



INFLUENCE OF MIXING METHOD AND CHEMICAL FUNCTIONALIZATION OF CARBON NANOFIBERS ON COMPOSITE PROPERTIES

Rui M. Novais, José A. Covas and Maria C. Paiva
Department of Polymer Engineering
E-mail: rui.novais@dep.uminho.pt

KEYWORDS

Carbon nanofibers; Polymer composites; Melt mixing.

ABSTRACT

The present work reports the study of the dispersion of carbon nanofibers (CNF), as-received and chemically functionalized, in polypropylene (PP) using two different mixing methods. A prototype mixer was tested, and the results were compared to melt mixing in a twin-screw extruder. The effect of functionalization of the CNF on dispersion was also evaluated. The composites formed using the two different methods were compared in terms of CNF distribution and dispersion, electrical properties and CNF/polymer interface.

INTRODUCTION

Carbon nanofibers present excellent mechanical and electrical properties. They are now produced at a high rates and reasonably low price, becoming a very interesting material for composite applications (Tibbetts et al.). Polymer/CNF nanocomposites can be prepared using different mixing methods, including in-situ polymerization, solution processing and melt mixing (Breuer et al 2004), the former being the most commonly used method. The explanation for this selection was given by S. Ray et al, they stated that the melt intercalation method is environmentally benign due to the absence of organic solvents and also due to its compatibility with current industrial process, like extrusion and injection moulding (Ray et al 2003). O. Breuer et al, also highlighted these reasons as well as the speed and simplicity of this conventional processing technique.

Conventional melt processed polymer composites are prepared in mixers such as twin-screw extruder, internal batch mixers, micro-compounders (DACA, DSM). Previous studies show that the dispersion of the filler is strongly dependent on the melt mixing equipment (Lin et al 2006; Sundararaj et al 1995; Maric et al 2001). The dispersion of nanofillers has been extensively studied in the past years, since it can affect strongly the final nanocomposite properties

(Pegel et al 2008; Luo et al 2008; Haggenueller et al 2000; Narh et al 2007).

The dispersion results obtained by these conventional methods seem to lack some consistence. Our objective here was to find a better small dispersive mixer, which could be used following extrusion in a twin-screw extruder, in order to improve the dispersion of the carbon nanofibers into a polymer matrice.

Another purpose of this report consists on proving that the functionalization of CNF can improve the composite dispersion independently of the melt mixing method. The treatment of the CNF surface should decrease the high chemical inertia of the pure CNF, and improve dispersion on the matrix material (Araújo et al 2007; Paiva et al 2010).

The dispersion of CNF homogeneously into a polymer is still a challenge, because of their highly entangled form and strong van der Waals forces between the nanofibers, nevertheless this tendency can be minimized if shear is applied during mixing (Haggenueller et al 2000).

Good dispersion needs strong shear flows, however dispersion forces in extensional flows are higher than those arising in equivalent shear flows. Pure extensional flows are difficult to generate in practice, but it is possible to generate flows with a strong extensional component. Therefore, it makes sense to investigate the effect of extensional flow on the dispersion of carbon nanotubes or nanofibers in thermoplastic matrices.

In this paper, the main goals were to evaluate the influence of extensional flow on the dispersion of carbon nanofibers in polypropylene using a mixing device designed for the purpose, compare the results with mixing in a twin-screw extruder, and finally conjugate the two methods, first the twin-screw extruder and then the new mixing device, and analyze the influence of this second mixing step.

The comparison of the level of dispersion achieved with as-received and chemically functionalized CNF will also be discussed.



EXPERIMENTAL

Materials

The carbon nanofibers used in this work were obtained from Applied Sciences Inc., PR-24-PS grade. The fibers are cylindrical and hollow, characterized by a wide diameter range varying from 60 to 150 nm, and a length that can reach 100 μm (Tibbetts et al.).

The polypropylene used was Stamylen P 13E10 from DSM, and the polypropylene modified with maleic anhydride (PP-g-MA), containing 1% of maleic anhydride, was Orvac CA 100 from Arkema.

