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Production and Dispersion of Plasma Functionalized Carbon Nanotubes in PAN Fiber Spinning Solution with Different Surfactants

Plazma ile İşlem Görmüş Karbon Nanotüp Üretimi ve Farklı Yüzey Aktif Maddelerle PAN Lif Çekim Çözeltisinde Dağılımı

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PRODUCTION AND DISPERSION OF PLASMA FUNCTIONALIZED CARBON NANOTUBES IN PAN FIBER SPINNING SOLUTION WITH DIFFERENT SURFACTANTS

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ABSTRACT: In this study, the distribution of plasma-functionalized multi-walled carbon nanotubes in polyacrylonitrile nanocomposite fibers produced by wet spinning method using different surfactants (Triton-X and sodium dodecyl sulfate) was investigated. Firstly, we produced CNTs by chemical vapor deposition (CVD) technique. Secondly, low-pressure plasma functionalization of CNTs was realized. Finally, nanocomposite polyacrylonitrile fibers doped by CNTs were obtained using wet spinning technique. Properties of produced carbon nanotubes, functionalized carbon nanotubes and nanocomposite polyacrylonitrile fibers were examined by the analyses of chemical composition, surface structure, structural and mechanical properties.

Keywords: CNT, plasma, chemical vapor deposition, PAN, dispersion

PLAZMA İLE İŞLEM GÖRMÜŞ KARBON NANOTÜP ÜRETİMİ VE FARKLI YÜZEY AKTİF MADDELERLE PAN LİF ÇEKİM ÇÖZELTİSİNDE DAĞILIMI

ÖZ: Bu çalışmada plazma ile fonksiyonelleştirilmiş karbon nanotüplerin farklı yüzey aktif maddeleri kullanarak (Triton-X ve sodyum dodesil sülfat) yaş çekim yöntemi ile üretilen poliakrilonitril nanokompozit liflerinin içerisindeki dağılımı incelenmiştir. İlk olarak, karbon nanotüpler kimyasal buhar biriktirme yöntemi ile tarafımızdan üretilmiştir. Ardından karbon nanotüplerin düşük basınç plazma ile fonksiyonelleştirilmesi gerçekleştirilmiştir. Son olarak, yaş lif çekim yöntemi ile karbon nanotüp katkılı nanokompozit poliakrilonitril lifleri elde edilmiştir. Karbon nanotüplerin, plazma ile fonksiyonelleştirilmiş karbon nanotüplerin ve nanokompozit poliakrilonitril liflerinin özellikleri, kimyasal kompozisyon, yüzey yapısı ve yapısal - mekanik özelliklerin analizleri ile incelenmiştir.

Anahtar Sözcükler: CNT, plazma, kimyasal buhar biriktirme, PAN, dispersiyon

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1. INTRODUCTION

Since their recognition in 1990s, carbon nanotubes have received a lot of attention. Carbon nanotubes (CNTs) are widely used as nanofillers for polymer nanocomposites due to their inherent, superior properties. They have high electrical and thermal conductivity and mechanical strength. CNT doped nanocomposite fibers receive attention because of their potential performance properties to obtain technical textiles. CNT nanocomposites are important for the next generation high performance materials for aerospace, automotive, construction industries. Particularly, CNT/poliacrylonitrile nanocomposite fibers are of further interest because they are used as precursors for high performance carbon fibers due to PAN fibers of high carbon yield upon carbonization. Polyacrylonitrile fibers are produced by wet spinning method because of its solubility in polar solvents and fiber structure is formed liquid-solid phase separation under stretching. Commercially, acrylic fibers are produced as copolymers of other vinyl monomers (like vinyl acetate, vinyl alcohol, etc.) and must be composed of at least 85% by weight of acrylonitrile. Literature shows that polyacrylonitrile are used for production of nanofibers and carbon fibers. For effective production of CNT doped polymer nanocomposites, very strong van der Waals bonds between CNTs should be overcome to obtain homogenous dispersions of them in polymer melts or solutions during manufacturing of composite materials. [1-10].

