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ORIGINAL ARTICLE

Improving the dispersion of multiwalled carbon nanotube in polypropylene using controlled extensional flow[a]

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Abstract

The use of controlled extension flows associated with processing with predominant shear flows can bring gains in the dispersive capacity of nanofillers during the processing of nanocomposites. In this work, we use a controlled flow device coupled to the matrix of a single-screw extruder to process PP matrix composites containing 0.5% and 2.5% (v/v) of MWCNT. The nanocomposites were evaluated by optical microscopy and oscillatory rheological analysis. The clusters size analysis showed that in PP/0.5MWCNT-el, 70.5% of all its clusters were below 1μm^2 while its analog processed without the extensional flow showed 59.8% of its clusters below this value. The rheological analysis allowed to verify that the compositions processed with the presence of the extensional flow have their crossover frequencies shifted to lower values, that is, longer relaxation times corroborating that improved degrees of dispersion were achieved.

Keywords: *processing, extensional flow, dispersion, nanocomposites.*

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1. Introduction

Several theoretical models elaborated show that there is a large difference between the measured values and the theoretical values of properties for composites containing multiwalled carbon nanotubes (MWCNT) nanofillers[1-3]. For the vast majority of these cases, these differences are mainly due to the poor dispersion level of the MWCNT in the polymer matrix and its tendency to agglomerate associated to the high surface area[3]. Due to the geometry of the carbon nanotubes that are long and twisted, they tend to entangle themselves making it even more difficult to break and redistribute the agglomerates inside polymer matrices[4]. Many different strategies have been studied to improve the dispersion level of the MWCNT and to reduce the difference between the theoretical values for the properties and those obtained, such as chemical functionalization[5], use of ultrasonic waves[6], polymer wrapping[7], shearing and extensional flows[8,9].

The use of controlled flows to increase the degree of particle dispersion is already a known method due to the possibility of allowing greater applications in terms of production scale[10-12]. It is known that the extensional flow is more efficient, when compared to the shear flow, with regard to the ability to break agglomerates and also in their redistribution throughout the polymer matrix[11]. Several studies have been carried out to evaluate the dispersive effect of the extensional flow by developing small-scale processing devices or using small mixers which are applicable to small scales of processing[11-17]. To nanofiller such as MWCNT[18-21] and graphene[8] in polypropylene (PP) matrixes was found that the dispersion of both fillers were highly improved due extensional forces. For example, in Son's[22] study, composites containing 0.5% w. of MWCNT in PP comparing the dispersion of the processing via twin screw extrusion and an extensional batch mixer (EBM), developed by the author's; their results shown an increase of up to 30% in the dispersion for processing with EBM, measured by the area of the agglomerates. A more recent approach in this field seeks to evaluate components to enhance the extensional flow in twin-extrusion processing, which provides gains in dispersive power in the production of immiscible blends[23,24], for example, the validation of this approach showed that in the processing of immiscible polypropylene/polystyrene blends it was possible to provide an increase in dispersion of up to 30% for processing with extensional mixing element (EME).

In general, shear flows are commonly applied in typical melt processing devices, such as extruders and mixers[14,21]. Increase the extensional flow component present in melt processing, adding to the shear component commonly present in extrusion, can significantly increase the erosion and the kinetics of breakup of agglomerates. For composites containing montmorillonite (MMT) and MWCNT in PVDF matrix, this approach has demonstrated its effectiveness in reducing the particle size of MWCNT agglomerates by up to 55%[25].

This study proposes to evaluate the effect of improving the dispersion of MWCNT particles in PP matrix, by associating a controlled extensional flow during extrusion processing. This approach is an innovative methodology to contribute to the improvement of fillers dispersion in the molten state processing of thermoplastic polymer matrix composites. In a previous work by this research group[25], we described in greater detail the device developed to be coupled to an extruder die.

2. Materials and Methods

2.1 Materials

Polypropylene (PP), H301, supplied by Braskem. The density and melt flow index (MFI) were 0.905 g/cm^3 and 10 g/10 min (at 230 ºC/2.16 kgf), respectively. PP was submitted to the micronization process in a mill (Micron Powder Systems, model CF Bantam) at 100 rpm with liquid nitrogen in order to obtain a micronized powder. After grinding the material was sieved (80 mesh). The micronization process was carried out to improve the premix (before extrusion) of the components. Multilayer Carbon Nanotubes (NTCMC) supplied by the company Nanocyl under the trade name NC7000 were used as supplied. The average diameter and length of the MWCNTs are 9.5 nm and 1.5 µm, respectively; transition metal oxide less than 1% and surface area between 250-300 m^2/g.

