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CHARACTERIZATION OF CNTs /CARBON NANOFIBRIL COMPOSITES VIA POSITRON ANNIHILATION

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ABSTRACT
Three groups of Carbon Nano Tubes (CNTs) of three different diameters, and each with five different weight concentrations were dispersed in a polyacrylonitrile (PAN)/ dimethylformamide (DMF) polymer solution. Electrospinning technique has been utilized to produce nanofibril composite fabrics from PAN/DMF with CNTs dispersions . Then, the collected fabrics were thermally stabilized and carbonized under static pressure to activate the high surface energy aiming to build firm and strong fabrics. The resultant carbonized sixteen fabrics showed reddish color with strong (as maximum as 60MPa strength) and flexible (as maximum as 5% strain) behaviors. Morphological characterization by using SEM showed minimum average fibril diameter of 130±20 nm for the smallest CNTs diameter. The effect of CNTs size on the electrospun fiber diameter has been investigated. Also, evaluation of the presence of CNTs inside the carbon nano fiber has been investigated by using HRTEM. Mechanical properties (strength and modulus of elasticity) of the fabrics have been investigated. AFM has been used to measure the modulus of single nano fibril composite. Thermal conductivity has been measured precisely to study the effect of CNTs on thermal properties. Positron annihilation lifetime spectroscopy (PALS) was employed to measure the free volume properties of the fabrics and correlated it to fabric's morphological, mechanical and thermal properties. It has been noticed that in general the presence of CNTs decreased the free volume values resulted in dense structure and improved its thermal conductivity. Also, as CNTs diameter decreases the free volume decreases resulted in improvement in fabric's strength and thermal conductivity.

(خصائص المؤتلفة من الالياف الكربونية النانومترية والمدعمة بأنابيب الكربون النانومترية باستخدام تقنية فناء البوزيترون)

فى هذا البحث تم أختيار ثلاثة مقاسات مختلفة من أنابيب الكربون النانومترية من شركة سيجما الدريتش ووضع كل منها بالخليط وبنسب وزنية متفاوتة بين البولي أكريلونيتريل مع الداي ميثيل فورمامايد فى محلول بوليمرى .ثم أستخدام المزيج مع طريقة الغزل الكهروستاتيكى لإنتاج ألياف نانومترية مؤتلفة من أنابيب الكربون النانومترية مع ألياف الأكريلك النانومترية ومن ثم تم تفعيل الطاقة السطحية وتحسين خواص هذه المؤتلفات النانومترية بالمعالجة الحرارية وذلك باستخدام الطريقة المستحدثة بالانضغاط الحرارى المرحلى لإنتاج النسيج الكربونى المؤتلف بأقطار وصلت الى 150 نانومتر. وفى هذا البحث تم ربط الخواص المورفولوجية والميكانيكية والحرارية للنسيج الكربونى المؤتلف النانومترى بقيم الفراغ النانوى المقاس باستخدام أطياف البوزيترون والمقاس بقيم الفترات الزمنية لحركة البوزيترون فى فراغ النسيج الكربونى المؤتلف. وقد توصلت الدراسة الى قياس تأثير وجود أنابيب الكربون النانومترية فى الخواص الحرارية والميكانيكية للنسيج الكربونى وربطها بقيم الفراغ المقاس وخلصت الدراسة الى تحديد النسبة المناسبة لأنابيب الكربون بالمحلول البوليمرى وكذلك المقاس المناسب لأنابيب الكربون النانومترية من بين الثلاث مقاسات المستخدمة والتى تم تقيمها وقياسها لتعبر عن الحجم النانومترى الأدنى للفراغ المقاس داخل النسيج الكربونى المؤتلف والذى أدى الى تحسن ملحوظ تم رصده بشكل واضح لحجم الفراغ ومن ثم للخواص الحرارية للنسيج الكربونى المؤتلف.