Chemical functionalization of the carbon nanofibers

The functionalization method was based on the 1,3-dipolar cycloaddition reaction of azomethyne ylides (Georgakilas et al. 2002). The reaction of a specific α -amino acid and paraformaldehyde was studied under solvent free conditions (Araújo et al. 2007) and scaled up to allow the homogeneous functionalization of tens of grams of CNF (Paiva et al 2010). The reaction was carried out under the conditions described in reference (Paiva et al. 2010). The amino acid used was N-benzyloxycarbonylglycine (Z-Gly-OH, 99%, from Aldrich) and paraformaldehyde was reagent grade, purchased from Sigma. CNF, paraformaldehyde and Z-Gly-OH were combined in a mortar in 1:5:1 molar ratio. The mixture without solvent was heated to 250 $^{\circ}\text{C}$ for 12-14 hours. The resulting product was washed with methanol and dried in the vacuum oven.

Composite preparation

Pellets of the matrix polymer were ground into powder form in a Retsch grinder ZM 100, under liquid nitrogen. Composites with 95% polypropylene (PP) and 5% of CNF (weight %) and a blend of 80% PP, 15% PP-g-MA and 5% of functionalized CNF, were prepared. The PP-g-MA has used to react with the chemical groups introduced by functionalization on the CNF surface. The different compositions of PP/CNF and PP/ PP-g-MA/CNF were mixed in the powder form and then melt mixed using different methods:

- i) by twin screw extrusion, on a prototype mini twin-screw extruder; the extrusion was performed at a flow rate of 270 g/h and a flat temperature profile of 220 $^{\circ}\text{C}$.
- ii) forcing the melt through a series of dies inducing a converging/diverging flow sequence; the device that generated the converging/diverging flow was formed by a series of twelve dies stacked in a sequence of large diameter/small diameter, fitted inside a capillary rheometer, as represented in Figure 1. The polymer and CNF, previously mixed,

were heated to 220 $^{\circ}\text{C}$ in the rheometer, and the piston moved down at a constant speed of 6.25 mm/min, forcing the material to flow along the converging/diverging circular flow channels. The entire set-up could be removed from the rheometer and disassembled so that samples of the composite could be collected along the flow axis.

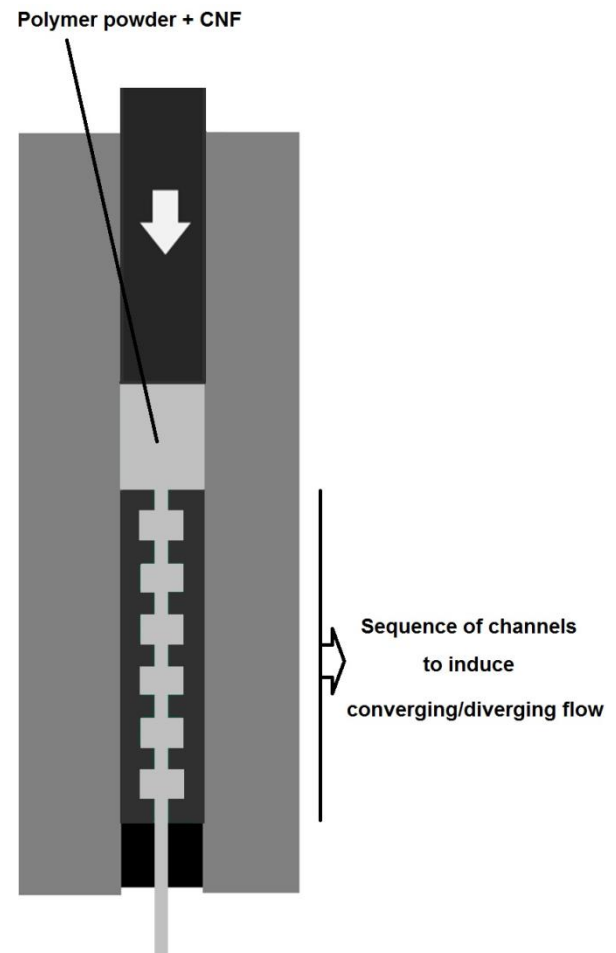


Figure 1: capillary rheometer with converging/diverging assembly.