2.2 Processing

The nanocomposites were processed in the form of filaments by extrusion using a single-screw mini-extruder Filmaq3d STD (22 mm screw diameter and L/D = 9.1) adjusted to 30 rpm and at a temperature of 200 ºC. For processing by accentuating the extensional flow component, a flow-controlled device consisting of a sequence of 7 rings with internal diameters alternating between 2 and 4 mm was developed. The matrix acted as a support for the assembly of the 7 rings and also as an "eighth ring", with an internal diameter of 4 mm, this device has already been described in a previous work by this research group[25]. The device associated with the extruder die is capable of adding an estimated[26] extensional flow rate of 33.19 s^{-1}. Extruded filaments were collected using a filament winder that has a water-cooling system.

All different compositions shown in Table 1 were prepared twice each, aiming to carry out two processes for each, the first in a conventional manner and the second using the extensional flow device. In the nomenclature the suffix -el was added for those processed using the device coupled to the extruder die.

2.3 Characterization of nanocomposites

The samples used in this analysis were prepared from the microtomy of the extruded filaments. The cuts, with a thickness of 10 µm, were made with an American Optical 820 manual rotating microtome. The images were captured with the Olympus BX51 polarized light optical microscope operating in transmitted light mode, equipped with an Olympus QColor 3 camera. Using 5 images from different regions, an evaluation was made regarding the distribution of the average particle size with the ImageJ software. The automatic particle size analysis tool was used to count and measure (in area) the particles present in each image.

Table 1. Compositions of MWCNT nanocomposites.

Compositions	PP (%v.)	MWCNT (%v.)
PP	100.00	0.00
PP/0.5MWCNT	99.50	0.50
PP/2.5MWCNT	97.50	2.50

The rheological behavior of the nanocomposites was evaluated using an oscillatory rheometer, Discovery Hybrid Rheometer (DHR-2) from TA Instruments, using parallel plates of 25 mm diameter, working distance between the plates of 1 mm (gap), temperature 200 ºC, mode: stress-controlled force, angular frequency (ω) from 0.1 to 100 hz at 0.3% shear strain. The samples were obtained from the extruded filaments, which were cut into pieces of around 3 mm and then added between the rheometer plates. The measurements were done in the linear viscoelastic regime. The following properties were measured as a function of frequency: storage moduli (G'), loss moduli (G"), complex viscosity (η*), real viscosity (η') and imaginary viscosity (η"). The short relaxation time (t_r) was calculated for all nanocomposites as a function of the value of ω_c which corresponds to the frequency at which G'= G", according to Equation 1[27]:

$$t_r = \frac{1}{\varpi_c}.(2\pi) \tag{1}$$

3. Results and Discussions

3.1 Optical microscopy and particle size analysis

Figure 1 shows the image of the morphology of the nanocomposites processed with (Figure 1b and d) and without the presence of the extensional flow device (Figure 1a and c). For the composition PP/0.5MWCNT-el and PP/2.5MWCNT-el it is noted that the size of the clusters are smaller, which points to a greater efficiency in reducing the size of the clusters with the processing occurring with the aid of extensional flow.

With the collected data in the clusters size analysis made with ImageJ software, the size distribution curves shown in Figure 2 and Table 2 were constructed. The PP/0.5NTCMC-el composition presented 70.5% of all its clusters below 1µm^2 while its analog processed without the extensional flow device showed 59.8% of its clusters below this value. For the composition PP/2.5MWCNT-el, a value of 58.7% of the clusters below 1 µm^2 and 4.2% above 10 µm^2 was found, on the other hand, its corresponding processed without the extensional flow presented 54.3% of the clusters below 1 µm^2 and 7.5% above 10 µm^2. The size reduction effect of the clusters was more significant for the composition containing 0.5%v. of MWCNT. It is known

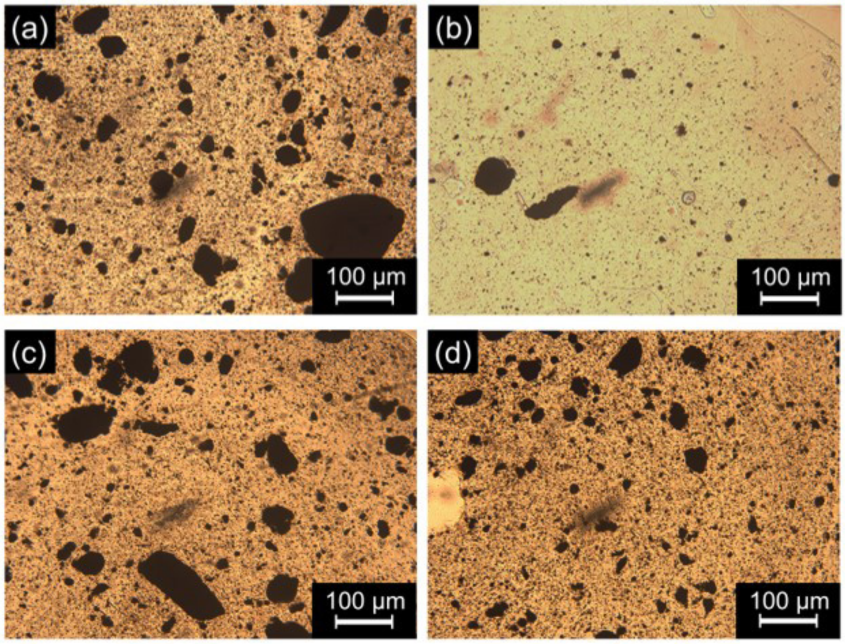

Figure 1. Morphology of nanocomposites: (a) PP/0.5MWCNT, (b) PP/0.5MWCNT-el, (c) PP/2.5MWCNT and (d) PP/2.5MWCNT-el.

