Polymer nanocomposites based on functionalized carbon nanotubes: Improvement of dispersion, mixing and composite properties

J. Zhang[a, b], M. Sahli[a], J-C. Gelin[a]

a. Institut FEMTO-ST, Départ. Mécanique Appliquée, 24, chemin de l'épitaphe, Besançon France.
b. Institut FEMTO-ST, Départ. MN2S, 32 avenue de l'observatoire, 25000 Besançon France.

Résumé:

Le but principal de notre étude est de produire un matériau qui verrait ses propriétés mécanique et électriques améliorées par l'incorporation de NTC bien dispersés. Les NTC sont donc dans un premier temps mélangés à la matrice thermoplastique puis broyés de manière à obtenir différents mélanges de granulés chargés à 0.1, 1 et 10%wt. Des testes d'homogénéisations et d'observation microscopique ont été réalisés pour déterminer la qualité finale des mélanges obtenus et la variation de la distribution des NTC. Des informations supplémentaires ont été obtenues grâce à l'étude du comportement rhéologique à différentes températures comprise entre 180 à 210°C. Après injection, des éprouvettes de traction ont été obtenues à partir de ces mélanges de manière à pouvoir les caractériser sous sollicitations mécaniques.

Abstract:

The main purpose of this study is to produce the materials which have the mechanical and electrical properties improved by the incorporation of CNTs well dispersed. The CNTs are initially mixed with the thermoplastic matrix and then crushed so as to obtain different mixtures of pellets loaded at 0.1, 1 and 10wt%. Homogenization of the testes and microscopic observation were performed to determine the final quality of the resulting mixtures and variation in the distribution of CNTs. Additional information was obtained through the study of the rheological behavior at different temperatures between 180-210 °C. After injection molding process, the tensile specimens were obtained from these mixtures to be able to characterize under mechanical stress.

Mots clefs: nano-composites, nanotubes de carbone, polymères chargés, dispersion, électromécanique.

1 Introduction

In recent years, carbon nanotubes (CNTs) have been more and more widely used in various fields; As a novel material, the carbon nanotubes have attracted the large attention of researchers after its first discovery in 1991 [1] because of its remarkable characteristics. CNTs are allotropes of carbon made of graphite; they have a tubular shape with a diameter in nanometer scale, and a length in micrometer scale. Due to this structure, carbon nanotubes possess some excellent physical, mechanical, thermal and electrical properties [2-5], these properties make them a very unique material with a whole range of promising applications including in nanocomposite (material reinforcement), nanotube-based field emitters, chemical sensing, biomedical (drug delivery), and nano electromechanical system (NEMS).

Owing to the extremely high stiffness and strength, carbon nanotubes are usually used as a reinforcement material to improve the mechanical performance of composite; a lot of research works have been carried out to develop the CNTs/Polymers composites and investigate the evolution of their properties such as mechanical and rheological properties [6-8], it is discovered that a little content of CNTs can improve evidently the various physical properties of composites [9]. Moreover, through extensive research, one can also find that for the elaboration of CNTs/Polymers composites, the dispersion of carbon nanotubes is a key who can affect the final mechanical and electrical properties of nanocomposites [10]. However, actually the homogeneous dispersion of CNTs in polymer is difficult because of the inherently inert (hydrophobic) nature and tendency to agglomerate and entangle due to their size and shape [11], which lead to the decline of the composites mechanical and electrical properties; therefore, the research for improving the dispersion of CNTs is also very significant.

In this paper, we focused on the application of carbon nanotubes in the polymer based nano-composites systems (CNTs/Polymer). Firstly, we have investigated the dispersion of CNTs in different solution by using a particle size distribution analyser, and then the optimal solution has been used to realize CNTs/PP composite by melt mixing process; the rheological and mechanical properties of obtained nanocomposites have been investigated; the evaluation of homogenization for the composite have been executed by TGA (Thermogravimetric analysis). At last, the suitable dispersion of CNTs in polymer was realised and CNTs based homogenous nanocomposites were obtained with desired quality.

