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Research Article

Measuring of Electrical Properties of MWNT-Reinforced PAN Nanocomposites

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Nano-web sheets of polyacrylonitrile (PAN) reinforced by carbon nanotubes (CNT) were prepared by electrospinning process. Multi wall nanotubes (MWNT) were dispersed mechanically by high shear mixing using a homogenizer device. It has been found that the spinning solution presented an electrical percolation threshold less than 0.5 wt.% of MWNT. Electrical volume and surface conductivity of the obtained nano-webs was studied by measuring the electrical volume resistance and surface resistance thanks to home-made plate electrodes. Scanning electron microscope (SEM) has been used to characterize the nano-web sheets produced. The average filament diameters range from 320 to 750 nm depending on the concentration of CNT and of PAN. From an electrical point of view, it has been observed that the electrical volume conductivity increases by about six orders of magnitude from 2×10^{-12} S/m for pristine PAN to 4×10^{-6} S/m for PAN charged by MWNT. Increasing the pressure on the specimen induces an exponential decrease of the volume resistivity while surface resistivity shows no significant changes, neither between pristine PAN and reinforced nano-webs, nor among reinforced nano-web in relation to MWNT concentration (in the limit of the study). This observed behavior is very interesting in the context of sensor developments.

1. Introduction

Carbon nanotubes (CNTs) are a new shape of carbon, first identified by Iijima in 1991 [1]. Since their discovery, they have attracted a great interest in research field and in industrial applications as well, owing to their magnificent thermal, electrical, and mechanical properties [2–4]. The electrical properties of carbon nanotubes are to a large extent derived from their 1D character and peculiar electronic structure of graphite [5]. In addition, they can carry the highest current density of any known material, measured as high as 10^9 A/cm^2 [6].

To employ CNTs as effective reinforcement in polymer nanocomposites, the proper dispersion and appropriate interfacial adhesion between the CNTs and polymer matrix have to be guaranteed [7]. There is a sizable volume of literature on the techniques developed for CNT dispersion in polymer matrix [8–11]. These techniques can be classified into two distinct approaches: the mechanical approach, such as ball milling, ball milling followed by ultrasonication, and high shear mixing, and the chemical approach designed to alter the surface energy of the solids. Chemical methods use surface functionalization of CNT to improve their chemical compatibility with the target medium (solvent or polymer solution/melt), that is, to enhance wetting or adhesion characteristics and reduce their tendency to agglomerate. Chemical treatments include boiling in acids (H_2SO_4 + HNO_3), soaking in concentrated acids under ultrasonication, and annealing at high temperature followed by boiling in concentrated acids [12, 13].

Their high aspect ratio makes carbon nanotubes capable of possessing a percolation threshold at low CNT loading in nanoweb [14]. Du et al. [15] have studied the influence of loading percentage of single-wall carbon nanotubes

(SWNTs) on the rheological properties of CNT-reinforced poly(methyl methacrylate), PMMA, nanocomposites. Their rheological and electrical measurements were performed on solid aligned and unaligned composite reinforced by CNT specimens prepared by the coagulation method. They found that the threshold of rheological percolation (0.12 wt.%) is significantly smaller than the threshold of electrical percolation (0.39 wt.%). Ounaies et al. [16] have investigated the electrical properties of SWNT-reinforced polyimide (aromatic colorless polyimide, CP2) composites prepared by in situ polymerization under sonication. The volume electrical conductivity of pristine CP2 polyimide was about 6.3×10^{-18} S/cm. A sharp increase of the volume conductivity value of solid samples was observed between 0.02 and 0.1 vol.% in solution, where the conductivity changed from 3×10^{-17} to 1.6×10^{-8} S/cm. Kota et al. [17] have studied the electrical and rheological percolation of MWNT-reinforced polystyrene composite prepared by a solvent evaporation method. They found that the volume conductivity of pure polystyrene is about 10^{-20} S/m, but adding MWNTs increased the volume conductivity of the composites by 20 orders of magnitude, approaching a value of about 1 S/m at 8 vol.% loading percentage of MWNTs in solution. Guo et al. [18] have investigated polyacrylonitrile (PAN)/carbon nanotube composites prepared by a solvent evaporation method and their reinforcement efficiency using different types of CNT, including single wall carbon nanotubes (SWNTs), double-wall carbon nanotubes (DWNTs), multiwall carbon nanotubes (MWNTs), and vapor-grown carbon nanofibers (VGCNFs). It was found that PAN/SWNT films at 20 wt.% exhibit the highest surface electrical conductivity among all composite films prepared with the same loading of CNT forms. Ra et al. [19] have researched the influence of MWNT on morphological and electrical conductivity of carbonized PAN nanofibers produced by electrospinning process. They discovered that the surface electrical conductivity of the carbonized PAN/MWNT aligned nanofiber sheets is highly anisotropic, and they pointed out that the percolation threshold was not reached, even at 10 wt.% of MWNT loading percentage.