To overcome this problem, several surface modification methods have been studied. These surface modification techniques either increase the dispersibility of CNTs or increase the affinity between polymers and newly formed polar groups of CNTs. The most used surface modification technique is chemical modification containing living polymerization, acidic oxidation and gamma radiation. However, due to their heavy conditions, these chemical methods cause damages on CNTs, opening their ends and breaking their walls. Besides, these methods are hard to adopt to the production processes. Plasma modification for CNTs results in functionalization of surfaces of CNTs and etches their uppermost surface layer without causing any harm. CNTs modified by plasma were used for carbon fibers, polymeric composite materials, especially epoxy/CNT composites, and nanofibers mostly. Plasmas of H_2, N_2, NH_3, CF_4 and SF_6 for fluorination, Ar, acrylic acid and O_2 were common gases for surface modification at radio frequency, microwave frequency and direct current. Atmospheric plasmas were researched usually as air plasma for functionalization of CNTs. Water and dimethylformamide were seen predominantly as solvent in the literature. Addition of surface active agents are another way to obtain homogenous particle dispersions in fiber spinning solutions. The role of them is to surround CNTs to be able to apply electrostatic or steric repulsion forces to resist van der Waals forces between CNT particles. Obtained balanced structure is effective to separate even single wall CNTs. The biggest problem that arises when working with surfactants is finding a way to remove them in the final product. Surfactants remain in the structure in which they are produced. We applied several plasmas as ethylenediamine, ammonia, octylamine, nitrogen, air and acrylic acid plasmas to modify surfaces of CNTs in our preliminary experiments. Dimethylformamide and dimethylacetamide were used as solvents [2, 11-19].

The aim of the study is to produce and disperse CNTs smoothly in PAN fiber spinning solution with the aid of plasma technology. Dimethylacetamide was chosen as solvent because of the company we spun our fibers. To our knowledge up to now, dispersions of CNTs in dimethylacetamide solvent – PAN wet spinning solution comparing nonionic and anionic surface active agents and plasma treatments were not investigated. Effects of plasma functionalization on properties of nanocomposite fibers were compared with surfactant additions. The study was completed in three parts: The first one was the production of CNTs, the second one was functionalization of CNTs by plasma technology to be able to disperse them in fiber spinning solvent and the last one was the obtaining of CNT doped PAN fibers by wet spinning method in pilot scale.

2. EXPERIMENTAL

2.1 Production of CNTs

In this study, CNTs were grown by using Co-Mo/MgO nanocatalyst particles that were prepared by gel-combustion method [20, 21]. The initial gel contained 1.06 wt.% Co and 0.86 wt.% Mo. In catalyst preparation process, $Co(NO_3)_2{\cdot}6H_2O$, $(NH_4)_5Mo_7O_{24}{\cdot}4H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ salts and as sorbitol $C_6H_{14}O_6$ were all mixed and dissolved in deionized water. To obtain homogenous gel, the solution was dried at 100 °C for 3 h and followed by the flash calcination of the gel that was carried at 550 °C for 30 min. The material was then pulverized in a mortar and the powder form was sieved through meshes with the pore sizes of 75–250 µm.

The thermal CVD method was used to synthesize CNTs atmospheric pressure in a quartz tube. The catalyst with the amount of 13.0 mg was used in each quartz sample holder for CNT growth. The catalyst pretreatment was carried with heating up the system to 850 °C with ramping rate of 5.15 °C/min followed by the annealing at the same temperature for 1 h under 200 sccm H_2 gas flow. After the annealing process, the system was heated up to 1000 °C with 5 °C/min ramping rate. When the temperature 1000 °C was achieved, 50 sccm CH_4 precursor gas flow was applied for 40 min. Then, the system was left cooling to room temperature under H_2 gas flow. The schematic of the growth process is shown in Figure 1.

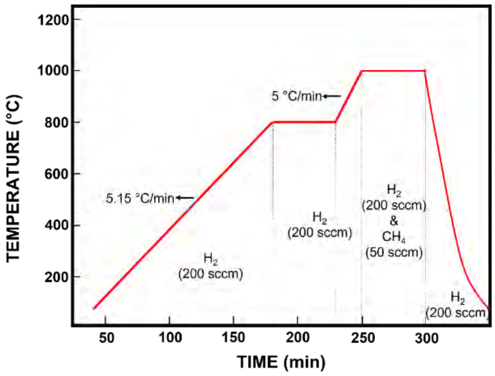


Figure 1. Schematic temperature diagram of CNT growth process.