***Keywords*:** Positron Annihilation; Mechanical Properties; Thermal Conductivity; SEM; TEM; AFM

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1. Introduction

Polymer nanofibers have been fabricated using an electrospinning process that produces nanofibers from an electrically charged jet of polymer solution. The nanofiber diameters range from 40 nm to 2µm, depending on the polymer types, bias voltage, viscosity of the solution, and so on [1]. One advantage of nanofibers is the high specific surface area developed by creating pores on the nanofiber surface [2]. Mechanical strength of an individual nanofiber is also expected to be enhanced with decreasing diameters [3]. This material has been widely applied to filters [4], scaffolds [5], protective clothing [6], and sensors [7]. Polyacrylonitrile (PAN) has been widely used to fabricate nanofibers owing to their easy carbonization process. PAN nanofiber fabrics can be used directly for electrode materials after stabilization and carbonization, which cannot be realized in other types of polymers. Another advantage of the carbonized PAN nanofiber is that; the nanofiber surface can be modified and functionalized by activation process under different ambient conditions [2]. G. Sui et al. [8] concluded that; the PP nanocomposite containing 5 wt. % CNF exhibits a high dielectric constant under wide sweep frequencies attended by low dielectric loss. Bal [9] showed an addition of 1 wt% of carbon nanofibers brought improvement in electrical properties of epoxy composite. Spitalsky et al. [10] studied nanotube/ polymer composites in which the presence of interconnected nanotube network results to a dramatic increase of their electrical conductivity. Also, nanocomposites based on Polymethylmethacrylate (PMMA) and MWCNTs as filler show a significant enhancement in the electrical conductivity. The multi wall carbon nanotubes (MWCNTs)/ PAN (20/80) Wt% composite papers without carbonization possess electrical conductivities of up to 0.5–1.0 S/cm at ambient temperature. However, the PAN-based carbon nanofibers are often required in many applications, which accompany inevitably stabilization and carbonization process. For instance, the PAN-based carbon nanofiber papers have been directly used for super capacitor electrodes, where high capacitance of 173 F/g at 10mA/g was obtained but the power density was poor due to large electrical resistivity of the PAN-based carbon nanofibers [11]. Higher electrical conductivity is always desired to have high capacitance and high power density in super capacitors [12]. This is the main reason to introduce CNTs in PAN nanofibers. While CNT/ PAN nanofibers were prepared in organic solvent, CNT/polyethylene oxide (PEO) was electrospun in water with additional surfactant [13]. Dielectric properties vary with the compositions of iron (III) chloride dopant [14]. The permittivity behavior of the device at the frequency below 102 Hz shows the relaxation contribution along with the electrode polarization. Dielectric loss peak in loss tangent also confirms the presence of relaxing dipoles in TNFs. The AC conductance as a function of frequency confirms the semiconducting nature of TNFs and obeys Jonscher's power law except a small deviation in the low frequency region. DC conductivity increases with increase in temperature [15]. Ali [16-20] published a series of publications studying the characteristics of the electrospun PAN/DMF polymer solution in both wet and dry collectors before and after heat treatment as well as with and without nano reinforcements. Positron annihilation Lifetime spectroscopy (PALS) is an important method for measuring the change in properties of structural defects in many solids [21, 22]. In PALS, when a positron emitted from a positron source and injected in a polymer sample, it undergoes several processes (scatter and thermalize in the sample within a time of the order of 10 ps). The positron may eventually annihilate with an electron (free positron annihilation) or may extract an electron from the surrounding material to form a positronium atom (Ps). Ps is formed in two states; a singlet state (p-Ps) with anti-parallel spins has an intrinsic lifetime of 0.125 ns and a triplet state (o-Ps) with parallel spins has an intrinsic lifetime > 0.5ns. In o-Ps, the positron can annihilate with an electron from the surrounded atom by pick off annihilation and emit three photons. The pick off lifetime is directly related to the size of the free volume in a polymer. Therefore, PALS has been used to characterize the properties of free volume of polymer nanocomposites, such as free-volume hole size, concentration, and its distribution [23-26].The present study is an attempt to study the effect of CNTs size and weight % on morphological and thermal properties of electrospun and treated (hot-pressed) CNTs/carbon flexible nano fibril fabrics as well as to correlate the presence of CNTs in the fabric's morphological and thermal properties to its intermolecular distances and free volume by using positron annihilation technique.

2. Experimental Work

2.1. Materials

Three different sizes of CNTs from Aldrich of the following numbering and dimensions; CNT#1: O.D. =10-30 nm, I.D.= 3-10 nm, L=1-10 µm, CNT#2: O.D.= 30-50 nm, I.D.= 5-15 nm, L= 0.5-200 µm, and CNT#3: O.D.= 40-60 nm, I.D.= 5-10 nm, L= 0.5-500 µm. have been well dispersed by 24 sonication hours within five different weight concentrations from 1% to 5% in Dimethylformamide (DMF) solvent and then Polyacrylonitrile (PAN) of 150000 g/mol molecular weight from Aldrich catalog no. (181315) has been

added with 10wt% then whole polymer solution and dispersions have been hot stirred at 60°C for 3 hours to ensure a complete PAN solubility.

