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Evolution of dispersion of carbon nanotubes in Polyamide 11 matrix composites as determined by DC conductivity

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A B S T R A C T

Double-walled Carbon NanoTubes (DWCNTs) have been dispersed in a Polyamide 11 (PA11) matrix by two routes: in the solvent way, Polyamide 11 was first dissolved in its solvent to ensure a liquid state dispersion of carbon nanotubes by ultrasonic way; in the melt mixing way, an optimization of the extrusion parameters, such as mixing time, mixing speed, mixing temperature and screw rotation direction allow to reach satisfactory dispersion. Dispersion and percolation threshold have been compared thanks to the evolution of DC conductivity with carbon nanotubes weight fraction in Polyamide 11.

An electrical percolation threshold of 1% in weight was found by the solvent way while the melt mixing way offers one of the lower percolation thresholds for a semi-crystalline matrix (0.93% in weight). An interpretation of the limitation of the electrical percolation threshold value in a semi-crystalline matrix will be proposed.

Keywords:

A. Carbon nanotubes
A. Polymer–matrix composites (PMCs)
B. Electrical properties
E. Extrusion

1. Introduction

A lot of work has been devoted to the introduction of conductive fillers in polymeric matrices to make them conductor. Different kinds of fillers have been incorporated to increase polymer conductivity: carbon black particles [1,2], carbon nanofibers [3,4], metallic fillers [5], nanowires [6]. Mixing of conductive carbon black and CNT has also been explored [7]. For applications requiring electrostatic dissipation or electromagnetic radiation shielding [8,9], carbon nanotubes (CNTs) present themselves as the best candidate, by bringing to the nanocomposite a good compromise between weight and conduction. One of the remarkable properties of the CNTs, discovered by Iijima [10], is their high aspect ratio. The interest of the aspect ratio in carbon fillers has been analysed extensively in the literature [11–13]. It permits to obtain very low percolation threshold. Percolation theory outlines that this threshold corresponds to an insulator–conductive transition occurring at a defined concentration of particles labeled p_c . CNTs–polymer nanocomposites become conductor at very low filler content; then mechanical properties of the polymer are preserved.

Amorphous polymers give a wide variety of composites [14] which provide electrical conductivity exhibiting very low percolation thresholds [15]. Despite a more complex physical structure, semi-crystalline polymers have attractive processing properties. In

situ polymerization, solvent way, melt mixing are different processes used to elaborate thermoplastic based composites. Extrusion, by offering a fast and free solvent process, is the most promising one from an industrial point of view. An extruder has variable parameters such as mixing time, mixing speed and mixing temperature. They depend on the extruded polymer properties as melting point or viscosity: such relationships have been analysed for PolyEther Ether Ketone (PEEK) [16,17], PA 6 [18–21] and PA 12 [22].

Regarding Polyamide 6 and 66, Polyamide 11 has the advantage to be less hydrophilic. The hydrophilicity of PA 11 is close to the PA 12 one, but PA 11 has a higher thermal stability (higher melting point). This work is devoted to PA 11/DWCNTs composites. Two methods of nanocomposite elaboration have been used: the solvent way and the extrusion way. The dispersion state of DWCNTs in Polyamide 11 is investigated by DC conductivity measurements in both cases. These electrical measurements give also information about nanoparticles aspect ratio and are useful to investigate extrusion parameters. The palmitic acid influence, as an amphiphilic molecule, is also studied and percolation theory will be applied to explain experimental results.

2. Experimental section

2.1. Materials and nanocomposites elaboration

Polyamide 11 will be studied either in granules or in powder (30 μm). The carbon nanotubes have been synthesized by Marion

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Technologies (France) and Arkema (France). Both of them were synthesized by catalytic chemical vapor deposition [23] (CCVD). The first ones are mostly double-walled (80% DWCNTs) whereas the second ones are sold as multi-walled (MWCNTs).

