NANOCOMPOSITES BASED ON POLY(VINYL ALCOHOL)/MULTI-WALLED CARBON NANOTUBES FOR POTENTIAL APPLICATION AS BIOMATERIALS

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Abstract
Nanocomposite films of poly(vinyl alcohol) (PVA) and multi-walled carbon nanotubes (MWNT) were synthesized with 0.2wt% nanotube concentrations. The nanocomposites were characterized regarding morphological, physical, and mechanical properties. The nanotubes were chemically modified, and the functionalization was confirmed by FTIR and RAMAN spectroscopy techniques. Young's modulus of the nanocomposites, as compared to the pure polymer, was increased by approximately 40%. In summary, the overall properties of the new PVA-CNT films have given preliminary evidence of their suitability as a potential alternative for wound dressings and skin tissue replacement.

1 Introduction

Currently, the interest in nanostructured materials has been growing at an extraordinary pace due to its potential in diverse scientific and technological areas, such as catalysis, development of biosensors, optoelectronic materials, controlled release of drugs, and tissue engineering. Nanoscience and nanotechnology involve processes and products on a scale which varies between 1 and 100 nanometers and has benefitted many segments, including the food industry, electronics, pharmaceuticals, biotechnology, cosmetics, medical-hospital industry, agriculture, and national security [1]. Materials and devices produced in nanometric scale present advanced physicochemical properties due the size reduction, large interfacial area in turn giving way to an enormous opportunity for human creativity in various segments of science and technology [2]. Due to their one-dimensional structure, fascinating mechanical properties, and thermal and electrical conductivity, carbon nanotubes (CNT) have been attracting the attention of physicists, chemists, and materials scientists, with medicine and biology representing the most prominent emerging areas for their application [3]. These factors make these materials interesting for use in chemical and biological sensors as well as in nanocomposites. Such CNT properties make them important materials in the development of nanotechnology for structural purpose. The combination of CNT with other materials (such as polymers) can generate nanocomposites with new electrical, mechanical, and thermal properties. Due to the van der Waals interactions formed among the graphene ("one-atom-thick sheets of carbon") hydrophobic surfaces, the nanotubes minimize their free surface energy, forming aggregates, and become chemically inert. This chemical inertia hinders the

CNT processibility and blocks their potential use in many applications. Hence, the functionalization of the nanotubes through chemical methods has been seen as a means through which to stimulate the interaction of CNT with other substances and materials, such as polymers, making it possible to use these carbon compounds in composites and sensors, as well as in their interaction with organic solvents. CNT functionalization through their walls has been seen as a means through which to explore the potential of these materials in chemical and biological applications [4,5]. Many polymeric materials have been studied for applications in epithelial tissue engineering due to their excellent characteristics, including flexibility, controllable degradability, and the ease of modification, in turn adapting their characteristics to the function that they will necessarily perform [6]. The choice of a polymer for use as a biomaterial is of utmost importance. Among the existing synthetic polymeric materials, the poly(vinyl alcohol) – PVA – has been used in diverse studies regarding applications in biomaterials. PVA contains excellent transparency and considerable consistency when in the membrane form, and is biologically inactive and biocompatible [6,7]. Research on the production of biocompatible materials that will be used to regenerate the skin is important in the treatment of patients worldwide. As the largest body organ, the skin is exposed to a wide range of chemical, physical, and biological agents, as well as diseases, such as diabetes, which reduces blood circulation and causes serious epithelial lesions [6,8]. The synthesis of polymeric nanocomposites made of CNT and PVA becomes quite relevant, given that it uses the combination of properties of these materials, which form a unique system with the possibility of applications as biomaterials.

The present work aimed to synthesize and characterize PVA nanocomposite films and multi-walled carbon nanotubes (MWNT) using the solution casting technique for potential application as biomaterials.

2 Materials and testing methods

2.1 Materials

All reagents were used in analytical grade and Milli-Q water was used in all solutions (18MΩ). The following reagents were used: poly(vinyl alcohol), Sigma-Aldrich, molar mass at 9,000 to 10,000g/mol and 80% degree of hydrolysis (DH); MWNT synthesized by chemical vapor deposition CVD with a 95% purity, 5-15μm length, and 10-30nm diameter supplied by SES Research and nitric acid (HNO_3) from Synth.