2.2. Electrospinning of Dispersed CNTs/PAN Nano Fibril Composites

Electrospinning set-up assembled at NTC, Faculty of Engineering, Zagazig University, Egypt was used through the following steps; the PAN/DMF+MWCNTs polymer solution and dispersions were poured to fill a clean syringe of 10 ml volume. The syringe was connected to a metal tube of orifice inner diameter 0.9 mm. The metal tube was connected to the power supply at 25kV of positive potential. A metal screen collector of 15x15 cm dimensions was centered vertically at a 20 cm distance away from the orifice of the metal tube and covered with aluminum foil. The electrospun fibers were collected for about 16 hours to reach to collect CNTs/PAN nano fibril composite fabrics.

2.3. Production of Carbonized Fabrics

About 2 cm from each side of the collected fiber mat was trimmed then the mat was placed in between two aluminum plates of 120x120 mm dimensions and 10 mm thickness after being covered with aluminum foil. The mold with the fabric in between was placed in a hot-press set to reach 220°C with no applying pressure for 1 hour until the plate's temperature reached the maximum set temperature. Then 1 metric ton was applied for another one hour. The hot-press was then allowed to cool down for another 1 hour while keeping the pressure on until it reaches 100°C then the pressure was released completely from the fabric except the weight of the upper aluminum plate until it has cooled down to room temperature. This process stabilized the PAN structure by adding an oxygen atom to PAN structure as well as activating the high surface energy accompanied with the nanofibril composites and use it as a cohesive bond to produce firm and uniform white fabrics. SEM and Raman investigations for such white fabrics have been conducted. Then, another hot-pressing for 3-hour in between single plate and double aluminum foils with 5 metric tons at 380°C has been applied then the pressure has been released after cool down to 100°C. This technique allowed to cyclize the carbon double bond and form graphitic hexagon structure from PAN. Reddish flexible and strong fabrics have been produced. Morphological, Chemical, Electrical, Thermal and Positron annihilation characterizations for the reddish sixteen fabrics has been conducted.

2.4. Characterization

2.4.1. Electron Microscopy

Scanning Electron Microscopy (SEM, JEOL JSM-5600LV) in the Central Laboratory for Elemental and Isotopic Analysis (Atomic Energy Authority Nuclear Research Center, Egypt) was used to characterize the fiber morphology, average diameter and its distribution of the both resultant white and reddish fabrics. High Resolution Transmission Electron Microscopy (HRTEM) (JEOL model JEM 2100) in Petroleum research Institute, Egypt) was used to investigate the morphologies of the fibers and the presence of CNTs in the resulting reddish fabrics.

2.4.2. Thermal Properties Measurements

A thermal device at physics department, Faculty of Science, Tanta University, Egypt has been used at room temperature to measure the thermal conductivity and coefficient of thermal expansion.

2.4.3. Mechanical properties Measurements

An optical extensometer attached to UTM has been used to measure the strength and modulus of the fabrics. Also AFM at "Atomic Energy Authority Nuclear Research Center " has been employed to measure the modulus of single nanofibril CNTs/carbon hybrid.

2.4.4. Positron Annihilation Spectrometer Measurements

A conventional fast−fast coincidence spectrometer (ORTEC) with a time resolution 395 ps was used for PALS measurements [27], and the ^{22}Na isotope with 10 μCi activity was used as a positron source. This source was prepared using a droplet of ^{22}NaCl solution dried onto two identical Kapton foils (7.6 μm thick), which were afterward glued by epoxy glue, placed between two identical samples. The measured PAL spectra were fitted by LT computer program of Kansy [28]. The measurements carried out in air at room temperature. 1-2 million counts were accumulated for each spectrum. Only results with FIT values with deviation range from 1.05 up to ~ 1.2 were considered as optimal ones. After source correction, each lifetime spectrum of the investigated samples was resolved into three lifetime components (τ_1, τ_2, τ_3) and their relative intensities (I_1, I_2, I_3) respectively. The τ_1 is attributed to the para positronium (p-Ps) annihilation. The τ_2 is attributed to the annihilation of positrons or positronium in defect of the ordered structure. The long-lived lifetime component τ_3 is attributed to the ortho-positronium (o-Ps) pick-off process in free volume holes in polymers. It directly correlates with the size of the free volume holes. A quantitative correlation between o-Ps lifetime τ_3 and the mean radius of holes R in a spherical

geometry is known as Tao-Eldrup equation [29, 30]:

$$\tau_3 = 0.5[1 - (\frac{R}{R_o}) + (1/2\pi)\,\mathrm{Sin}(\frac{2\pi R}{R_o})\,]^{-1} \quad (1)$$