To elaborate the composite using a solvent method, PA 11 granules need to be first added in dimethylacetamide (DMAc), previously heated at 160 °C. At the same time, CNTs are dispersed by ultrasounds in DMAc (previously heated at 160 °C) and then added to the PA11-DMAc liquid blend. At ambient temperature, the mixture precipitates. It is then filtrated, water washed and vacuum dried at 160 °C during 12 h to eliminate all solvent residues. The nanocomposite is hot pressed at 210 °C in order to realize films of 100 μm in thickness. The twin screw extruder is the second way to make nanocomposites. The extruder is a Haake Minilab II from Thermo Scientific. The extruder needs a sample volume of 7 ml. The screw rotation direction, the screw rotation speed, the mixing temperature and the mixing time are variable parameters. Two modes are available: the re-circulation mode allows the control of the mixing time and the extrusion mode is enabled by opening the bypass valve. This is a free solvent process which is a huge advantage for industrial applications. Moreover, thanks to the use of PA 11 powder, DMAc is totally excluded from the process. Process parameters will be presented hereafter.

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed using a Perkin–Elmer DSC 7 calorimeter. The sample temperature was calibrated using the onset of melting of Tin ($T_m = 231.88$ °C) and Indium ($T_m = 156.6$ °C). The heat-flow was calibrated with the heat melting of Indium ($\Delta H = 28.45$ J g^{-1}). Sample weight varied from 5 to 10 mg. In order to remove the effect of previous thermal history, only second and third runs are investigated. Crystallinity ratio is calculated from the melting peak and normalized to the polymer mass. Experiments were carried out in the temperature range 20–210 °C with a constant heating rate of 20 °C min^{-1} .

Fig. 1a shows the evolution of heat capacity for neat PA 11 and its composites elaborated by extrusion with 0.3, 0.85, 1.3, 2, and 4 wt.% of CNTs. Thermograms are recorded during the second temperature scan. The evolution of the melting peak corresponding to the crystalline phase shows that higher the CNTs content is, broader the peak is. Fig. 1b shows that crystallinity ratio is maintained constant until 2 wt.%. At higher CNT concentration (4 wt.%), additional crystallites are not created (the area under the melting peak stays constant) but the original ones are modified with presence of

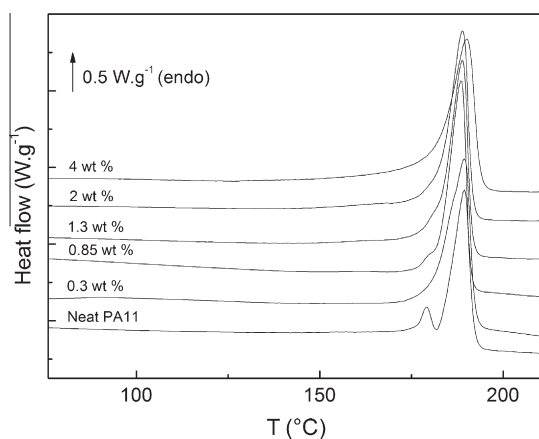


Fig. 1a. Melting peak for neat PA 11 and its composites elaborated by extrusion with 0.3, 0.85, 1.3, 2, and 4 wt.% of CNTs. Thermograms are recorded during the second temperature scan.

CNTs. Indeed, the thermograms of Fig. 1a shows that the melting peak of the composite at 4 wt.% has shifted to higher temperature. It indicates that the melt of crystallites requires more thermal energy, i.e. the morphology of crystallites has been slightly modified.

2.3. Dynamic conductivity measurements

Electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$ using a Novocontrol broadband spectrometer. Measurements were done in the frequency range from 10^{-2} to 10^6 Hz at room temperature. The real part, $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was investigated. The value of $\sigma'(\omega)$ at 10^{-2} Hz was taken as dc conductivity σ_{dc} . The sample surfaces were silver coated (the coating does not contain a solvent of the PA11) to insure a good electrical contact with the cell electrodes.