2.2 Functionalization of CNTs by Plasma Modification

To prevent agglomeration in fiber solutions, CNTs were modified in a barrel in the chamber of PICO Low Frequency (40 kHz) Plasma System (Diener-Germany). Because of many trials of our previous works to find proper conditions and effective plasma gas/monomer and fiber spinning, commercial multiwalled CNTs (KNT-M31: 3-10 nm diameter, 500 m^2/g surface area, >95% purity) were purchased from Grafen, Turkey [19]. Plasmas of some gases and monomers like oxygen, nitrogen, air, octylamine, acrylic acid, ethylenediamine, etc. were applied to commercial multiwalled CNTs for smooth dispersion in fiber wet spinning solvent, dimethylacetamide. None of the plasmas of monomers was successful. Plasma gas was chosen as air, due it was the most effective and the cheapest one to be used. Plasma duration and power were 30 minutes and 50 Watts. Starting pressure was 10 Pa, gas pressure and plasma pressure were both 12 Pa, and argon pressure was 10 Pa.

2.3 Manufacturing of CNT Doped Nanocomposite PAN Fibers

Polyacrylonitrile –co- vinylacetate copolymer (AKSA Acrylic, Turkey) was used to obtain fibers in a pilot scale wet spinning system. Effects of LF air plasma modification on the distribution of multiwalled CNTs were compared to surface active agent additions. Triton-X and sodium dodecylsulfate (SDS) were used as additional surface active agents. Usage rates are taken as 3 times the amount of CNT used. [22]. To prepare wet spinning solution, firstly, solvent dimethylacetamide (DMAc), CNTs and surface active agent, if there was any in the recipe, were mixed for 5 minutes by ultrasound probe. If there is no surface active agent in the recipe, ultrasonic mixing was continued for 15 minutes. Secondly, 10 g of polymer was added and mixed at 16.000 rpm in a mechanical mixer. Lastly, remaining polymer was added and mixed by hand mixer. These solutions were stored at 60 °C and then send to the wet-spinning system. Fibers were formed by passing through a spinneret having 1506 holes whose diameters were 65 µm into a coagulation bath. Coagulation bath contains 50% solvent (DMAc) and there were two more bath containing 25% DMAc and 10% DMAc, respectively. Finally, fibers were wrapped on a bobbin. Wet spinning recipes are shown in Table 1.

Distribution of doped CNTs in nanocomposite PAN fibers were investigated by optical microscope (Olympus BX43, Japan). JEOL-JSM 6060 was used for scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy. Fineness and tenacity properties of nanocomposite PAN fibers were measured by Textechno Favigraph with 100 cN load cell. Distance of measurement and speed were 20 mm and 20 mm/min, respectively. Fourier Transform Infrared Spectroscopy device was Brutex Vertex 80 V and it was performed between 8000-400 cm^{-1} with 1200 scans. Resolution was 4 cm^{-1}. Surface atoms were investigated by Thermo Scientific K Alpha surface analysis system using Al-Kα source. Limiting oxygen index (LOI) is simply the oxygen percentage that is needed by a material to continue its burning. LOI values were measured by homemade LOI measurement device at Dokuz Eylül University Textile Engineering Department. Surface resistance values of fibers were obtained by Keithley 6517A electrometer/high resistance measurement device in a Faraday cage at 400 V.

Table 1. Wet spinning recipes

Recipe 0 (Standard Dope)	**Recipe 1**	**Recipe 2**	**Recipe 3**	**Recipe 4**	**Recipe 5**
1445 g DMAc 500 g PAN-co-VA	1445 g DMAc 500 g PAN-co-VA 1 g CNT (0.2%) 3 g SDS	1445 g DMAc 500 g PAN-co-VA 1 g CNT (0.2%) 3 g Triton X-100	1445 g DMAc 500 g PAN-co-VA 2 g CNT (0.4%) 6 g SDS	1445 g DMAc 500 g PAN-co-VA 5 g CNT (1.0%) 15 g SDS	1445 g DMAc 500 g PAN-co-VA 1 g CNT (0.2%)

3. RESULTS AND DISCUSSION

Smooth dispersion of CNTs in wet fiber spinning solution was obtained by applying low frequency plasma technology to CNTs. Air plasma surface modification was a suitable and ecological method that there were no use and cost of chemical and water and resultantly no wastewater.

3.1 Production of CNTs

The synthesized CNTs on quartz boat holder is shown in Figure 2.