Where: τ_3 and R, are expressed in ns and Å, respectively, R_0=R+ΔR, ΔR is the fitted empirical electron layer thickness (1.66 Å). The average radius of the free volume hole R is related to the mean free volume, Vf (in Å3) by a simple relation [31, 32]:

$$V_f = (4/3)\,\pi R^3 \quad (2)$$

3. Results and Discussion

3.1. SEM and HRTEM characterization

SEM image Fig. 1 show the fiber morphological characterization and distribution of CNTs/Carbon nano fibril composites pattern for the 5 wt% CNT#1/Carbon reddish fabric. About 130 nm ± 32 nm average fibril diameter has been reported. HRTEM image (Fig. 2) shows CNT#1 bundle with diameter ranged from 6 to 16 nm wrapped by carbon nano fibers and aligned along the fiber axis.

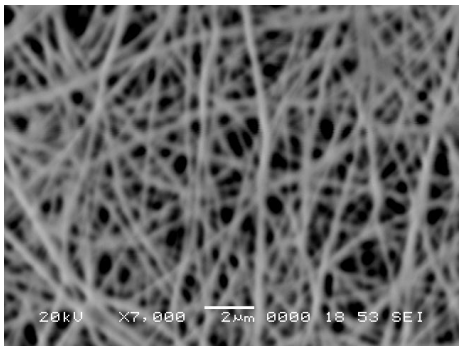

Fig. 1: SEM micrograph of CNTs/Carbon Reddish Fabrics

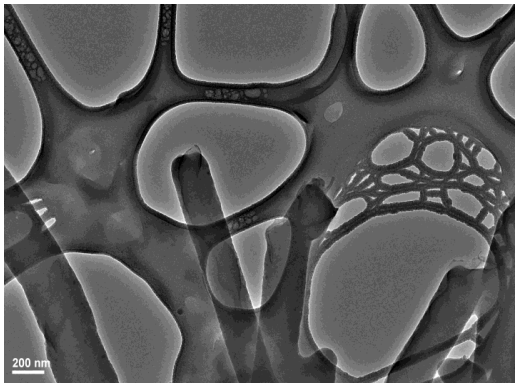

Fig. 2: HRTEM micrograph of CNTs/ Carbon Reddish Fabrics

3.2. Thermal Analysis

The effect of CNTs weight % on thermal properties of the fabrics have been measured and presented as shown in Figure (3)

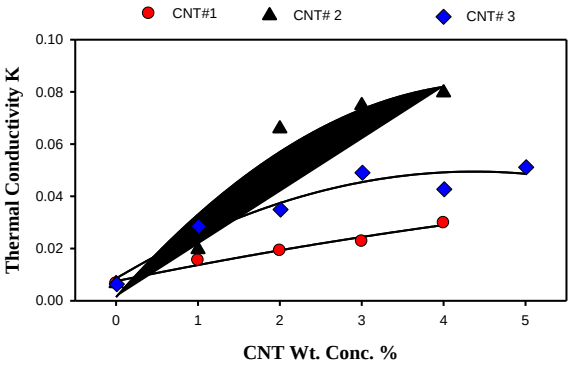

Fig. 3: CNT wt% and size vs. Thermal Conductivity

3.3 Mechanical Testing Analysis

Figure 4 represents the strength values of all CNTs wt.% for all three sizes. It is obvious from the figure that as CNTs size increases in diameter and became close and compatible with the carbon fiber diameter a better strength values reported. On the other hand, as shown in Figure 5 the calculated values of modulus from stress-strain Fabrics results after it has been corrected by using optical extensometer showed same behavior and effect for CNTs sizes. Figure 6 represents the measurements of single fibril composite modulus by using AFM for 5wt% samples and it goes as the same of size compatibility between CNTs and carbon nano fiber.