3. Results and discussion

3.1. Nanocomposites elaborated by solvent way

The solvent way has been already used to disperse CNTs in various polymers and presents itself as an easy method, only requiring ultrasounds and suitable solvent. Two composites have been elaborated with different DWCNTs weight fraction. From each one, two samples have been pressed at 210 °C in order to perform conductivity measurements. The direct conductivity average (σ_{DC}) and the standard deviation of each CNTs weight fraction have been considered to plot the electrical percolation threshold defined by percolation theory [24] as an insulator-conductor transition and reported in Fig. 2. The eight decades gap between insulator-conductor behaviors highlights the electrical percolation phenomenon. The linearity between $\log \sigma_{\text{dc}}$ and $\log(p-p_c)$ confirms this observation. The low standard deviation shows a good reproducibility of the dispersion method. The following scaling equation, proposed by Kirkpatrick [25], links the evolution of the conductivity to four parameters:

$$\sigma = \sigma_0(p - p_c)^t$$

where σ_0 is a constant, p the CNTs weight fraction, p_c the CNTs weight fraction at the percolation threshold, and t the critical exponent. The best fitted values are for $p_c = 1$ wt.%, $\sigma_0 = 2 \times 10^{-5}$ S m^{-1} and $t = 2.02 \pm 0.23$. The t exponent is closed to the universal value predicted by Stauffer [24] associated with a 3D percolation network. Nevertheless, the solvent toxicity is a drawback for industrial application. This is the reason why the extrusion way is also inves-

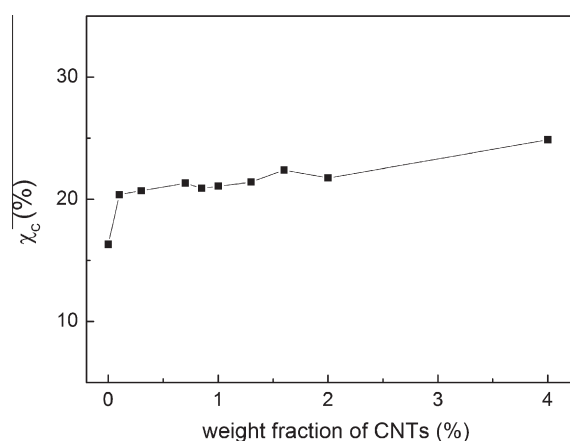


Fig. 1b. Evolution with the CNTs content of the crystallinity deduced from thermograms of Fig. 1a.

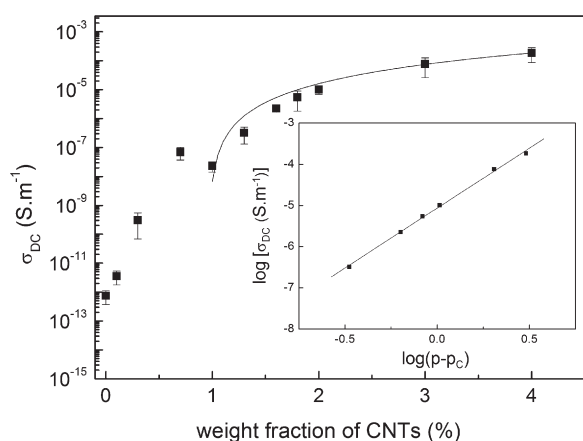


Fig. 2. Dependence of the σ_{DC} conductivity on the CNTs weight fraction p at 25 °C for composites elaborated by solvent way. The percolation threshold p_c is about 1 wt.%. The solid line is a fit to the scaling law of the percolation theory. The insert shows $\log \sigma$ versus $\log(p-p_c)$ and the solid line corresponds to the best fit.

tigated in order to ensure CNTs dispersion in the melting state by avoiding the dissolution step.