2.2 Functionalization of carbon nanotubes

For the functionalization of nanotubes, 1g of MWNT was added to 50mL of 14mol.L^{-1} HNO_3 solution and stored in a reflux system at a temperature of 120°C for 15 hours. The functionalized nanotubes (MWNT-F) were vacuum filtered, using a Millipore® glass fiber filter; washed abundantly with deionized water until a pH of approximately 7 had been reached; and dried for 48 hours in an oven at 60°C.

2.3 Synthesis of nanocomposite films

The nanocomposites were synthesized by dispersing the nanotubes in deionized water using ultrasound at a concentration of 0.2wt.%. The PVA was added to this dispersion at room temperature with polymer concentrations (wt. %) of 5, 10, and 28. The system was placed in a water bath at 70°C for 3h to completely dissolve the PVA. The nanocomposites were obtained in the form of films through casting for 24 hours at room temperature (25±2)°C and for 48 hours in a greenhouse at 40°C. Ten different films were synthesized, as presented in Table 1, with three types of polymeric films containing only PVA in three distinct concentrations (5, 10, and 28wt.%) and 6 types of nanocomposites containing the constant concentration of MWNT and MWNT-F of 0.2wt.% in three different PVA concentrations. Different PVA

concentrations were used for the nanocomposite synthesis, in an attempt to determine which polymer/nanotube relation would be best for the preparation of homogeneous materials and appropriate physical and chemical properties. The ratio (R_n) among the percentage concentrations within the PVA and nanotubes was calculated according to equation 1.

$$R_n = \frac{[PVA]}{[MWNT]} \tag{1}$$

where [PVA] is the concentration of PVA (wt.%) in the aqueous suspension of the nanocomposite, and [MWNT] is the concentration of the nanotube (wt.%) in the aqueous suspension of the nanocomposite.

	Sample	[PVA] (wt.%)	[CNT] (wt.%)	Ratio (R_n) PVA/MWNT
Ref.	PVA 5%	5	0	∞
	PVA 10%	10	0	∞
	PVA 28%	28	0	∞
Nanocomposites	5%PMWNT	5	0.2	25
	5%PMWNT-F	5	0.2	25
	10%PMWNT	10	0.2	50
	10%PMWNT-F	10	0.2	50
	28%PMWNT	28	0.2	140
	28%PMWNT-F	28	0.2	140

Table 1. Identification and concentration of the synthesized nanocomposites.

2.4 Fourier Transform Infrared spectroscopy (FTIR)
In an attempt to characterize the presence of chemical groups in the functionalized carbon nanotubes and in the PVA films, an infrared analysis (IR) was performed, using Attenuated Total Reflectance (ATR). The spectra were obtained in the wave range from 4000 to 650 cm^{-1}, during 64 scans, with a 2 cm^{-1} resolution (Spectrum One, Perkin-Elmer, USA). The IR spectra were normalized, and the vibration bands were associated with the main chemical groups present in the samples.

2.5 Raman spectroscopy
In an attempt to characterize the graphene structure of the carbon nanotubes and the effect of the chemical functionalization on these, Raman spectroscopy analysis was performed. The spectra were obtained at room temperature by the CCD Raman spectrometer, 1024x256 pixels, using the He-Ne laser with a wave length of 632nm and a potency of 20mW.

2.6 Swelling assay
The degree of swelling (DS) of the nanocomposite films was obtained by using the saline phosphate buffer solution (PBS – Saline Phosphate Buffer Solution) was prepared at room temperature (approximately 25ºC), dissolving the reagents in de-ionized water under constant magnetic stirring, and the pH corrected for the value of (7.40±0.05) with a 1.0 mol.L^{-1} HCl solution. To determine the degree of swelling (DS), the samples (two-dimensional samples) were cut in dimensions of 10×10mm, in triplicate, set for 24 hours in a greenhouse at 40ºC to remove the humidity and extra weight. After having been weighed, the samples were placed

in recipients containing the PBS solution. The samples were maintained at room temperature in a water bath. After pre-set time intervals had been executed (0.5h, 1h, 2h, 4h, 24h, 96h) the samples were removed from the recipient and weighed. To remove the excess fluid, the samples were placed quickly (< 20s) on a filter paper and then weighed on an analytical scale. The DS was obtained according to equation 2.

$$DS = \frac{M_I - M_S}{M_S} \times 100 \qquad (2)$$

where M_I is the swelling mass and M_S is the dried sample mass. Each trial was performed in triplicate, and the average value and standard deviation were used to validate the results.

