Controlled Dispersion of Carbon Nanotubes Wrapped in Amphiphilic Block Copolymers: Elaboration of Polymer Nanocomposite

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ABSTRACT

In this work, we aim to prepare polymer nanocomposites by the dispersion of multiwall carbon nanotube (MWCNT) in aqueous solution using amphiphilic block copolymers. First, we report our success in wrapping MWCNT with amphiphilic block copolymers in aqueous solution. We selected poly(ethylene oxide) (PEO) as the hydrophilic block because of its strong affinity for water and its easiness synthesis, while for hydrophobic block we used one of the following polymers: polyethylene, poly(propylene oxide), polythiophene. The dispersions were characterized by different techniques including optical microscopy (OM) and transmission electron microscopy (TEM), along with UV-visible adsorption and dynamic light scattering. Of particular interest, are our findings related to nanocomposites composed of the PEO or poly(methyl-methacrylate)-wrapped MWCNT. We investigated through of their rheological and electrical (percolation) behavior, about the structure and the dispersion of the nanoparticles in the polymer matrix. In terms of the rheological behavior, both dynamic modulus G' and complex viscosity η* increased especially at low frequencies as the CNT loading increases. We observed two rheological percolations. Electrical measurements showed one electrical percolation.

Keywords: multiwall carbon nanotube, amphiphilic block copolymers, polymer wrapping, nanocomposite, rheological measurement.

1 INTRODUCTION

The next generation of high-performance nanocomposites would certainly benefit from both the numerous properties of carbon nanotubes (CNT) and the processability of polymers [1]. However, the scope of CNT applications in practical devices has been hampered by poor dispersion and weak interfacial bonding with polymer matrices [2]. Therefore, effective methods for CNT dispersion and consequently for dispersion characterization are required for industrial applications.

In recent years, many groups worked on the dispersion of CNT using amphiphilic bloc copolymers [3; 4]. In this paper, we describe a noncovalent process for surface functionalization of MWCNT using amphiphilic block copolymers.

Our work shed the light on elaborating and characterization of nanocomposite with a well dispersed wrapped MWCNT inside to benefit from all the properties for the CNT [5].

2 EXPERIMENTAL

The MWCNT used in this study are Graphistrength® supplied by Arkema. The MWCNT synthetized by the chemical vapor deposition have an outer diameter within the range 12-20 nm and an initial average length between 1 and 10 μm.

2.1 Aqueous solution

CNT was stored in a wet form (90% of water) and mixed with an aqueous solution of amphiphilic block copolymers. The mixture were sonificated for 15 minutes (15 Watts) using an ultrasonic probe (Vibra Cell model 75186). To evaluate the solutions obtained with different concentrations of CNT and copolymers different techniques at different stages were used. First, we observe dispersions with optical microscopy and analyzed their adsorption using Varian® Cary 3E between 200 and 800 nm. The most effectively dispersed system was further characterized by TEM and dynamic light scattering. The TEM images were obtained by on HITACHI H7650. Dynamic light scattering measurements were performed to determine the dimension (length, diameter) of CNT in suspension according to the model describe by Badaire and Coll [6].

2.2 Nanocomposite

The dispersions MWCNT-copolymer were used to elaborate nanocomposites with a polymer matrix made of

POE (evaporation technique) or PMMA (melt mixing technique). Viscoelastic properties of nanocomposites were assessed with a strain controlled parallel-plate rheometer (AR 2000) equipped with aluminum disks of 25 mm in diameter. Measurements were performed with oscillatory shear method at 120°C and 230°C. In the linear viscoelastic domain a dynamic strain sweep was carried out to determine both dynamic moduli (G', G'') and complex viscosity (η*). The dielectric measurements were performed using a frequency response analysis system consisting of Solartron 1250, at room temperature; in a frequency domain ranging from 0.01 to 1000 Hz. Typically the sample thickness and diameter were respectively around 0.9 and 10 mm.

