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# POLYACRYLONITRILE–MWCNT HYBRIDS OBTAINED BY FREE RADICAL POLYMERIZATION IN MINIEMULSIONS

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## Abstract

Polyacrylonitrile (PAN) and poly(acrylonitrile-co-vinylcarbazole) (PAN-VK) hybrids were obtained in presence of multiwalled carbon nanotubes (MWCNT) by a one-step free radical polymerization in miniemulsions. MWCNTs, in an unmodified state, as well as MWCNTs functionalized with maleic anhydride or monoethoxy dimethylvinyl silane, were used. The presence of MWCNT increased the molecular weights of the polymers and affected the polydispersity index. The polymers obtained next to the MWCNT showed a high value in their crystallinity index (33 %). The method was proven as an efficient route for dispersing nanotubes in the polymer matrix. Functionalized MWCNTs restrict the transfer reaction to areas next to the walls of the nanotubes during the polymerization and increase the dispersability in the final polymer matrix. MWCNT –polymer hybrids showed perspectives in membrane fabrication, as well as a specific profile, for carbon fibers precursors (with advantages in the three main stages: cyclization, dehydrogenation and decomposition).

**Keywords:** polyacrylonitrile; miniemulsion polymerization; multiwalled carbon nanotubes; grafted nanotubes; membranes

## Introduction

The use of carbon nanotube (CNT) nanofillers has gained importance over the last five years in the development of polymer nanocomposites for use in various applications that require improvement in their physical properties, i.e., mechanical, electrical, and thermal properties [1-12]. The aforementioned review papers discussed a wide spectrum of published data and focused on how to clarify the optimal dispersion in the polymer matrix, including various concentrations and techniques, in order to determine the final properties of the composite. Following on the publication dynamics of nanocomposites with CNT, reveals a higher rate in comparison with other nanofillers (3D, 2D). CNT are used as reinforcing agents due to their maximal available aspect ratio (L/D) being the largest among the known nanofillers [1, 4]. The differences between the polarities of the CNTs and the polymer matrix have been shown, through research, to be the key factor in achieving good composite properties. Van der Waals forces between the CNTs promote a high degree of association in the final aggregation of the elementary particles. The advanced dispersion in the polymer matrix is very difficult because of the enthalpic phenomena induced by the unfavorable interactions between the polymer and the CNTs [9]. In a recent study, Grady [9] identified and described the major techniques for obtaining polymer-CNT nanocomposites: dispersion-reaction, dissolution-dispersion-precipitation, dispersion-dispersion-precipitation, melt-powder mixing, and fluid mixing. The first method, a dispersion-reaction, seems to eliminate the complex interactions between the CNTs and the polymer in the synthesis stage [9]. Monomers, with a low viscosity, can assure a good dispersion of CNTs in the initial stage. This dispersion can be improved by introducing a supplementary ultrasonication stage [9]. In this context, the miniemulsion polymerization technique possesses all of the desired and favorable conditions [13, 14]. Monomer particles, in fine droplets, are stabilized by a surfactant and a hydrophobic agent in nanoreactors for the radical polymerization to take place. The presence of the hydrophobic agent, i.e., hexadecane, assures the stability of the monomer particles over the Oswald ripening side effects seen in classical emulsions. The hydrophobic agent influence is also considered significant in the stabilization of the monomer-polymer particles through the polymerization process to the final conversion. These features, previously developed in miniemulsions, are useful for obtaining polymer-CNT composites which involve monomers compatible with the forming polymer: polystyrene (PSt) [15-18], polybutylacrylate [19], and copolymers styrene-isoprene [20]. Polymerization kinetics for miniemulsion polymerization are regarded as pseudo-bulk kinetics, with the reaction rates being influenced by the surfactant type (non-ionic, anionic, or cationic) [19].

The main objectives of the present work are to investigate a new approach for the synthesis of PAN-MWCNT hybrids and to obtain specific correlations between the structure of the hybrids and their physical properties. The polymer PAN was chosen due its use in a wide variety of industrial applications, especially in the field of synthetic fibers [21]. The specificity of PAN synthesis lies in the incompatibility in solubility between the acrylonitrile (AN) and the final polymer. That is the reason why the indicated method for this synthesis in an aqueous system is miniemulsion polymerization [22]. By stabilizing the monomer droplets through the miniemulsion, the diffusion of AN becomes secondary as these nanoreactors maintain a pseudo-steady interface from the very beginning of the polymerization process and form the reaction loci for the radical polymerization [22]. The partitioning of the polymerization system

into droplets in the presence of CNT is one of the most challenging aspects of the miniemulsion technique, especially with the interaction between the monomer and the nanofillers in general [23]. To the best of our knowledge, AN polymerization conducted by the miniemulsion technique, in the presence of CNTs, was not investigated until now. There are papers that report AN polymerization in presence of CNT nanofillers utilizing different techniques that include soap free emulsion [24] and deposition polymerization under ultrasonication (US) [25]. To increase the probability of CNT dispersion, MWCNTs that were used were either purified or functionalized with small molecular compounds such as ethoxydimethylvinyl silane (VMe2TES) and maleic anhydride (MA). In this paper, we present new results involving AN polymerization in the presence of vinylcarbazole (VK), which is a comonomer intended to enhance the interaction with the CNTs [26]. The final nanocomposites were analyzed by dynamic light scattering (DLS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and gel permeation chromatography (GPC). Several correlations were investigated between the physical properties and the concentration and nature of the MWCNTs. These correlations could be useful for future applications with new PAN-CNT hybrids used as carbon fiber precursors [27-35]. Hybrids that were analyzed in previous papers [28-35] were obtained by spinning a PAN solution that was mixed with CNT, previously described as the dissolution-dispersion-precipitation technique [9]. Ensuring the advanced dispersion of the MWCNTs by miniemulsion polymerization could increase the final properties of the carbon fibers obtained after the stabilization and carbonization of the PAN-CNT hybrids. These effects have been already emphasized for SWCNT [28,30,32,34,35] and for MWCNT [28,29,31-33] from the hybrids obtained by solution spinning.