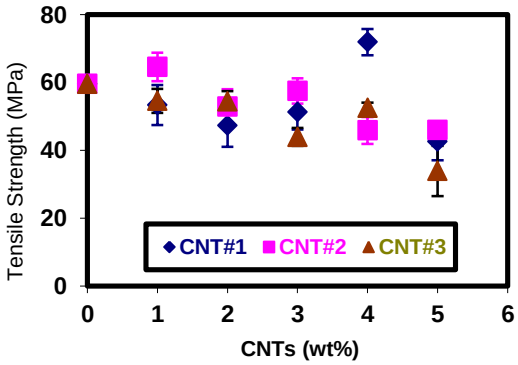

Fig. 4: Tensile strength vs. CNTs wt.% and size

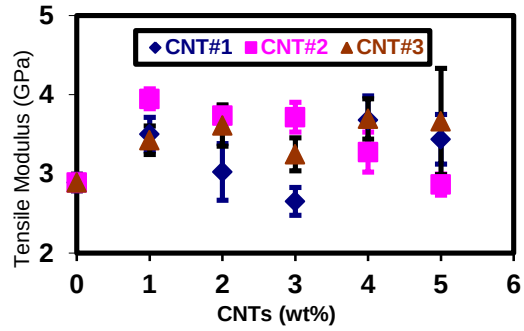

Fig. 5: Fabrics tensile modulus vs. CNTs wt.% and size

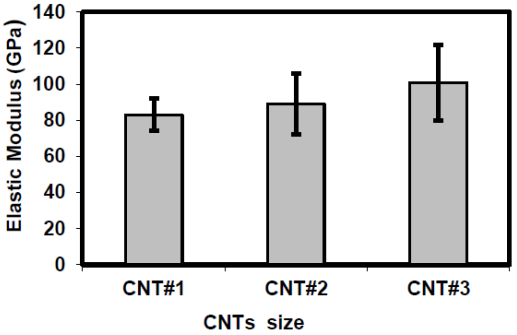

Fig.6: Single nano fibril composite tensile modulus vs. CNTs size

3.4. Positron Annihilation Analysis

The measured positron lifetime spectra for Carbon nano tubes (CNTs) of three different diameters, and each with five different weight concentrations were resolved into three lifetime components. These components are attributed to various states of positron annihilation. The first lifetime component τ_1 (fixed to 0.125 ns) and with intensity I_1 (I_1 =57-73 %) is attributed to p-Ps. The intermediate component τ_2 (0.376- 0.486 ns) with its intensity I_2 (I_2 = 23-37.5%) is related to annihilation of positrons without forming Ps, i.e., free positron annihilation. The longest lifetime component τ_3 (τ_3 = (1.77-2.2 ns) with its intensity I_3 (**I_3** = 3.4-5.9%) is due to the pick-off annihilation of o-Ps in the free volume sites present in the amorphous regions of the polymer matrix [33]. These two parameters τ_3 with intensity I_3 are important and are of interest in this investigation, because τ_3 is related to the average free volume size and I_3 is related to the relative number density of free volume holes. The average lifetimes (τ_2, τ_3) and the relative intensities (I_1, I_2, I_3) values measured for CNT#1, CNT#2 and CNT#3 are listed in Table 1. As illustrated in Table 1, the o-Ps lifetime components, τ_3, with different CNTs concentration % does not have a systematic change with changing CNTs concentration. This is may be due to CNTs presence effect. On the other hand, I_3, the o-Ps probability formation also does not change systematically. This may be interpreted as I_3 depends on chemical and physical properties of the nanofibril composites, and the trend of change in I_3 may be related to whether or not polymer chains are covalently bonded to the surface of the nanotubes.

Table 1: The calculated values of Positron annihilation lifetime components with their corresponding intensities for the Carbon nanotubes (CNTs) of three different diameters