3.2. Nanocomposites elaborated by extrusion

3.2.1. Standard twin screw extruder parameters

First, nanocomposites were elaborated by extrusion with standard mixing parameters (time, speed, temperature and screw rotation direction). It has been chosen 30 min, 80 rpm, 210 °C and counter-rotating respectively. For each double-walled CNTs weight fraction, the DC conductivity was measured on two pellets coming from the same extruded composite and average value was calculated.

Fig. 3a displays the evolution of the DC conductivity as a function of CNTs weight fraction. The percolation phenomenon was not completely observed, but the corresponding threshold can be estimated near 3.7 wt.%. This high value can be explained by a relatively bad dispersion or a deterioration of the fillers. It can be admitted as a possible explanation that CNTs have been deteriorated during the process. Balberg et al. [26] shows that the aspect ratio multiplied by p_c is equal to a constant; i.e. if the percolation threshold value increases, the aspect ratio decreases. The nanofiller aspect ratio has been reduced, which can explain the increase of

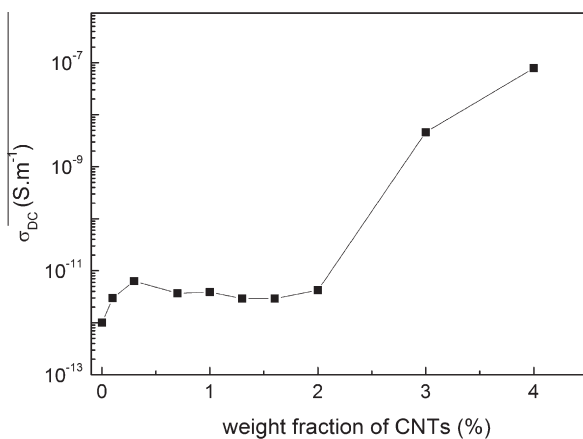


Fig. 3a. Dependence of the σ_{DC} conductivity on the p CNTs weight fraction at 25 °C for nanocomposites elaborated by extrusion (mixing time: 30 mn, mixing speed: 80 rpm, mixing temperature: 220 °C, screw rotation direction: contra-rotating). The percolation threshold p_c is about 3.7 wt.% CNTs.

the percolation threshold. Work on the different extruder parameters has to be performed to reach an optimal process.

3.2.2. Evolution of mixing time, mixing speed, screw rotation direction and mixing temperature

This following part is devoted to the determination of the most adapted parameters to elaborate nanocomposites by melt process. As these experiments are CNTs consuming, MWCNTs have been used. Composites at 4 wt.%, well above the percolation threshold, have been elaborated. Fig. 3b shows the influence of mixing time, mixing speed and screw rotation direction on the DC conductivity. Concerning the mixing time, longer the composite is extruded, lower is the DC conductivity. This effect becomes stronger for 30 min of mixing. Dissipated energy increases with mixing time and nano-charges are progressively deteriorated; i.e. the aspect ratio decreases and p_c shifts to higher values. Co-rotating screws compared to counter-rotating ones allow us to reach the higher conductivities by reducing shearing rate and conserving CNTs aspect ratio. Co-rotating screws offer higher conductivity for the slower rotation speed. This conductivity decreases with the increase of the rotation speed. This result is consistent with a similar study in PA 6 [18]. Extrusion during 15 min at 30 rpm with co-rotating screws is the optimal process.

Nevertheless, conductivities obtained with the counter-rotating screws give also information. The lower conductivity is obtained at very high speed near 130 rpm: it is equivalent with the results coming from co-rotating screws. However, a difference is observed at 30 and 80 rpm. Two phenomena seem to occur as a compromise: in counter-rotating case, the energy dissipated by the screws disperses and deteriorates fillers. At 30 rpm, fillers are deteriorated but the rotation speed is not high enough to disperse them. At 80 rpm, fillers are more deteriorated but the speed is sufficient to disperse CNTs. During extrusion, shearing rate through screw rotation direction plays an important role.

