixing mechanisms.

Direct assessment of (distributive and dispersive) mixing necessitates the use of electron microscopy techniques that are expensive and time consuming, often involve elaborate sample preparation and entail an extensive statistical analysis of a sufficiently high number of filler particles/fibers. Thus, the indirect characterization of dispersion by other techniques (such as X-ray diffraction, rheology, infra-red analysis), or the direct measurement of relevant final features (tensile properties, electrical conductivity) are often adopted. It has been extensively shown that the rheological response of nanocomposites is sensitive to changes at different length scales (Huang et al., 2006; Lertwimolnun and Vergnes, 2006; Ray, 2006; Vermant et al., 2007; Cassagnau, 2008; Park et al., 2008; Ma et al., 2008; Vergnes, 2011). Thus, as rheometers are readily available in most laboratories, sample preparation is not too complicated and measurements are relatively straightforward, rheology is currently one of the most used methods to characterize dispersion. For example, the linear viscoelastic response of extruded samples produced under a variety of processing conditions can be employed to select the most adequate compounding condition for a specific nanocomposite. Rheological measurements of samples along the screw are much rarer. Lertwimolnun and Vergnes (2007) reported results from dead-stop experiments with nanoclay composites, where the machine was stopped after reaching steady state operating conditions, the barrel was rapidly cooled, the screws were removed and material samples were collected from several axial locations. For a few processing conditions, the authors reported a reversion of the evolution of dispersion along the screws, which they attributed to a combination of local high temperature and long residence time, that induced either a degradation of the organic intercalant or an expulsion of the already intercalated polymer chains. In fact, these phenomena could also eventually develop under quiescent conditions while the barrel was being cooled, during compression molding of a disk for the subsequent rheological test, or even while waiting for thermal equilibrium between the plates of the rheometer, prior to the measurement. Similarly, in the case of CNT nanocomposites aggregate re-agglomeration has been reported when flow is interrupted, or when the material is subjected to repetitive thermal cycles (Pe – gel et al., 2008; Jamali, 2010).

The advantages of on-line measurements are obvious: i) the number of thermal cycles necessary for sample preparation and thermal equilibrium are minimized, ii) if the rheological measurements can be performed along the length of the equipment, the evolution of physical-chemical processes can be followed, iii) periodic measurements at a certain location can be useful for quality and process control. Most commercial online instruments transfer melt from the main stream, which then feeds a capillary or slit die at constant rate by means of a gear pump. Generally, after the measurement the by-passed melt merges with the main stream. However, practice has shown that oscillatory rheometry is more adequate for the characterization of nanocomposites than capillary rheometry, because it preserves the initial sample morphology, is sensitive to small variations in dispersion and can deliver a rather complete rheological description. The authors (Mould et al., 2011) have recently presented and validated experimentally a computer controlled on-line rotational rheometer capable of quickly collecting material samples from within an extruder at different axial locations and performing the same measurements of typical bench top commercial instruments. The instrument was designed to: i) minimize the time-lag between sample collection and measurement, ii) prevent material morphology changes both during sampling and measurement, iii) enable measurements along the axis of the extruder iv) perform trials at temperatures other than the processing temperature.

The present work aims at demonstrating the usefulness of the new device to monitor the evolution of the rheological response of nanocomposites along the axis of a twin screw extruder and the effect of some material and process parameters (composition and screw-speed), thus contributing to a better understanding of the mixing mechanisms in this type of equip-
ment and to process optimization. The paper is organized as follows. The on-line rheometer is briefly presented and the conditions selected for the experimental work are described. Then, the sensitivity of the device to changes in several process parameters, for different polypropylene and polyamide based nanocomposites with organoclay or CNT is demonstrated. Finally, the main conclusions are drawn.

The On-line Oscillatory Rheometer

From the time the original concept of the on-line rheometer was implemented and successfully validated (Covas et al., 2008), efforts have been made to improve its design, reliability and precision, as well as minimize the dependence on the user skills upon operation. For that purpose, all movements were fully automated using motion control hardware and control software was developed. As shown in Fig. 1, which depicts the on-line rheometer coupled to the barrel of the extruder at a specific location, the system comprises a linear motor (A) to control the position of the lower plate, a rotational motor (B) to open/close the valve (C) through which flows the melt that is withdrawn from the extruder, a linear actuator (D) to displace a cleaning ring and a commercial rotational rheometer head (E) (Anton Paar DSR301) that controls the actual rheological test. As in conventional off-line rheometry, the device can operate in steady and oscillatory modes and measurements can be made during isothermal steady shear, small amplitude oscillatory shear, amplitude sweep, stress relaxation, creep & recovery. A detailed description and validation of the instrument is reported elsewhere (Mould et al., 2011).

Fig. 2 illustrates the sequence of operation steps taken for one rheological test. Fig. 2A shows the extruder operating normally while the rotating valve is closed, eventually for mainte-