In order to understand the morphological properties of the grown CNTs, SEM images were investigated (Figure 3.). Previously, it was indicated that increasing the growth temperature leaded to decreasing the amount of tangled CNTs and at the temperature of 1000 °C, CNTs were observed as much more ordered and untangled [21]. Therefore, as we carried CNTs growth process at 1000 °C, homogenous and ordered CNTs were obtained.

The average CNT diameter size is measured as 12.8±2.32nm in Figure 4.(a). The diameter size distribution is shown in Figure 4.(b).

Raman spectra of the synthesized CNTs is given in Figure 5. (a). Raman spectroscopy is a useful tool for carbon-based materials to investigate their vibrational and electronic properties. The so-called G-band (1580 cm^{-1}) corresponds to the tangential vibration of carbon atoms and indicates the characteristic features of the graphitic layers. The other characteristic band is D-band (1340 cm^{-1}) which is a typical sign of disordered graphitic structures. The intensity ratios of D peak to G peak gives information about the quality of the bulk samples. The low intensity of the D-band relative to the G-band of the synthesized CNTs indicates the low defect density and high crystallinity. I_G/I_D ratio of the grown CNT samples was obtained as 3.78.

Figure 2. The photograph of synthesized CNTs in quartz boat

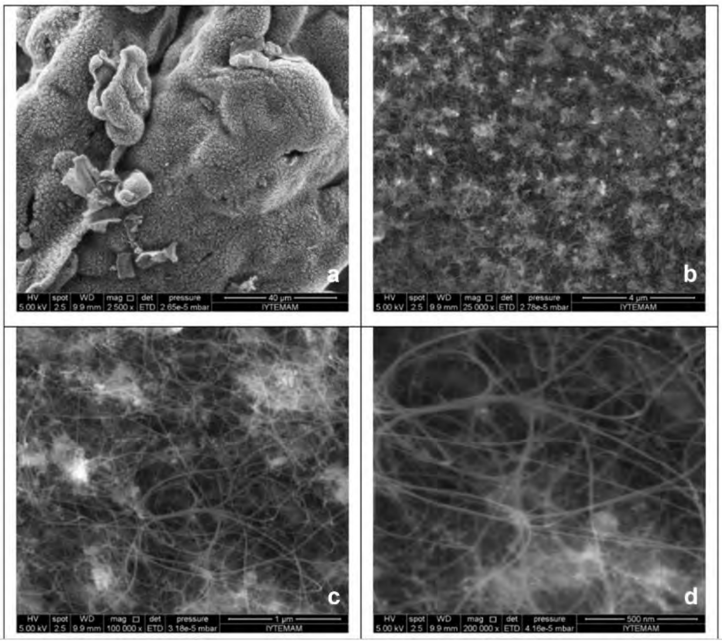


Figure 3. SEM images of CNTs with magnifications of (a) 2500x, (b) 25000x, (c)100000x and (d) 200000x. Note that each figure has a bar scale.

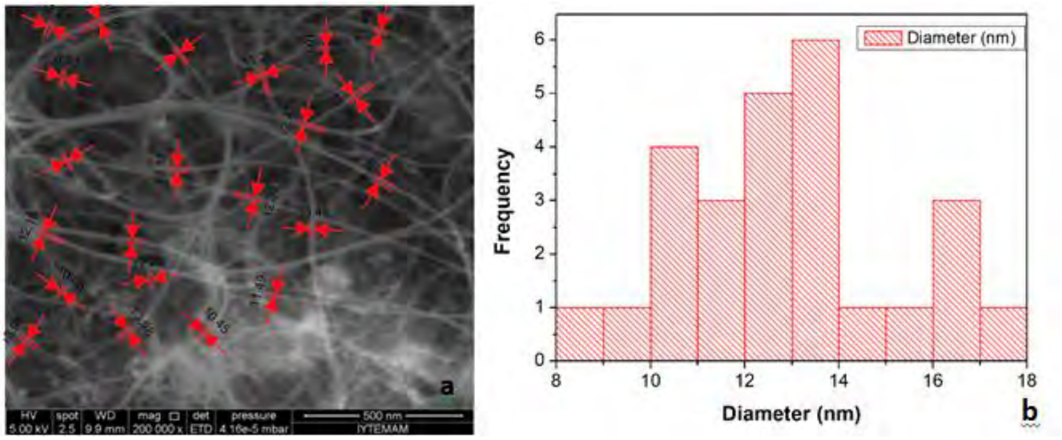


Figure 4. CNT diameter (a) measurement and (b) distribution.