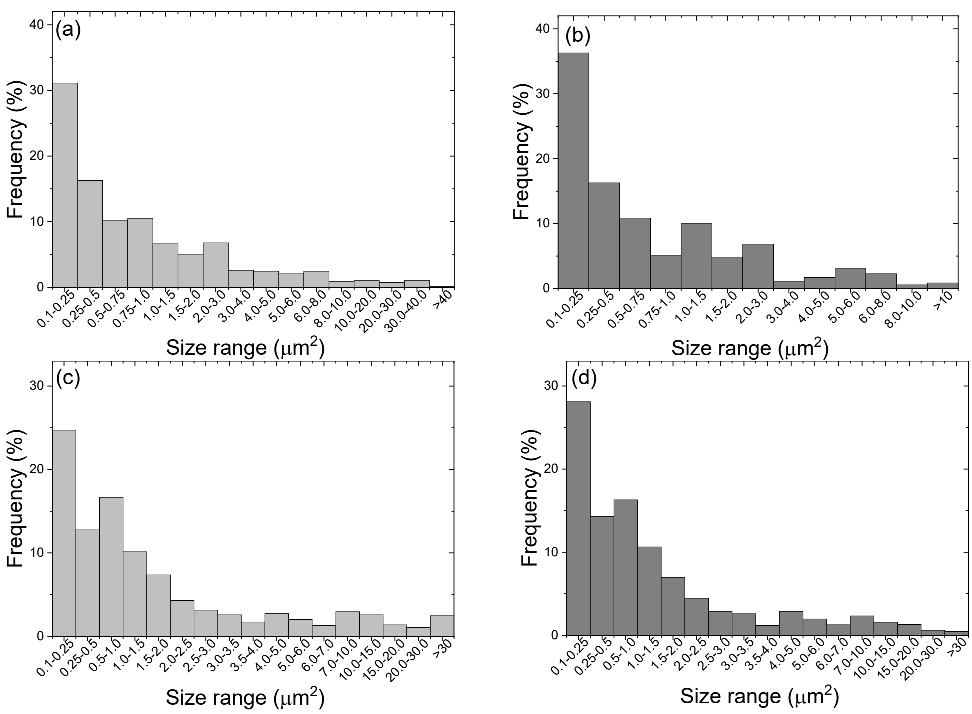

Figure 2. Clusters size distribution for the processed nanocomposites: (a) PP/0.5MWCNT (b) PP/0.5MWCNT-el, (c) PP/2.5MWCNT and PP/2.5MWCNT-el (d).

Table 2. Size measurements of MWCNT aggregates in PP.

Compositions	Nº *	X<1 μm² (%)	1<X<10 μm² (%)	X>10 μm² (%)
PP/0.5MWCNT	2865	*59.8*	*36.6*	*3.6*
PP/0.5MWCNT-el	*3490*	*70.5*	*26.0*	*3.5*
PP/2.5MWCNT	3559	54.3	38.2	7.5
PP/2.5MWCNT-el	*3472*	*58.7*	*37.1*	*4.2*

* Nº corresponds to the total number of analyzed particles.

that carbon nanotubes can easily entangle themselves and with polymers chains[3,6]. Also, Jamali[18] demonstrated that a higher extensional rate represents a greater breaking force for MWCNT clusters, when processing nanocomposites containing 4% w. of MWCNT, in a device coupled to a capillary rheometer.

This clusters size reduction behavior is associated with greater efficiency of the extensional flow in generating higher levels of dispersive and distributive mixture[12,18,22,24,28,29]. The results shown in Figure 2 and Table 2 also corroborates with the effect observed in our previous work[25], that is, the reduction in the size of the MWCNT agglomerates when processing with the extensional flow device coupled to the extrusion matrix. Here we have more significant results in terms of cluster size, due to the large number of clusters analyzed (Table 2) in this measure. We can say with greater reliability that when we accentuate the elongational flow in the extruder die, we contribute to achieving higher levels of dispersion for MWCNT aggregates in PP matrix.

3.2 Parallel plate rheometry

Rheological measurements in oscillatory regime, allow to assess the internal interaction between macromolecules and nanofillers in polymer matrix nanocomposites[20,29,30]. Figure 3 shows storage moduli (G'), loss moduli (G") and complex viscosity (η*) versus oscillatory frequency (ω) of the MWCNT nanocomposites. As expected, both G' and G" increased remarkably with frequency, while η* presented a decrease.