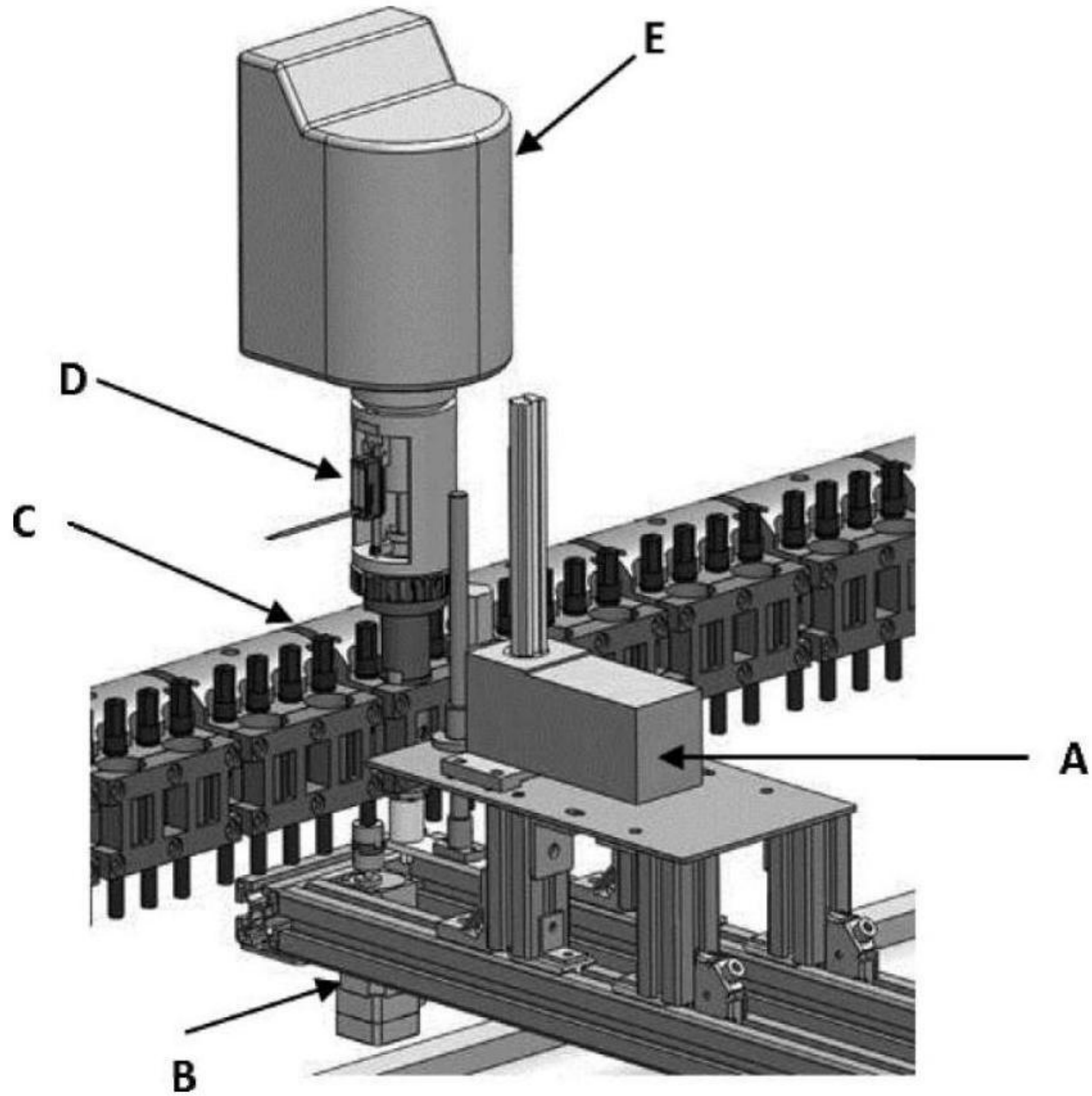


Fig. 1. On-line oscillatory rheometer

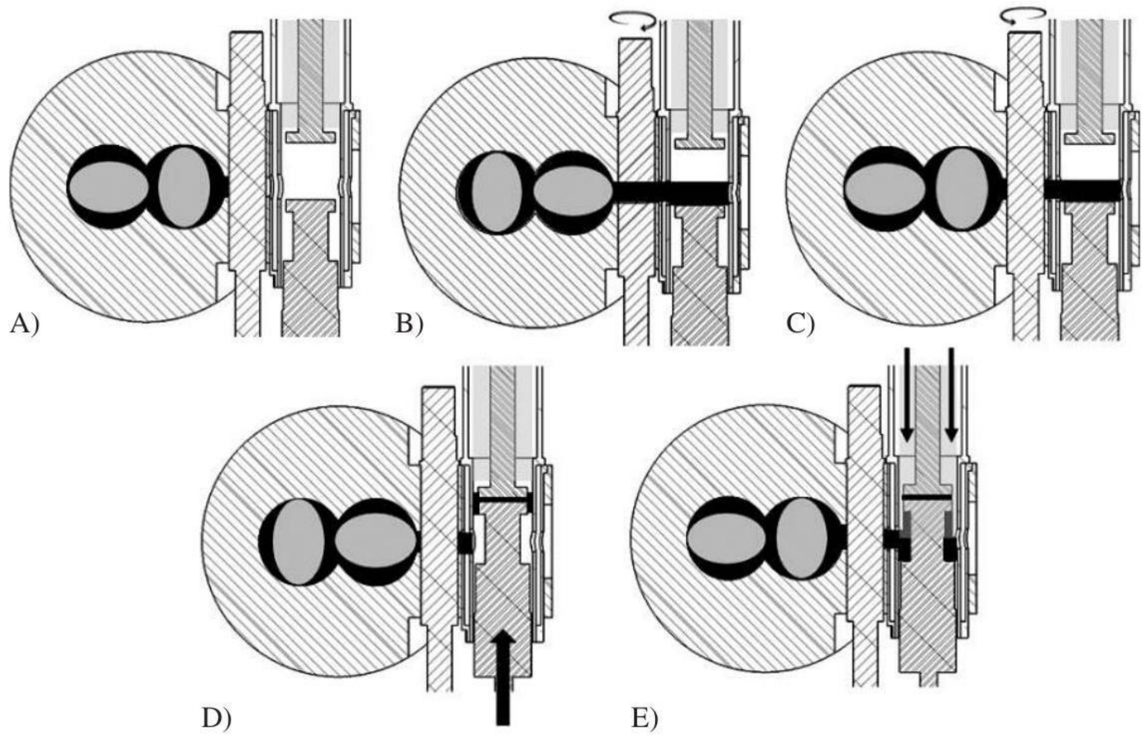


Fig. 2. Operation sequence of the on-line oscillatory rheometer (adapted from Covas et al., 2011)

nance, cleaning and/or calibration of the on-line device. When the rotating valve opens (Fig. 2B), the melt is diverted from the extruder and flows towards the testing chamber, due to the pressure difference between the two regions. The shear rates developing during sample collection are negligible, preventing any significant changes on morphology or chemical conversion. After collecting enough melt from the extruder barrel, the rotating valve closes (Fig. 2C). The sample is then squeezed between the two plates, as the lower one rises vertically to the pre-defined gap (Fig. 2D). The excess material around the edge of the plates is wiped out by a cleaning ring sliding downwards (Fig. 2E). The rheological test starts when the temperature of the sample reaches thermal equilibrium at the set temperature of the experiment. Once the rheological measurement is concluded the cleaning ring and the lower plate return to their initial positions and the measuring system can be removed for cleaning.

Materials and Experimental Data

This section contains a description of the materials, processing conditions and rheological tests performed.

Materials

The materials used in this study are listed in Table 1, together with their main characteristics. They include commercial polypropylene (PP), polypropylene grafted with maleic anhydride (PP-g-MA), polymide-6 (PA6) and nanoclays (Cloisite 20A, Dellite 43B and Dellite 67G). The compositions produced are given in Table 2. For each polymer matrix, the amount and type of nanoclay was varied. When comparing nanoclay types, the amount of the latter was changed to keep the same inorganic content.

Processing Conditions

All nanocomposites were manufactured in a Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder. Fig. 3 shows schematically the screw profile, the barrel configuration, as well as the locations where on-line measurements were performed. For all PP and PA6 compositions, a flat barrel and die set temperature profile was adopted, at 200°C and 240°C, respectively. The throughput was fixed at 3 kg/h via a gravimetric feeder, the screw speed(s) being identified in Table 2.

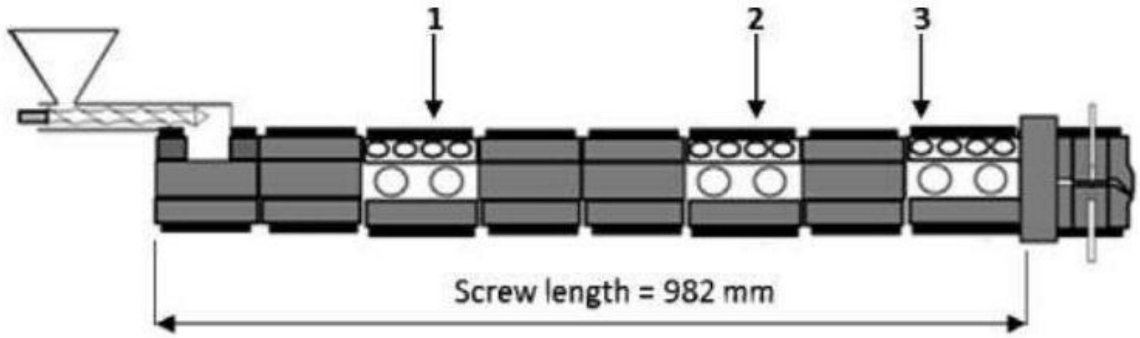
Designation	Material	Producer	Grade
PP	Polypropylene	Basell	HP500N
		Rhodia	Technyl C206
PP-g-MA	Modified Polypropylene with Maleic Anhydride		Polybond 3200
D67G	Montmorillonite	Laviosa	Dellite 67G
D43B	Montmorillonite	Laviosa	Dellite 43B
C20A	Montmorillonite	Southern Clay Products	Cloisite 20A
C30B	Montmorillonite	Southern Clay Products	

