

On-line Rheometry: A Tool to Monitor Polymer Nanocomposites Production

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Abstract

The high potential of polymer nanocomposites has attracted the interest of both industrial and scientific communities. The final properties of these materials depend not only on the characteristics of the matrix and nanofillers, but also on the degree of dispersion of the nanofiller in the polymeric matrix. There are different methods to promote the dispersion of nanofillers in polymeric matrices, but the most promising is based on melt mixing, where the dispersion is achieved through the application shear and elongational stresses on a mixture of the polymer melt and nanofiller, usually performed on complex mixing devices. In order to improve the knowledge of the phenomena involved in the melt mixing process, several research groups are developing on/in-line adequate monitoring techniques, among these the online rheometry has shown to be a suitable choice. This work presents a new accessory conceived for a previously developed automated on-line rheometry system, which allows to couple easily the rheometer to any extruder. The developed system was subsequently used to study the effect of some process parameters related to the melt mixing process, which evidences the adequacy of these tools for monitoring purposes.

Keywords: On-line rheometry, Polymer nanocomposites, Melt mixing, Monitor production.

INTRODUCTION

Polymeric materials reinforced with nanofillers are receiving a tremendous attention by both the scientific and industrial communities, due to their extraordinary potential enhancement of properties [1], such as, mechanical performance, barrier resistance, optical clarity, flame retardancy, thermal stability, wear resistance, as well as electrical and magnetic properties [2]. The nanofillers can be one-dimensional (examples include

carbon nanotubes and nanofibers) [3], two-dimensional (e.g. layered silicates) [4], and three-dimensional (spherical nanofillers).

In general, polymer nanocomposites can be prepared in three different ways [5, 6]: in-situ polymerization, solution or by melt mixing. In-situ polymerization involves inserting a monomer into the nanofiller stacks and then expanding and dispersing the nanofillers into the matrix by polymerization. Similarly, solution methods involve the dispersion of nanofillers agglomerates in a polymer solution. Although these two methods are effective in obtaining well exfoliated nanocomposites, they are not suitable for industrial practice. Melt mixing seems to be the most promising way to produce nanocomposites with different degrees of nanofiller dispersion [7] at industrial scale. Melt mixing involves dispersing nanofillers stacks or agglomerates by means of shear/elongational stresses generated by the compounding equipment (usually a twin screw extruder), in the absence of solvents. Unfortunately, controlling the final dispersion levels, yielded by melt mixing, has proven to be much more difficult than anticipated [8]. Therefore, aiming to improve the knowledge related to nanofiller dispersion mechanisms, that take place during the melt mixing process, several research groups have been involved on the development of adequate on/in-line monitoring devices, that are based on rheometry [9-11], spectroscopy [12-14] or light scattering/transmission [15].

On-line oscillatory rheometry tools have been successfully applied to monitor phenomena that take place during the extrusion process, like in situ compatibilization of polymer blends (where a major - often complex - morphology evolution takes place within a short screw length) [16] and the peroxide-induced degradation of polyolefins (which is dictated by the degradation rate of the peroxide) [17]. Recently, a new automated version of these tools have been developed [11] that allowed to improve the its reliability and reduce its dependency on the skills of the user.

This work presents a recently developed accessory that allows to easily couple the previously developed automated on-line oscillatory rheometer [11, 18] to any extruder, both at laboratorial or industrial scales. Subsequently, their applicability to monitor the production process of polymer nanocomposites, by melt mixing, is illustrated, by the evaluation of their capability to discriminate the effect of some process parameters.

ON-LINE OSCILLATORY RHEOMETRY SYSTEM

The previously developed automated version of the on-line oscillatory rheometer [11] is illustrated in Figures 1 and 2, it comprises motion and measuring subsystems. The former is responsible for collecting the sample and positioning the system for the test, while the later (a commercial rheometer head supplied by Anton Par - DSR301) controls the test and collects the required data. Each subsystem is controlled by a specific control software; for the motion subsystem a in-house software was developed and the measuring subsystem uses a commercial control software (supplied by Anton Paar).

In the conventional system [11], taking the advantage of the modular construction of the modern extruders, the on-line rheometer had to be coupled to a special designed extruder barrel module, as illustrated in Figure 2. However, this approach restricts the possibility of performing the test on different extruders, since a special barrel segment was necessary

for every extruder model where the device was intended to be used.