Although an electrical percolation threshold volume of polymer/CNT composites can be reached for a low loading percentage of CNT, obtaining percolated nanocomposite of a polymer charged by CNTs with a very low concentration of treated carbon nanotubes is an interesting challenge.

Our study is focused on the use of electrospinning device in order to obtain a nanoweb of PAN charged with MWNT. Two different conductivities are measured: volume and surface ones. The fact that volume and surface electrical behaviors could be different will present advantages for sensor and actuator applications and developments.

2. Experimental

2.1. Materials. Polyacrylonitrile (PAN) with molecular weight $M_w = 150000\,\mathrm{g\cdot mol^{-1}}$ was supplied by Sigma-Aldrich (France). N,N-Dimethylformamide pure (DMF) (impurities less than 152 ppm in which water is less than 50 ppm) was purchased from Fisher Scientific (France). Purified multiwall carbon nanotubes was prepared by vapor deposition on a catalytic support, supplied by Arkema (France). The purity of MWNT is about 93% with a mean external diameter of 11 nm and a thickness of about 3.2 ± 1 nm.

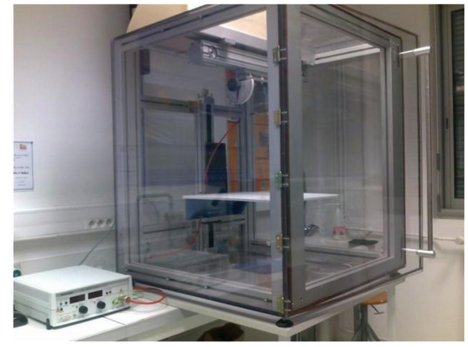


Figure 1: Electrospinning setup.

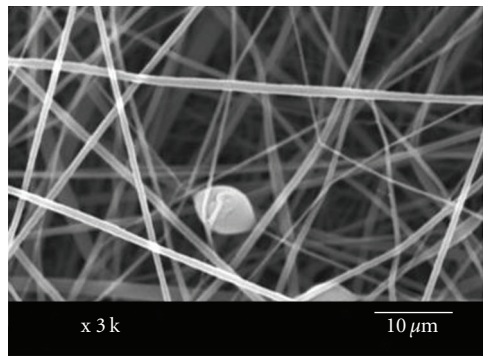
2.2. Protocol of Work

2.2.1. Preparing Solutions and Electrospinning Parameters. Six dispersions of multiwall carbon nanotubes in DMF with different loading percentages (0.2, 0.4, 0.5, 0.7, 1.0, and 1.5 wt.%) were prepared using high shear homogenizer from IKA (France) with the following conditions: 18 000 rpm during 15 min. In order to avoid overheating nanotubes due to high shear mixing, an aqueous bath was used for this purpose. Then, samples were ultrasonicated for 30 min at 50°C.

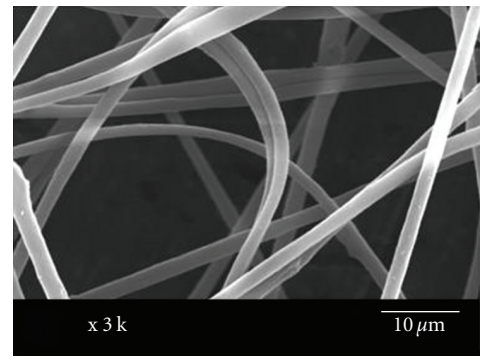
To prepare the charged colloids to be electrospun, proper quantities of PAN equivalent to a concentration of 10 wt.% were added to the treated dispersions of MWNTs in DMF. Samples were stirred for 24 h at 70°C to insure the homogeneity of the final spinning polymeric solutions.