Table 1. Materials and main characteristics

PP wt.%	PP-g-MA wt.%	PA6 wt.%	Nanoparticle type, wt.%	Screw-speed min^{-1}
95	5	-	-	100
86.2	5	-	D67G, 8.8	50, 100, 200
90.6	5	-	D67G, 4.4	100
77.4	5	-	D67G, 17.6	100
87.3	5	-	C20A, 7.7	100
-	-	100	-	100
-	-	91.7	D43B, 8.3	50, 100, 200
-	-	95.8	D43B, 4.2	100
-	-	83.4	D43B, 16.6	100

-	-	92.9	C30B, 7.1	100

Table 2. Compositions produced and corresponding set screw speed



30R2/60R/60R4/45R2/30R2/4KB+60%/5KB90%/4KB-60%/20R4/30R/5KB90%/45R/30R/30R4/30R2/20R4L/20R2/1KB
Fig. 3. Extruder lay-out and screw configuration

On-line Rheological Measurements

For each sample, frequency sweeps from 100 to $0.1 \mathrm{rad/s}$ were performed under a constant strain of 1%, at $200^{\circ}\mathrm{C}$ (PP matrix) or $240^{\circ}\mathrm{C}$ (PA-6 matrix), using parallel-plate geometry. The gap and diameter of the plates were 1 mm and 2.0 cm , respectively.

X-ray diffraction (XRD) - The diffraction patterns were obtained using a Bruker diffractometer (AXS Nanostar-D8 Discover) equipped with a $\mathrm{CuK}\alpha$ generator ($\lambda =$ 1.5404Å) at 40 kV and 40 mA , in a 2λ range from 0.08 to 10°. The organoclays were analyzed directly, whereas the nanocomposites were beforehand compression molded into disks with a diameter of 20 mm and a thickness of 4 mm .

Monitoring the Production of Polymer Nanocomposites

The effect of material and process parameters (composition and screw-speed) on the linear viscoelastic response will be discussed first, all the rheological measurements having been performed at sampling location 3 (see Fig. 3). Then, the evolution of the rheological behaviour along the extruder axis of some compositions will be reported.

Effect of Composition

Fig. 4 and 5 illustrate the effects of the addition of filler to PP and percentage, respectively. As expected, these results show that nanocomposite melts exhibit an anomalous rheological response. PP+5 % PP-g-MA behaves as a typical polymer melt, with a loss modulus (G'') larger than the storage modulus (G') throughout the frequency range analysed and slopes of ap-

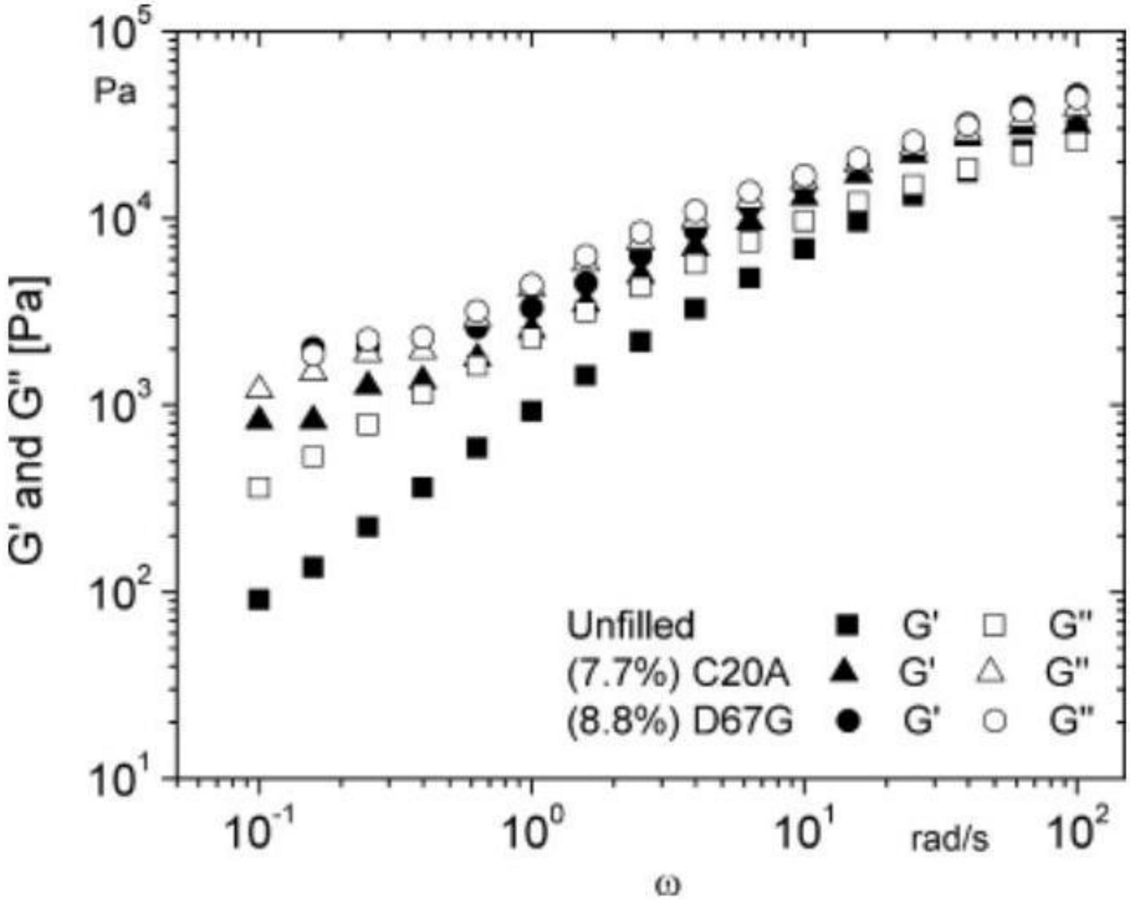


Fig. 4. Effect of the addition and type of nanofiller for PP +5% PP-gMA compositions