3 RESULTS AND DISCUSSION

3.1 Aqueous dispersion characterization

On the base of collected data, we could establish the influence on CNT dispersion quality of the molar mass of copolymers, the nature of the hydrophobic block and the length of hydrophilic block. For example, as shown in table 1, the decreased of molar mass of the copolymers corresponds to a significant improvement in dispersion. Further evidence for the dispersion state of the different solutions was provided by UV- visible adsorption as shown in figure 1; homogeneous dispersion absorb more because of a higher number of MWCNT dispersed in aqueous solution and the almost total absence of aggregate.

Block copolymers	Molar mass	Molar % of blocks	Dispersion state	
			1 week after	3 month after
PPO-POE	5200	27-73	No aggregation	
	10200	28-72	Presence of aggregation	

Table 1: Molar mass effect of block copolymers

Transmission electron microscopy (TEM) allows the polymer adsorbed onto the nanotubes to be observed. Figure 2 shows that in the presence of PPO-POE (Mn 5200), the average MWCNT diameter increases from 18nm to 25nm and that CNT are coated with an amorphous layer of copolymers.

Systems stabilized by PPO-POE are perfectly homogenous and can be characterized using depolarized light scattering. Considering the nanotubes as rigid rods and using the Broersma equations [7], we measure the depolarized component of the scattered light using dilute suspensions. From the corresponding diffusion coefficients, the average length L and the average diameter d can be calculated. We find L = 250 nm and d = 40 nm. The calculated diameter is larger than the diameter deduced from TEM observations on dried materials. This difference is not surprising since the polymer in solution is expected to be swollen. In addition, dynamic light scattering measures the hydrodynamic diameter which is always to some extent larger than the actual one.

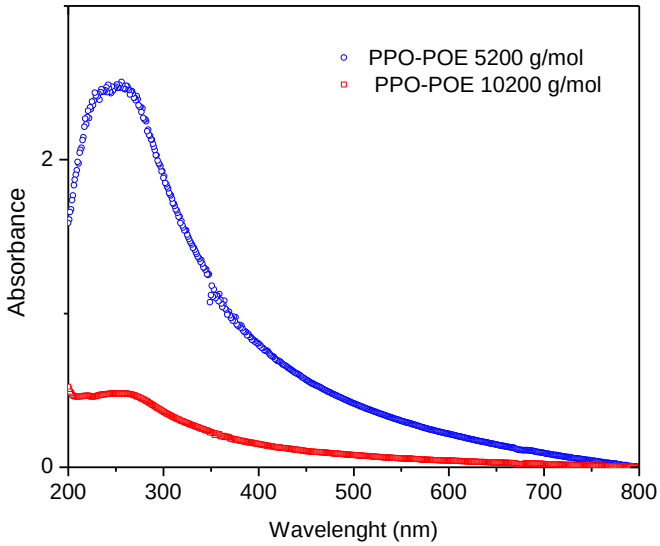

Figure 1: UV-visible absorption spectrum of PPO-POE wrapped MWCNT in water solution.

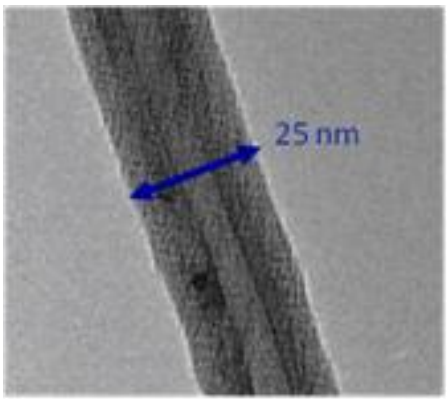

Figure 2: TEM image of MWCNT wrapped with PPO-POE, (average diameter 25 nm)

3.2 Polymer nanocomposite characterization

Rheological behavior of wrapped - MWCNT

Melt rheology is a powerful technique for studying dispersion of MWCNT in polymer matrix. The frequency dependence of the complex viscosity η* is shown in log-log plots in figure 3 for nanocomposite made with PEO and MWCNT wrapped with 10 wt. % PE-POE.