2.7 Characterization of mechanical properties
The tensile strength test was performed to evaluate the mechanical behavior through: the ultimate tensile strength (UTS), the Young´s modulus (E), the yield strength (σ_e), and toughness (T) of the produced films. The test was performed in an EMIC DL 3000 equipment, using a load cell of 50N, at speed of 5mm.min^{-1}, and samples in the form of strips of 50mm in length and 15mm in width. Average values of the five samples were obtained according to ASTM D882/02 [9], assay temperature of $22 \pm 2^{\circ}$C, and a relative humidity of $60 \pm 8\%$. The selected samples were previously inspected and any discontinuities, such as air bubbles and holes, with a dimension of above 5% of the thickness were rejected.

3 Results and Discussions Materials and testing methods
3.1 Qualitative evaluation
The PVA and nanocomposite films presented an average thickness of ($200 \pm 50\mu$m), but by adjusting the solution volume in the mold, one can obtain varied final thicknesses. The visual analysis of the PVA films (reference) showed that they were optically transparent and uniform. The aspects of the 5%PMWNT and 5%PMWNT-F nanocomposite films were similar, as one could observe nanotubes that were agglomerated and dispersed evenly throughout the polymeric matrix. In addition, the presence of the chemical functionalization in nanotubes can lead to a greater interaction by means of hydrogen bonds between the nanotubes and the polymer.

3.2 Raman spectroscopy
Figures 1 (a) and (b) illustrate the Raman spectra obtained for the samples of non-functionalized multi-walled carbon nanotubes and MWNT-F, respectively. In both spectra, the characteristic bands from carbon materials, bands D, G, and G', could be observed.
Within the spectroscopic techniques used in the characterization of fullerenes and CNT, the Raman spectroscopy is one of the most valuable, making it a widely used technique in the characterization of carbon material, identifying the types of bonds and providing information concerning the degree of disorder from the crystalline network [10]. In the case of CNT, these allow for the differentiation among the nanotubes, graphite, and amorphous carbon. One typical spectra of a carbon nanotube sample generally contains two quite characteristic bands: the G band, centered around 1580-1590 cm^{-1}, associated with the graphite tangential vibration, and the D band, centered around 1350 cm^{-1}, associated with the defects and/or disorder [11]. The D band is characteristic of the disordered carbon, given that its width and intensity are factors which vary with the degree of material disorder. Thus, the analysis of the form, position, and intensity relative to these bands allows for the identification of the presence of simple-walled and/or multi-walled nanotubes, as well as the identification of the degree of purity and/or defects in the sample. The degree of disorder in the structure of the

carbon nanotubes can be estimated by the ratio among the relevant intensities of the D and G bands (I_D/I_G) [12]. The lower the I_D/I_G ratio value, the greater the degree of graphitization that is attributed to the lower the concentration of structural defects within the tubes (sp^3 carbons). Also, the greater the I_D/I_G value, the greater would be the extension of the chemical functionalization. For the non-functionalized carbon nanotubes, the I_D/I_G ratio was equal to 1.25. For the functionalized carbon nanotubes, the I_D/I_G ratio was equal to 1.44. The evaluation of the relevant intensities of the D and G bands indicates the presence of defects in the carbon nanotubes induced by chemical functionalization.
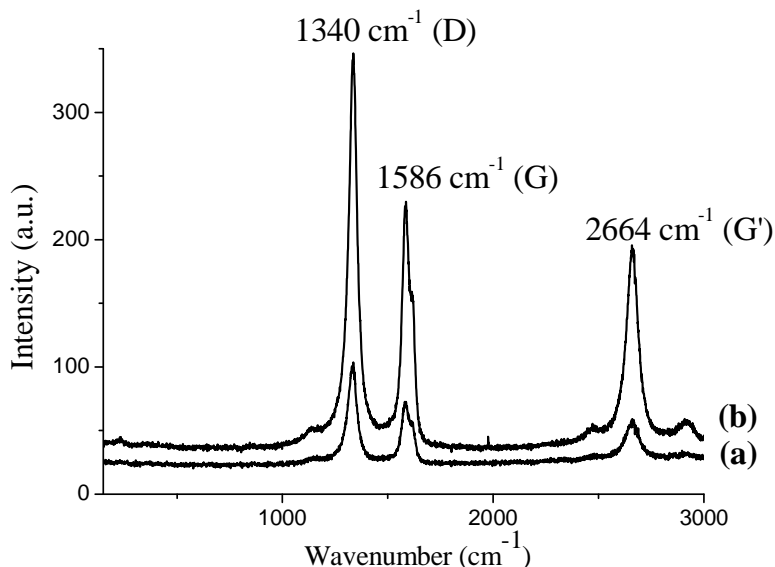

Figure 1. Raman spectra for the (a) MWNT and (b) MWNT-F.

