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Ultrasound Assisted Extrusion of Polyamide 6 Nanocomposites Based on Carbon Banotubes

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Summary: Polyamide 6 (PA6)/multiwall carbon nanotubes (MWCNTs) nanocomposites have been prepared by an extrusion process assisted by ultrasounds. The ultrasounds system has been incorporated at the extrusion die, when the material is flowing through the exit channel. The application of an ultrasound field to a polymer melt has been shown a very efficient method to improve productivity of the process. When ultrasounds are applied, the extrudate flow is highly enhanced maintaining the same processing conditions. In addition, the ultrasounds contribute to the deagglomeration of CNTs into the matrix, as can be conclude from the drop in the electrical resistivity values of the nanocomposites observed when ultrasounds are applied. For the system PA6/MWCNT 7wt%., the electrical resistivity increases three orders of magnitude when ultrasounds are employed during the extrusion. In addition, a high reduction in the electrical percolation index is obtained for nanocomposites extrudated by the assistance of ultrasounds.

Keywords: carbon nanotubes; extrusion; nanocomposites; polyamides; ultrasound

Introduction

Multiwall carbon nanotubes (MWCNTs) have attracted considerable attention due to their inherent extraordinary electrical, thermal, structural and mechanical properties.[1] Therefore, they have been expected to be excellent fillers for polymer composites with application as conductive composites, energy conversion devices, sensors, to nanometer-sized semiconductor devices.[2] However, their high aspect ratio and the strong π-π interaction between the carbon nanotubes lead to a strong bundle arrangement. Therefore, the biggest challenge in effectively using MWCNTs is their lack of dispersion in a polymeric matrix, representing the main drawback for their processability and application.

Between the different techniques available for nanocomposite processing, extrusion is the most extensively used method for thermoplastics processing in industrial applications and one of the most promising methods to disperse carbon nanotubes in a polymeric matrix, because it is rapid, environmentally friendly and it can be easily scale up. Numerous efforts have been made to improve extrusion processing, and the application of ultrasounds to polymer melt seems to be an efficient way.[3–6] The application of ultrasounds when polymers flow through channels with vibrating walls may alter the conventional wall-stick condition during the flow, and cause the slippage by means of the thin layer with decreased viscosity next to the wall.[3] Furthermore, the application of ultrasounds on the flowing polymer melt is a complex phenomenon, involving physical and chemical factors, which could affect the macroscopic flow behaviour and

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also the chemical structures of the original molecules. In the present paper, the effects of ultrasounds not only on the processability of PA6/MWCNT nanocomposites, but also on the dispersion degree of MWCNT in the matrix have been analyzed.

Experimental Part

Industrial grade MWCNTs, Nanocyl grade 7000, were used as starting material. PA6 was chosen as polymeric matrix due to its combination of mechanical and thermal properties and to its wide use in industry for different applications, automotive, aeronautic,... PA6 from DSM, Akulon F223D range, was dried 48 hours in an oven with vacuum and mixed with MWCNTs into a corrotating conical twin screw microextruder (Haake Minilab II) equipped with a closed loop for recirculation. The ultrasonic vibration at 20 kHz is applied in the exit zone of the extruder normal to the polymer flow, being the vibration amplitude 8–12 microns. The ultrasonic piezoelectric actuator is located in an enlarged exit channel where the temperature and the flow section are controlled. Nanocomposites with 0, 3, 7 and 10 wt. % of carbon nanotubes were obtained applying ultrasounds and without their application. Processing conditions were similar in both modes: 10 minutes under recirculation at 255 °C applying a rotation screw speed of 150 rpm and working in corrotating mode.

Electrical conductivity of the nanocomposite was measured with a Fluke 1520 MegaOhmeter. The scanning electron microscope (SEM) micrographs have been carried out by a Carl Zeiss Ultra Plus FESEM to characterized morphology of nanocomposites. The flow rate of the material in the extruder was determined as the grams of material extruded in one minute. Fourier Transform Infrared spectroscopy was employed to study the presence of new bands generated due to the use of ultrasounds. Thermal behaviour of the nanocomposites was studied by differential scanning calorimetry (DSC) and thermogravimetric (TGA) measurements.