- iii) using the mini twin-screw extruder followed by the converging/diverging flow sequence assembly.

The composite rod obtained from each set of experiments was chopped into pellets, and composite plates with 1mm thickness were prepared by compression moulding on a heated press, at 230 $^{\circ}\text{C}$.

Characterization

The CNF were characterized by thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy



(XPS). TGA was performed on a Q500 thermobalance from TA Instruments. The samples were heated at 5 °C/min under a constant flow of N₂ (g). XPS spectra were obtained with a ESCALAB 200A-VG. The effect of inducing predominantly i) shear flow, ii) extensional flow or iii) shear followed by extensional flow, on the distribution and dispersion of the CNF was analyzed by OM and SEM. The electrical resistivity of the composites produced was measured.

The volume resistivity of the samples was obtained by measuring the characteristic I-V curves at room temperature with a Keithley 6487 picoammeter/voltage source. The samples were previously coated by thermal evaporation with aluminium electrodes, where the probe tips touched the sample, and placed on the sample holder. The current and voltage were measured and the resistivity was calculated accounting for the geometrical factors.

Optical microscopy (OM) analysis was performed on 5 μm thick samples cut from the compression moulded plates using a Leitz 1401 microtome. At least five specimens were prepared for each composite, with an average area of $3,1 \times 10^5 \mu\text{m}^2$ analyzed per specimen. A BH2 Olympus transmission microscope was used. The images were acquired with a digital camera LEICA DFC 280 coupled to the microscope. The number of CNF agglomerates, agglomerate size and area ratio (represents the area of the sample that is covered by visible carbon nanofibers agglomerate) were quantified using the Leica Qwin Pro program.

Scanning electron microscopy (SEM) of the CNF and of the cryo-fractured surfaces of the composites was performed on a LEICA-S360 equipment.

RESULTS AND DISCUSSION

The present work focuses on the study of the CNF/polypropylene composite formation by melt mixing under different flow regimes. The distribution of the CNF agglomerates through the PP, the CNF dispersion and interface achieved under the different mixing conditions was analyzed for composites with as-produced and chemically functionalized CNF (FCNF).

The functionalization was tailored to bond pyrrolidine (cyclic amine) groups at the CNF surface. A blend of PP and PP grafted with maleic anhydride as used as matrix for the FCNF/PP composites.

The PR-24-PS CNF used in this work are cylindrical nanofibres characterised by graphitic layer structure with “stacked-cup” morphology, as described by Tibbetts (Tibbetts et al. 2007). The functionalization method leads to the formation of the pyrrolidine 1, as represented in figure 2. This functionalization method is carried out under mild reaction conditions and does not lead to CNF structural damage (Araújo et al 2007; Paiva et al 2010). After washing with methanol and drying, the typical round-shaped agglomerates of entangled CNF that constitute the as-received CNF present an open structure, as observed before (Paiva et al 2010).

Carbon nanofiber functionalization

The FCNF were analyzed by TGA and XPS. The results obtained are presented in Table 1. The higher weight loss observed for the FCNF when heated from ambient to 800 °C under inert atmosphere, compared to the untreated CNF, was considered indicative of functionalization. XPS provides the analysis of the atomic composition of the CNF surface, quantifying the amount of nitrogen and oxygen atoms bonded to the CNF carbon surface, providing evidence for the formation of nitrogen containing functional groups. The XPS results evidence a considerable degree of oxidation of the as-received CNF. The oxygen content remains approximately constant before and after chemical functionalization while the nitrogen content, almost absent on the as received CNF, reaches a value close to 5% of the surface atomic composition. The chemical functionalization of the CNF surface is expected to improve the CNF/matrix interface through the chemical reaction between the anhydride grafted on the PP and the cyclic amine groups at the CNF surface, forming amide links and covalently bonding PP molecules to the CNF surface as in product 2 represented in figure 2.