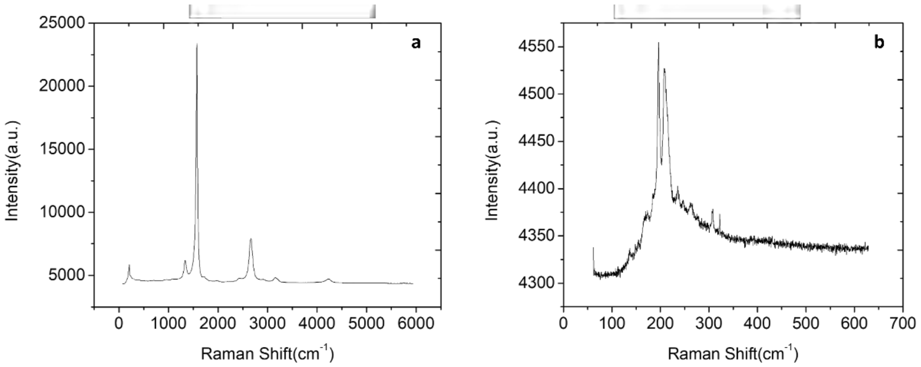


Figure 5. Raman spectra of synthesized CNTs (a) and (b) RBM peaks.

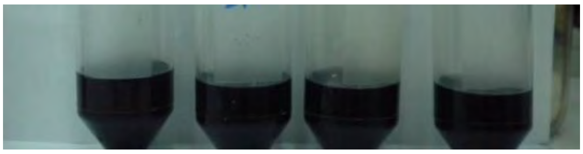
In Raman spectrum, a third mode is observed which is named as the radial breathing mode (RBM) which is sensitive to the diameter of CNTs. Especially, H_2 flow amount during synthesis determines the existence of RBM peaks. For synthesized CNTs, the RBM peaks were appeared in the wavenumber range of 100-300 cm^{-1} with different wavelengths and intensities. Generally, RBM peak existence is a significant indicator of single-wall CNT structure, however, lower I_G/I_D ratio (~3.8) may be explained as the mixture of both single and multi-wall CNTs in the structure.

3.2 Functionalization of CNTS by Plasma Modification

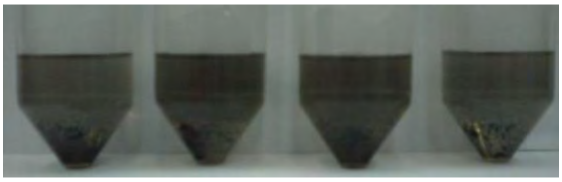
Figure 6 shows low frequency (LF) and radio frequency (RF) plasma functionalized CNTs. LF was chosen for the study because RF plasma functionalized CNTs were precipitated after 24 hours.

Air plasma was found the most effective one to have homogenous dispersion in DMAc solvent. In addition, it was the cheapest choice to use in plasma treatment. X-ray photoelectron spectroscopy was used to investigate the plasma surface modification on CNTs (Figure 7).

5min RF



5min LF



24h RF

24h LF

Figure 6. RF (after 5min,-after 24h) and LF (after 5min,-after 24h) plasma modified CNTs