## **Experimental**

### *Materials*

AN was purified by rectification and preserved at a low temperature (2 °C) before polymerization. Sodium dodecylbenzenesulfonate (DBS) (Fluka), maleic anhydride (MA) (Fluka), 9-Vinylcarbazole (VK) (Aldrich), monoethoxydimethylvinyl silane (VMe2TES) (Alfa Aesar),  $\alpha,\alpha'$ -azoisobutyronitrile (AIBN) (Fluka), N,N-dimethylformamide (DMF) (Fluka), toluene (Chimreactiv), and hexadecane (Merck) are commercial products that were used as received. MWCNTs that were purified and functionalized with OH- (MWCNT-OH) were obtained from FutureCarbon GmbH and used as received.

### *Synthesis Methods*

#### *MWCNT functionalizing*

In a three-neck glass flask equipped with a reflux condenser and a mechanical stirrer operating at 500 rpm, 200 ml of toluene was introduced after drying on molecular sieves and nitrogen purging. 5 g of MWCNT-OH were added to the flask under nitrogen bubbling, followed by either 0.7 g of MA or 1.4 ml VMe2TES. Ten minutes after homogenization, the temperature was increased to 60 °C, where it remained constant for the entire reaction time (5 hours). The resulted samples (labeled MWCNT-MA for the nanotubes functionalized with MA, respectively MWCNT-VMe2TES for the nanotubes functionalized with VMe2TES) were filtered, dried under vacuum and then analyzed by TGA.

#### *PAN-MWCNT by AN synthesis through miniemulsion polymerization*

To achieve the miniemulsion dispersion, two homogenous phases were prepared. The first phase, phase A, consisted of the monomer (100 g AN, 0 or 1 g VK) and a dissolved initiator (5 g AIBN). –The second phase, phase B, contained the surfactant solution in water (2 g DBS, 400.3 g H<sub>2</sub>O) with 1 g of CNT (MWCNT or functionalized MWCNT). Phase B was obtained by US (35 000 Joules) (Cole Parmer ultrasonic processor) and hydrophobic agent (4.17 g hexadecane) adding drop by drop under mechanical stirring (600 rpm). Phase A was added to phase B under intense mechanical stirring (800 rpm; 30 min.) in order to promote creaming and the formulation of the miniemulsions. The entire mixture was then sonicated (265 000 Joules and 89% Amplitude). All of the solution preparation and mixing was conducted in ice baths, bubbling with nitrogen and monitored by a temperature probe controller, in order to overcome the heat from the US treatments. The final miniemulsion (AB) was loaded on a glass autoclave (ARTER VMSRD30F) equipped with a reflux condenser, a thermometer, a heating jacket with thermostat, a gas purging circuit and mechanical stirrer, and bubbled with nitrogen. The polymerization was conducted under nitrogen atmosphere at 250 rpm and 65 °C for 5 hours. The final grey homogenous latex was cooled down with water that was directly pumped into the autoclave jacket. A small part of the latex was isolated for analysis, and the rest was treated with a 2/3 volume ratio of 1N HCl to the solution under intense mechanical stirring (1000 rpm) in order to remove the surfactant. The dispersion was washed and filtered several times. The polymer drying was performed in normal atmosphere and the final drying was performed in the oven under vacuum.

#### *PAN-MWCNT obtained from physical mixtures*

Physical mixtures of the MWCNT-PAN were also prepared by the miniemulsion polymerization of PAN (s.36) and MWCNT 1% wt. In a round flask equipped with magnetic stirrer, 0.5 g of PAN was added to 25 ml of DMF. The dispersion was kept stirred at 300 rpm at 60 °C for 3 hours. Then, 0.005 g of MWCNT was added to the solution. After a US treatment (sonication bath) of 1 hour at 60 °C, the mixture was precipitated through the addition of 300 ml

distilled water under constant stirring. The product was then washed with acetone and dried in a vacuum oven at 60 °C. The final hybrid (s.24-Table 1) was then analyzed thermogravimetrically.

### Methods of Analysis

The distribution of the particle dimensions and the average diameter of the particles was measured by dynamic light scattering (DLS) with a Malvern-Zetasizer Nano ZS instrument. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were accomplished with Q5000 and Q2000 TA Instruments, respectively, in a nitrogen atmosphere, with a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns in the Bragg-Brentano system (by reflection) were obtained using a DRON UM 1 with data acquisition interface and Co K $\alpha$  ( $\lambda=1.79021$  Å) radiation filtered with Fe for the removal of the K $\beta$  component. For the interplane distance ( $d_{hkl}$ ) calculation, the Bragg relation,  $d_{hkl}=\lambda/2\sin\theta$ , was used. Crystalline dimensions were determined by the Sherrer relation:  $D_{hkl}=k\lambda/\beta_c\cos\theta$ ,  $k=1$  and  $\beta_c$  is the integrated value of the half-width corresponding to the instrumental  $\beta_i$  according to the equation  $\beta_c=\sqrt{(\beta^2-\beta_i^2)}$ . Images of the membrane were taken with a scanning electron microscope (LEO Gemini 1550 VP from Zeiss). The sample preparation for the cross-sectional analysis was conducted under cryogenic conditions. The membrane samples were sputtered with a very thin layer of Au/Pd. Gel permeation chromatography (GPC) measurements were performed using a Waters instrument. The instrument is equipped with four PSS columns, with a porosity range from 102 to 105 Å, coupled with a differential refractometer (WatersTM 2410 RI) and a UV detector (WatersTM 486, at 254 nm). The samples were dissolved in N,N'dimethyl acetamide and measured at 30°C. The results were calibrated with polystyrene standards. Transmission electron microscope (TEM) images were obtained using a FEI Tecnai F20 operated at 200 kV. The separated dry polymer/polymer-MWCNT bulk phase from polymerization was prepared as film from DMF, then sliced in 50nm sections at ultramicrotome and analyzed in bright field.