The morphology of MWCNT contributes for this material to become entangled themselves and with polymers chains[3,6]. This structure presents both, high modulus and high viscosities[2,31,32], this behavior was exhibited by the nanocomposites processed, as shown in Figure 3, and is more evident for the composition containing 2.5%v.. With regard to the effects of adding the extensional flow in processing, it was noted that MWCNT nanocomposites obtained under extensional flow had remarkable higher G', G" and η* than the others. For example, at 0.1rad/s, PVDF/MWCNT presented G'=1616.2 Pa, G"= 4176.1 Pa and η *=4496.8 Pa.s, while PP/2.5MWCNT-el presented G'=2562,8 Pa, G"= 5387.1 Pa and η*=5990.7 Pa.s. From a rheological point of view, this result shows that improved degrees of dispersion of MWCNT were achieved for MWCNT nanocomposites extruded under extensional flow compared to their counterparts extruded without extensional flow. Similar results were obtained in other works[33-37], for example in the study of Ke et al.[33], were compared the effects of melt and solution mixing on the dispersion and on rheological properties of MWCNT/PVDF nanocomposites. They found higher G' for solution mixed samples than for their counterparts obtained by melt mixing. This result was attributed to the better dispersion of MWCNT achieved in the solution mixed samples than in the melt mixed ones, for MWCNT loadings lower than 5 wt.%.

In order to more clearly assess the effects of extensional flow on the rheological properties, the values of the crossover frequency (ω_c) and also the short relaxation time (t_r) were determined, which are shown in Table 3. The relaxation process referred to in the measurement is associated with relaxation of the PP chains, probably by the reptation mechanism[38-40]. We can verify that when processed with the flow-through device, the compositions have their crossover frequencies shifted to lower values, that is, longer relaxation times, which are involved with higher degrees of interaction between MWCNT and PP chains, corroborating that improved degrees of dispersion were

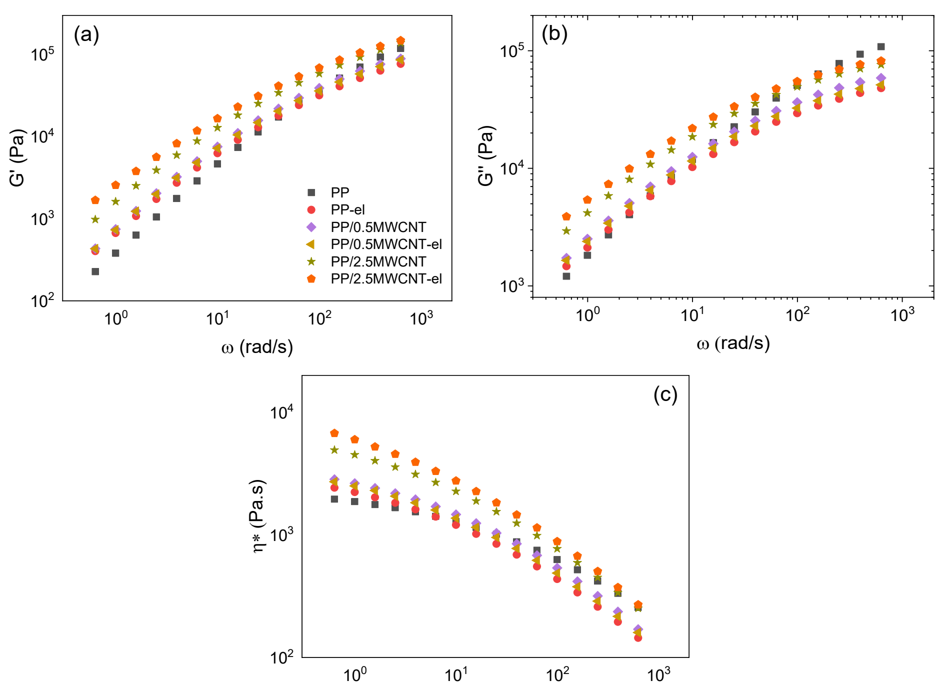

Figure 3. (a) Storage moduli (G'), (b) Loss moduli (G"), (c) Complex viscosity (η*) of the MWCNT nanocomposites.

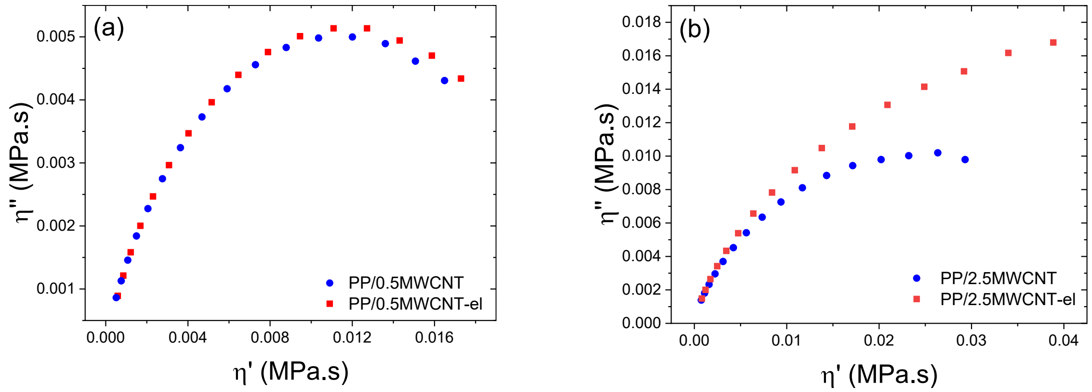

Figure 4. Cole-Cole plots for compositions with and without extensional flow device: (a) PP/0.5MWCNT and (b) PP/2.5MWCNT.