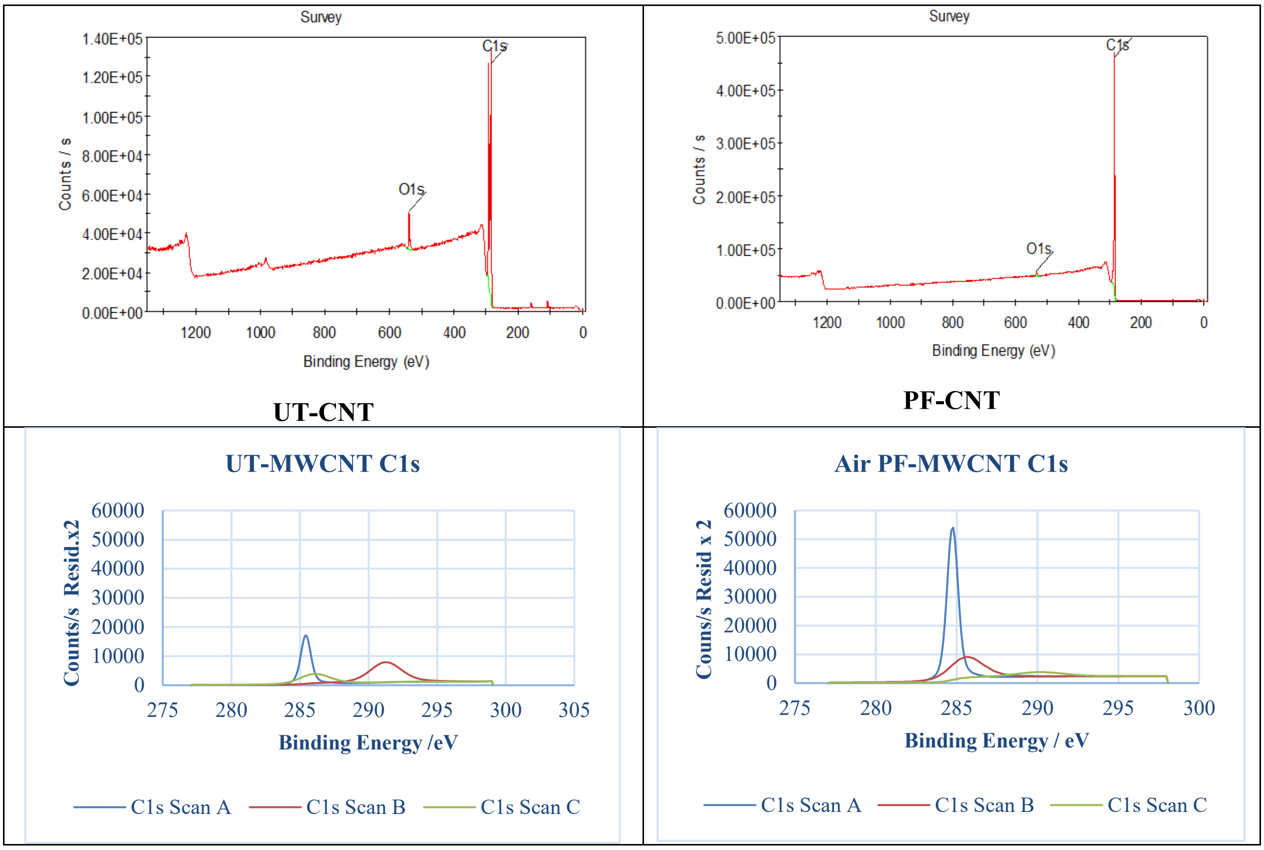


Figure 7. XPS spectra of untreated and air plasma treated CNTs.

Before and after 30 minutes - 50W air plasma treatment, there were only carbon (C) and Oxygen (O) atoms on the surfaces of CNTs. Atomic ratios of these atoms were given in Table 2.

Table 2. Elemental composition of the surfaces of air plasma treated and untreated CNTs

Sample	**C%**	**O%**
Untreated multiwalled CNT	95,33	4,67
Air plasma treated multiwalled CNT	98,32	1,68

UT-CNT is the spectra from as-purchased multi-walled CNTs. Ratio of carbon atoms were convenient to purity of purchased multi-walled CNT. From curve fitting of pristine multi-walled CNT, there are three peaks approximately at 285.eV, 286eV and 290eV that can be attributed to sp^2 carbon atoms of original multi-walled CNT, sp^3 carbon atoms indicating amorphous carbon layer on the surface and oxygen-carbon from air contamination, respectively [23]. After air plasma modification, ratio of carbon atoms was higher than ratio of oxygen atoms detected. Deconvolution showed increase in the peaks areas of sp^2 and sp^3 carbon atoms and decrease in the peak area of oxygen-carbon from air contamination. The increase in the peak area at approximately 286eV was 2 times more than that of pristine CNT. The difference may be attributed to the interference of a new peak at approximately 286.5eV from oxidation carbon [23]. The peak of Sp^2 carbon atoms from original CNT was increased and the peak of oxygen-carbon from air contamination was decreased showing cleaning of the surface groups on the CNTs. The reason for this can be the dominance of etching effect of low frequency plasmas. The effect can be higher when plasma process duration increase [23-26].