### Results and Discussion

#### MWCNT-OH functionalization

To confirm that MWCNTs were functionalized, the final products were analyzed by TGA in a nitrogen atmosphere (Figure 1). MWCNT-OH showed a small weight loss (0.78%) in the temperature interval 0-500 °C, which is attributed to the loss of water from the hydroxyl functional group. For the MWCNTs that were functionalized by VMe2TES (MWCNT-VMe2TES), the weight loss increases notably (2.6% wt.) for the same temperature interval, and a maximum decomposition temperature of 150 °C is observed. The functionalization of the MWCNTs with MA (MWCNT-MA) demonstrated an even more pronounced weight loss over the same temperature interval, 4.2%, and a maximum decomposition temperature (Tmax) of 139.8 °C was observed. It should be noted that MA adds a larger amount of mass onto the unit, which leads to an increased susceptibility to temperature, as seen by the decrease in Tmax. The TGA profiles indicate the capacity of MWCNT initially functionalized with OH groups to further react with other functionalizations, seen by the esterification reaction with MA and the etherification reaction with VMe2TES.

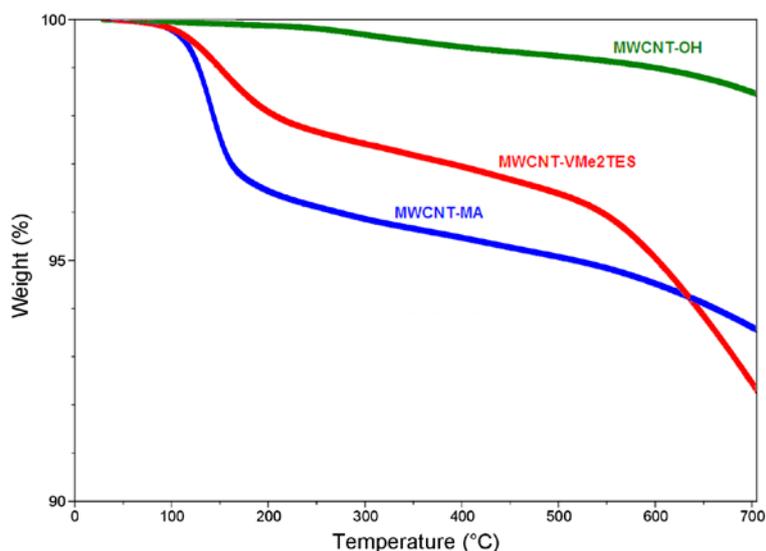


Figure 1 TGA profiles for MWCNT-OH and their functional derivatives obtained by MA esterification (MWCNT-MA), respectively etherification VMe2TES (MWCNT-VMe2TES)

The functionalization percent was calculated based on the hypothesis that MWCNT-OH weight loss is the only result of the organic group elimination during the decomposition stage. Based on the molar weights of the units the approximate number of sites able to be condensed was calculated. In the case of MWCNT-VMe2TES and MWCNT-MA the increase in weight loss (in comparison with the initial MWCNT-OH), was attributed to the increase in organic amount respectively to the units able to condense (from MA and VMe2TES). Then based on the initial units (and molar weight of the new attached units) the functionalization percent was calculated to 60 % for the VMe2TES etherification

and 80% for the MA esterification. The TGA data, shown in Figure 1, is in good agreement with other studies for the functionalization with MA [36-38]. However, no comparisons can be drawn with the functionalization with monoalcoxysilane due to the lack of reported results until now.

#### *PAN and PAN-VK MWCNT nanocomposites*

The synthesis conditions previously described in this manuscript represent a system which was able to offer the highest degree of stability in the initial state after emulsification (mechanical stirring and US). The mixture was homogeneous, as shown in Figure 2 A, with an intense dark color. After the polymerization occurs, the color of the solution changes from black to a light grey, as seen in Figures 2B and C. The final dispersions are highly concentrated with solids without any separations in phase, and with a color intensity that is dependent on the amount of MWCNT used in the synthesis. Several miniemulsion systems were created by varying the MWCNT concentration and the type as well as the co-monomer (VK) amount with 1:1 wt. ratio with the MWCNTs; these systems are described in Table 1. Miniemulsion polymerization was not the only polymerization method studied using water as a continuous media. Several attempts at dispersion polymerization, as well as with suspension polymerization, were conducted. These polymerization systems were formulated either according to the specific interactions described in literature and/or by the geometrical volume necessary for MWCNT encapsulation in the polymer particles. These systems included the following components and methodologies: peroxydisulfates alone or in combination with peroxides, single peroxides, redox systems, precipitation polymerization, in situ generated solid stabilizers for suspension polymerization, fatty co-stabilizers (to increase the hydrophobic interaction between the final polymer and the CNT, butyl stearate, small amounts of stabilizers with segments able to offer  $\pi$ - $\pi$  interactions with the CNTs (i.e., DBS below and above critical micelle concentration), wave breaker and stirring adaptations, and different polymerization temperatures, just to name a few. All of the aforementioned components and methodologies exhibited a severe phase separation in the final stage where the MWCNTs were drastically rejected, seen as a bright white polymer and dark black aggregated MWCNTs, even if the initial polymerization system proved a certain stability and homogeneity under stirring. There are three main reasons why all of the aforementioned components and methodologies failed: i) AN water solubility, ii) the incompatibility between the forming PAN and the CNTs and iii) the temperature control of a highly exothermic reaction system is strongly dependent on the cooling capacity available. The miniemulsion dispersion was proven to be the only viable solution to synthesize PAN-CNT in water dispersion. By conducting the polymerization in the miniemulsion, the reaction was able to be performed at 65 °C with a negligible exothermic effect.