The FCNF were analyzed by TGA and XPS. The results obtained are presented in Table 1. The higher weight loss observed for the FCNF when heated from ambient to 800 °C under inert atmosphere, compared to the untreated CNF, was considered indicative of functionalization. XPS provides the analysis of the atomic composition of the CNF surface, quantifying the amount of nitrogen and oxygen atoms bonded to the CNF carbon surface, providing evidence for the formation of nitrogen containing functional groups. The XPS results evidence a considerable degree of oxidation of the as-received CNF. The oxygen content remains approximately constant before and after chemical functionalization while the nitrogen content, almost absent on the as received CNF, reaches a value close to 5% of the surface atomic composition. The chemical functionalization of the CNF surface is expected to improve the CNF/matrix interface through the chemical reaction between the anhydride grafted on the PP and the cyclic amine groups at the CNF surface, forming amide links and covalently bonding PP molecules to the CNF surface as in product 2 represented in figure 2.

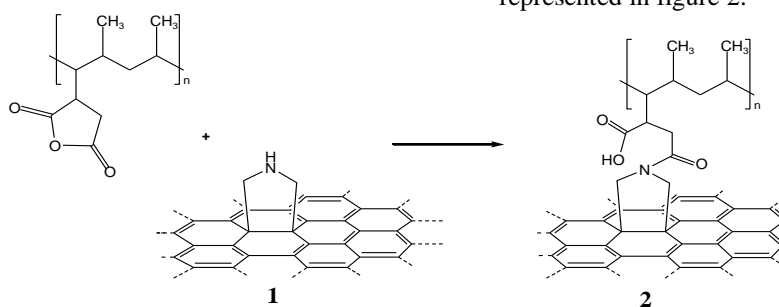


Figure 2: Reaction of the functional group at the surface of the CNF with the maleic anhydride grafted on PP.



Table 1. Carbon, nitrogen and oxygen atomic composition of the CNF obtained by XPS, and weight loss results measured by TGA.

Sample	C (at%)	O (at%)	N (at%)	Weight loss (%)
As received CNF	93.2	6.2	0.6	2 ± 1
FCNF	88.5	6.8	4.7	17 ± 2

Melt mixing of the carbon nanofibers in the polymer

Composites with PP and CNF, as-received and functionalized, were prepared by mixing the polymer in powder form with 5% of CNF or FCNF. The different compositions were melt mixed following three different routes: i) by twin screw extrusion (Extru); ii) by forcing the melt through a rheometer equipped with a series of dies inducing a converging/diverging flow sequence (Rheo); iii) finally, by twin screw extrusion followed by forcing through the rheometer with the series of dies (Extru/Rheo).

The results obtained by optical microscopy for the agglomerate area ratio, average agglomerate area and average number of agglomerates, for the composites produced by the different melt mixing routes, are presented in Table 2.

These results illustrate the level of CNF dispersion achieved using each technique. It was observed that the non-reactive system PP/CNF is reasonably well dispersed by twin screw extrusion, the agglomerates are well distributed across the composite, although presenting a large variation of agglomerate sizes. The converging/diverging induced flow system originates very poor distribution of the CNF in PP with large agglomerates covering a large area %, indicating that a low dispersion level was attained. Interestingly, the application of this method to the composite formed by extrusion lead to an improvement on the dispersion level, decreasing the average agglomerate size and the agglomerate area ratio relative to the extruded composite, and considerably reducing the variability of the results.

The reactive system of PP + PP-g-MA/FCNF presented a different behavior. The FCNF were equally well distributed and dispersed by extrusion and by converging/diverging induced flow. The later method showed a slightly higher variation of the agglomerate size and larger number of agglomerates, but the differences were minor. The application of this method to the composite formed by extrusion showed an evolution towards smaller agglomerate size. The agglomerates formed during extrusion were broken into smaller agglomerates by application of the

converging/diverging flow, but the total number of agglomerates doubled.