3.3 CNT/PAN Nanocomposite Fiber Production

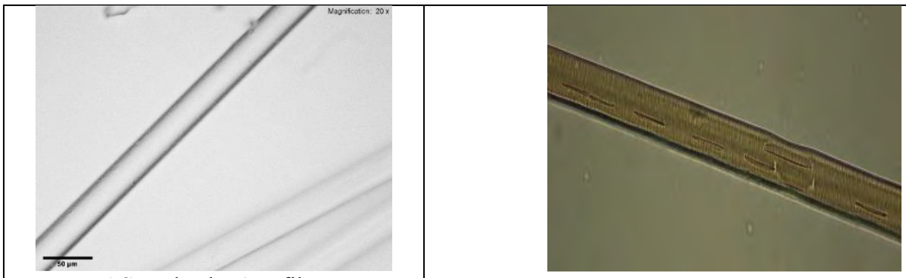
Pristine CNT doped PAN polymer fibers could not be obtained because the CNT aggregates did not get out from the spinneret. Anionic and nonionic surface active agents were added to fiber spinning formulations to understand whether they enhanced distribution of plasma functionalized CNTs or not [12]. Photos of PAN-CNT fibers were given in Figure 8 where (fiber 0): standard fiber solution, (fiber from former studies-CNT3): 0.02% acrylic acid PF-CNT +Sodium dodesilbenzene sulfonate-SDBS, (fiber 1): 0.2% PF-CNT + SDS, (fiber 2): 0.2% PF-CNT + Triton X100, (fiber 5): 0.2% PF-CNT, (fiber 4): 1.0% PF-CNT + SDS and (fiber 3): 0.4% PF-CNT + SDS in the front.

Figure 8. PAN /CNT nanocomposite fibers: (Fiber0) PAN, (Fiber-CNT3) fiber produced by former studies (0.02% acrylic acid PF-CNT + SDBS), (Fiber1) 0.2% PF-CNT + SDS, (Fiber 2) 0.2% PF-CNT + Triton X100, (Fiber 5) 0.2% PF-CNT, (Fiber 4) 1.0% PF-CNT + SDS and (Fiber3) (front) 0.4% PF-CNT + SDS

Optical microscope images of the same fibers shows distribution of PF-CNTs in the fiber structures (Figure 9). One of the CNT doped fiber sample (0.02% acrylic acid (aa)-PF-CNT+SDBS surfactant) from former studies was also included for comparison of images. There is a scale bar of 50micrometer on the photo for comparison.

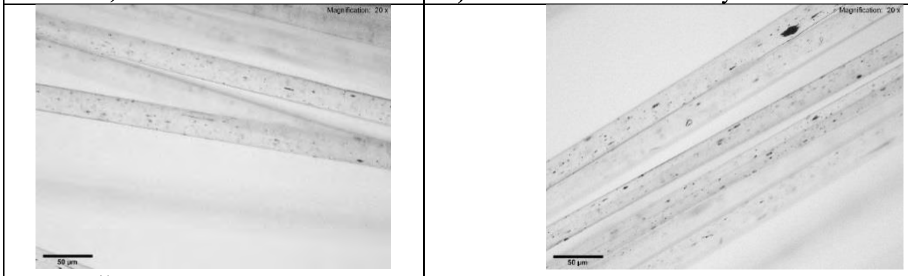
CNTs inside fibers can be seen in the photos. There are small aggregates in the fibers and distributed in the structure. There can be seen formation of CNT aggregates in very small amount. 1.0% CNT+SDS doped fiber has dense CNT content inside fiber structure which was thought being the reason of dark color of the fiber4. This fiber's fineness was the lowest one (Table 3) among all and here we can see that they are finer than the other fibers. F3-0.4% CNT+SDS doped fiber could not be produced because it break continuously while wrapping on cylinder. Big agglomerates can be seen in the Figure 9 and might be the cause of the breaks that prevent obtaining fiber structure. 1.0% PF-CNT doped fiber could be spun; therefore, CNT amount cannot be the reason for aggregation but mixing just before spinning may be insufficient for this fiber. Former sample CNT3 was in light gray color and CNTs in the fiber could not be seen in the longitutional view.

Fibers obtained with surfactants (Triton-X, SDS) and only PF-CNT contain 0.2% CNTs inside. When we compare them, fibers containing PF-CNT+SDS and only PF-CNT show smooth distribution of CNTs, while bigger agglomerates can be seen clearly in fiber with PF-CNT+Triton-X. The best distribution was in the fiber containing air-PF-CNTs alone (Figure 9.g). Additionally, color of the fiber with air-PF-CNTs alone (Figure 9.g) is a little darker (Figure 8) than the other same amount of CNT doped fibers with surfactants (Figure 9.c,d).