As the CNT loading increases, η* increases especially at low frequencies. In fact, we observe a progression from liquid-like to solid-like behavior, the Newtonian region disappeared and only the shear-thinning region remained [8]. The progression is attributed to a presence of a well organized network which is called percolation network of MWCNT [9; 10]. In order to observe clearly the rheological

transitions the reduced viscosity η^*_r, was plotted versus wrapped MWCNT content. η^*_r is defined as:

$$\eta_r^* = \frac{\eta^*}{\eta_0^*}$$

Where η^*_0 is the zero shear viscosity of the pure copolymer mixing polymer and calculated at 0.1 rad/ (figure 4). The plot clearly indicates two rheological percolations, the first one at 0.085% and the second one at 2%.

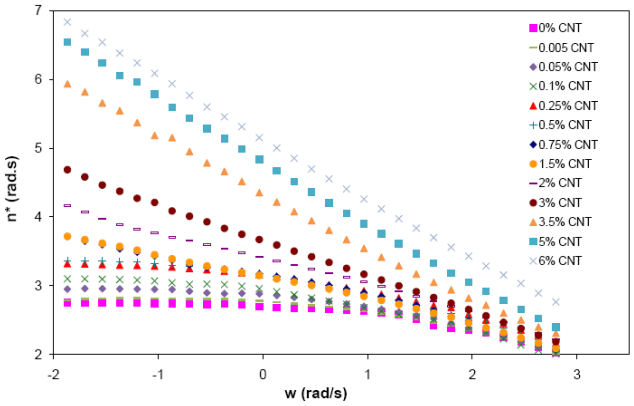

Figure 3: the complex viscosity η* as a function of frequency for different PE-POE wrapped MWCNT dispersed wrapped in PEO polymer matrix.

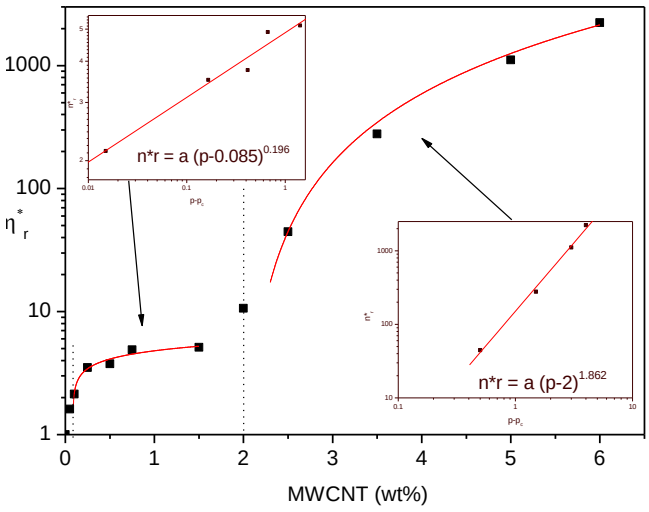

Figure 4: The reduce viscosity η*r versus MWCNT concentration calculated at 0.1 rad/s for PE-POE-MWCNT/POE nanocomposites.

Electrical behavior of wrapped MWCNT-

To understand the impact of MWCNT on the nanocomposite microstructure, we compare rheological behavior with electrical conductivity variation. The concentration of MWCNT in nanomposite has a strong impact on the electrical conductivity [11]. Figure 5 shows a percolation behavior with only one electrical percolation a 2%.

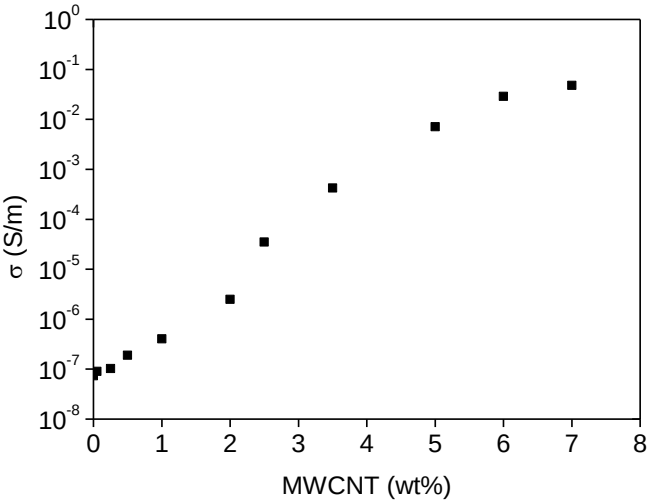

Figure 5: The conductivity σ versus MWCNT concentration for PE-POE-MWCNT/POE nanocomposites.