The electrical percolation of composites with this type of CNF is expected to be attained at CNF content higher than 10% weight (Lozano et al. 2001). For that reason the composites produced were still far from electrical percolation, nevertheless the volume resistivity measured for all the composites was several orders of magnitude lower than that of PP (10^{14} to 10^{16} $\Omega.m$), placing the composites with non functionalized and functionalized CNF in the antistatic behavior region.

SEM of the composite cryo-fracture surfaces is a complementary technique of the OM observations. It illustrates the presence of CNF agglomerates, reveals the presence of CNF dispersed in the agglomerate free areas, and clearly shows the quality of the polymer/CNF interface. These results are illustrated in table 2. The SEM micrograph of the PP/CNF fracture surface prepared by extrusion shows the poor CNF/PP interface result in the long fiber lengths protruding from the fracture surface and a large number of holes produced by the pulled out fibers. The composite with FCNF prepared by the same method shows the excellent interface established between the FCNF and the PP+PP-g-MA, leading to the fiber breakage close to the fracture surface.

The SEM micrograph of the PP/CNF fracture surface prepared with extensional flow shows again poor dispersion compared to the composite with FCNF.

Carbon nanofiber dispersion along the sequence of dies

Samples of the composite melt as it was forced through a series of dies mounted on a rheometer were collected along the flow axis, after passing through each die channel.

The collected samples along the die channels were analyzed by OM (see table 3). The results obtained for the agglomerate area ratio and average agglomerate area, for the non-reactive system PP/CNF are summarized in the column charts in Figure 3.

These results illustrate the level of CNF dispersion achieved after passing through each die channel. For the non-reactive system PP/CNF the observations



showed that, after passing the first channel, the composite was formed by large CNF agglomerates. The agglomerate size decreased after the fourth channel, and then the average agglomerate area remains almost unchanged for the next three channels.