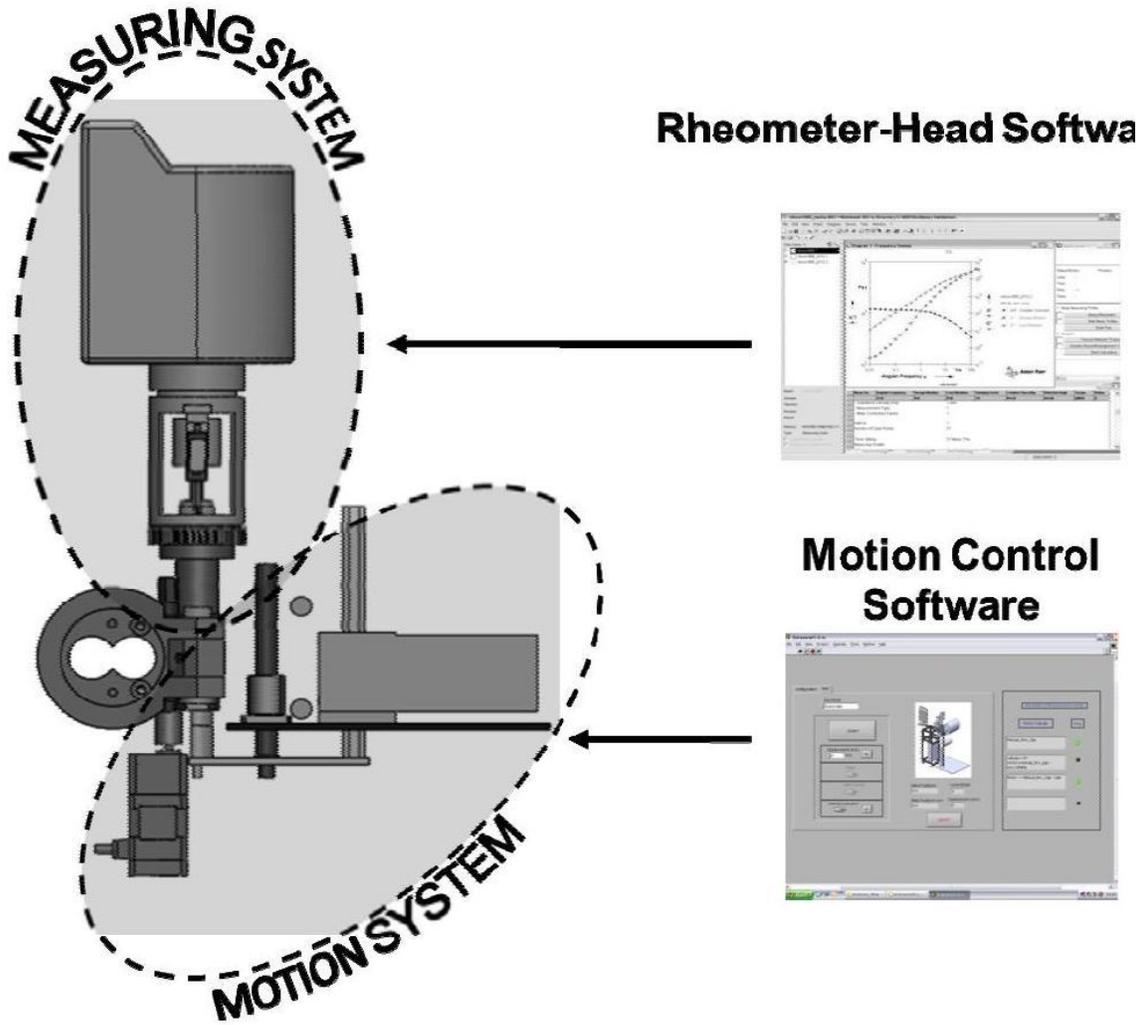


FIGURE 1. Automated on-line oscillatory rheometer: motion and measuring subsystems.

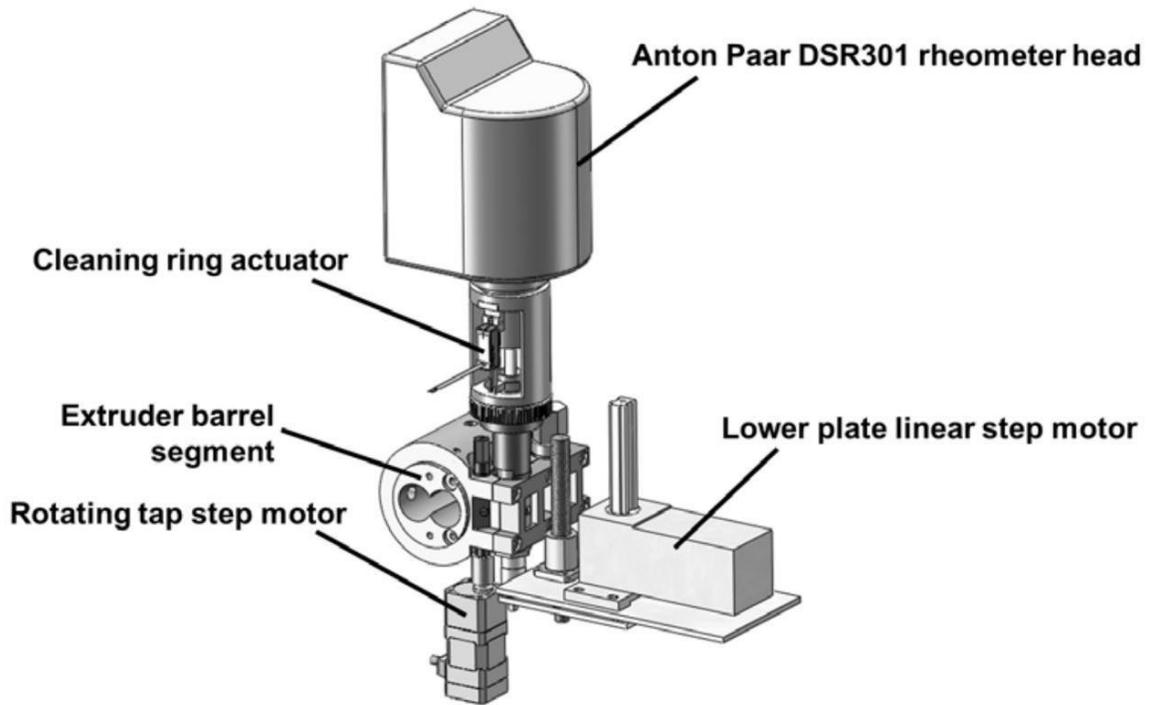


FIGURE 2. Components of the on-line oscillatory rheometer. In order to overcome these limitations, a new module that allows to connect the on-line rheometer to the extruder and to perform the test outside the extruder was manufactured, as illustrated in Figure 3. Using this part, the connection to the extruder can be accomplished by any available connection, e.g. a pressure transducer hole, or by manufacturing a simple adaptor.