Table 3. Frequency of cross over (ω_c) and short relaxation time (t_r) for the nanocomposites.

Compositions	ω_c	t_r
PP/0.5MWCNT	75.41	0.083
PP/0.5MWCNT-el	*63.08*	*0.100*
PP/2.5MWCNT	47.92	0.131
PP/2.5MWCNT-el	*34.97*	*0.180*

achieved for these compositions due to the finer dispersion of MWCNT through the PP matrix. This possibly occurs because the polymer chain relaxations are more restricted by the nanotubes when there is a better dispersion in the nanocomposites. A similar phenomenon was reported by Rostami et al.[41], for PC/ABS/MWCNT composites; and in the study by Poothanari et al.[42] for PC/PP/MWCNT composites; in addition, we also reported this behavior in a previous study for PVDF/MWCNT nanocomposites[25].

The influence of extensional flow on relaxation times can also be seen in the Cole-Cole plots, shown in Figure 4.

The presence of extensional flow induced smoother curves (red dots) which is related to longer relaxation times, reaffirming what was calculated and shown in Table 3. This effect was much more pronounced for the composition containing 2.5%v. of MWCNT (approximately 4.6%w.). It is known that rheological percolation is a phenomenon that can be easily noticed by the significant increase in rheological properties[43-46] and in Banerjee's[47] work this phenomenon was observed between 3-4%w. for processing with a melt-state mixer with twin-screw components, however in our study we have no evidence of this phenomenon. Possibly, due to the proximity to the rheological percolation range for this type of nanocomposite, the effects of greater dispersion promote more significant gains contributing to the growth of PP/MWCNT and MWCN/MWCNT interactions, making the interconnected network more consistent, thus leading to longer relaxation times, for processing with accentuated extensional flow.

4. Conclusions

It was possible to process all the proposed compositions with and without the extensional flow device during extrusion. Clusters size analysis demonstrated that there was a reduction in MWCNT clusters size when processing the nanocomposites with the addition of the extensional flow rate (33.19 s^{-1}) in the processing. The most significant effect was observed for the composition PP/0.5NTCMC-el that presented 70.5% of all its clusters below 1µm^2 while its analog processed without the extensional flow device showed 59.8% of its clusters below this value.

Furthermore, the rheological analysis allowed to verify that the compositions processed with the presence of the extensional flow have their G', G" and η* values higher compared to their homologous compositions processed without the addition of the extensional flow. In addition, the crossover frequencies shifted to lower values, that is, longer relaxation times, which are involved with higher degrees of interaction between MWCNT and PP, corroborating that improved degrees of dispersion were achieved.

5. Author's Contribuition

- **Conceptualization** – Marcel Andrey de Goes; João Paulo Ferreira Santos; Benjamim de Melo Carvalho.
- **Data curation** – Marcel Andrey de Goes.
- **Formal analysis** – Marcel Andrey de Goes; João Paulo Ferreira Santos.
- **Investigation** – Marcel Andrey de Goes.
- **Methodology** – Marcel Andrey de Goes.
- **Project administration** – Benjamim de Melo Carvalho.
- **Resources** – Benjamim de Melo Carvalho.
- **Software** – Marcel Andrey de Goes.
- **Supervision** – NA.
- **Validation** – Marcel Andrey de Goes.
- **Visualization** – NA.
- **Writing – original draft** – Marcel Andrey de Goes.
- **Writing – review & editing** – Marcel Andrey de Goes; João Paulo Ferreira Santos.