The prepared solution was, then, electrospun by means of an electrospinning setup manufactured at LPMT (France), (see Figure 1). This setup is based on the vertical projection of polymeric solution, where this later is fed to a syringe using a pump located outside the electrospinning cabin. The electrospinning process is carried out between the tip of the needle, which is connected to the positive output of a high-voltage-supplier-type (Heinzinger) LNC 30 kV, and a grounded plat of copper covered with a foil of aluminum.

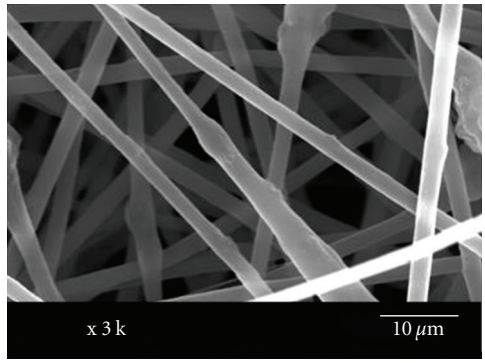
Table 1 gives the parameters of the electrospinning process. The sheets produced were characterized by scanning electron microscopy type (SEM, Hitachi S-2360N). Figure 2 shows a SEM micrograph of pristine PAN and CNT-reinforced PAN nanocomposites, respectively, charged with 0.2, 0.4, 0.5, 0.7, 1.0, and 1.5 wt.% of MWNTs. On these photos, 50 different fibers of each specimen were measured by using Photoshop 6.0 ME in order to evaluate their diameters.