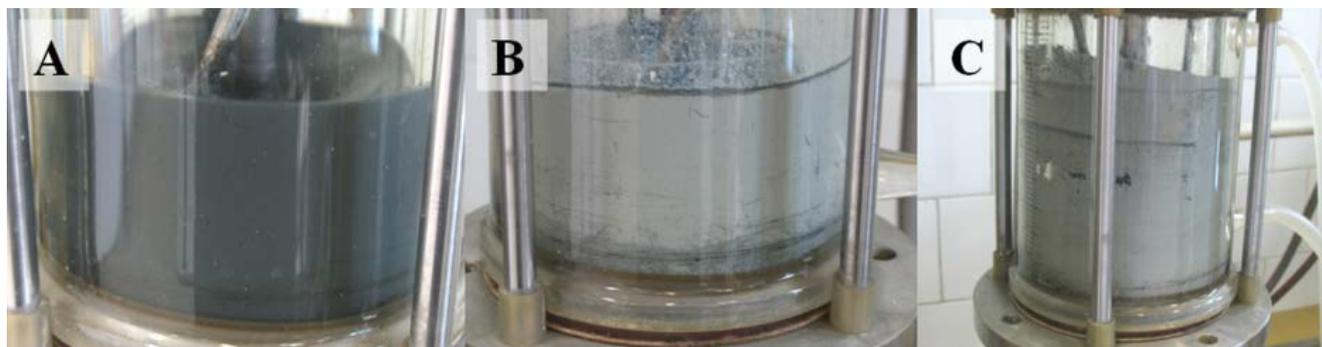


Figure 2 Appearance of the reaction homogeneity initially (before polymerization) (A) and after polymerization reaction of AN in miniemulsion (B), AN with VK copolymerization (C) (all samples with 0.2% wt. MWCNT).

To verify the homogeneity of the composites and the PAN grafted onto the MWCNTs, purified samples were solubilized in DMF (0.2% wt.). The appearance of the solutions, shown in Figure 3, with their degree of transparency and stability over time, is indicative of a good dispersion of CNT in the associated hybrid solutions, where the intensity of the color of the solution increases with the concentration of the nanofiller. Solution stability over time (over 3 months in this case) can be considered a first indication for the polymer grafting onto the MWCNTs. The grafted copolymers that were formed by radical polymerization in DMF solutions, similar to what has been described above, have been observed in previous studies (Donescu et al unpublished study). In the same study, it was observed that the physical mixtures of PAN and CNT in the DMF solution cause a precipitation of the nanofiller. Moreover, the study also demonstrated that with AN solution polymerization, the molecular weights of the polymer decrease with the corresponding increase in MWCNT concentration. By miniemulsion polymerization (Table 1) the monotone modification of the molecular weights with respect to MWCNT concentration is not happening.

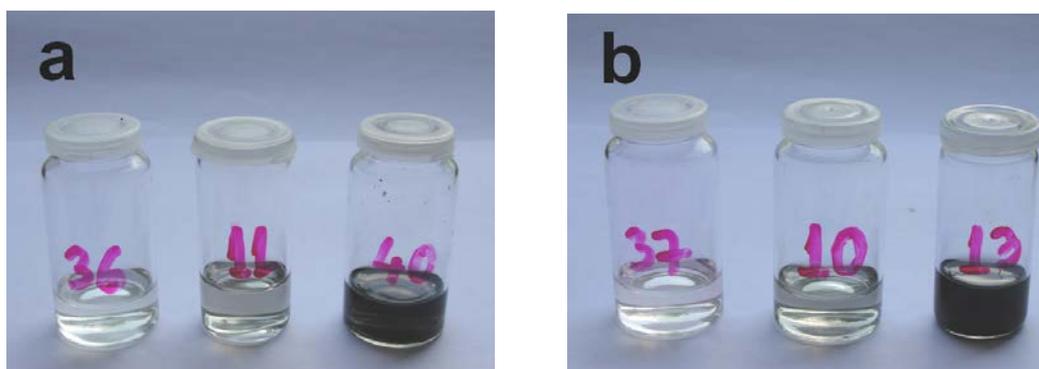


Figure 3 Appearance after 3 months of the polymer solutions in DMF (samples from Table 1) (a) PAN with 0, 0.1 and 1 % MWCNT (s.36, 11, 40) and (b) PAN-VK with 0, 0.1 and 1 % MWCNT (s.37, 10, 13)

The changes seen in the polydispersity indices (PDI) for PAN and PAN-VK as a function of the initial CNT concentration used in the synthesis (Figure 4) is similar in behavior with the changes in the polydispersity index observed in the case of other monomers polymerization with CNT [39, 40]. The main reason for the increase in the PDI is due to several factors: the addition reaction promoted by the radical's attack (of the initiator) on the MWCNT [40, 41], the transfer reactions of the growing macro-radicals, and the grafting process, etc. The major difference between miniemulsion and solution polymerization was observed in the case of molecular weights were a bimodal distribution is obtained for miniemulsion process (Figure 5).

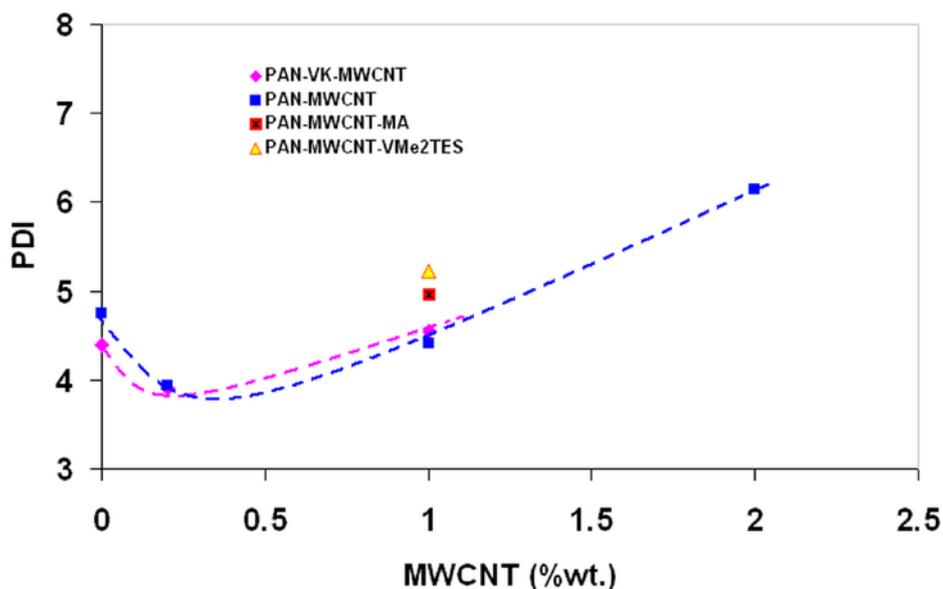


Figure 4. PAN polydispersity index profile as function of MWCNT used in the polymerization process