	W %	τ_2	τ_3	I_1	I_2	I_3
CNT #		0.405± 0.007	2.034± 0.0330	69.2± 0.71	26.9± 0.720	3.90± 0.1
	1%	0.376± 0.002	2.009± 0.017	66.28 ±0.13	29.94 ±0.13	3.784± 0.038
	2%	0.410± 0.007	2.236± 0.035	67.15 ±0.46	28.13 ±0.47	4.72± 0.100
CNT#1	3%	0.417± 0.006	1.969± 0.038	66.17 ±0.41	29.82 ±0.41	4.01± 0.120
	4%	0.402± 0.004	2.137± 0.025	73.20 ±0.24	23.38 ±0.23	3.42± 0.052
	5%	0.433± 0.007	2.040± 0.023	70.67 ±0.67	25.24 ±0.69	4.09± 0.079
	1%	0.4474± 0.007	2.023± 0.04	70.22 ±0.67	26.08 ±0.68	3.70± 0.12
	2%	0.4299± 0.006	1.991± 0.022	67.89 ±0.64	28.03 ±0.65	4.08± 0.085
CNT#2	3%	0.4206± 0.0035	2.026± 0.02	63.92 ±0.49	30.60 ±0.51	5.48±0 .068
	4%	0.4865± 0.0086	1.864± 0.034	72.85 ±0.65	23.15 ±0.66	4.00± 0.12
	5%	0.4640± 0.010	2.000± 0.038	70.48 ±0.65	24.85 ±0.66	4.66± 0.14
	1%	0.428± 0.007	1.868± 0.028	60.57 ±0.40	33.51 ±0.39	5.92± 0.1
	2%	0.433±. 0.002	1.864± 0.025	67.37 ±0.37	28.19 ±0.38	4.44± 0.16
CNT#3	3%	0.418± 0.005	1.775± 0.020	57.22 ±0.64	37.47 ±0.64	5.31± 0.09
	4%	0.431± 0.007	1.953± 0.025	68.59 ±0.62	27.25 ±0.63	4.16± 0.12
	5%	0.390± 0.001	1.975± 0.013	64.93 ±0.29	31.16 ±0.29	3.91± 0.04

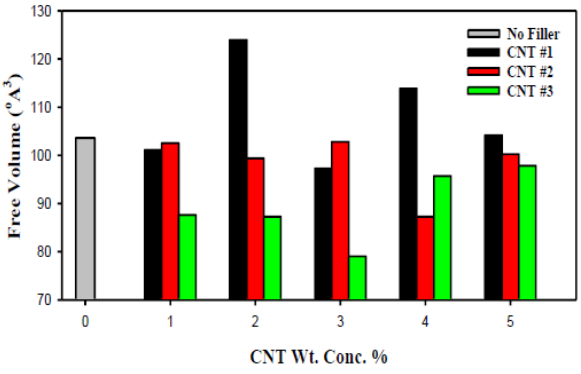

Fig. 7: Mean free volume (Å^3) as a function of filler concentration in Carbon nanotubes (CNTs) of three different diameters

The volume V ($Å^3$) of free volume nanoholes is calculated according to eqn. (2), where R is radius of the nano-holes calculated through eqn. (1). The variation of V ($Å^3$) as a function of CNTs concentrations of three different diameters is shown in Fig 7. The results showed that the average size of free volume for CNT#1, CNT#2 and CNT#3 are 108±10.8 ($Å^3$), 98.4±6.4 ($Å^3$) and 89.5±7.5 ($Å^3$) respectively. It can be noted that with increasing the average size of CNTs leads to decrease the average size of free volume. The obtained results of o-ps lifetime τ3 and consequently the average size of free volume are in a good agreement with that reported in the literatures [34]. Other studies showed that ortho-positronium principally annihilates from interfacial regions of polymer and nanotubes in the nanocomposite [35]. The increase of the average size of CNTs leads to an increase of the external surface area as well as the interstitial region volume among the CNTs and decreased free volumes at the fibroses interface in the fabrics. The LT program of Kansy [28] is used to fit the obtained positron annihilation lifetime data into free volume distributions based on the Tao–Eldrup equation (1). Figure 8 (A-C) shows the probability distribution of free volume size, V (nm^3) as a function of free volume nano holes (nm^3) as well as lifetime dispersion σ_3 from LT analysis for all the CNTs measured samples. It is interesting to observe that the average lifetime components of o-Ps and their intensities from continuous distributions were in good agreement with the discrete component analysis. Sharma et al. [35] have reported similar results for PF–CNTs composites.