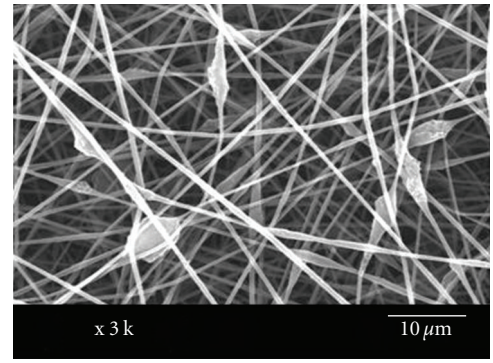
(a) 10% PAN



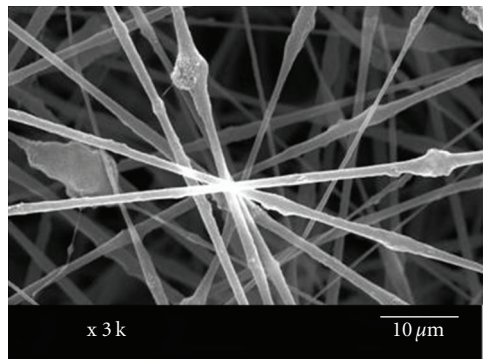
(b) 10% PAN + 0.2 wt.% MWNTs



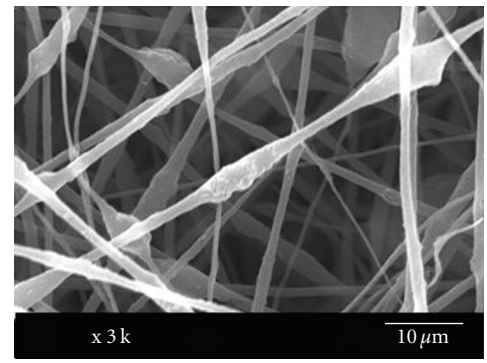
(c) 10% PAN + 0.4 wt.% MWNTs



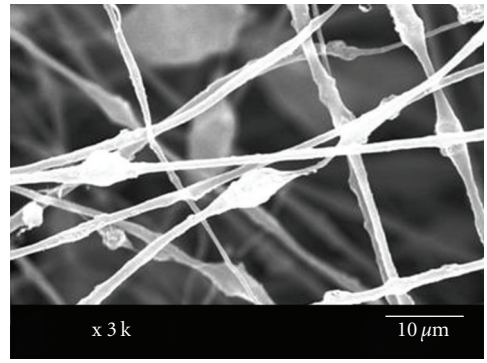
(d) 10% PAN + 0.5 wt.% MWNTs



(e) 10% PAN + 0.7 wt.% MWNTs



(f) 10% PAN + 1.0 wt.% MWNTs



(g) 10% PAN + 1.5 wt.% MWNTs

Figure 2: SEM micrograph of (a) 10% PAN and CNT-reinforced PAN electrospun nanocomposites with (b) 0.2 wt.%, (c) 0.4 wt.%, (d) 0.5 wt.%, (e) 0.7 wt.%, (f) 1.0 wt.%, and (g) 1.5 wt.% loading percentage of MWNTs.

Table 1: Parameters of electrospinning process.

	10% PAN	10% PAN 0.2% CNT	10% PAN 0.4% CNT	10% PAN 0.5% CNT	10% PAN 0.7% CNT	10% PAN 1.0% CNT	10% PAN 1.5% CNT
Voltage (kV)	11	12	12.5	11	14	14	12
Gap needle collector (cm)	30	30	30	30	30	30	30
Feed rate (mL/h)	0.354	0.212	0.212	0.283	0.424	0.424	0.283
Period of spinning (min)	60	60	60	60	60	60	60

2.2.2. Preparing Electrospun Specimens for Resistance Measurements. A set of three specimens of each electrospun sheet was cut in dimensions of 2×2 cm for measuring the volume resistance, and another set composed of three specimens was also cut in dimensions of 2×6 cm for measuring the surface resistance. Surface and volume resistance were measured up to the American standard ASTM D 257-61 by using an assembly of plate electrodes. Table 2 illustrates the parameters of electrical resistance measurements. An assembly of loads was also used to study the effect of compression on resistivity, as shown in Figure 3.

3. Results and Discussion

3.1. Influence of CNT on the Morphology of Nanofibers. Electrospun fibers of 10% PAN have a mean diameter of 568 nm, and reinforced fibers have average diameters that range from 325 to 795 depending on the percentage of MWNTs, as shown in Figure 4. It can be assumed that adding CNT will increase the conductivity of the solution that leads to accelerating the jet and therefore reduces the diameter of filaments. In the case of 0.5 wt.% MWNTs, this phenomenon is observed. With higher MWNT concentrations, this behavior comes from a competing effect between the previous described phenomenon and the size of MWNT aggregates that still are not dispersed and generate coarse diameter.

3.2. Percolation Threshold of Reinforced Nanocomposites and the Influence of CNT on Volume Resistivity of Nanocomposites. Figure 5 illustrates the relationship of electrical volume conductivity in S/m of pristine PAN (at 0% loading percentage of CNT) and CNT-reinforced PAN nanocomposites. According to the results obtained, it is obvious that CNT-reinforced PAN nanofibers have a clear percolation threshold between 0.4 and 0.5 wt.% loading percent of carbon nanotubes. The volume conductivity of less than 0.5 wt.% shows no significant change compared to the initial status, that is, PAN nanofibers with no reinforcement, while the conductivity after adding 0.5 wt.% or more increases by five orders of magnitude from 1.85×10^{-11} S/m at loading percent of 0.4 wt.% of CNT to 4.15×10^{-6} S/m at 0.5 wt.% of CNT. This means that the electrical state of the material (nanocomposite) has changed from an insulative material (where conductivity equals or less than 1×10^{-11} S) into static dissipative material (where conductivity is between 1×10^{-4} S and 1×10^{-11} S) [20].

On the other hand, plotting the volume resistivity values of the mentioned nanocomposites after percolation threshold, as shown in Figure 6, reveals that the volume resistivity of the nanocomposite decreases exponentially when a load is applied. It can be concluded from this result that these nanocomposites can be used as pressure sensors and could be integrated into an electrical circuit in the context of smart textile applications.

3.3. Influence of CNT on Surface Resistivity of Nanocomposites. Figure 7 shows a comparison of surface electrical resistivity of the 7 produced nanowebs. It can be noted that there is no significant change in the values of surface resistivity among all specimens; that is, both pristine PAN electrospun fibers and CNT-reinforced fibers have surface resistivities of the same magnitude (teraohm). On the other hand, there is no significant change in surface resistivity in relation to the applied load (Figure 7).