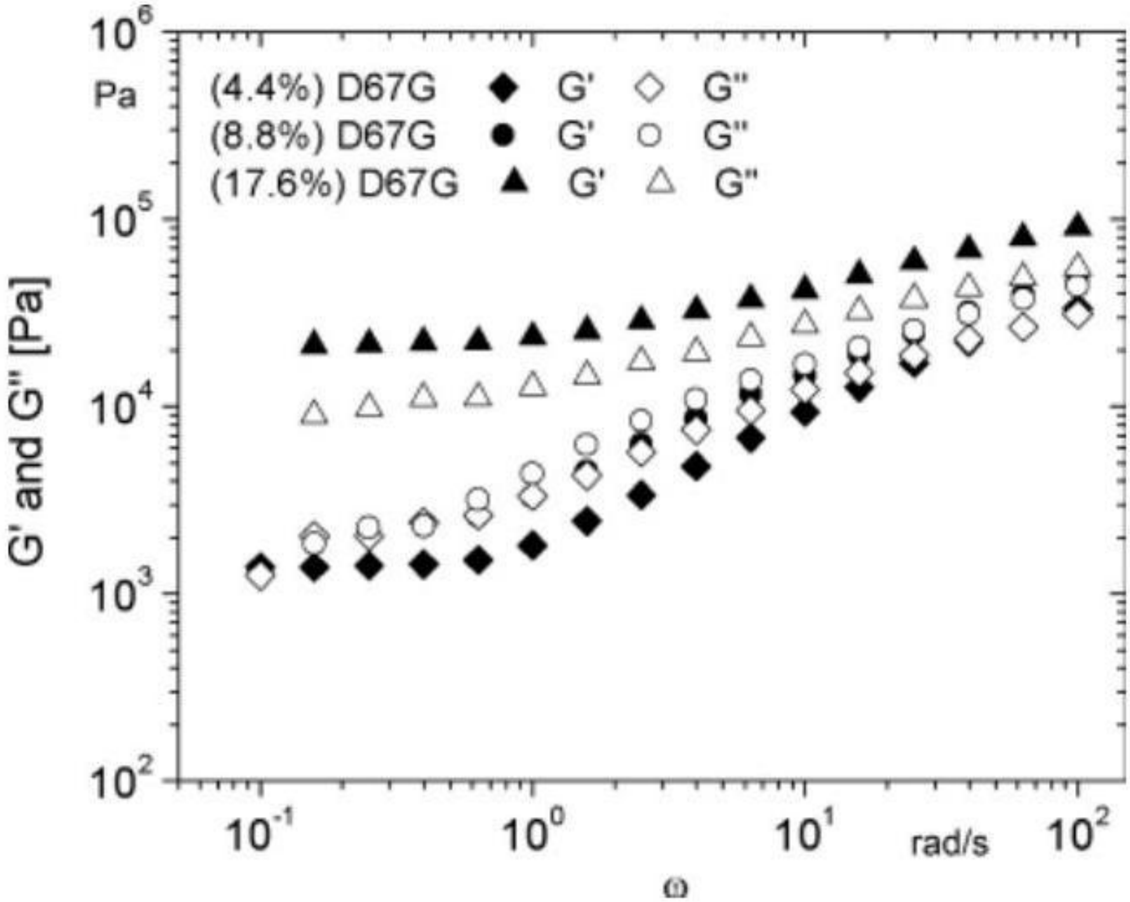


Fig. 5. Effect of the amount of nanofiller (Dellite) for PP+5 %PP-gMA compositions proximately 1 and 2, respectively, in the terminal region. The addition of nanoclay (C20A or D67G) brings about an increase of G′ particularly at low frequencies, or the development of a nonterminal plateau solid-like behavior, which is often reported and associated with the existence of a network microstructure containing solid particles (see, for example, (Solomon et al., 2001) and (Cassagnau, 2008). This increase is more noticeable for D67G. As expected, both G' and G'' increase as the amount of the nanoclay increases (Fig. 5). At the high frequency range, G′ approaches the value of the matrix, which may be interpreted as indication that segmental motion of the polymer matrix determines the material response at short time scales (Lee et al, 2006).

The level of dispersion of the nanoclays in the polymer matrix was assessed by XRD. As shown in Figs. 6 and 7, which also display the XRD pattern of the fillers, the peaks corresponding to the lamellar structure of the nanoclays are still present in the nanocomposites, evidencing that the growth in elasticity was mainly obtained by melt intercalation. The lower intensity of the peak for the compositions with 4.4% of Dellite (Fig. 7) is due to the lower amount of nanoclay. Therefore, these results confirm the well-known difficulty of dispersing organoclays in a PP matrix, even with the addition of a compatibilizer (Lertwimolnun and Vergnes, 2006; Lertwimolnun and Vergnes, 2007). XRD and rheological data are not always coherent. The dynamic data in Fig. 5 for 4.4% and 17.6% DG7G show solid-like behaviour at low frequencies, unlike the 8.8 % composite. XRD data in Fig. 7 indicates identical dispersion in all cases. In fact, XRD and rheology not only probe materials at different length scales, but also analyse quite different volumes of sample.

Upon incorporating organoclays in PA6, similar rheological effects were observed, as seen in Figs. 8 and 9 for the type and amount of filler, respectively. As before, Dellite induces a higher raise of the moduli, especially in the low frequency

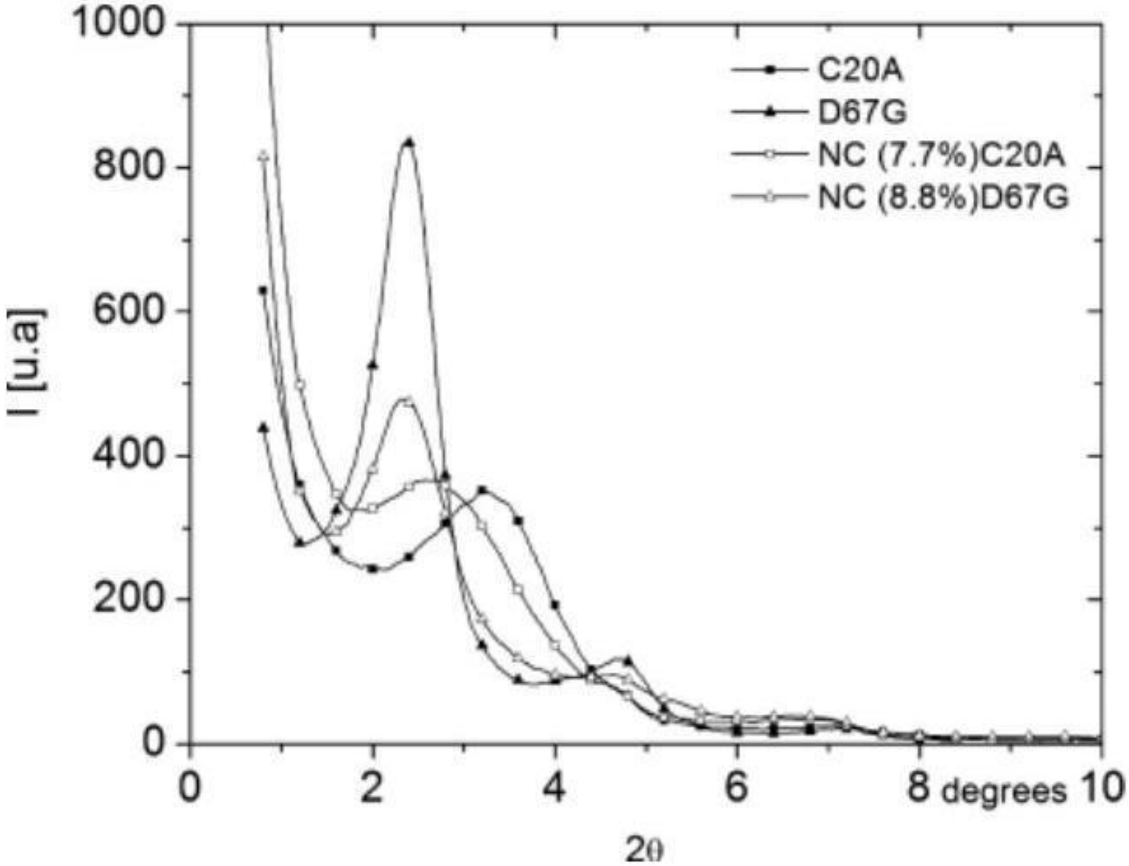


Fig. 6. XRD of C20A, D67G, PP +5% PP-g-MA+7.7%C20A and $PP + 5\% PP - g - MA + 8.8\% D67G$