The explanation for the bimodal distribution of the molecular weights could be the coexistence of two phases in the initial state of the polymerization system; one phase consists of the monomer stabilized nanodroplets and the second phase consists of the monomer solution in water [42]. The solubility of the monomer in water can influence the PDI [43, 44]. For our systems, the polymerization of AN in the water phase was inherent (9.1% wt. solubility in water). Moreover, the concentration of AIBN in the water at the polymerization temperature can produce free radicals [45] that are active towards the solubilized monomer present in the water phase.

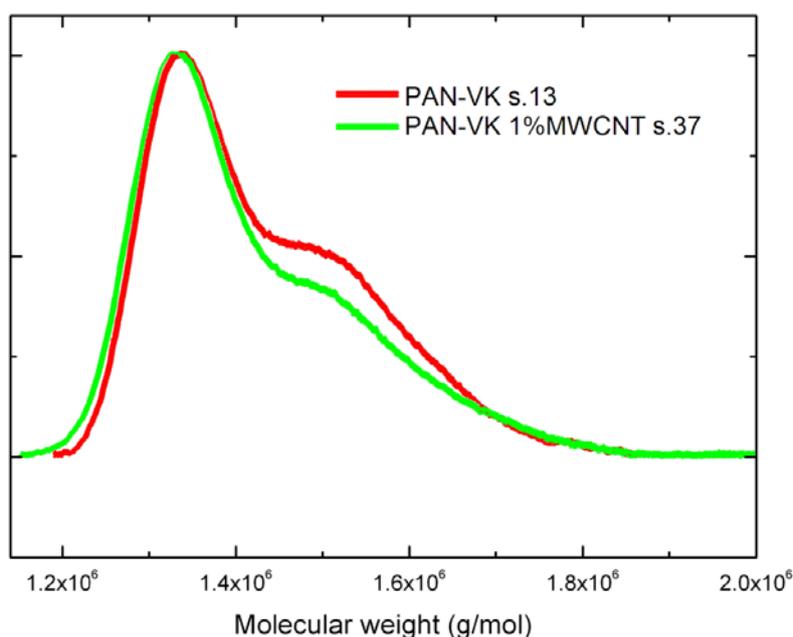


Figure 5 GPC curves for PAN-VK (PAN-VK s.13) and PAN-VK obtained in presence of 1% wt.MWCNT (PAN-VK 1% MWCNT s.37) by miniemulsion polymerization

Another specific of the miniemulsion polymerization process used in this study is in final particle structures, which consist of agglomerated nanoparticles with defined crystalline structure that are formed during the reaction process [22]. The initial miniemulsion particles (droplets) before polymerization are stable, and their sizes are not dependent upon the concentration or nature of the MWCNTs (DLS measurements indicated diameters of  $100 \text{ nm} \pm 5\%$ ). After the polymerization process was finished, the particles formed aggregates in sizes ranging from 500 nm up to 2-3 microns. The phenomena can be explained by the influence of two main factors on the final particles stability. The insolubility of the formed polymer and the crystalline nature are inducing a concerted action in the aggregation process. Even if homogenous nucleation should be considered in miniemulsion polymerization (of the initial particles in presence of oil soluble initiator) according to literature, PAN macromolecular chains crystallization and precipitation during the polymerization are inducing a different structure from traditional latex particles driven by the aggregation of polymer crystalline phase [22]. Through further XRD investigations, we were able to determine the crystalline dimensions and the crystallinity index (CI) of the final polymer (Table 1).

Table 1 Influence of the MWCNTs on PAN-VK and PAN polymers obtained by miniemulsion polymerization

Sample No.	MWCNT % wt. to AN	VK (% wt. to AN)	$M_n \times 10^5$	$M_w \times 10^5$	XRD	
					$d_{\text{cryst}} (\text{\AA})$	CI (%)
36	0	0	1.64	7.83	69.1	33.0
11	0.2	0	1.74	6.86	69.6	33.7
40	1	0	1.93	8.55	69.4	32.3
31	2	0	1.14	6.99	68.9	33.3
37	0	0.2	1.69	7.5	69.7	33.3
9*	0.2	0.2	2.4	9.5	-	-
10	0.2	0.2	1.96	7.18	69.5	32.8
13	1	1	1.85	8.42	68.9	31.6
38	-MA/ 1	0	1.42	7.22	68.4	33.5
39	-VME <sub>2</sub> TES /1	0	1.2	6.6	68.9	34.0

\* initiator 1.4% wt. to AN

PAN, synthesized in this study with results displayed in Table 1, showed a superior structural arrangement in the macromolecular chain level when compared with previously reported PAN that was obtained by miniemulsion polymerization [22]. The difference was observed in two ways: smaller crystals approximately 7 nm (in comparison

with approximately 10 nm); and a crystallinity index of 33 % (26% was previously reported) [22]. These new findings are also seen in the presence of MWCNTs and functionalized MWCNTs (s.38, 39 Table 1). The nucleation effect from PAN crystallization can be explained by the MWCNT dispersion, an effect that is more pronounced in the case of the functionalized MWCNTs because of the small groups attached onto the body of the MWCNT [9]. During the polymerization the phase separation tendency involved by the crystallization of the forming polymer can be mediated in terms dispersability by the surface treated MWCNT (the modified MWCNTs are less aggregated in the final bulk phase of the composite). The advanced dispersion of the CNTs in the PAN matrices is observed in TEM images (Figure 6). AN-VK copolymers (s.37, 10, 13 Table1) possess a lower degree of crystallinity in comparison with PAN due to the primary units involved in the nucleation process that perturb the arrangements of the initial molecular architecture.