The mixing temperature was varied in the range from 200 to 240 °C and data are reported in Fig. 3c. The results are obtained with the following extrusion parameters: a mixing time of 15 min, a mixing speed of 30 rpm and the screw rotation direction in the co-rotating configuration; i.e. the ones which present the best conductivity values in Fig. 3b. A five decades gap is observed between the composites prepared at 200 and 240 °C. At 200 °C, the mixing temperature is too low, leading to a high viscosity, and preventing a good CNTs dispersion whereas mixing at 240 °C induces a clustering of the fillers because of a too low viscosity. The ideal mixing temperature is 220 °C, situated 20° above the melting point. The study done on mixing conditions in PA6 [11] highlights similar observation: an optimum mixing temperature

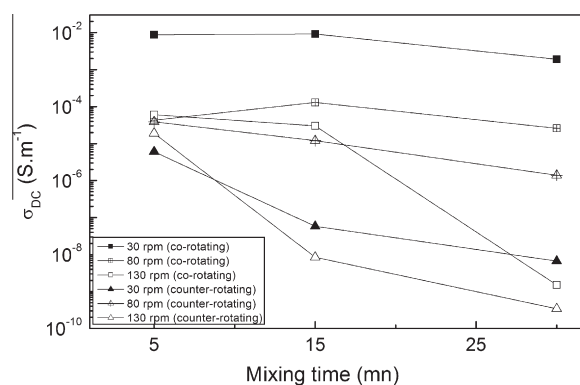


Fig. 3b. Dependence of the DC conductivity on mixing speed, screw rotation direction and mixing time for the composite at 4 wt.% CNTs obtained with a mixing temperature of 220 °C.

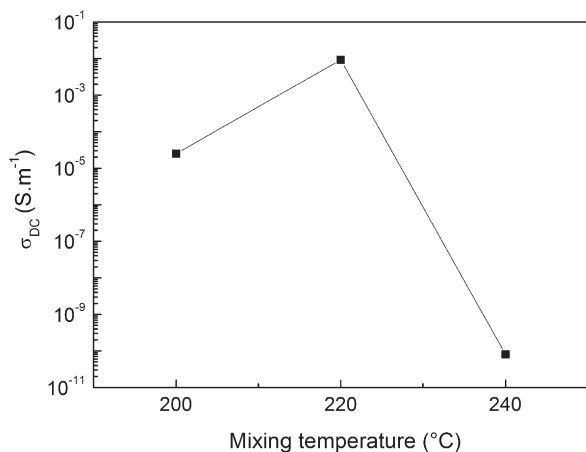


Fig. 3c. Dependence of the DC conductivity on mixing temperature for the composite at 4 wt.% CNTs with a mixing time of 15 min, a mixing speed of 30 rpm and screw rotation direction in the co-rotating configuration (best parameters obtained in Fig. 3b).

has been found at 280 °C for a PA6 melting point at 263 °C. A medium viscosity allows a better diffusion of the polymer chain in the CNTs network.

3.2.3. Optimized twin screw extruder parameters.

The extrusion parameters of a composite CNT – Polyamide 11 have been optimized. For each concentration, PA 11 powder was mixed with DWCNTs and injected in the extruder. The chosen parameters are the ones determined previously: a mixing speed of 30 rpm, 15 min of mixing time, co-rotating screws and a mixing temperature of 210 °C ($=T_m + 20$ °C; PA 11 powder has a melting point at 189 °C). For each concentration, PA 11 powder was mixed with DWCNTs and injected in the extruder.