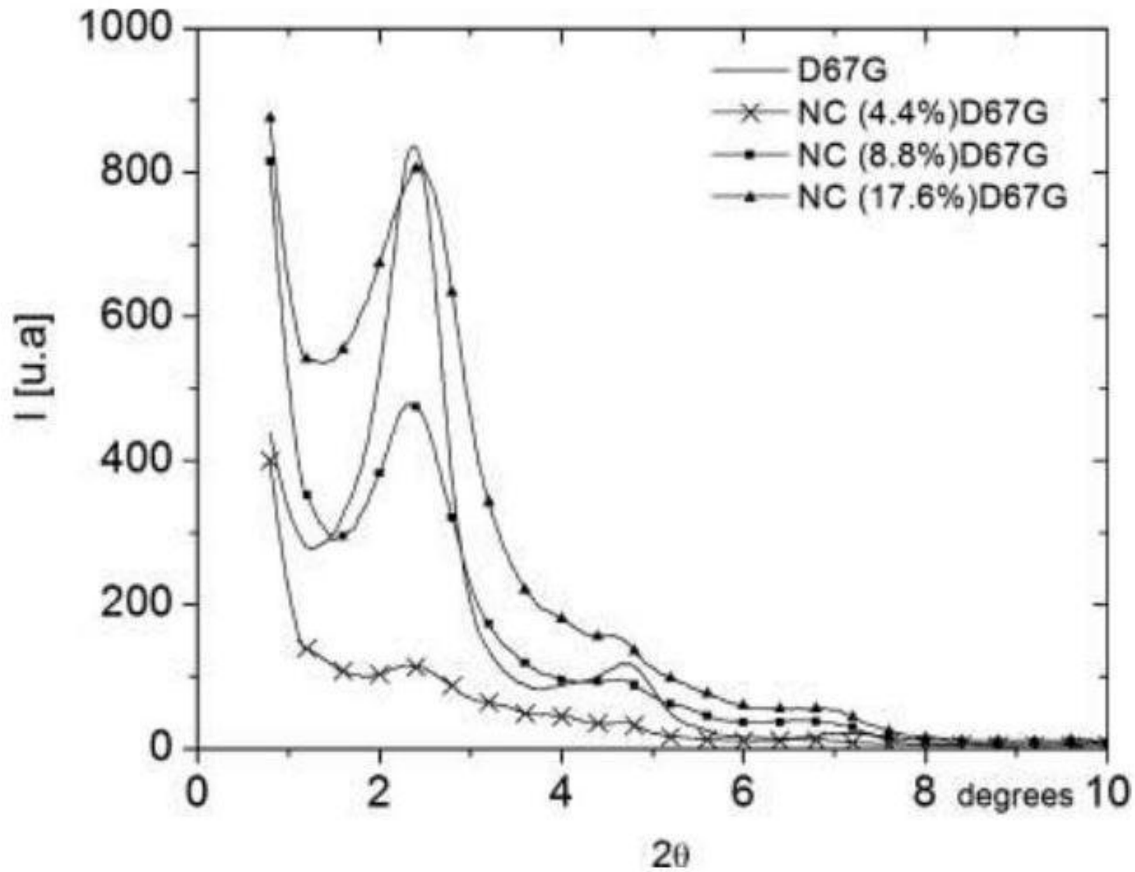


Fig. 7. XRD of PP+5 %PP-g-MA with different amounts of D67G

range. Also, as the percentage of filler progressively increases, G′ increases from values lower than G′′ (at 4.1%), to values of the same order of magnitude (at 8.3%), and to G′ > G′′ and a quasi-solid behaviour at 16.6%. A comparison of Figs. 5 and 9 cannot be done, as the nanocomposites contain different grades of organoclay, due to the different polarity of the matrices. Nevertheless, it is still interesting to observe that similar levels of filler added to PP (with compatibilizer) and PA6 induce different magnitudes of the moduli, with higher values being attained for the latter. The polarity of PA6 should facilitate reaching a finer dispersion. In the case of the composite with 8.3%D43 B, G′ becomes lower than G′′ at higher frequencies and higher than G′′ at lower frequencies (Fig. 8), which is unusual and is difficult to account for.

The XRD characterization of the C30B and D43B clays and their PA6 nanocomposites is made in Fig. 10. In the composites, the peak corresponding to the lamellar structure of D43B disappears, while the peak concerning C30B remains, but shifted to lower angles.

These results indicate a better dispersion of D43B than C30B, an exfoliated morphology being anticipated. This is in good agreement with the curves of Fig. 8, which show that the nanocomposite containing D 43 B has a higher G′ and a better defined plateau at low frequencies.