2 Materials and Methods

2.1 Materials

Commercially isotactic polypropylene (PP - EP548N) were supplied by Sabic company® with melt flow Index (MFI) = 11g/10min (230 ºC/2.16 kg) and density = 0.892g/mm^3. Multi-walled carbon nanotubes (MWNTs) - NC7000 were purchased from Nanocyl Company (Belgium) and were produced with purity higher than 90% and diameter range of 15-30 nm with a typical length of 1-10 um. The morphology of carbon nanotubes was observed by scanning electron microscopy (figure 1).

Table 1. Material characteristics of Polypropylene

Material	Polypropylene (PP), EP548N
density [g/mm^3]	0.892
Transition temperature [°C]	-10
Melting temperature [°C]	160
Thermal conductivity [W/mK]	0.14
Melt flow index (MFI) [g/10min]	[230°C/2.16kg]:11

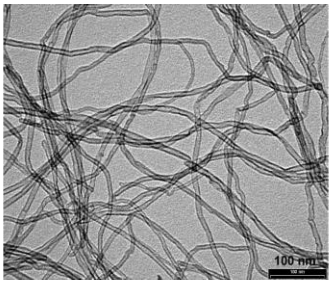

FIG. 1 – SEM Photo of carbon nanotubes – NC7000.

2.2 CNTs dispersion process

In this work, the used CNTs are powdery; they have been dried in an oven at 80 °C for 24h before using. Before mixing process, particle-size distributions of multi-walled CNTs were measured using a Horiba model LA-950V2 laser scattering particle size analyzer. The dried powders of multi-walled CNTs were dispersed either in distilled water containing a Sodium dodecyl sulfate (SDS dispersions) or in acetone (act), and with dishwashing liquids (v) added later. The conditions of dispersions were circulation speed (C), ultrasound frequency (US) and agitation speed (A).

2.3 Elaboration of CNTs/PP composites

All Prior to the preparation of nanocomposites, all of the materials were dried in an oven for 24h at 80ºC. PP/MWNT nanocomposites were carried out in a Brabender® mixer with a pair of rotor blades. The rotation speed and temperature of the mixing chamber were set at 30 rpm and 180 ºC, respectively, and blending continued for 30 min. During the mixing process, the PP was firstly introduced in the mixing chamber, then the solution containing CNTs was gradually introduced; because of the high mixing temperature, the water and all the other dispersion agents will be evaporated during the process. After pelletizing, blend granules were injection-molded into standard test specimen using Billon injection molding machine. The mould temperature was kept at 25°C and the barrel temperature ranged from 200 to 220 ºC. The injection pressure and injection speed 100bar and 40rpm, respectively.

3 Results and discussion

3.1 Analysis of particle size distribution

With the help of the particles size distribution analyzer, we can investigate the dispersion stat of CNTs in solution with different solvents. The figure 2 demonstrates the CNTs size distribution in four different solutions, we can observe that the measured CNTs median diameter and average diameter are respectively 8.80, 8.29, 43.10, 3.48µm and 9.38, 8.39, 49.28, 3.64µm in four solutions: dishwashing liquids, dispersions (SDS), acetone, and solvent mixed with acetone and dishwashing liquids. Comparing to the average diameter (1.5µm) provided by CNTs supplier, one can conclude that the solvent mixed with acetone and dishwashing liquids can improve effectively the dispersion of CNTs in the solution; the measured high values of CNTs average diameter in the other solutions are due to the agglomeration of CNTs, these values are actually the diameters of the agglomeration of CNTs.