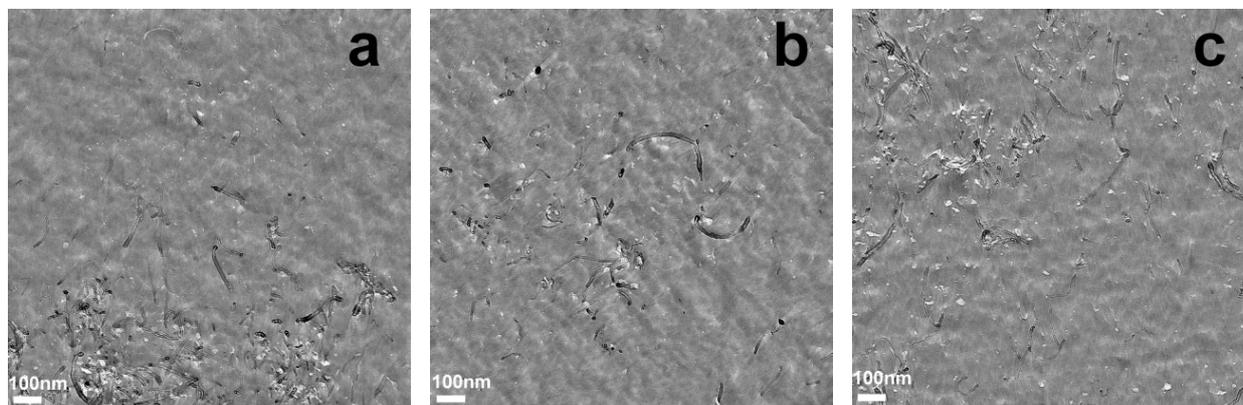


Figure 6 TEM images for PAN hybrids obtained with 1% wt.: purified MWCNT (a), MWCNT-MA (b) and MWCNT-VMe2TES (c)

Because PAN-CNT hybrids are used as precursors for carbon fibers [25, 27-35], a useful feature that should be considered is their thermal behavior profile. With a temperature increase to between 150-300 °C, the ladder structure formed by the polymerization of the nitrile will occur. The cyclization of the CN groups (in air or in nitrogen) is accompanied by dehydrogenation and thermo-oxidation. Heating the cyclized hydrides improves the carbon quality in the final carbon fibers [25]. In this study we focus on the thermal behavior of the synthesized composites (Table 2) formed in the nitrogen atmosphere.

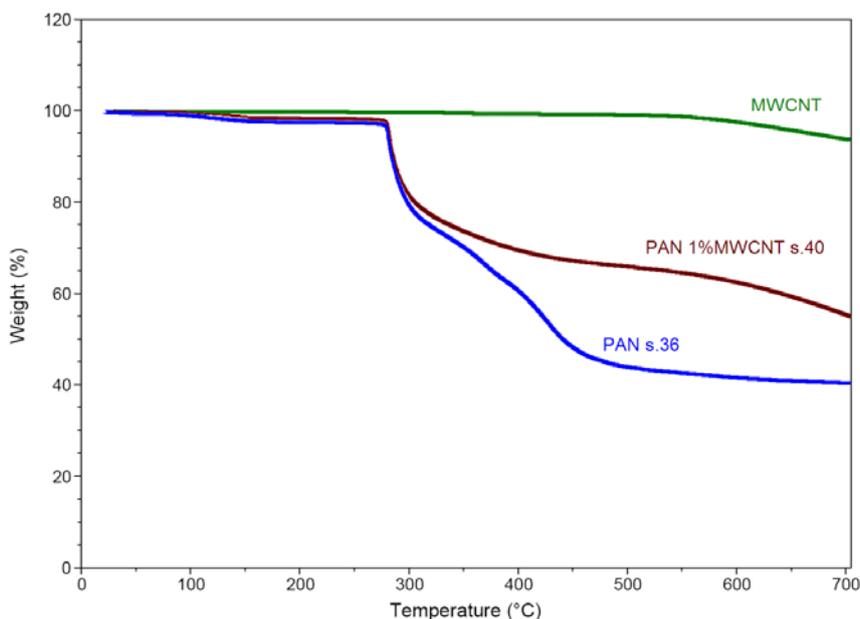


Figure 7 TGA curves for neat MWCNT, PAN s.36 and PAN 1% MWCNT s.40, obtained by miniemulsion polymerization

Table 2 Influence of MWCNTs and VK on the thermal behavior for the corresponding PAN hybrids obtained by miniemulsion polymerization

No.	CNT %	TGA, N <sub>2</sub>			DSC	
		0-350 °C ΔG/Tmax(1;2)	350-500 °C ΔG/Tmax(1;2)	500-700 °C ΔG (wt.%)	Residue wt. %	T (°C) ΔH (J/g)

		(wt.%/ °C)	(wt.%/ °C)		700 °C		
36	0	29.41/ (124.02;284.43)	26.39/ (371.24;425.73)	3.53	40.65	289	569.9
11	0.2	26.08/ (135.12;294.34)	6.048	13.2	54.66	293	467.2
40	1	26.1/ (119.97;284.81)	7.833	10.41	55.73	285	548
31	2	25.46/ (128.06;290.11)	7.869	10.37	56.31	289	462
37 <sup>¥</sup>	0	28.83/ (132.1;285.77)	27.37/ (373.26;427.75)	3.866	39.92	290.8	611
10 <sup>¥</sup>	0.2	27.45/ (135.97;295.18)	6.179	13.05	53.39	295	539.1
13 <sup>¥</sup>	1	27.48/ (136.13;297.21)	7.563	10.43	54.51	296	461.5
38 <sup>*</sup>	1	30.47/ (103.84;280.73)	27.78/ (377.3;427.75)	4.186	37.59	285	392
39 <sup>±</sup>	1	30.29/ (131.53;284.13)	27.77/ (376.95;430.31)	4.389	37.47	289	515.6
24 <sup>*</sup>	1	27.03/ (268)	25.53 (369;424)	3.598	43.5		