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7. References

1. Bauhofer, W., & Kovacs, J. Z. (2009). A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology*, *69*(10), 1486-1498. http://dx.doi.org/10.1016/j.compscitech.2008.06.018.
2. Kaseem, M., Hamad, K., & Ko, Y. G. (2016). Fabrication and materials properties of polystyrene/carbon nanotube (PS/CNT) composites: A review. *European Polymer Journal*, *79*, 36-62. http://dx.doi.org/10.1016/j.eurpolymj.2016.04.011.
3. Ma, P.-C., Siddiqui, N. A., Marom, G., & Kim, J.-K. (2010). Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. *Composites. Part A, Applied Science and Manufacturing*, *41*(10), 1345-1367. http://dx.doi.org/10.1016/j.compositesa.2010.07.003.
4. Du, F., Scogna, R. C., Zhou, W., Brand, S., Fischer, J. E., & Winey, K. I. (2004). Nanotube networks in polymer nanocomposites: rheology and electrical conductivity. *Macromolecules*, *37*(24), 9048-9055. http://dx.doi.org/10.1021/ma049164g.
5. Zhu, B., Bai, T., Wang, P., Wang, Y., Liu, C., & Shen, C. (2020). Selective dispersion of carbon nanotubes and nanoclay in biodegradable poly(ε-caprolactone)/poly(lactic acid) blends with improved toughness, strength and thermal stability. *International Journal of Biological Macromolecules*, *153*, 1272-1280. http://dx.doi.org/10.1016/j.ijbiomac.2019.10.262. PMid:31758994.
6. Santos, J. P. F., Arjmand, M., Melo, G. H. F., Chizari, K., Bretas, R. E. S., & Sundararaj, U. (2018). Electrical conductivity of electrospun nanofiber mats of polyamide 6/polyaniline coated with nitrogen-doped carbon nanotubes. *Materials & Design*, *141*, 333-341. http://dx.doi.org/10.1016/j.matdes.2017.12.052.
7. Voge, C. M., Johns, J., Raghavan, M., Morris, M. D., & Stegemann, J. P. (2013). Wrapping and dispersion of multiwalled carbon nanotubes improves electrical conductivity of protein-nanotube composite biomaterials. *Journal of Biomedical Materials Research. Part A*, *101*(1), 231-238. http://dx.doi.org/10.1002/jbm.a.34310. PMid:22865813.
8. Vilaverde, C., Santos, R. M., Paiva, M. C., & Covas, J. A. (2015). Dispersion and re-agglomeration of graphite nanoplates in polypropylene melts under controlled flow conditions. *Composites. Part A, Applied Science and Manufacturing*, *78*, 143-151. http://dx.doi.org/10.1016/j.compositesa.2015.08.010.
9. Harris, A. M., & Lee, E. C. (2008). Improving mechanical performance of injection molded PLA by controlling crystallinity. *Journal of Applied Polymer Science*, *107*(4), 2246-2255. http://dx.doi.org/10.1002/app.27261.
10. Feast, W. J., Tsibouklis, J., Pouwer, K. L., Groenendaal, L., & Meijer, E. W. (1996). Synthesis, processing and material properties of conjugated polymers. *Polymer*, *37*(22), 5017-5047. http://dx.doi.org/10.1016/0032-3861(96)00439-9.
11. Tokihisa, M., Yakemoto, K., Sakai, T., Utracki, L. A., Sepehr, M., Li, J., & Simard, Y. (2006). Extensional flow mixer for polymer nanocomposites. *Polymer Engineering and Science*, *46*(8), 1040-1050. http://dx.doi.org/10.1002/pen.20542.
12. Covas, J. A., Novais, R. M., & Paiva, M. C. (2011). *A comparative study of the dispersion of carbon nanofibres in polymer melts.* In *Proceedings of the 27th World Congress of the Polymer Processing Society* (pp. 1-5). Morocco: International Polymer Processing.
13. Oxfall, H., Rondin, J., Bouquey, M., Muller, R., Rigdahl, M., & Rychwalski, R. W. (2013). Elongational flow mixing for manufacturing of graphite nanoplatelet/ polystyrene composites. *Journal of Applied Polymer Science*, *128*(5), 2679-2686. http://dx.doi.org/10.1002/app.38439.
14. Pierson, H. O. (1993). *Handbook of carbon, graphite, diamond and fullerenes: properties, processing and applications*. USA: Noyes Publications.