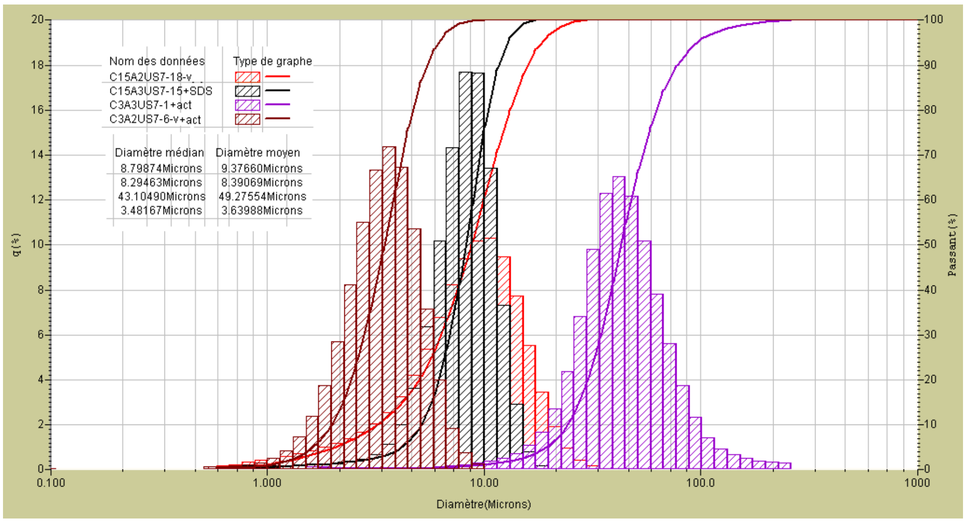

FIG. 2 – The CNTs particles size distribution in solution for different solvents.

3.2 Mixing characterization

The curves in figure 3 shows the final mixing torque variation of the PP and CNTs/PP composite (loading ratio between 0.1 to 10 wt.%), vs. mixing time. Uniform mixing is achieved when the torque reaches a steady state value. From the results, it reveals that: 1) adding the CNTs can increase the final mixing torque of the composites; 2) increasing the CNTs content can increase the final mixing torque, when the CNTs content is below to 1wt.%, there is no evident difference comparing to the pure PP; when the CNTs content is beyond 1wt.%, an evident increase of the mixing torque for the composite is observed.

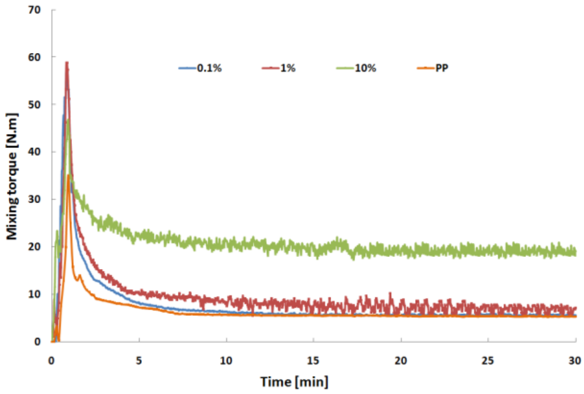

FIG. 3 – Mixing torque vs. time for PP and PP loaded CNTs at 180°C during 30 mins.

3.3 Homogeneities analysis

In order to investigate the homogeneity of the CNTs/PP composite, the electronic scanning microscopy (SEM) has been used to observe the dispersion state of the CNTs in the polypropylene. The result is illustrated in figure 4a, it can be observed that the carbon nanotubes have been almost dispersed homogenously in the polypropylene. Besides, the thermo gravimetric analysis (TGA) was also carried out to investigate composites homogeneity from 20°C to 500°C, the figure 4b demonstrated the TGA results of same nanocomposite for three tests, we can see that the TGA curves decreased from about 400°C, which means the beginning of the degradation for PP; it can be also found that the TGA curves of the tree tests are almost superimposed; thence one can conclude that the obtained composite by melt mixing process is homogenous.

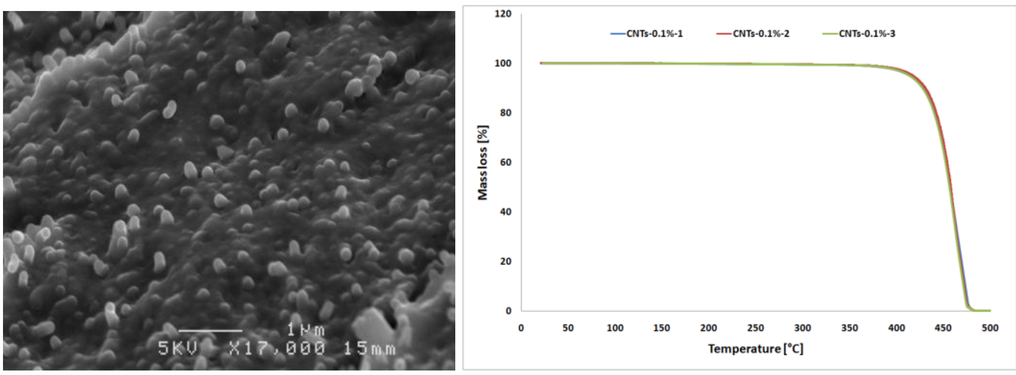

FIG. 4 – (a) SEM photo of the composite loaded with 10wt.% of CNTs, (b) mass loss of the nanocomposite loaded with 0.1 wt% of CNTs for three tests.