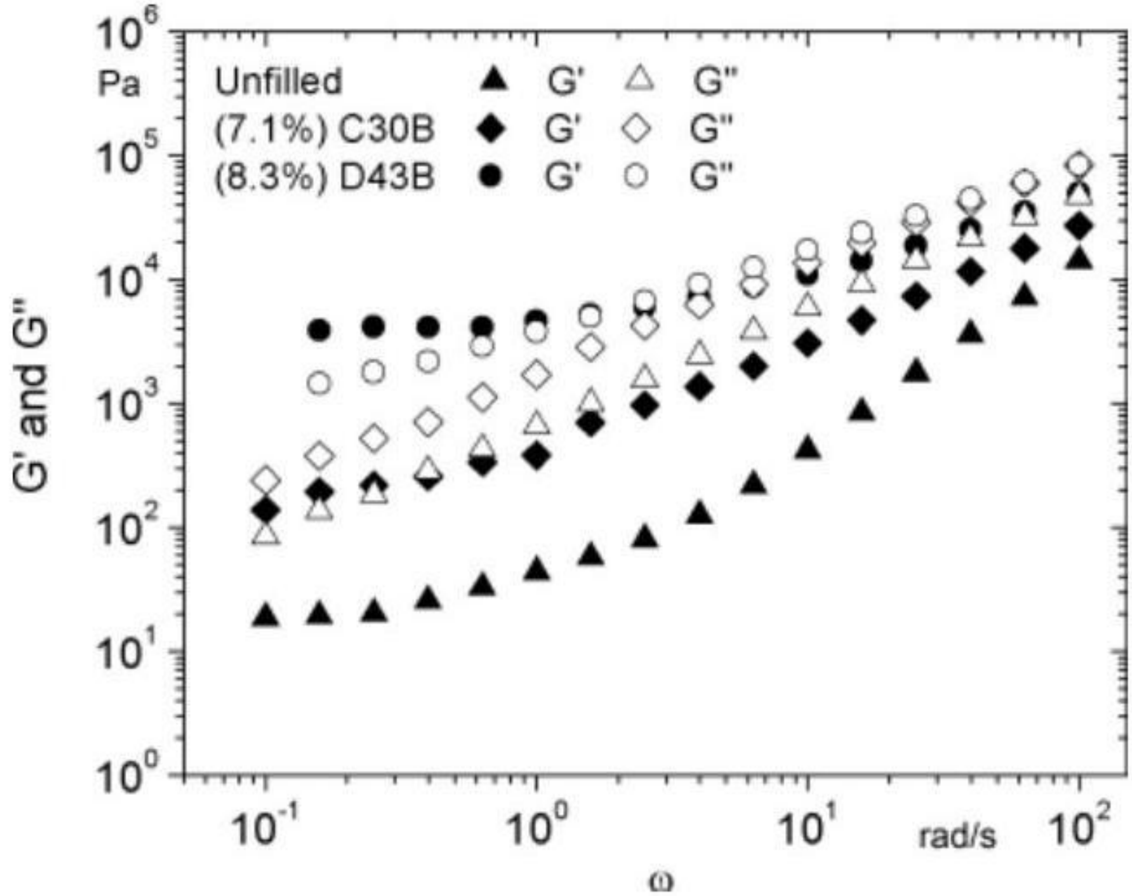


Fig. 8. Effect of the addition and type of nanofiller for PA6 compositions

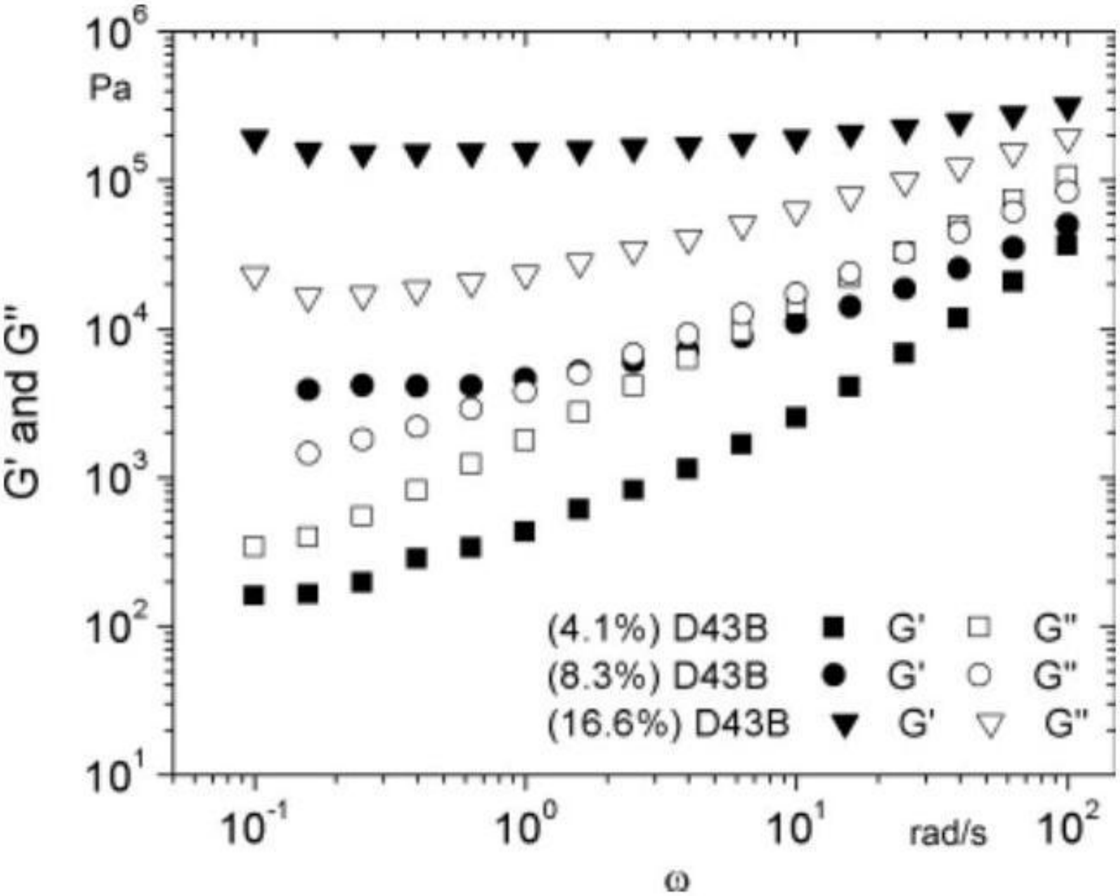


Fig. 9. Effect of the amount of nanofiller (Dellite) for PA6 compositions

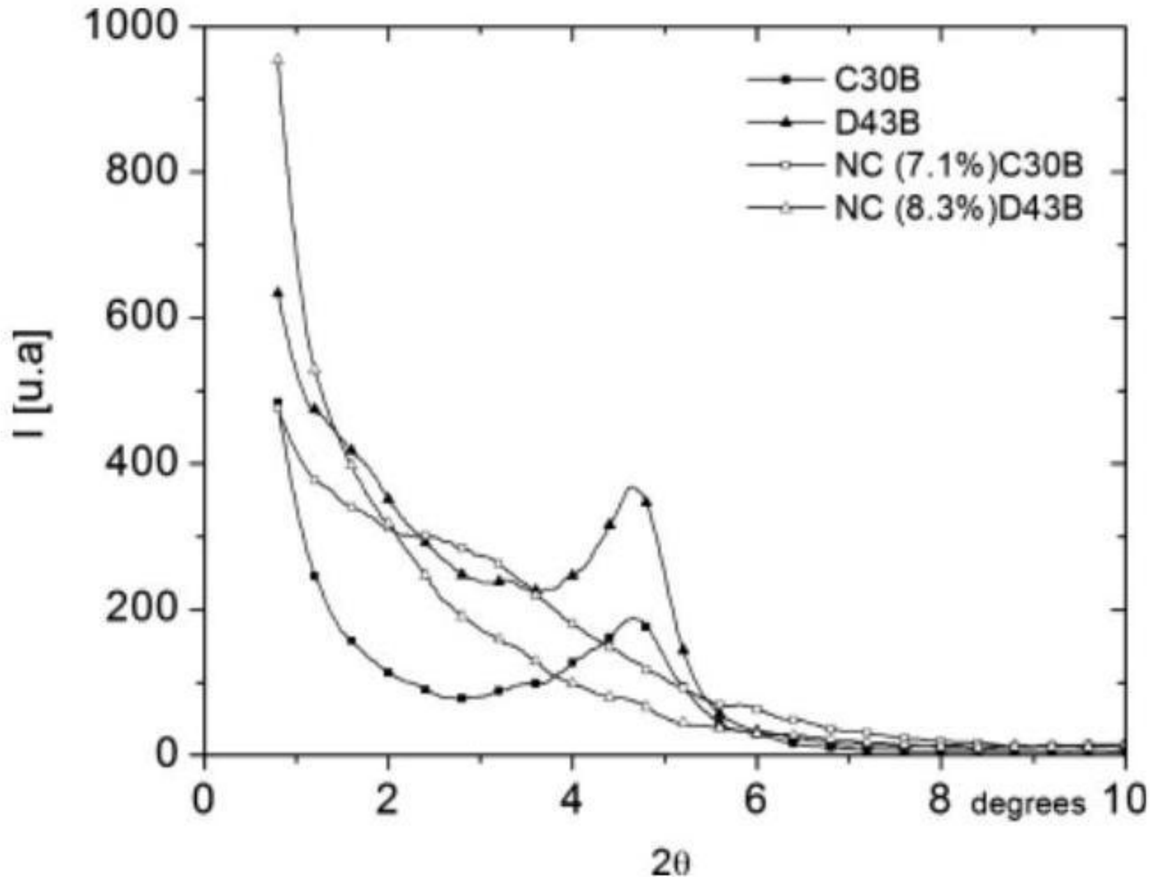


Fig. 10. XRD of C30B, D43B, PA6+5%+7.1%C30B and PA6+ 8.3 %D43B

Effect of Screw Speed

The effect of screw speed (at constant feed rate) on the rheological parameters of the PP and PA6 nanocomposites is illustrated in Figs. 11 and 12, respectively. No direct correlation seems to exist between G' and G'' and screw speed. Nevertheless, in both cases the highest dispersion (higher G') is achieved at the highest screw speed tested. For PP+PP-g-MA+Cloisite20A nanocomposites, Lertwimolnun and Vergnes (2006)