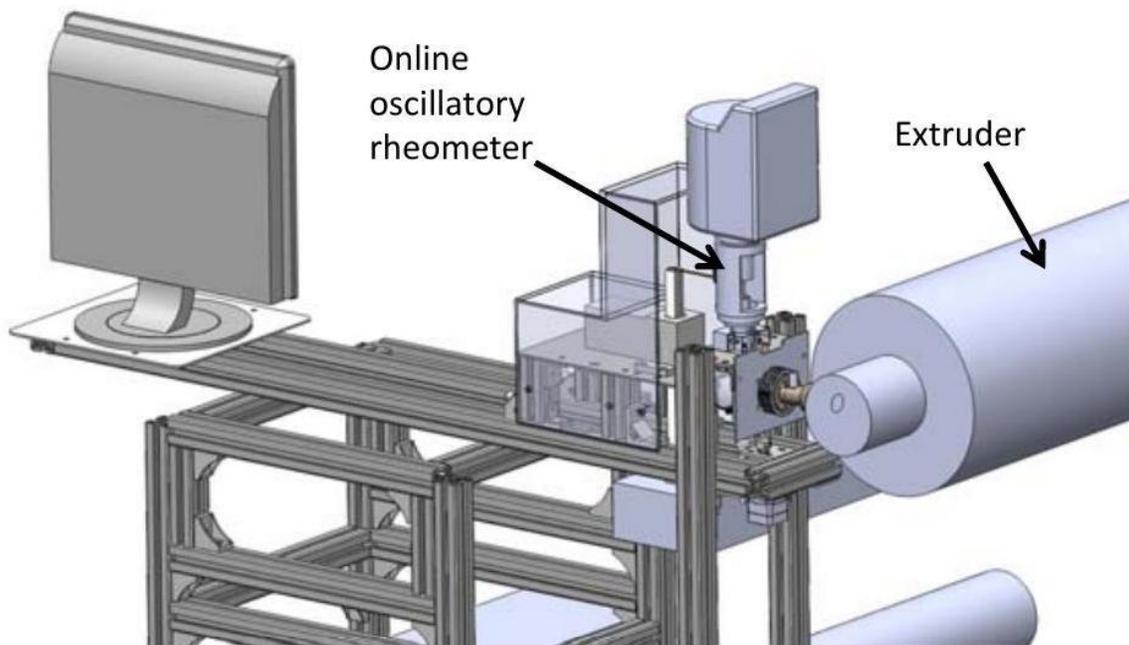


FIGURE 3. General overview of the on-line rheometry system. A detailed cross sectional view of the new module, coupled with the on-line oscillatory rheometer, is shown in Figure 4, where the main system flow channel is presented.