3.4 Rheological characterizations

In our work, the viscosity of CNTs/PP composites have been measured by a rheometer HAAKE MARS III with a cone-and-plate geometry of a diameter 35mm and an angle 2°. The test temperature is set from 180 to 210°C beyond the melting temperature of polypropylene and below its degradation temperature. The shear rate has been chosen in a range from 10^{-1} to $10^{2}s^{-1}$. Figure 5a shows the dependence of the melt shear viscosity of the PP loaded with 0.1wt.% CNTs on shear rate, it can be seen that the viscosity of CNTs/PP composite decreases with an increase of shear rate. It can also be observed that the melt shear viscosity decreases with a rise of temperature when shear rate is constant. The conclusion that increasing the temperature and shear rate can decrease the viscosity of CNTs/PP composite and improve their fluidity can be obtained.

3.5 Mechanical properties

For investigating the influence of the CNTs to the composites mechanical properties, some specimens with dumbbell shaped were obtained by injection molding with the mixed CNTs/PP composites. The results of tensile tests are shown in figure 5b, it describes the evolution of the tensile stress as a function of strain for PP and CNTs loaded PP. One can observe that the increasing of CNTs loading ratio leads to a rapid increase in the Young's modulus; for 1wt.% and 10 wt.% CNTs loading, the Young's modulus of composites increases respectively 13% and 40% comparing to the no-loaded PP. One conclusion is obtained that the addition of carbon nanotubes can significantly increase the mechanical properties of the final composites.

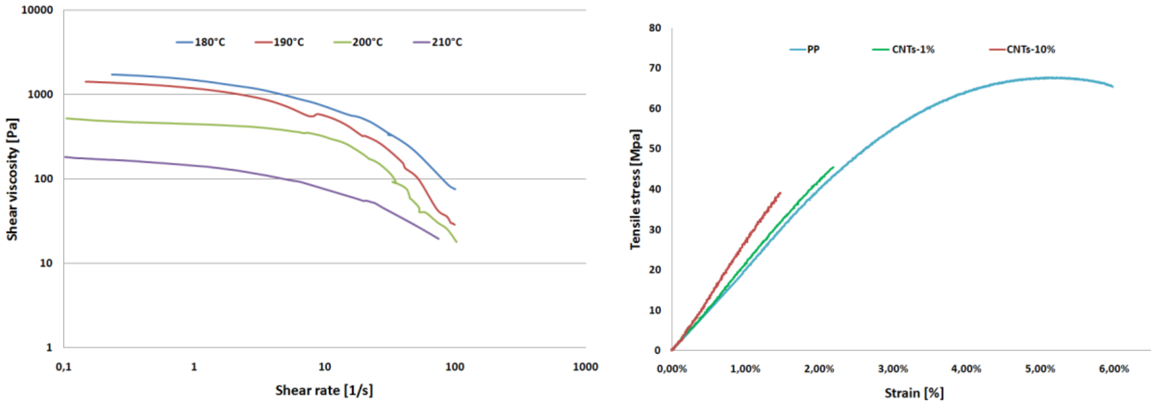

FIG. 5 – (a) The shear viscosity of PP loaded with 0.1wt% CNTs vs. shear rate at different temperature, (b) Evolution of tensile stress vs. strain for PP and CNTs loaded PP at ambient temperature.

4 Conclusion

In this work, the multi-walls carbon nanotubes (MWCNTs) have been mixed with polypropylene to realize the CNTs/PP composites. Firstly, the dispersion state of CNTs in different solutions has been investigated; the optimal solvent has been selected and used in the mixing process to improve the CNTs homogenous dispersion in PP. Then, the CNTs/PP composites with different loading ratio from 0.1 to 10.wt% have been obtained by melt mixing process; the homogeneity of elaborated composite has been evaluated by the micro observation and thermo gravimetric analysis; more over their rheological and mechanical properties were also characterized. Finally, the results indicate that the solvent mixed with acetone and dishwashing liquids can improve effectively the dispersion of CNTs in solution and the addition of CNTs in the polypropylene can effectively increase the polypropylenes mechanical property.

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