Discussion

The presence of two rheological percolations and only one electrical percolation can be explained by the presence of different types of interaction in the nanocomposite and as a result of the quality dispersion. On one hand, the viscosity increases with increasing the concentration of MWCNT in two phases. First, at low concentration, particle-polymer interactions predominate. Then, at higher concentration the particle-particle interactions appears (figure 6). As a result, we observe two rheological percolations. On the other hand, the change in conductivity (conduction) will not occur until we reached the particle-particle interaction domain; this is why we observe only one percolation threshold.

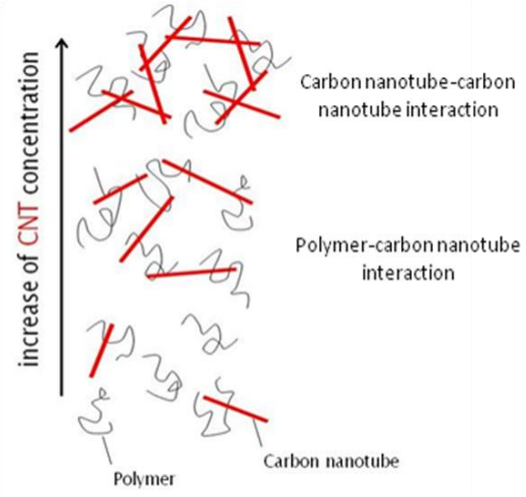

Figure 6: Schematic representation of MWCNT dispersion in polymer nanocomposites

Wrapping effect on nanocomposite

As shown in figure 6, the value of reduce viscosity of nanocomposite made with MWCNT without wrapping is greater, in the particle-particle interaction domain, than that of wrapped MWCNT. This can be explained by the level of dispersion of MWCNT in the PEO matrix. A better dispersion of MWCNT in the polymer matrix leads to a decrease of viscosity. Moreover, the tube-tube connections (frictions) are decreased by the copolymer layer.

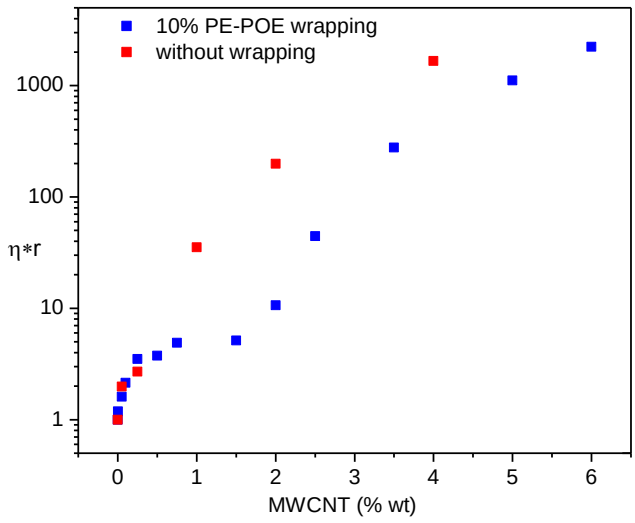

Figure 3: Comparison of the reduce viscosity η*r versus MWCNT concentration with or without copolymer wrapping

4 CONCLUSION

In summary, we have shown the efficiency of different amphiphilic block copolymers to wrap MWCNT. PEO-PE, PEO-PPO and POE-PT block copolymers were the most effective for the dispersion of MWCNT in aqueous phase. The wrapped MWCNT were well dispersed in water with PEO block exposed to the aqueous phase and PE or PPO or PT adsorbed to CNT. We also create PEO-wrapped MWCNT nanocomposites. Rheological and electrical analyses show the existence of two rheological percolations and one electrical percolation.

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