Results and Discussion

The application of ultrasounds during the extrusion affects greatly the material flow when pristine and MWCNT modified PA6 are processed. Ultrasonic vibration during extrusion affects the throughput of extrudate. As an example, the extrusion of the system PA6/10wt% MWCNT results in a flow of 0.25 g/min, but when US are applied 0,44 g/min were obtained under the same process conditions. Furthermore, lower rotation speeds and lower extrusion temperatures, which mean longer duration of the ultrasonic treatments, lead to larger throughput of extrudate. The effects of ultrasounds in the macroscopic behaviour observed during the extrusion can be due to different factors. Firstly, part of the ultrasound energy could be converted into heat energy by the internal friction between the molecules in the melt state. The increase in the temperature could be responsible of the higher flux, as the viscosity of the melt polymer is reduced. However, the measurement of the temperature of the extrudate in the die did not show any significant change when ultrasounds are applied. On the other hand, ultrasounds could cut the length of the polymer molecular chains or degrade the polymer reducing its viscosity. But the FTIR spectra of PA6 extruded with the assistance of ultrasounds did not show the generation of new oxygen containing groups, and the curves corresponding to the thermogravimetric analysis of PA6 didn't show the degradation of the polymer. The reduction of the die pressure with the application of ultrasounds seems to be responsible of the higher flow rate, as observed by other workers.[3–6] When ultrasounds are applied, an average reduction of 7 Pa is observed in the extrusion of the PA6 modified with10 wt % MWCNT (Figure 1), with a maximum reduction of 17 Pa.

Treating the extruding die as a dynamic capillary rheometer (equations 1–3), it can be observed that the pressure drop along the capillary and the increase in the flow rate can results in the reduction of the

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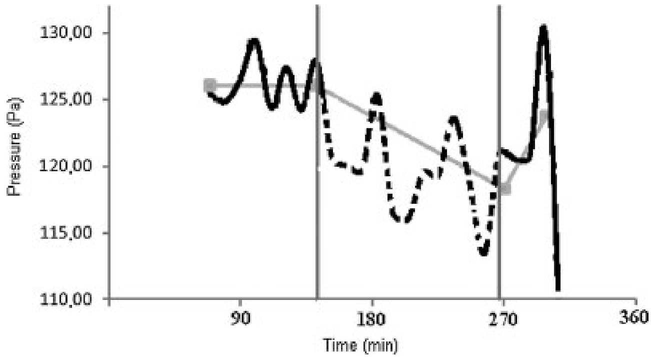

Figure 1.
Die pressure during the extrusion of PA6/MWCNT 10 wt % with (---) and without (—) the assistance of ultrasounds.

apparent viscosity of the extrudate.

$$\tau_w = \frac{P \cdot D}{4 \cdot L} \quad (1)$$

$$\dot{\gamma}_w = \frac{32 \cdot Q}{\pi \cdot \rho \cdot D^3} \quad (2)$$

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \quad (3)$$

It seems that the ultrasounds can accelerate molecular motion and make long entangled molecular chains unravel with no significant degradation of the polymer.

Concerning the dispersion degree of MWCNT into the PA6 matrix, the analysis by SEM showed a high degree of dispersion of the nanotubes in ultrasound assisted and non-assisted extruded nanocomposites, but clear differences in MWCNT dispersion degree were not observed due to the high amount of MWCNT employed. Figure 2 showed the micrographs obtained for the system modified with 7 wt % MWCNT, but similar results are observed for all the nanocomposites. The MWCNTs seem not to be damaged or shortened by the ultrasounds.

Interestingly, a great difference in electric resistance is observed for nanocomposites extruded with or without assistance of US. The electrical resistivity values, collected in Table 1, showed that the resistivity of the neat matrix is too high for being measured with the employed equipment (higher than $4\,M\Omega \cdot m$).