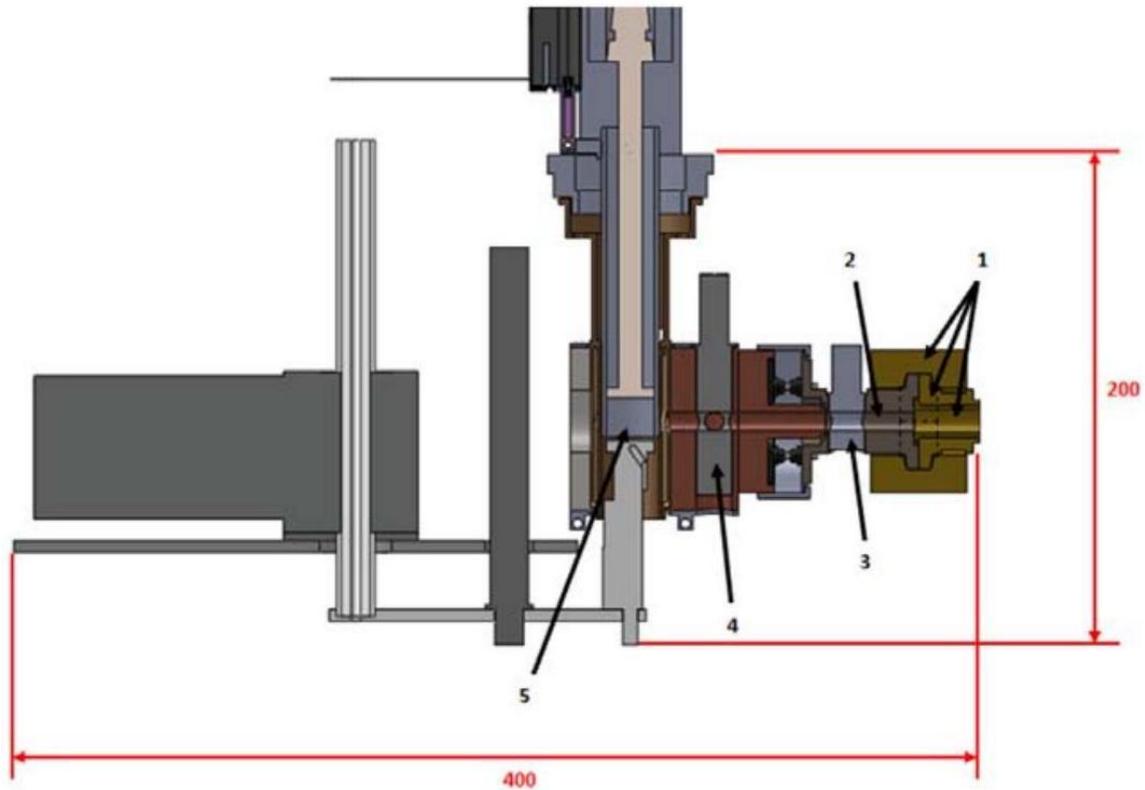


FIGURE 4. Cross section view of the designed module coupled with the on-line oscillatory rheometer (dimensions in mm).

The connection (1), which is linked to the extruder barrel, is capable to divert the melt from the main stream. The melt flows through a flow channel (2) towards the parallel plate rheometer chamber (5) depending on the position of the blocking valve (3). When the latter is opened the melt flows towards the rheometer, when closed the melt passage is not possible. There is still another valve, that we called it sample collection valve (4), which is position controlled and operates automatically. This valve is used for collecting a representative sample either for on-line rheometry test or for purging. The active part of the system, i.e. the on-line rheometer is the same of the conventional on-line rheometer.

MONITORING THE POLYMER NANOCOMPOSITES PRODUCTION

Validation and assessment of the on-line oscillatory rheometry system was presented in previous works [18]. Therefore, in the present study the system will be used to evaluate its sensitivity to some process parameters involved in polymer nanocomposites production by melt mixing. Hence, the results obtained will allow to evaluate the possibility of using this device for process monitoring purposes.

The materials and the formulations employed in the experimental work, are listed in Tables 1 and 2, respectively.

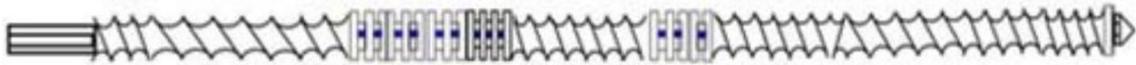
TABLE 1. Materials characteristics.

Material	Producer	Acronym	Grade	MFR/lamellar distance
Polypropylene	LyondellBasell	PP	Moplen HP500N	12 g /10 min(230°C /2.16 kg)
Polypropylene-grafted-Maleic anhydride	Crompton	PP-g-MA	Polybond 3200	115 g /10min(190°C /2.16 kg)
Polyamide	Rhodia	PA6	Technyl C206	--
Montmorillonite clay	Laviosa	D67G	Dellite 67G	$d_{001} = 3.45$ nm
Montmorillonite clay	Laviosa	D43G	Dellite 43G	$d_{001} = 1.86$ nm
Cloisite clay	Southern clay	C20A	Cloisite 20A	$d_{001} = 2.42$ nm
Cloisite clay	Southern clay	C30B	Cloisite 30A	$d_{001} = 1.85$ nm

TABLE 2. Formulations tested.		
POLYMER	COMPOSITION	W/W (%)
PP	PP	100
	<i>PP + PP - g - MA</i>	85/5
	<i>PP + PP - g - MA + D67G</i>	86.2/5/8.8
		90.6/5/4.4
		77.4/5/17.8
<i>PP + PP - g - MA + C20A</i>	87.3/5/7.7	
PA 6	PA 6	100
	PA + D43 B	91.7/8.3
		95.85/4.15
		83.4/16.6

	PA + C30B	92.3/7.7
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The nanocomposites were prepared in a Leistritz LSM 30.34 laboratorial modular intermeshing co-rotating twin screw extruder, using the formulations shown in Table 2, a set temperature of 200 °C, a throughput of 2 kg·h⁻¹, a screw speed of 200 rpm . The screw configuration is illustrated in Figure 5. The rheometry system was attached to the extruder at the extrusion die, using the new developed module, as shown in Figure 6.



**R2/60R/60R4/45R2/4KB+60%/5KB90
%/4KB-
60%/20R4/30R/5KB90%/30R/20R4L/
45R/30R4/30R2/20R2/1KB**

FIGURE 5. Extrusion screw configuration employed for the experimental work.



(a)



(b)

FIGURE 6. On-line rheometry system used for the experimental work: (a) general overview, (b) detailed overview of the connection with the extrusion die.

The results obtained during the experimental work are plotted in Figures 7 to 10. As shown, both materials present the same trend, the addition of nanofillers promotes an increase of the storage modulus (G'), with a more pronounced effect in the low frequencies region. Additionally, with the addition of nanofillers, G' seems to level-off at low frequencies, a typical behavior reported in the literature that is usually attributed to

the deformation and recovery of the dispersed filler [6, 19-21].