Fig. 4 shows an abrupt variation of the conductivity indicating the existence of a percolating path via connecting DWCNTs. The data are well fitted to the scaling law mentioned previously. The best fitted values are obtained for $p_c = 0.93$ wt.%, $\sigma_0 = 8 \times 10^{-2} \text{ S m}^{-1}$ and $t = 2.46 \pm 0.32$. The t value is closed to the one predicted by the universal value given by Stauffer: the percolation phenomenon occurs in the 3D network. The high aspect ratio and the good dispersion

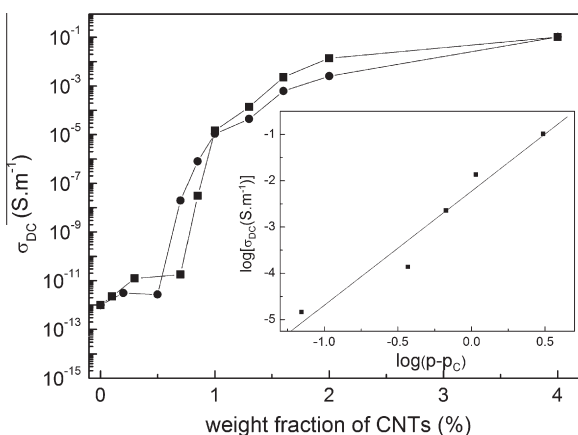


Fig. 4. Dependence of the DC conductivity on the CNTs weight fraction p at 25 °C for nanocomposites elaborated by extrusion (mixing time: 15 mn, mixing speed: 30 rpm, mixing temperature: 210 °C, screw rotation direction: co-rotating) without palmitic acid (■) and with palmitic acid (●). Palmitic acid has been added to the mix of PA11 powder and CNTs before the extrusion step with a ratio of 1:1 with CNTs. The inset shows $\log \sigma$ and $\log (p - p_c)$ where the solid line corresponds to the best fitted line for nanocomposites without palmitic acid.

of DWCNTs in the PA 11 matrix are confirmed by a percolation threshold at a low weight fraction of nanotubes. The percolation threshold value obtained in PA 11 by extrusion is one of the lowest observed in literatures [15,17,27–37], showing that the dispersion method has been optimized.

The influence of palmitic acid has already been studied as amphiphilic molecules in CNTs–epoxy composites. The palmitic acid ($\text{C}_{16}\text{H}_{32}\text{O}_2$) has a hydrophobic part, i.e. long alkyl chain $\text{CH}_3-(\text{CH}_2)_{16}-$, which is adsorbed onto the nanotubes surface. An acid hydrophilic head group ($-\text{CO}-\text{OH}$), induces electrostatic repulsions between nanotubes preventing their aggregation. Barrau et al. [38] showed that the palmitic acid allows an efficient dispersion of CNTs in the epoxy matrix. Electrical conductivity was optimal using 1:1 CNTs to palmitic acid weight ratio. The percolation threshold was shifted from 0.19 wt.% CNT to 0.1 wt.% CNTs, dividing by two the fillers concentration at the electrical percolation threshold. Fig. 4 compares the DC conductivity dependence on the CNTs content at 1:1 CNTs to $\text{C}_{16}\text{H}_{32}\text{O}_2$ weight ratio. Respectively, data fitted to the scaling law gives 0.73 wt.% and 0.93 wt.%. Palmitic acid acts as dispersant. However, its effect is weaker in PA11 than in polyepoxy: several hypotheses can explain this difference. The first one comes from the thermoplastic nature of the matrix; CNTs are mixed in the melt and the final composites cool during extrusion. In thermoset, the polymerization takes place under temperature influence by freezing the percolating network. Furthermore, palmitic acid influence has been reduced by the extrusion step at 210 °C: the thermogravimetric analysis of palmitic acid highlights a degradation temperature of 158 °C for 1% of weight loss and 19% at 210 °C. Then, CNTs agglomerates persist, considering that palmitic acid has not a stronger influence to maintain CNTs dispersed during extrusion. Finally, interactions between the hydrophobic tail and the matrix can be at the origin of this result. For Polyamide, the hydrogen bonds of the amide groups may increase interactions with palmitic acid hydrophilic head, reducing the repulsion between CNTs.