3.3 Swelling Assay

The swelling assays conducted on the PVA films presented a high dissolution rate, which was completed in approximately 15 minutes. This finding was expected, since the PVA with an 80% DH used in the preparation of films is highly hydrophilic and soluble in water. Considering that the PVA of the present study presented a relatively low DH (80%) and molar mass (9,000 to 10,000g/mol), its dissolution in water occurs at room temperature (20-25°C), given that in films containing PVA with these characteristics, the swelling is followed by the solvation of PVA chains by water until their complete dissolution has been attained, which occurs in only a few minutes [7]. The swelling assays with the synthesized films, as of the solutions with low PVA concentrations (5%PMWNT, 5%PMWNT-F, 10%PMWNT, and 10%PMWNT-F) have revealed that the presence of nanotubes within these materials did not affect the dissolution of the pure PVA film. The low dispersion of the nanotubes by the polymeric matrix forming the CNT agglomerate regions may well have promoted their low interfacial adhesion with the PVA matrix. The weak PVA interaction with the nanotubes led to the availability of the hydrophilic polymeric chains for their interactions with water and solvation until the complete dissolution of the film. The swelling assays with the nanocomposite films with higher PVA concentrations (28%PMWNT and 28%PMWNT-F) showed interesting results with samples maintained their forms over a period of 96 hours. This finding can be attributed to the interaction of the carbon nanotubes with the polymer, stabilizing the availability of the hydrophilic groups and making the dissolution unfavorable. The swelling behavior for the two different samples of nanocomposites proved to be similar, reaching a maximum value of 90% for 28%PMWNT and nearly 100% for 28%PMWNT-F, in

a period of three and one half hours. Figure 2 shows the histogram of swelling for the different nanocomposites. According to researchers [7], the swelling of PVA is approximately 500%. Therefore, it can be concluded that the presence of carbon nanotubes in the PVA network drastically reduces swelling due to the formation of a polymeric network that is denser and with a lesser capacity for expansion. Still, the increase in toughness of the polymeric chain, caused by the physical barrier of the nanotubes and the nanotube-PVA interaction, by means of hydrogen bonds for MWNT-F, make the polymeric matrix denser and less susceptible to attacks by water.
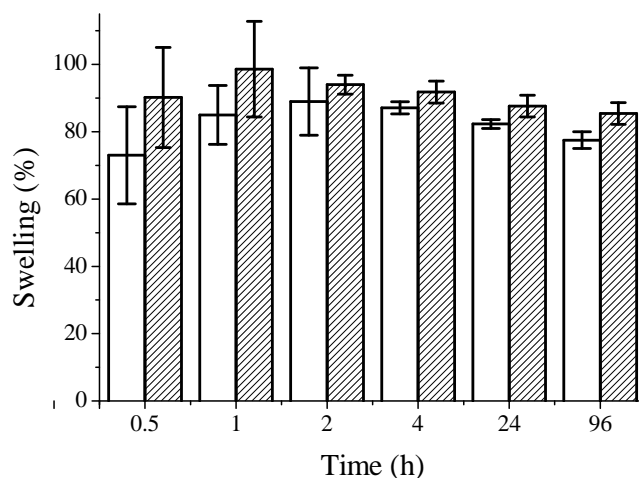

Figure 2. Swelling in the PBS generated by the nanocomposites of 28%PMWNT (white) and 28%PMWNT-F (dashed). Bottom: a scheme of a possible interaction mechanism between PVA and nanotubes.

Before the addition of carbon nanotubes, the PVA chains consist of a physical entanglement, forming a network. With the incorporation of CNT in the polymeric network, a reduction in the mobility of the chain can be observed, and consequently, in the mobility of the PVA hydrophilic groups, promoting a greater fixation, greater hardness of the polymeric chain, and a lesser swelling when compared to the pure polymer. The carbon nanotubes represent a physical block to the PVA hydrophilic groups and these, subsequently, become less available for interaction with water.

The present study found that the swelling behavior is still influenced by the presence of carboxyl groups present in the functionalized nanotubes. The chemical functionalization promotes the formation of hydrogen bonds between the PVA hydroxyls and the nanotube carboxyls, diminishing the availability of the polymer polar groups for interaction with water.