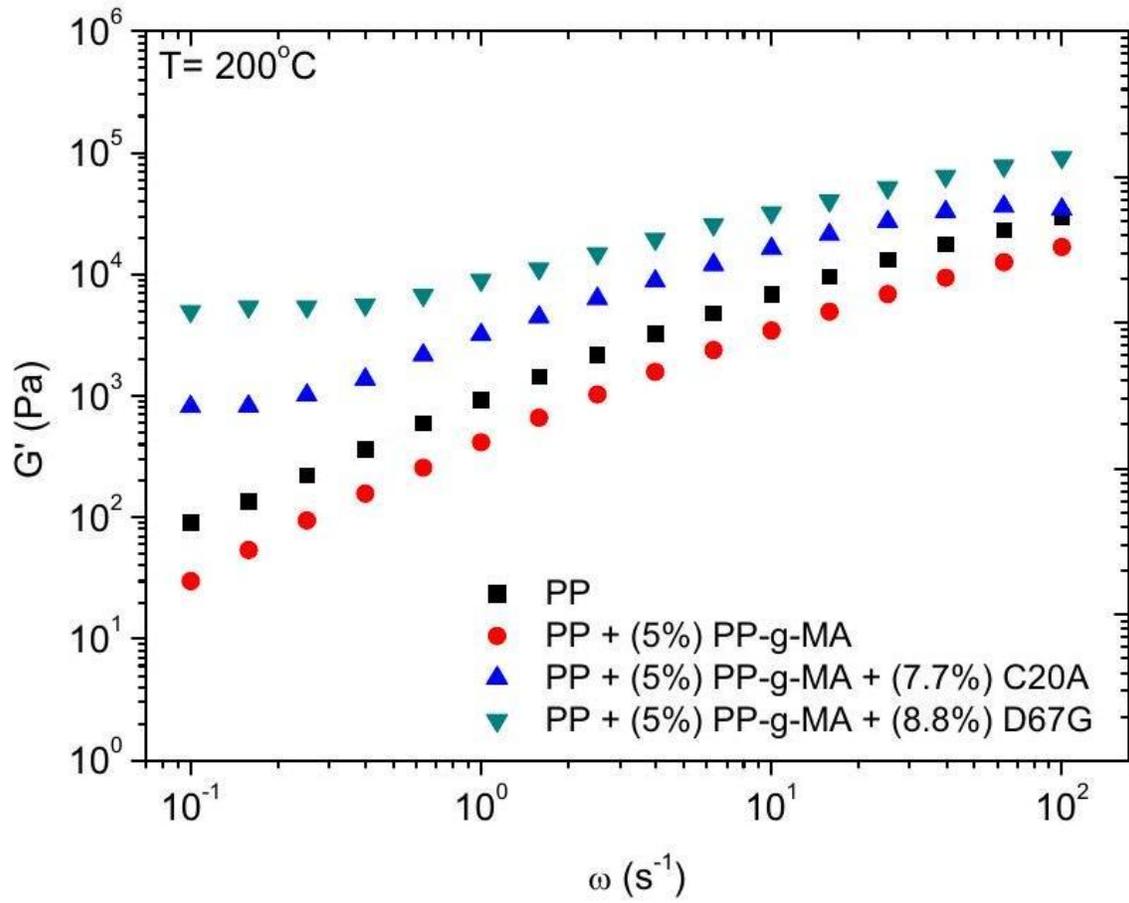


FIGURE 7. Linear viscoelastic behavior of PP formulations as measured on-line, the effect of nanofiller type.