15. Ibarra-Gómez, R., Muller, R., Bouquey, M., Rondin, J., Serra, C. A., Hassouna, F., Mouedden, Y. E., Toniazzo, V., & Ruch, D. (2015). Processing of nanocomposites PLA/graphite using a novel elongational mixing device. *Polymer Engineering and Science*, *55*(1), 214-222. http://dx.doi.org/10.1002/pen.23869.
16. Chellamuthu, M., Arora, D., Winter, H. H., & Rothstein, J. P. (2011). Extensional flow-induced crystallization of isotactic poly-1-butene using a filament stretching rheometer. *Journal of Rheology (New York, N.Y.)*, *55*(4), 901-920. http://dx.doi.org/10.1122/1.3593471.
17. Bischoff White, E. E., Henning Winter, H., & Rothstein, J. P. (2012). Extensional-flow-induced crystallization of isotactic polypropylene. *Rheologica Acta*, *51*(4), 303-314. http://dx.doi.org/10.1007/s00397-011-0595-5.
18. Jamali, S., Paiva, M. C., & Covas, J. A. (2013). Dispersion and re-agglomeration phenomena during melt mixing of polypropylene with multi-wall carbon nanotubes. *Polymer Testing*, *32*(4), 701-707. http://dx.doi.org/10.1016/j.polymertesting.2013.03.005.
19. Yuan, D., Wu, T., Chen, R.-Y., Zhang, G.-Z., & Qu, J.-P. (2018). Investigation on properties of polypropylene/multi-walled carbon nanotubes nanocomposites prepared by a novel eccentric rotor extruder based on elongational rheology. *Journal of Macromolecular Science, Part B: Physics*, *57*(5), 348-363. http://dx.doi.org/10.1080/00222348.2018.1462648.
20. Silvano, J. R., Rodrigues, S. A., Marini, J., Bretas, R. E. S., Canevarolo, S. V., Carvalho, B. M., & Pinheiro, L. A. (2013). Effect of reprocessing and clay concentration on the degradation of polypropylene/montmorillonite nanocomposites during twin screw extrusion. *Polymer Degradation & Stability*, *98*(3), 801-808. http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.009.
21. Graf, A., Zakharko, Y., Schießl, S. P., Backes, C., Pfohl, M., Flavel, B. S., & Zaumseil, J. (2016). Large scale, selective dispersion of long single-walled carbon nanotubes with high photoluminescence quantum yield by shear force mixing. *Carbon*, *105*, 593-599. http://dx.doi.org/10.1016/j.carbon.2016.05.002.
22. Duc, B. N., & Son, Y. (2020). Enhanced dispersion of multi walled carbon nanotubes by an extensional batch mixer in polymer/MWCNT nanocomposites. *Composites Communications*, *21*, 100420. http://dx.doi.org/10.1016/j.coco.2020.100420.
23. Carson, S. O., Maia, J. M., & Covas, J. A. (2016). A new extensional mixing element for improved dispersive mixing in twin-screw extrusion, Part 2: experimental validation for immiscible polymer blends. *Advances in Polymer Technology*, *37*(1), 21653. http://dx.doi.org/10.1002/adv.21653.
24. Carson, S. O., Covas, J. A., & Maia, J. M. (2015). A new extensional mixing element for improved dispersive mixing in twin-screw extrusion, Part 1: design and computational validation. *Advances in Polymer Technology*, *36*(4), 21627. http://dx.doi.org/10.1002/adv.21627.
25. Goes, M. A., Woicichowski, L. A., Rosa, R. V. V., Santos, J. P. F., & Carvalho, B. M. (2021). Improving the dispersion of MWCNT and MMT in PVDF melts employing controlled extensional flows. *Journal of Applied Polymer Science*, *138*(17), 50274. http://dx.doi.org/10.1002/app.50274.
26. Feigl, K., Tanner, F. X., Edwards, B. J., & Collier, J. R. (2003). A numerical study of the measurement of elongational viscosity of polymeric fluids in a semihyperbolically converging die. *Journal of Non-Newtonian Fluid Mechanics*, *115*(2–3), 191-215. http://dx.doi.org/10.1016/j.jnnfm.2003.08.002.
27. Beatrice, C. A. G., Branciforti, M. C., Alves, R. M. V., & Bretas, R. E. S. (2010). Rheological, mechanical, optical, and