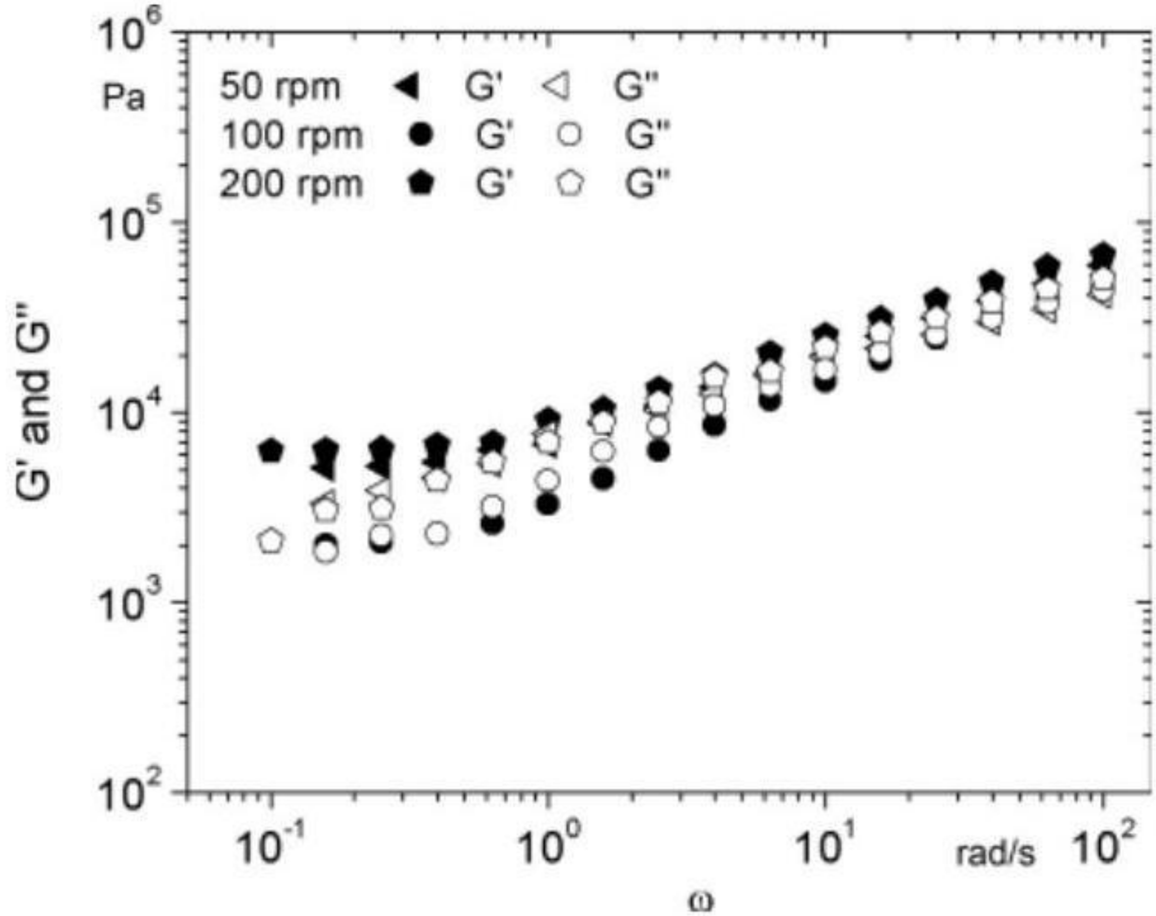


Fig. 11. Effect of screw speed on G' and G'' of PP +5% PP-gMA + 8.8 % D67G

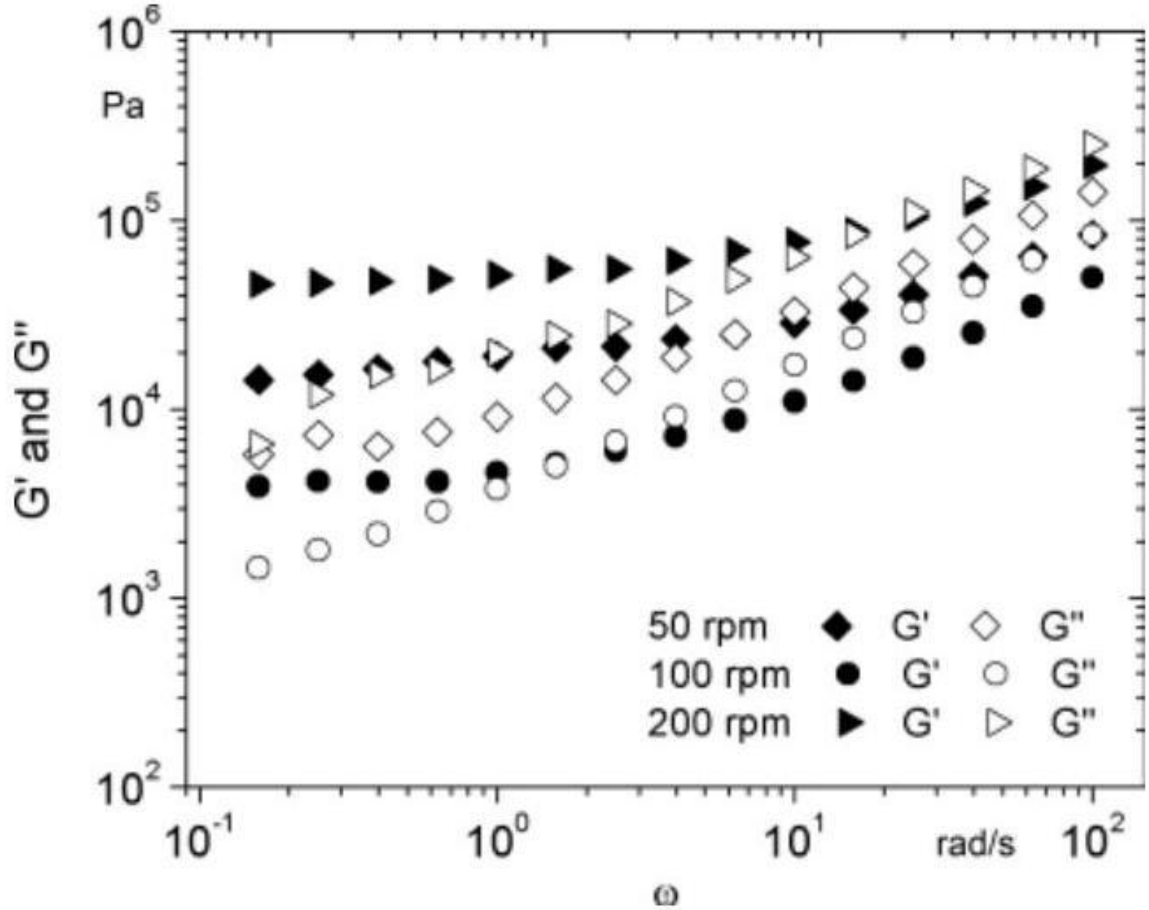


Fig. 12. Effect of screw speed on G' and G'' of PA6 +8.3% D43B

found out that the state of intercalation is globally unaffected by the processing parameters (independent variation of feed rate and screw speed), but the level of exfoliation grows when the feed rate decreases and the screw speed increases. In fact, dispersion should result from the creation of sufficiently high hydrodynamic stresses during enough time (Manas-Zloczower and Feke, 2009; Domingues, 2010).

Upon increasing the screw speed the shear intensity escalates, but the residence time for flow is reduced. The rheological properties of the components and the screw profile also play a role. Thus, monitoring the evolution of dispersion along the extruder axis could assist in better understanding the influence of processing conditions on dispersion.