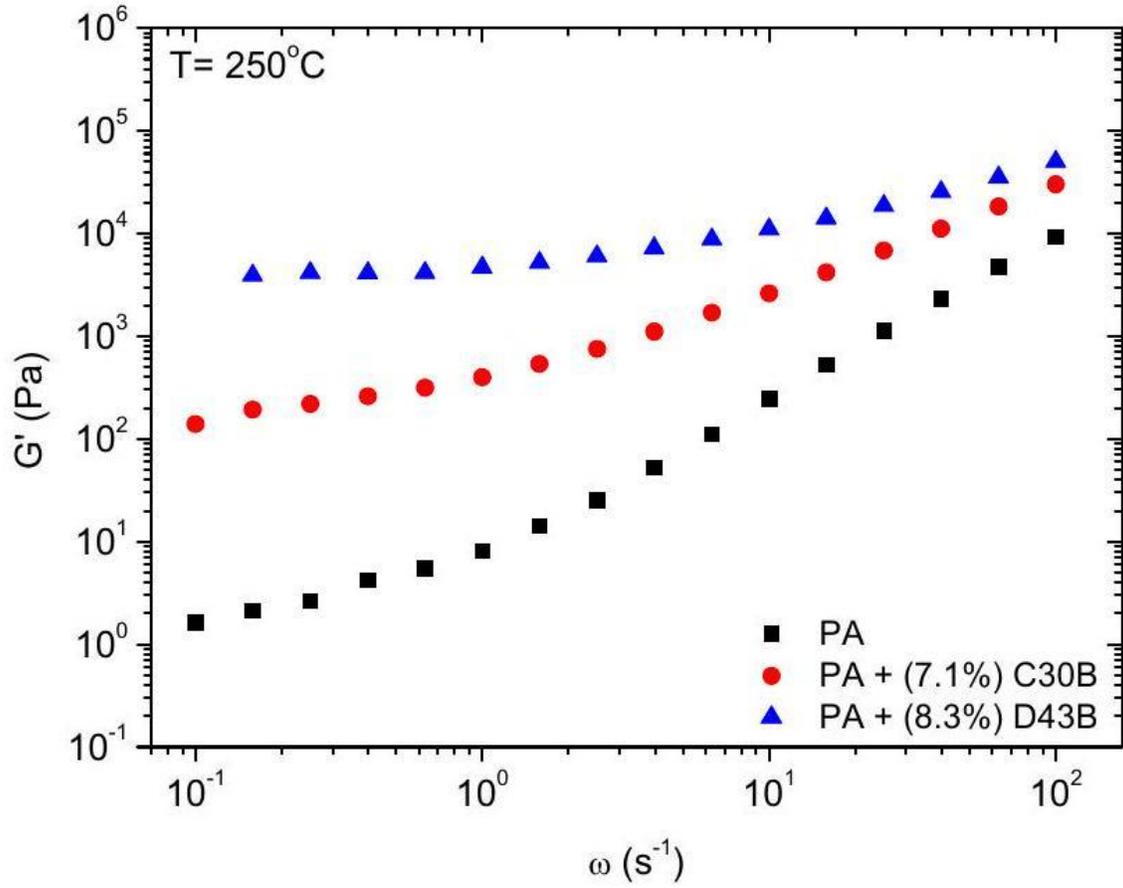


FIGURE 8. Linear viscoelastic behavior of PA formulations as measured on-line, the effect of nanofiller type.

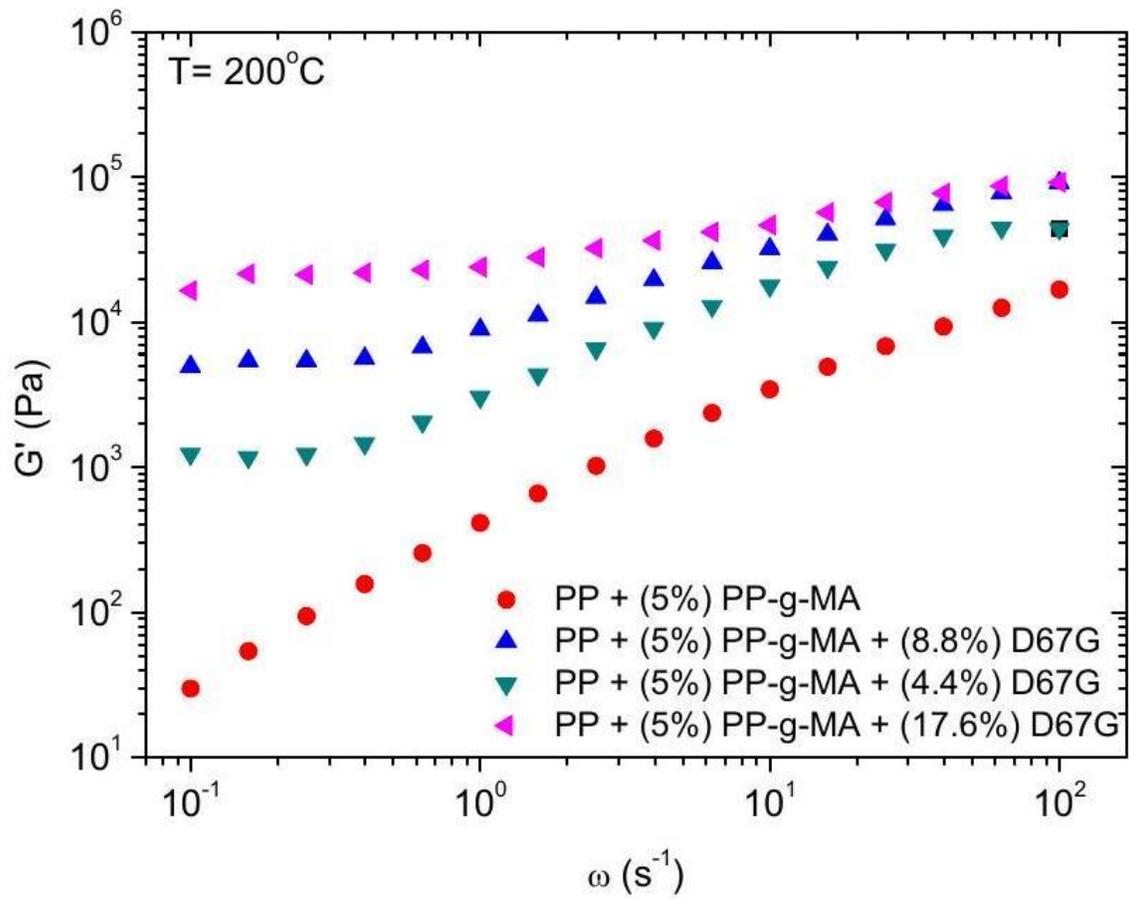


FIGURE 9. Linear viscoelastic behavior of PP formulations as measured on-line, the effect nanofiller content.