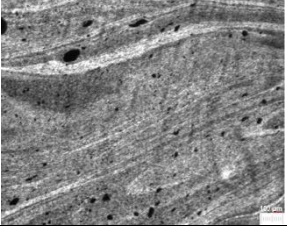
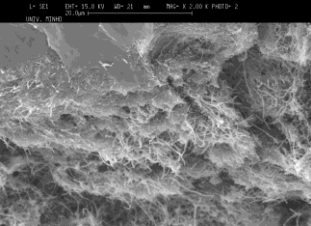
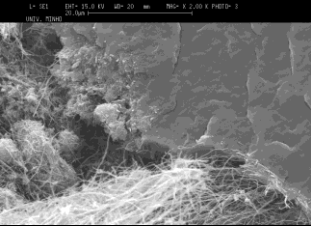
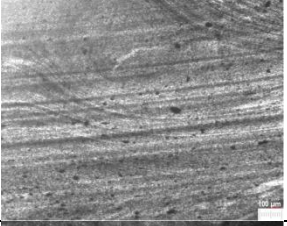
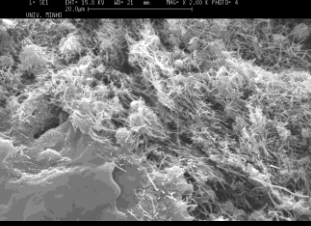
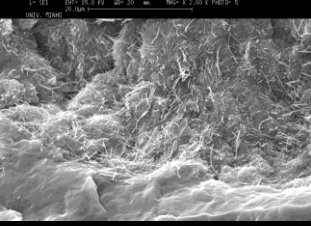
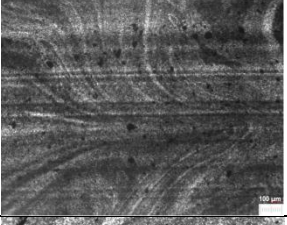
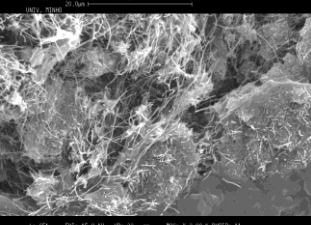
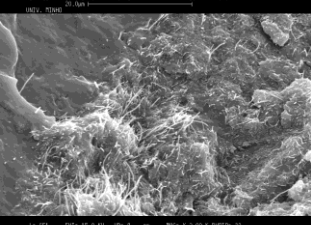
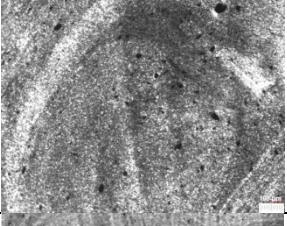
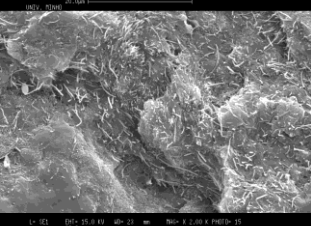
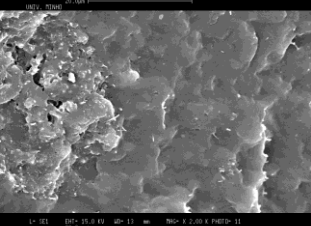
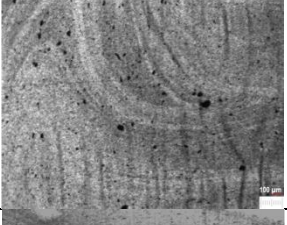
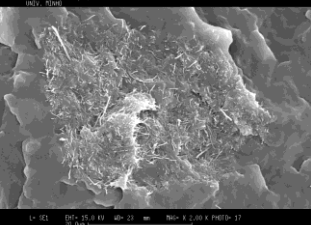
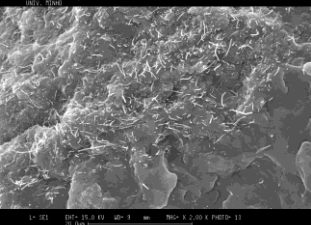
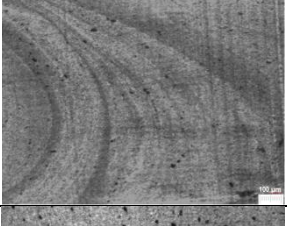
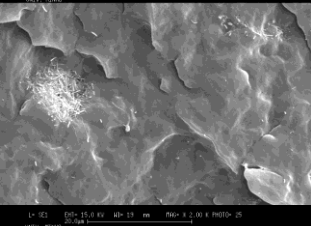
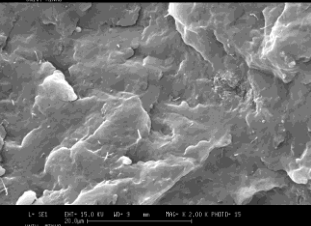
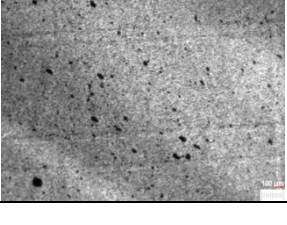
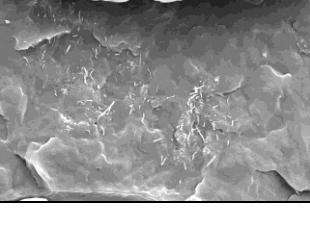
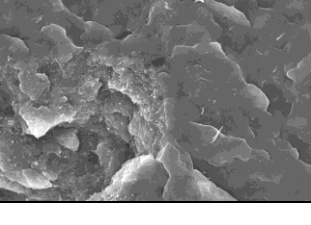
The agglomerates size decreases again after the eight channel.

Table 2. Optical microscopy and electrical resistivity characterization of the composites produced by the different melt mixing routes.