Measurements along the Extruder Axis

The evolution of the moduli of the PP and D67G nanocomposite (relative to the unfilled polymer) is shown in Fig. 13 at 3 frequency values. As expected, G' and G'' increase along the extruder up to $L/D = 20$, as a consequence of increasing dispersion. Most probably the rise is not linear, most of the dispersion taking place upon melting (Lertwimolnun and Vergnes, 2006). Surprisingly, a decrease between locations 2 and 3 was measured, which cannot be attributed to matrix degradation as

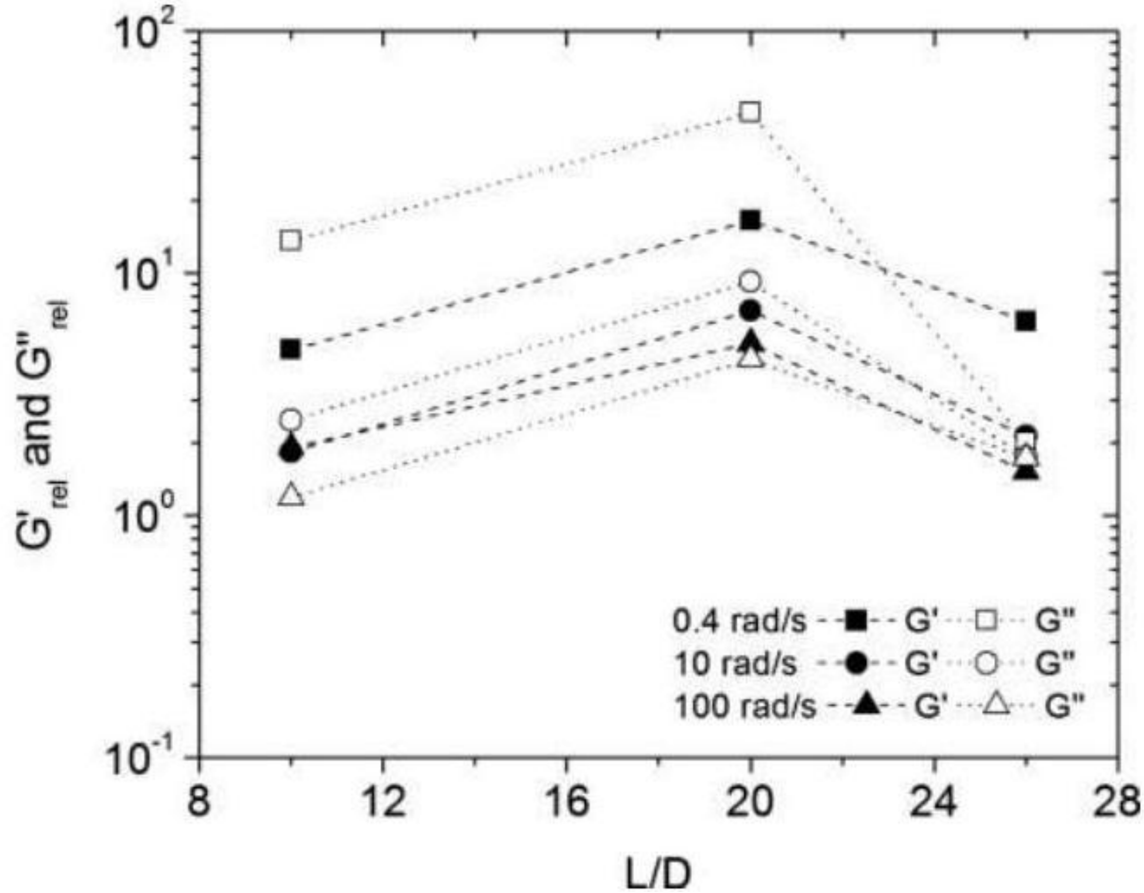


Fig. 13. Evolution of G' and G'' of PP+5%PP-g-MA+8.8%D67G along the screw axis

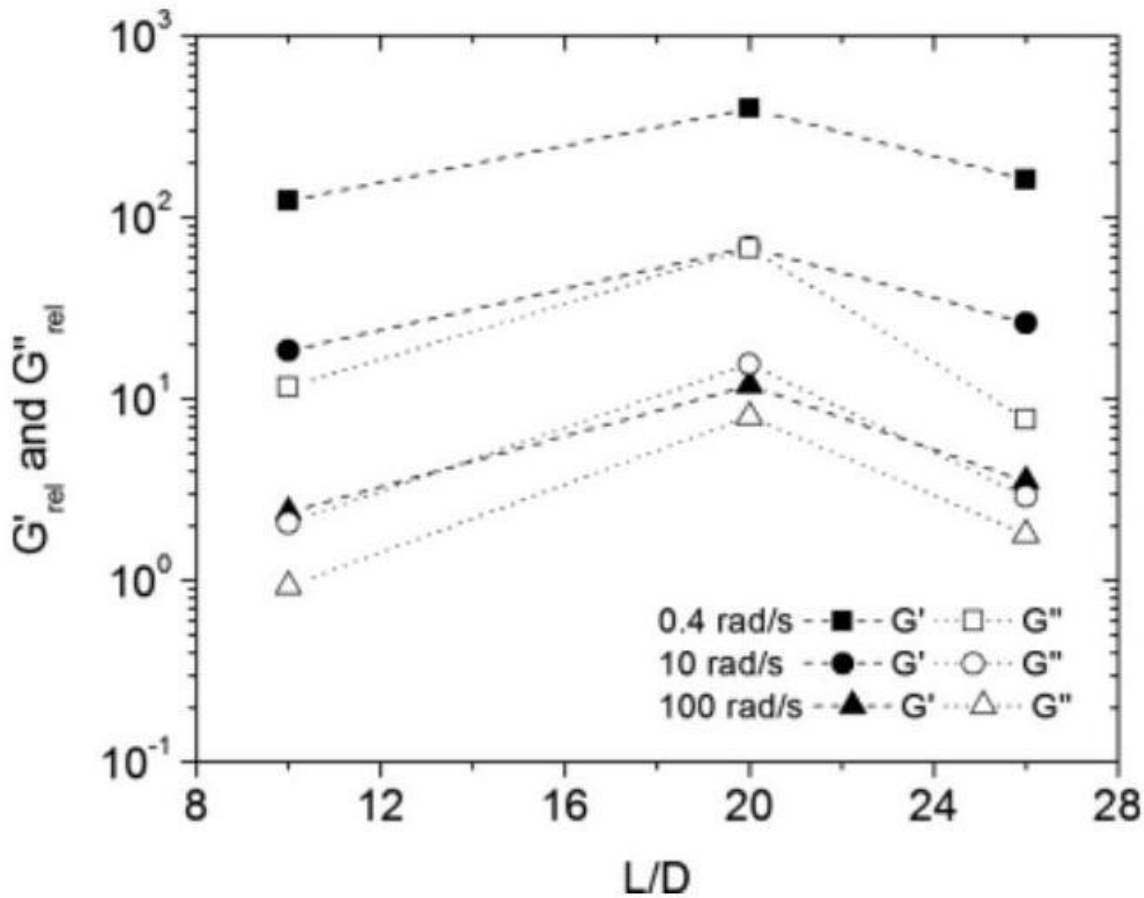


Fig. 14. Evolution of G' and G'' of PA6+8.3 % D43B along the screw axis shown in (Sacha et al., 2011). Similar results were reported by Lertwimolnun and Vergnes (2007), no explanation being offered.

The rheological measurements performed on an equivalent PA6 composition followed a similar trend (see Fig. 14). However, in this case the downstream deterioration of G' and G'' can be attributed to matrix degradation (Covas et al., 2011). Nonetheless, it is interesting to point out that before degradation sets in an increase of the storage modulus of circa 400 times was observed, i.e., extensive dispersion is achieved.

Conclusions

The prototype on-line oscillatory rheometer employed is sensitive to changes in morphology that result from variations in material, composition and processing conditions.

The addition of nanofillers promotes a significant increase of the linear viscoelastic moduli, particularly at low frequencies, that grows with dispersion and filler content. In general, the rheological data could be correlated with off-line XRD spectra.

Changes in screw speed induce a complex rheological material response, due to the interplay between hydrodynamic stresses, residence time and velocity fields, with the possibility of material degradation also playing a part. Measurements along small axial increments of the twin screw extruder would contribute to clarify this topic.

In general, the results demonstrate the practical utility of the new on-line device for research, quality control and optimization of the manufacture of polymer nanocomposites by melt compounding.

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