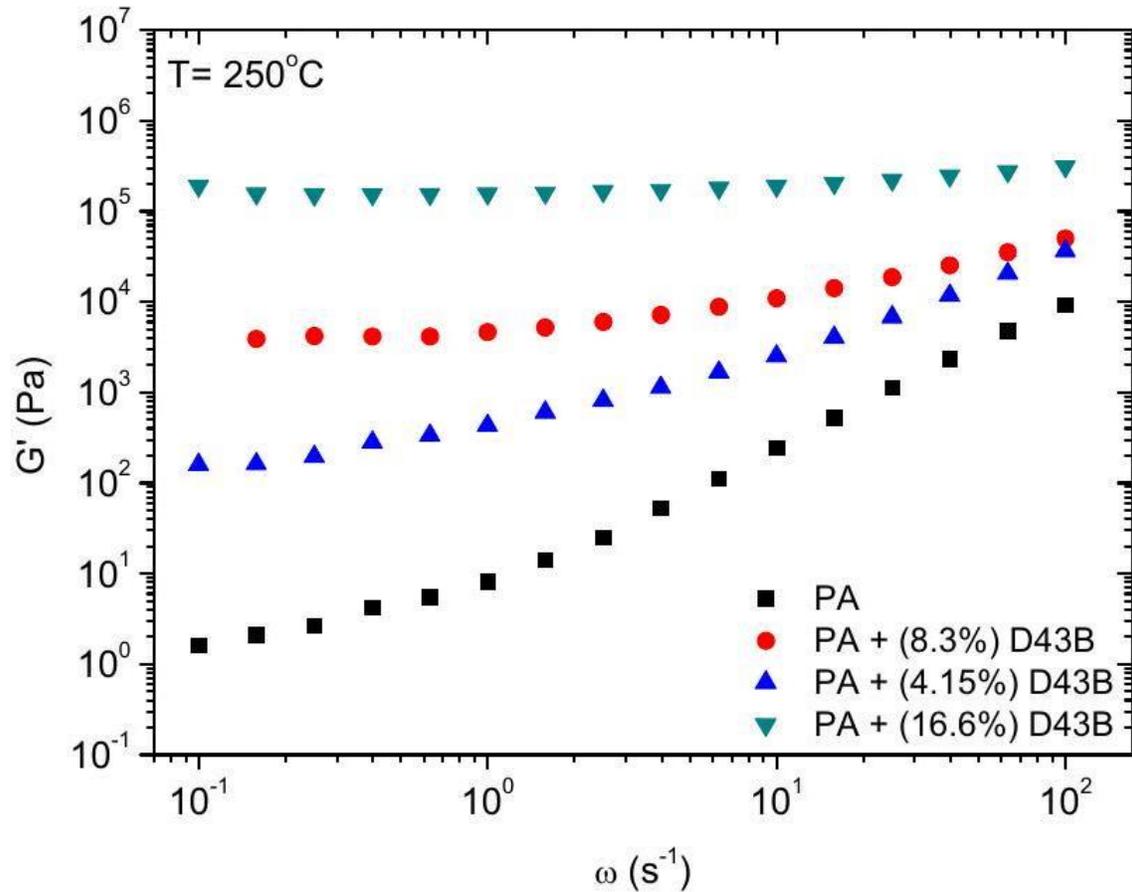


FIGURE 10. Linear viscoelastic behavior of PA formulations as measured on-line, the effect nanofiller content.

From the results plotted in Figures 7 and 10, it can be concluded that the material rheology is also sensitive to the type and amount of nanofiller employed.

In order to further assess the on-line rheometry system sensitivity, for the PA based formulations, the nanocomposites were produced using different screw speeds. The results plotted in Figure 11 show that the final rheological behavior, which is related to the morphology obtained, depends on two major factors residence time and level of induced shear. Consequently, a similar rheological behavior was obtained for the smallest and the highest screw speeds employed, since those conditions promote, an increase of the residence time or induced shear rate, respectively.