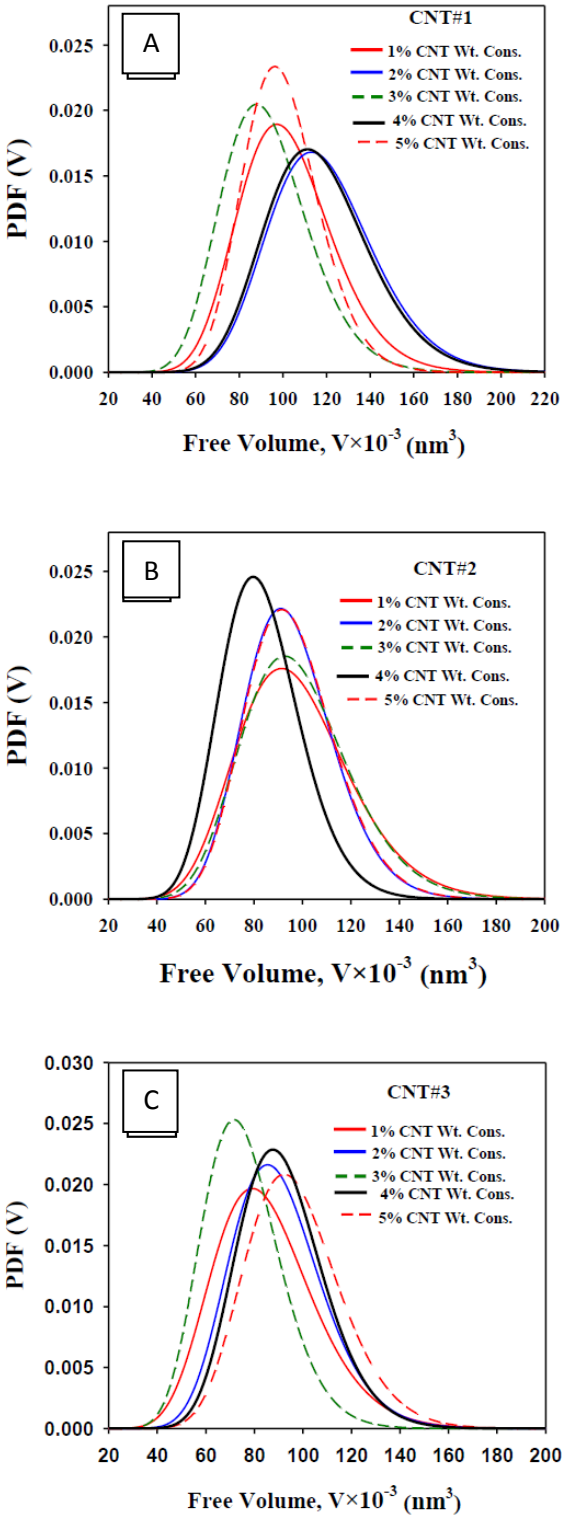

Fig.8:(A-C): The probability distribution of free volume size in different CNTs concentrations %

They showed that the peak position of the distribution shifts to a higher value with incorporation of CNTs, which is consistent with discrete component analysis. From the free volume hole size distributions, Figure 8(A-D), the calculated values of the full width at half maximum (FWHM) for the Carbon nanotubes (CNTs) of three different diameters are listed in Table 2. The results showed that in the case of CNT#1 and CNT#2 there are not systematic changes of the values of FWHM. In the case of CNT#3, the values of FWHM, Table 2, are decreased up to 3% CNTs concentrations indicating that the free volume size distribution becomes narrower with increasing the percentage of CNTs concentrations. The reduction in full width at half maxima with increasing the CNTs weight concentration% indicates that the nanotubes can lead to variation in packing density of chains in the vicinity of nanotubes, creating large size interfaces with the ''annihilation'' of smaller size nanoholes in the interphase region. A broader distribution of free volume size at a higher values > 3% CNTs weight concentration is observed, indicating the presence of larger interfaces as a result of agglomeration of CNTs in the polymer matrix.

Table 2: The calculated values of the full width at half maximum (FWHM) for the Carbon nanotubes (CNTs) of three different diameters

CNTs Wt. conc. %	CNT#1 FWHM (nm^3)	CNT#2 FWHM (nm^3)	CNT#3 FWHM (nm^3)
1%	0.044	0.048	0.042
2%	0.050	0.038	0.038
3%	0.040	0.044	0.032
4%	0.048	0.032	0.036
5%	0.036	0.036	0.040

4. Conclusions

Conclusions can be summarized as following:

1. As CNTs size is compatible in size with carbon nano fiber diameter a better fabrics mechanical and thermal properties have been reported.
2. Single nano fibril composites showed better modulus for CNTs#3 of lower free volume
3. Positron annihilation measurements indicated better mechanical and thermal properties are much correlated to fabrics minimum free volume values.

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