The results of the swelling assays revealed that the nanocomposites prepared beginning with the low concentration PVA precursor solutions (5%PMWNT, 5%PMWNT-F, 10%PMWNT, and 10%PMWNT-F) dissolve quickly and present a difference among the solution rates of pure PVA. As such, it is important to point out that some processing parameters, such as the DH of PVA, the pH of the solution, the drying profile of the solvent, the use of a plasticizer, and the mixture procedure, when used together influence all the mechanical properties of the nanocomposite films. Therefore, the present study chose to perform tensile strength assays only on the 28%PMWNT and 28%PMWNT-F nanocomposite samples.

3.4 Characterization of Mechanical Properties

Figure 3 presents the curves obtained by tensile strength assays for the nanocomposites of 28%PMWNT (a) and 28%PMWNT-F (b), as well as for the 28% PVA film (c). The Young´s modulus was estimated by determining the slope of the linear portion of the graph of the

stress-strain curve. The toughness corresponds to the area above the curve until the rupture of the bodies of evidence. It could be observed that a reduction in the specific shaping and the increase in the Young´s modulus could be observed for the nanocomposites as compared to the 28% PVA film.
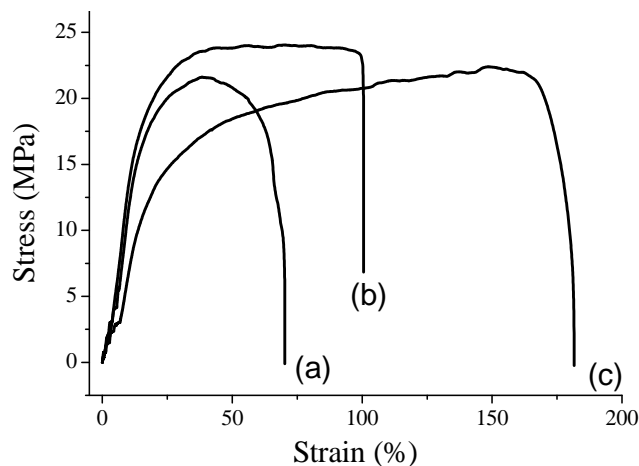

Figure 3. Tensile curves versus shaping for the nanocomposites of 28%PMWNT (a), 28%PMWNT-F (b), as well as for the 28% PVA film (c).

In general, the values of the Young´s modulus obtained for the nanocomposites were higher than the module obtained for the pure polymer film. The presence of the carbon nanotubes increases the hardness of the polymeric matrix. The crystallization of the polymeric matrix is caused by the presence of carbon nanotubes, and this fact leads to the improvement of the mechanical properties of nanocomposites when compared to the pure polymer [13]. Moreover, the presence of the hydroxyl and carboxyl groups on the surfaces of functionalized CNT promote the formation of strong interactions with the hydroxyl groups present in the PVA chains.

For the 28%PMWNT and 28%PMWNT-F nanocomposites, the Young´s modulus is approximately 33% and 48% higher, respectively, as compared to the 28% PVA film. As expected, the presence of the carbon nanotubes increases the hardness and, consequently, makes the shaping of the polymer matrix difficult [14]. The addition of the MWNT-F, as compared to the addition of the MWNT, most likely produced nanocomposites with higher Young´s modules due to the greater interfacial interaction of the carboxyl nanotubes with the polymeric matrix through hydrogen bonds.

The epithelial tissue presents maximum tensile strength values within the range from 2.5 to 16 MPa. As such, the mechanical properties of the synthesized nanocomposites revealed that these do in fact have a potential application as a substituent for skin. The addition of carbon nanotubes in the PVA matrix led to improvements in the mechanical properties of the polymer and illustrated more appropriate properties for the application of nanocomposites as substituents for epithelial tissue [7]. In addition, the evaluated systems proved to be appropriate as potential biomaterials in the repair of skin tissues, the degree of swelling, mechanical properties, and biocompatibility, as they are similar to natural skin.

4 Conclusions

PVA nanocomposites/multiwalled carbon nanotubes, with and without chemical functionalization, were synthesized by means of the simple method of solution casting and evaporation. The films were characterized by tensile stress assays and swelling assays in an attempt to evaluate the mechanical and physical properties of these films. The results, in

addition to the interfacial adhesion of the functionalized nanotubes with the polymer matrix, also present strong evidence that controlling the PVA concentration, in the precursor solution of the nanocomposite films, associated with the chemical functionalization of the nanotubes, shows that it is possible to obtain synthetic, organic-inorganic hybrid materials with the variation of the physicochemical properties according to application needs, including those from the biomedicine industry.

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