\*MWCNT-MA/ 1.0; <sup>±</sup> MWCNT-VMe<sub>2</sub>TES /1.0; <sup>¥</sup> with VK 1:1 wt. to CNT; <sup>\*</sup>solution mix

For pure MWCNTs, the weight loss (in nitrogen) ( $\Delta G$ ) for the temperature interval between 0-700 °C was observed to be 1.8 % (Figure 7). For the hybrids, the weight loss occurs in three distinct temperature intervals (Figure 9): 0-350 °C, 350-500 °C, 500-700 °C. MWCNT presence in general decreases the weight loss for the hybrids obtained by miniemulsion polymerization when compared with the polymer alone (PAN or PAN-VK). This behavior was emphasized in the case of decomposition temperatures ( $T_{max2}$ ), which, in favorable conditions, can increase by 10 °C (0.2% wt. CNT), indicating a certain interaction between the nanocomposite phases. This tendency of the results was the same also for the other two intervals. During the heating process, several reactions occur: cyclization, dehydrogenation and decomposition [25]. The main influence of the MWCNT was noticed in the cyclization stages undertaken by the CN groups (350-500 °C interval). This behavior was promoted by the specific interaction between  $\pi$  electrons of the CNTs and the CNs [34]. The mentioned above profile was observed for all of the PAN and PAN-VK hybrids synthesized in presence of unfunctionalized MWCNTs (Table 2). The influence of the MWCNT concentration can be observed (Figure 8) for all three temperature intervals. In the 500-700 °C interval, the weight loss was rather moderate; however, the increase in stability was still present when compared with the pure polymers. The residue increase at 700 °C verifies both the CNT presence as well as the associated thermostability of the analyzed hybrids.

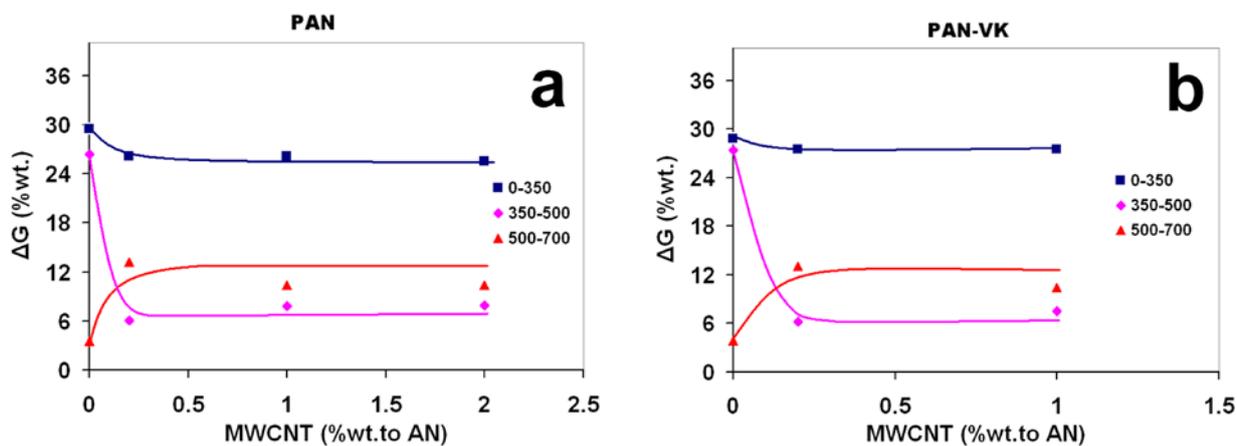


Figure 8 Influence of the MWCNTs concentration on the TGA results of the main stages of the programmed heating - PAN (a) and PAN-VK (b) cyclization, dehydrogenation and graphitization.

The sterical hindering effects induced by the chemical modification of the walls of the MWCNT drastically restrict the interaction between the  $\pi$  electrons. The effects of the functional groups were observed as the increased dispersion ability of the MWCNTs in the PAN matrix, which also provided a steric hinder for the agglomeration of the nanotubes (Figure 6).

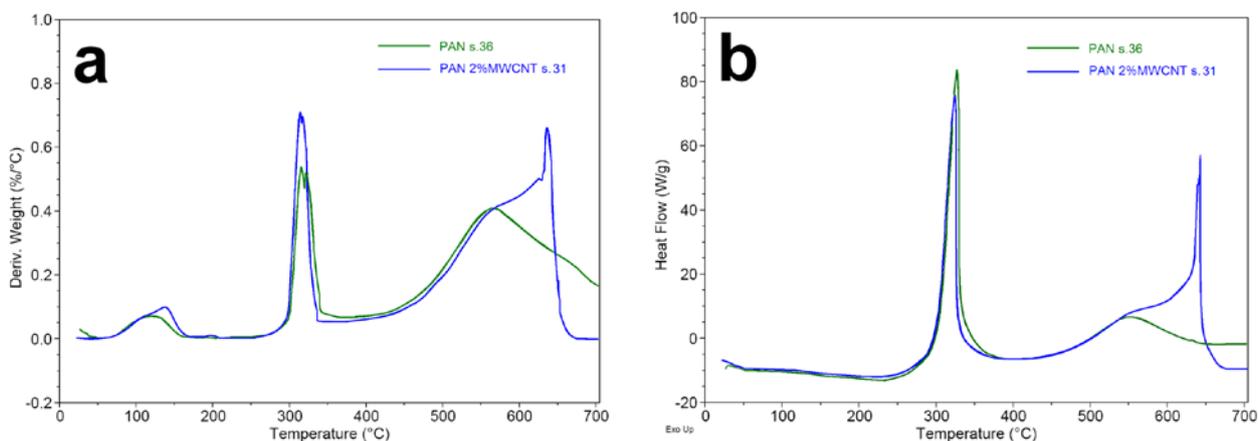


Figure 9 DTG (a) and DSC (b) curves for PAN (s.36) and PAN 2%MWCNT (s.31)

In the applications context the impact of the studied hybrids still remains in the thermal properties side. To have a complete picture a final element was added by preparing a physical mixture (sonication and solvent casting) (s.24 Table 2). The thermal profile of the material obtained as a physical mixture was considerably lower than for the thermal profiles of the samples obtained by miniemulsion polymerization. The observed weight losses increased in the programmed heating interval (up to 700 °C) while the decomposition temperatures and residues were radically decreased (Table 2).