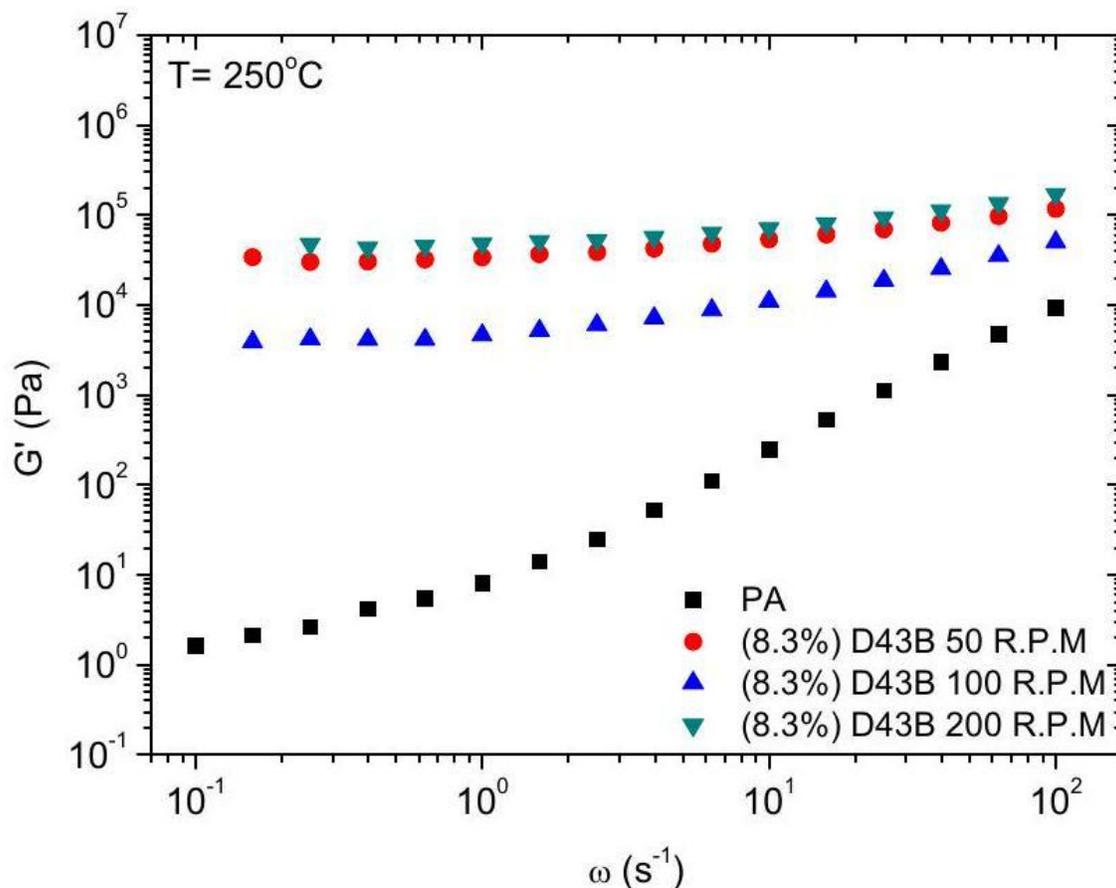


FIGURE 11. Linear viscoelastic behavior of PA formulations as measured on-line, the effect of the screw speed.

CONCLUSIONS

This work presents a new accessory that allows to easily couple a previously developed automated on-line oscillatory rheometry device to any extruder. The new system was employed to monitor the evolution of rheological behavior of polymer nanocomposites produced by melt mixing. The results obtained allow to conclude that the nanocomposites viscoelastic behavior is sensitive to the tested process parameters, and thus the developed system can be used to monitor the production process of polymer nanocomposites by melt mixing.

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REFERENCES

1. J. H. Koo, *Polymer Nanocomposite*, McGraw-Hill Professional, 2010, pp. 272.
2. S. C. Tjong, *Materials Science and Engineering: R: Reports* 53, 73-197 (2006).
3. S. G. Advani, *Processing and Properties of Nanocomposites*, World Scientific Publishing Company, 2006, pp. 162-168.
4. S. C. Tjong, "Synthesis and Structure-Property Characteristics of Clay-Polymer Nanocomposites" in *Nanocrystalline Materials*, Oxford: Elsevier Science Ltd., 2006, pp. 311-348.
5. M. Alexandre and P. Dubois, *Materials Science and Engineering: R: Reports* 28, 1-63 (2000).
6. S. Sinha Ray and M. Okamoto, *Progress in Polymer Science* 28, 1539-1641 (2003).
7. R. A. Vaia and E. P. Giannelis, *Polymer* 42(3), 1281-1285 (2001).
8. W. Lertwimolnun and B. Vergnes, *Polymer Engineering Science* 46, 314-323 (2006).
9. J. A. Covas, J. M. Nóbrega and J. M. Maia, *Polymer Testing* 19, 165-176 (2000).
10. J. A. Covas, J. M. Maia, A. V. Machado and P. Costa, *Journal of Non-Newtonian Fluid Mechanics* 148, 88-96 (2008).
11. S. T. Mould, J. M. Barbas, J. M. Nóbrega, A. V. Machado and J. A. Covas, *AIP Conference Proceedings* 1152, 175-182 (2009).
12. I. Alig, D. Fischer, D. Lellinger and B. Steinhoff, *Macromolecular Symposia* 230, 51-58 (2005).
13. D. Fischer, D. Pospiech, U. Scheler, R. Navarro, M. Messori and P. Fabbri, *Macromolecular Symposia* 265, 134-143 (2008).
14. J. Müller, S. Kummer and D. Fischer, *Measurement Science and Technology* 20, (2009).
15. L. Jourdainne, R. Matadi Boumbimba, B. Triki, M. Bouquey, R. Muller, P. Hébraud and P. Pfeiffer, *International Journal of Material Forming*, 1-9 (2010).
16. J. A. Covas, O. S. Carneiro, J. M. Maia, S. A. Filipe and A. V. Machado, *The Canadian Journal of Chemical Engineering* 80, 1065-1074 (2002).
17. A. V. Machado, J. M. Maia, S. V. Canevarolo and J. A. Covas, *Journal of Applied Polymer Science* 91, 2711-2720 (2004).
18. J. M. Nóbrega, S. T. Mould, J. M. Barbas, A. V. Machado and J. A. Covas, *Monitoring Nanoclay Dispersion in Polymer Matrix by On-Line Rotational Rheometry*, in 6th International ECNP Conference. 2010: Madrid, Spain.
19. M. J. Solomon, A. S. Almusallam, K. F. Seefeldt, A. Somwangthanoj and P. Varadan, *Macromolecules* 34, 1864-1872 (2001).
20. P. Cassagnau, *Polymer* 49, 2183-2196 (2008).
21. S. Sinha Ray and M. Bousmina, *Progress in Materials Science* 50, 962-1079 (2005).