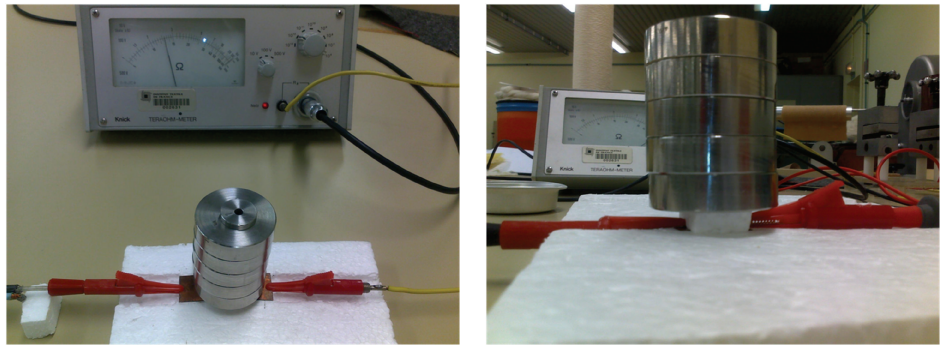
These results can be explained by two approaches: the first one is "electron hopping or tunneling," and the second one is "the percolation threshold theory." When the percolation threshold is reached, a conducting path of conclusions is formed, where a distinct distance between fillers is reached. Then, when the fillers are close enough but are not in direct physical contact, hopping or even tunneling [21] occurs. According to the percolation threshold, electrical conductivity σ_{dc} is fitted by

$$\sigma_{dc} \propto (P - P_c)^{\mu}, \quad P > P_c, \tag{1}$$

where P is the MWNT mass fraction, P_c is the threshold of electrical conductivity percolation, and μ is the critical exponent.

Concerning the conductivity of percolation clusters, there is no current below P_c that passes in the volume direction of the sample, while σ_{dc} increases exponentially by the low power indicated in formula (1). Within this mechanism, carbon nanotubes should be in direct contact so that they form a continuous conducting path [22–24].

Increasing the applied load decreases the distance between fibers more and more, and taking into consideration that carbon nanotubes exist both inside and outside of the surface of fiber [25], this enhances the formation of conducting networks which states the presence of direct contact between embedded MWNTs. In this case, the percolation theory is dominant.



(a) (b)

Figure 3: Setup for measuring the surface (a) and volume (b) resistances in relation to applied load.

Table 2: Parameters of electrical resistance measurements.

Shape and dimensions of specimen	Type and dimensions of electrodes	Conditioning of specimen	Test conditions	Applied voltage	Time of electrification
Square 2 × 2 cm Rectangular 2 × 6 cm	Plates of copper metalized by gold 2 × 2 cm	No cleaning No predrying 24 h of conditioning	20 ± 2°C 60 ± 2% RH	Surface resistance: 500 V Volume resistance: 10 V	2 min

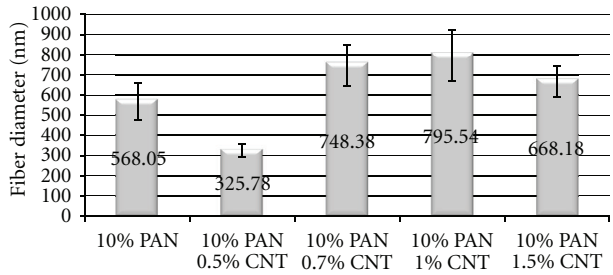


Figure 4: Fiber average diameters of CNT-reinforced PAN nanocomposites.

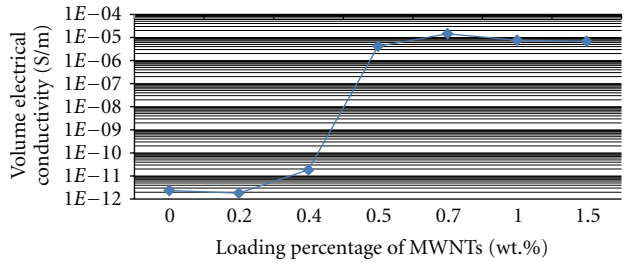


Figure 5: Volume conductivity of 10% CNT-reinforced PAN composite with different loading percentage of MWNTs.