All of the above should be considered for using the proposed method for the synthesis of carbon fibers with more efficient precursors.

Supplementary information about the thermal stability was obtained by DSC (Table 2, Figure 9). The obtained results were in good agreement with previously reported results in the literature [29]; however, the maximum enthalpy, which appears in the cyclization stage (over 285 °C), is higher for pure PAN and PAN-VK (s.36, 37 Table 2) than for the corresponding MWCNT hybrids. This behavior happens because of the hindering effect induced by the MWCNT in the PAN stabilization reaction, which is a consequence of the interaction between CN and CNT [34]. The presence of VK creates an even more pronounced affinity for MWCNTs [26], reflected in decreasing the cyclization enthalpy. If the results obtained by TGA and DSC (Table 2) are compared, we can observe that a weight loss also occurs in the cyclization stage. However, the results of the DSC demonstrate that the enthalpic effect (Table 2, Figure 9) was the major event and a consequence of the stabilization by cyclization. For the temperature interval of 350-500 °C, the weight loss of the MWCNT hybrids was reduced (Figure 8, Table 2). Comparative DSC analysis showed no enthalpic differences between PAN (s.36) (26.39% wt. loss) and PAN with 2 % MWCNT (s.31) (7.9% wt. loss).

All the data that has been discussed suggest that PAN in the vicinity of MWCNTs has a higher degree of thermal stability than PAN without the CNTs, and the associated enthalpic effect of the CNTs, as seen through the DSC measurements (Table 2, Figure 9), is a consequence of the cyclization of the CN groups [25, 27, 29, 30, 34, 46].

The aforementioned method for producing these polymer-MWCNT composites should be considered for carbon fiber synthesis as the obtained hybrids showed an ideal profile as carbon fiber precursors [46-48].

Mixed matrix micro- and ultrafiltration membranes for water purification and waste-water treatment can be fabricated from the synthesized polymer batches. The mixed matrix ultrafiltration membranes, prepared by blending PAN with CNTs, are reported to be resistant against compaction and showed superior separation performance compared to pure PAN [49, 50]. In this case, integral asymmetric ultrafiltration membranes were prepared by a phase inversion process using a sample with 0.2% wt. CNT (PAN and PAN-VK). A 12 wt% polymer solution was prepared in *N,N*-dimethylformamide and was cast onto a non-woven polyester support, followed by immediate immersion of the system into distilled water at 20°C. This created membranes with a porous structure. The morphology of integral asymmetric membrane (from the sample with PAN 0.2% CNT) is shown in an SEM image. In the tilted cross-sectional view, a thin separating layer is quite distinctive (Figure 10a), with the surface morphology possessing an average pore size of 17 nm (Figure 10b). The prepared membranes can be utilized in a membrane ultrafiltration process, where turbid aqueous suspensions containing particle sizes above 20 nm can be treated.

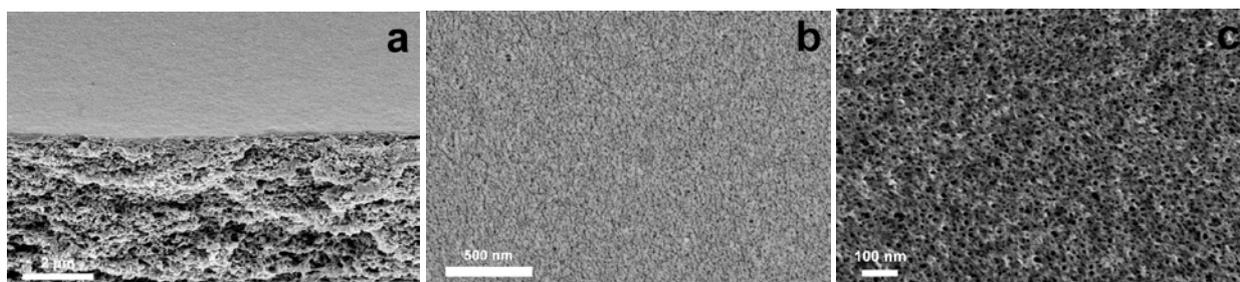


Figure 10 SEM images of the cross-section (a), top surface (b) and pores section (c) of PAN membranes prepared using sample PAN with 0.2% CNTs

### Conclusions:

Free radical polymerization in miniemulsions, as a method for obtaining hybrids comprised of polyacrylonitrile–MWCNT and poly(acrylonitrile-co-vinylcarbazole)-MWCNT, was demonstrated for the first time. The efficiency of the proposed route should be considered in the following terms: increasing (for particular optimal conditions) the molecular weights of the polymer generated next to the MWCNT particles, the absence of toxic solvents, the improvement in the thermal stability in comparison with the pure polymer, takeover the polymerization exotherm (the droplets dispersed in the water can be considered small reactors), the dispersion of agglomerated MWCNT into particles, increases in polymer crystallinity indices, the formation of polymer hybrids in wet media (MWCNTs in air suspensions are undesired as they create safety concerns), increasing the polymer polydispersity index; hybrids with uniform behaviour, specific to polymer decorated MWCNT (not simple mixtures).

The advanced functionalization of the MWCNTs limited the area for the transfer reaction of the radicals in the polymerization process to the wall defects of the nanotubes, which in turn lowered the molecular weights of the polymer. However, some limitations of this polymerization methodology should be emphasized, such as the sonication process and the presence of the surfactant, which was removed in supplementary steps by precipitation and further washing.

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