As the MWCNT content in the polyamide matrix increases, the resistance of the composite decreases, due to the increase in the number of contacts between the tubes. In addition, the ultrasonically

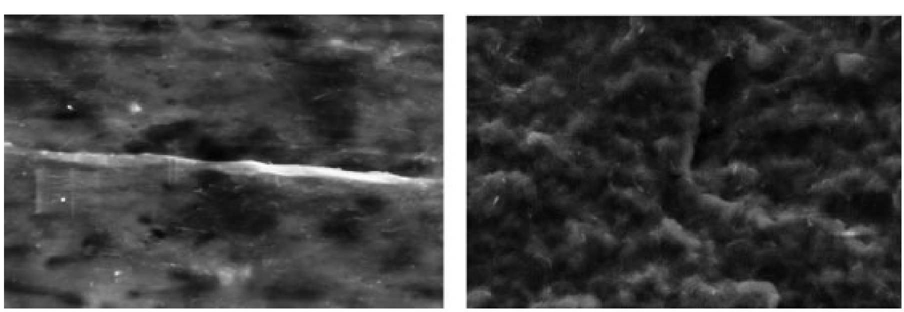

Figure 2.
SEM micrographs of PA6/MWCNT 7 wt % processed with (left) and without (right) the assistance of ultrasounds. Magnification 50 k X.

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Table 1.
Electrical resistivity values for the obtained nanocomposites with and without the assistance of ultrasounds.

SYSTEM	WITHOUT US	WITH US
PA6	>4 MΩ · m	>4 MΩ · m
PA6 + 3%CNT	>4 MΩ · m	743 kΩ · m
PA6 + 7%CNT	56.63 kΩ · m	63.42 Ω · m
PA6 + 10%CNT	17.67 Ω · m	6.3 Ω · m

treated nanocomposites showed a lower percolation index than the commonly processed nanocomposites. The resistance value can be monitored for MWCNT contents higher than 7 wt % in nanocomposites processed without the assistance of ultrasounds, however, when ultrasounds are applied during the extrusion the concentration of carbon nanotubes required for detecting the electric conductivity is reduced to a 3 wt %. The ultrasounds can make long entangled CNT unravel and the dispersion of the tubes is enhanced, being created a path for electric conduction with lowers contents of MWCNTs. The reduction in the apparent viscosity with the application of ultrasounds could also contribute to the increase of the electrical conductivity, as the dispersion of the tubes is better for lower viscosity systems.[7]

Conclusion

High power ultrasounds have been incorporated to corrotating twin screw microextruder in order to obtain MWCNT based nanocomposites with improved processability and with a good dispersion of MWCNT into the matrix. The results showed that ultrasounds are very efficient in improving the processability of pristine and MWCNT modified polymers. The ultrasounds increase the throughput of the extrudates, mainly due to a reduction in the die pressure that causes a reduction in apparent viscosity. In addition, the thermal stability of pristine and MWCNT modified polymers seemed not to be significantly affected by the ultrasounds. The influence of the ultrasounds in the extrusion flux is higher at lower temperatures and lower rotation speeds, due to the longer radiation time.

On the other hand, the ultrasonic vibration has also a significant effect on the nanocomposite conductivity. The percolation index of the polyamide/MWCNT system is reduced from 7 to 3 wt % when ultrasounds are employed during the nanocomposite processing. This indirectly could be ascribed to the improved dispersion of the nanotubes in the matrix. Ultrasounds can make long entangled CNTs unravel being created a path for electric conduction with lowers contents of MWCNTs. In addition, the ultrasounds reduce the apparent viscosity of the material at the die, contributing to a better dispersion of the nanotubes. The use of ultrasounds during the extrusion results in an increment of three orders in the electrical resistivity for the system PA6/MWCNT 7 wt %.

As a conclusion, the incorporation of high power ultrasound in the extrusion of thermoplastics nanocomposites improved its processability and could reduce greatly the amount of nanotubes required for conductive applications, without a significant detriment in their thermal properties.

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