Figure 6 reveals that the curves reached asymptotical values when the applied load is greater than 65 g (i.e., 2.5 kPa, where the active area of specimen is about 2.56 cm^2).

This means that a saturation value of percolated charges network has been attained. These results offered the possibility of using this nanocomposite of CNT-reinforced PAN (after percolation value) as a pressure sensor for low pressure applications.

The surface resistivity behavior can be explained as follows.

The carbon nanotubes are distributed inside and on the surface of the fiber [25]. In this case, the percolation threshold (P_c) for surface conductivity has not been reached; therefore, within the theory of percolation theory, the conducted network path is not formed.

4. Conclusion

Nanowebs of PAN nanofibers reinforced with MWNTs were produced by means of electrospinning. It was found that adding carbon nanotubes will reduce the diameter of nanofibers when they are well dispersed and when all process and ambience parameters are fully controlled. The reinforced nanofibers obtained possess an electrical volume percolation threshold at very low loading percentage of MWNTs corresponding to 0.5 wt.%. Simultaneously, the surface electrical percolation threshold has not been reached even for a concentration of 1.5 wt.%. An exponential relationship between the mechanical pressure applied and the volume conductivity was observed experimentally by assuming that the electrospun nanoweb of PAN reinforced with MWNTs could be used as a pressure sensor.

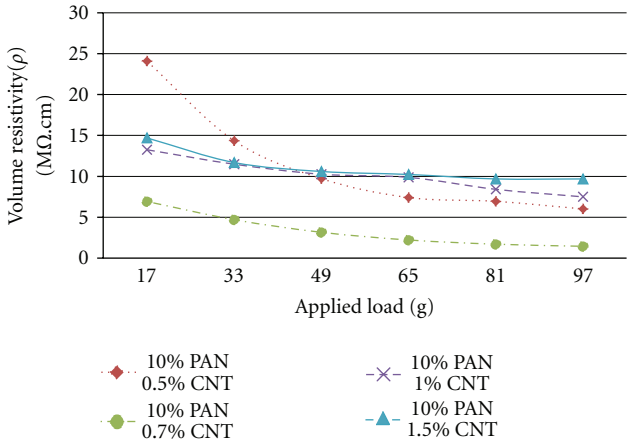


Figure 6: Volume resistivity of 10% CNT-reinforced PAN composite with different (wt) loading percentage of MWNTs after percolation threshold at 0.5 wt.%.

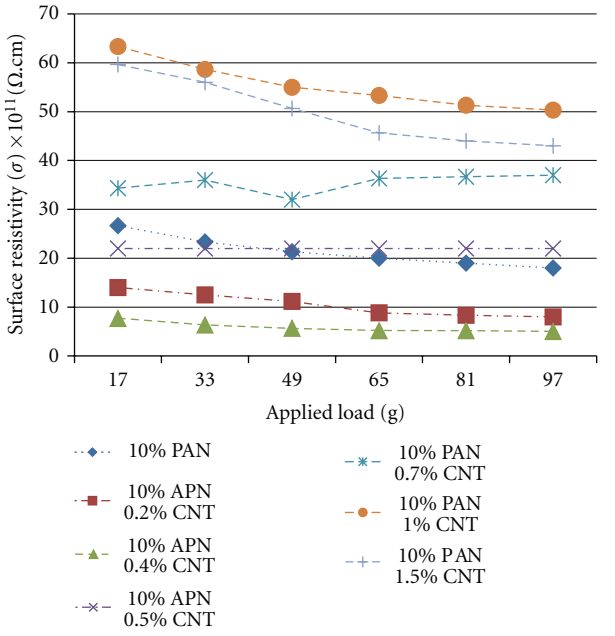


Figure 7: Surface resistivity of 10% CNT-reinforced PAN composite.

Perspectives

Additional characterization techniques, like TEM, Raman spectroscopy, and so forth, will be used quantitatively and qualitatively to characterize the nanowebs produced. In addition, a new device that enhances the distribution of carbon nanotubes on the surface of the fibers can be envisaged. Moreover, the increase of the MWNT concentration in order to obtain percolation threshold of the surface conductivity has to be implemented.

Acknowledgments

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