Sample	Melt mixing method	Area ratio (%)	Average agglomerate area (μm^2)	Number of agglomerate (per $10^5 \mu\text{m}^2$)	Volume resistivity/ ($10^{10} \Omega \cdot \text{m}$)	Typical OM image	Typical SEM image
PP + 5% CNF	Extru	10 ± 10	100 ± 100	80	$2,5 \pm 0,5$		
	Rheo	19 ± 13	800 ± 900	34	$0,6 \pm 0,5$		
	Extru/Rheo	6.1 ± 1	80 ± 30	81	$0,7 \pm 0,4$		
PP + PP-g-MA + 5% FCNF (containing 4.25% CNF)	Extru	5.8 ± 1	90 ± 20	67	$1,9 \pm 0,5$		
	Rheo	6.5 ± 3	90 ± 30	86	$0,2 \pm 0,3$		
	Extru/Rheo	7.4 ± 1	60 ± 20	143	$2,3 \pm 0,1$		



Table 3: typical MO and SEM micrographs of the composites prepared by forcing the melted polymer mixture through a series of dies. The number of dies passed is indicated on the left column.

Channel	CNF		FCNF
	Typical OM image	Typical SEM image	Typical SEM image
1			
2			
3			
5			
6			
8			
11			

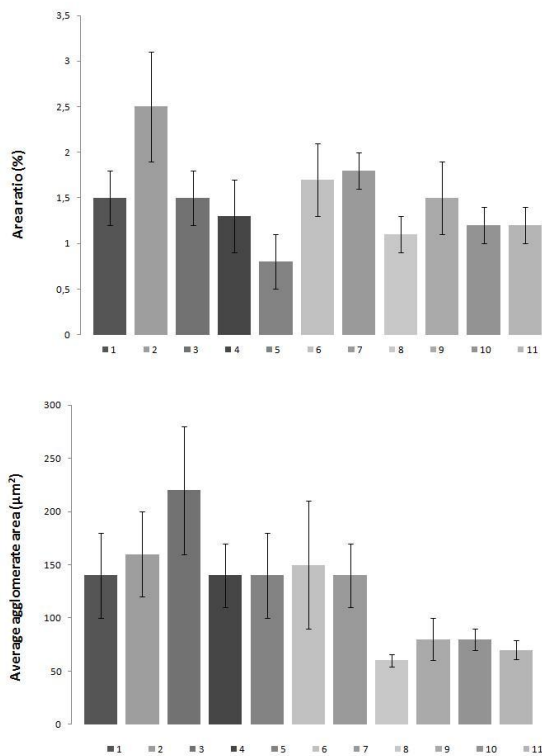


Figure 3: Variation of the agglomerate area ratio and average agglomerate area for the as received CNF composite using capillary rheometer.

The samples collected after each die channel were cryo-fractured and observed by SEM. The observations showed that, after passing the first channel, the composite was formed by large CNF agglomerates irregularly distributed through the polymer. The non-functionalized CNF agglomerates were not wet by the matrix until after passing through the fourth channel, while for the FCNF the wetting was evident after passing the third channel. The agglomerate size decreased and CNF wetting increased along the flow axis, as an increasing number of channels inducing converging/diverging flow were passed. These observations are illustrated in table 3 for a selection of micrographs of the fracture surface of the composite melt along the flow line.

These results are consistent with the previous MO results, showing that throughout the flow line the size of the agglomerates tends to decrease.

CONCLUSIONS

Composites with CNF, as-received and chemically functionalized, and PP, were prepared using two different melt mixing methods, separately and in sequence. The CNF distribution, dispersion and primary agglomerate size for the composites obtained by the different methods was analyzed by optical

microscopy. The effect of CNF functionalization on its dispersion, agglomerate size, and CNF/polymer interface was studied by optical microscopy and scanning electron microscopy.