transport properties of blown films of polyamide 6/residual monomer/montmorillonite nanocomposites. *Journal of Applied Polymer Science*, *116*(6), 3581-3592. http://dx.doi.org/10.1002/app.31898.

28. Khajehpour, M., Arjmand, M., & Sundararaj, U. (2016). Dielectric properties of multiwalled carbon nanotube/clay/polyvinylidene fluoride nanocomposites: effect of clay incorporation. *Polymer Composites*, *37*(1), 161-167. http://dx.doi.org/10.1002/pc.23167.
29. Hsissou, R., Bekhta, A., Dagdag, O., El Bachiri, A., Rafik, M., & Elharfi, A. (2020). Rheological properties of composite polymers and hybrid nanocomposites. *Heliyon*, *6*(6), e04187. http://dx.doi.org/10.1016/j.heliyon.2020.e04187. PMid:32566792.
30. Demarquette, N. R., & Carastan, D. J. (2016). *Rheological behavior of nanocomposites.* In J. Parameswaranpillai, N. Hameed, T. Kurian, & Y. Yu (Eds.), *Nanocomposite materials: synthesis, properties and applications* (pp. 233-264). USA: CRC Press, Taylor & Francis Group. http://dx.doi.org/10.1201/9781315372310.
31. Behera, K., & Chiu, F. C. (2020). Evident improvements in the rigidity, toughness, and electrical conductivity of PVDF/HDPE blend with selectively localized carbon nanotube. *Polymer Testing*, *90*, 106736. http://dx.doi.org/10.1016/j.polymertesting.2020.106736.
32. Zhang, Q., Fang, F., Zhao, X., Li, Y., Zhu, M., & Chen, D. (2008). Use of dynamic rheological behavior to estimate the dispersion of carbon nanotubes in carbon nanotube/polymer composites. *The Journal of Physical Chemistry B*, *112*(40), 12606-12611. http://dx.doi.org/10.1021/jp802708j. PMid:18785703.
33. Ke, K., Wang, Y., Liu, X.-Q., Cao, J., Luo, Y., Yang, W., Xie, B.-H., & Yang, M.-B. (2012). Composites : part B A comparison of melt and solution mixing on the dispersion of carbon nanotubes in a poly (vinylidene fluoride) matrix. *Composites. Part B, Engineering*, *43*(3), 1425-1432. http://dx.doi.org/10.1016/j.compositesb.2011.09.007.
34. Vermogen, A., Masenelli-Varlot, K., Séguéla, R., Duchet-Rumeau, J., Boucard, S., & Prele, P. (2005). Evaluation of the structure and dispersion in polymer-layered silicate nanocomposites. *Macromolecules*, *38*(23), 9661-9669. http://dx.doi.org/10.1021/ma051249+.
35. Durmus, A., Kasgoz, A., & Macosko, C. W. (2007). Linear low density polyethylene (LLDPE)/clay nanocomposites. Part I: structural characterization and quantifying clay dispersion by melt rheology. *Polymer*, *48*(15), 4492-4502. http://dx.doi.org/10.1016/j.polymer.2007.05.074.
36. Franchini, E., Galy, J., & Gérard, J.-F. (2009). Sepiolite-based epoxy nanocomposites: relation between processing, rheology, and morphology. *Journal of Colloid and Interface Science*, *329*(1), 38-47. http://dx.doi.org/10.1016/j.jcis.2008.09.020. PMid:18848336.
37. Carastan, D. J., Vermogen, A., Masenelli-Varlot, K., & Demarquette, N. R. (2010). Quantification of clay dispersion in nanocomposites of styrenic polymers. *Polymer Engineering and Science*, *50*(2), 257-267. http://dx.doi.org/10.1002/pen.21527.
38. Gaspar, H., Santos, R., Teixeira, P., Hilliou, L., Weir, M. P., Duif, C. P., Bouwman, W. G., Parnell, S. R., King, S. M., Covas, J. A., & Bernardo, G. (2019). Evolution of dispersion in the melt compounding of a model polymer nanocomposite system: A multi-scale study. *Polymer Testing*, *76*, 109-118. http://dx.doi.org/10.1016/j.polymertesting.2019.03.013.
39. Fernandez, M., Huegun, A., & Santamaria, A. (2019). Relevance of rheology on the properties of PP/MWCNT nanocomposites elaborated with different irradiation/mixing protocols. *Fluids*, *4*(1), 7. http://dx.doi.org/10.3390/fluids4010007.
40. Hassanabadi, H. M., Wilhelm, M., & Rodrigue, D. (2014). A rheological criterion to determine the percolation threshold in polymer nano-composites. *Rheologica Acta*, *53*(10), 869-882. http://dx.doi.org/10.1007/s00397-014-0804-0.
41. Rostami, A., Masoomi, M., Fayazi, M. J., & Vahdati, M. (2015). Role of multiwalled carbon nanotubes (MWCNTs) on rheological, thermal and electrical properties of PC/ABS blend. *RSC Advances*, *5*(41), 32880-32890. http://dx.doi.org/10.1039/C5RA04043D.
42. Poothanari, M. A., Xavier, P., Bose, S., Kalarikkal, N., Komalan, C., & Thomas, S. (2019). Compatibilising action of multiwalled carbon nanotubes in polycarbonate/polypropylene (PC/PP) blends: phase morphology, viscoelastic phase separation, rheology and percolation. *Journal of Polymer Research*, *26*(8), 178. http://dx.doi.org/10.1007/s10965-019-1833-2.
43. Pötschke, P., Fornes, T. D., & Paul, D. R. (2002). Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer*, *43*(11), 3247-3255. http://dx.doi.org/10.1016/S0032-3861(02)00151-9.
44. Kota, A. K., Cipriano, B. H., Duesterberg, M. K., Gershon, A. L., Powell, D., Raghavan, S. R., & Bruck, H. A. (2007). Electrical and rheological percolation in polystyrene / MWCNT nanocomposites. *Macromolecules*, *40*(20), 7400-7406. http://dx.doi.org/10.1021/ma0711792.
45. Wu, G., Lin, J., Zheng, Q., & Zhang, M. (2006). Correlation between percolation behavior of electricity and viscoelasticity for graphite filled high density polyethylene. *Polymer*, *47*(7), 2442-2447. http://dx.doi.org/10.1016/j.polymer.2006.02.017.
46. Huang, A., Wang, H., Ellingham, T., Peng, X., & Turng, L.-S. (2019). An improved technique for dispersion of natural graphite particles in thermoplastic polyurethane by sub-critical gas-assisted processing. *Composites Science and Technology*, *182*, 107783. http://dx.doi.org/10.1016/j.compscitech.2019.107783.
47. Banerjee, J., Kummara, S., Panwar, A. S., Mukhopadhyay, K., Saxena, A. K., & Bhattacharyya, A. R. (2021). Influence of carbon nanotube type and novel modification on dispersion, melt-rheology and electrical conductivity of polypropylene/carbon nanotube composites. *Polymer Composites*, *42*(1), 236-252. http://dx.doi.org/10.1002/pc.25821.

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