Fig. 5 gives an outline of electrical percolation threshold values of CNTs in polymers as thermosets [15], amorphous [13,32] and semi-crystalline thermoplastics [13,17,32–37]. Thermoset and amorphous thermoplastics offer the lowest percolation threshold values (from 0.024 wt.% to 0.5 wt.%). In semi-crystalline, p_c mean value is around 1.5 wt.% with the lowest one observed at 0.9 wt.% for PET-MWCNT [32] composite (a lower value has been obtained in a Poly(ϵ -caprolactone) [13] but the crystallinity level of this polymer has to be discussed). The elaboration process differs for thermoset and amorphous thermoplastics; i.e. curing process and melt mixing respectively. The semi-crystalline matrix based nano-

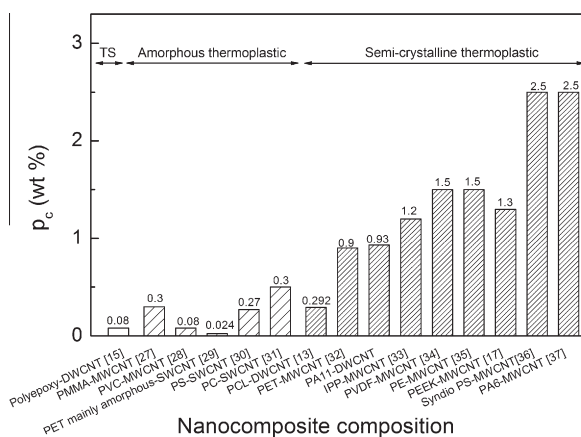


Fig. 5. Comparison of electrical percolation threshold values (wt.% of CNTs) for thermosets (TS), amorphous thermoplastics (TP) and semi-crystalline thermoplastics (TP).

composites are obtained by melt mixing in the same way than for amorphous matrix: the composite elaboration process can be rejected as a possible explanation of different percolation threshold values between thermoset/amorphous thermoplastics and semi-crystalline ones.

The main difference between these three types of polymers is the presence of an ordered phase in the semi-crystalline ones. Crystallites are too organized to allow the introduction of CNTs in this phase and then, interfere in the infinite cluster formation disturbing the CNTs percolating network.

Even if transcrystallinity can appear onto the surface of CNTs [39–41] perturbing the formation of the percolating path, the most reasonable explanation to the increase of p_c value in semi-crystalline polymers, is the increase of the percolating path length. The establishment of the conductive way need more charges and random dispersion of CNTs in the matrix is not optimized. The most comprehensible explanation to the increase of the ratio of required CNTs to reach percolation in case of semi-crystalline polymers is the increase of the tortuosity of the percolating path.

4. Conclusion

A solvent way and a melt mixing method, allowing the dispersion of DWCNTs in a semi-crystalline matrix, Polyamide 11, have been evaluated through the direct conductivity evolution. The electrical percolation threshold obtained by the first process is $p_c = 1$ wt.%. Conductor composites follow a scaling law. The linearity between the conductivity and the $p-p_c$ difference highlights a percolation phenomenon. In order to remove the use of a toxic solvent and to industrialize the process, a twin-screw extruder has also been used to elaborate composites. A percolation threshold value of 0.93 wt.% was obtained by optimizing the conductivity of the process parameters. The results exhibit again a percolation phenomenon which occurs in three dimensions. The palmitic acid, used as dispersant, allows to improve the dispersion state: p_c shifts from 0.93% to 0.73%. However, considering polyepoxy results detailed in the bibliography, further studies should lead to confirm the efficiency of such CNTs dispersant in a thermoplastic matrix. The influence of crystallites in the CNTs network formation has been brought up as a possible explanation to the systematic increase of electrical percolation threshold values in CNTs / semi-crystalline thermoplastic matrix composites.

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