The composites produced in the mini twin-screw extruder presented a good distribution of the CNF agglomerates, with much smaller agglomerate area and area ratio as compared to the composites prepared with the sequence of dies inducing converging/diverging flow of the melt. The later method induced a fluctuation in the agglomerate size and area ratio as the melt flow was forced through the sequence of dies, with an overall decrease as the number of dies passed increased. The effect of using the twin screw extruder followed by the sequence of dies inducing the converging/diverging flow lead to an improvement on the dispersion level of the non-functionalized CNF, decreasing further the average agglomerate size and the agglomerate area ratio relative to the extruded composite, and considerably reducing the variability of the results. The composites formed with functionalized CNF showed agglomerate size, ratio and distribution reasonably independent of the processing method, with a small improvement when applying the two methods in sequence.

The CNF functionalization improved the nanotube /polymer interface.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Portuguese Foundation for Science and Technology through project POCI/QUI/59835/2004 and PhD grant SFRH/BD/32189/2006.

REFERENCES

- Araújo, R.; M. Paiva; M. Proença; and C. Silva. 2007. "Functionalization of carbon nanofibres by 1,3-dipolar cycloaddition reactions and its effect on composite properties". *Composites Science Technology*, 67, 806–810.
- Baughman, R.; A. Zakhidov; and W. Heer. 2002. *Science*, 297, 787.
- Breuer, O. and U. Sundararaj. 2004. Big Returns from small fibers: A review of polymer/carbon nanotube composites. *Polymer Composites*, 25, 630.
- Georgakilas, V.; K. Kordatos; M. Prato; D.M. Guldi; M. Holzinger; and A. Hirsch. 2002. *Journal of the American Chemical Society*, 124(5), 760.
- Haggenmueller, R.; H. Gommans; A. Rinzler; J. Fischer; and K. Winey. 2000 *Chemical Physics Letters*, 330, 219-225.
- Heer, W.. 1999. *Current Opinion in Solid State and Materials Science*, 4, 355.



- Lin, B.; U. Sundararaj; and Petra Pötschke. 2006. Melt mixing of polycarbonate with multi-walled carbon nanotubes in miniature mixers. *Macromolecular Materials and Engineering*, 291, 227-238.
- Lozano, K.; J. Bonilla-Rios; E. V. Barrera. 2001. A study on nanofiber-reinforced thermoplastic composites (II): investigation of the mixing rheology and conduction properties. *Journal of Applied Polymer Science*. Vol. 80, 1162-1172.
- Luo, Z. and J. Koo. 2008. *Materials Letters*, 62, 3493-3496.
- Maric, M. and C. Macosko. 2001. Improving polymer dispersions in mini-mixers. *Polymer Engineering and Science*, 41,1.
- Narh, K.; A. Agwedicham; and L. Jallo. 2007. *Powder Technology*, 186, 206-212.
- Paiva, M. C.; R. M. Novais; R. F. Araújo; K. K. Pederson; M. F. Proença; C. J. R. Silva; C. M. Costa; and S. Lanceros-Méndez. 2010. *Polymer Composite*, 31 (3) 369-376.
- Pegel, S.; P. Pötschke; G. Petzold; I. Alig; S. M. Dudkin; and D. Lellinger. 2008. *Polymer*, 49, 974.
- Ray, S.; and M. Okamoto. 2003. *Progress in Polymer Science*. 25, 630.
- Sundararaj, U. ; C. W. Maosko A. Nakayama; and T. Inoue. 1995. Miligrams to kilograms: an evaluation of mixers for reactive polymer blending. *Polymer Engineering Science*. 35, 1, 100-114.
- Tibbetts, G. G.; M. L. Lake; K. L. Strong; and B. P. Rice. 2007. *Journal of Computer Science and Technology*, 67, 1709.



RUI M. NOVAIS was born in Fafe, Portugal in 1982. He graduated in Physics and Chemistry in 2005 at the University of Minho. He worked as a research assistant at the Institute for Polymers and Composites, contributing to the area of carbon nanofibre thermoplastic composites

and to the ESA Project PARMAX (New Thermoplastic Based Composites for Highly Demanding Space Applications). He was awarded a PhD grant from FCT (SFRH/BD/32189/2006) and has been working on his PhD in the area of polymer/carbon nanotube composites at the University of Minho since 2007. His e-mail address is: ruim.novais@dep.uminho.pt