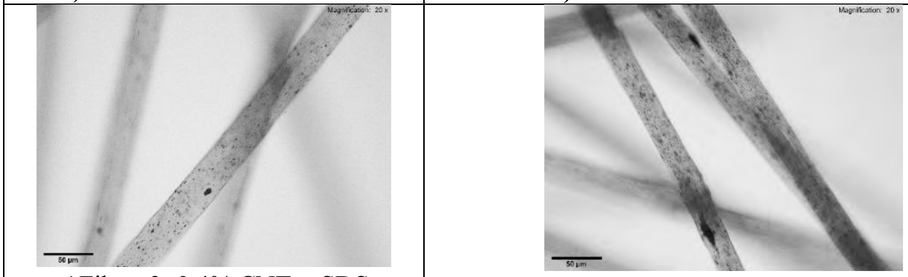
a)Standard PAN fiber

b)Fiber-CNT3: 0.02% acrylic acid PF-CNT + SDBS



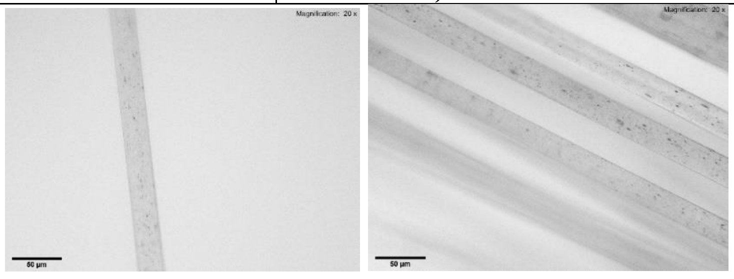
c)Fiber 1: 0.2% CNT + SDS

d)Fiber 2: 0.2% CNT + Triton X



e)Fiber 3: 0.4% CNT + SDS

f)Fiber 4: 1.0% CNT + SDS



g)Fiber 5: 0.2% PF-CNT

Figure 9. Optical microscopy views of PAN/CNT nanocomposite fibers (Fiber0 to fiber5 with former sample 0.02% aa-PF-CNT+SDBS)

In FTIR analysis of fibers (Figure 10), F0-PAN fibers showed characteristic peaks, which may be assigned as C≡N stretching (nitrile peak) at 2244 cm−1, C=O groups in the PAN chain at 1734 cm−1, –CH bending vibrations at 1456 cm−1 and at the peaks near 2850–3000 cm−1. Comparison of the spectra of PF-CNT doped PAN fibers with the standard PAN fibers, especially air PF-CNT doped PAN fibers exhibit a weak intensity at characteristic PAN peaks. Characteristic peaks especially nitrile peak of PAN decreased after CNT addition. These findings indicate that formed groups on the CNT surface after modification may have interacted with groups (i.e. peaks) of PAN chains, hindering nitrile polymerization as a result of mutual π–π interactions. [1, 27, 28]. These may also the cause of enhancement in electrical properties [28].

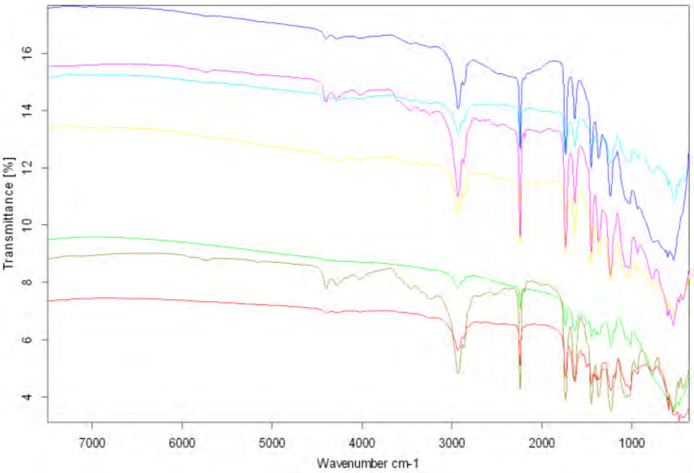


Figure 10. FTIR analysis results of fibers: pink: F0-Standard PAN fiber, yellow: F1-0.2% PF-CNT + SDS, navy: F2-0.2% PF-CNT + Triton X, red: F3-0.4% PF-CNT + SDS, green: F4-1.0% PF-CNT + SDS, turquoise: F5-0.2% PF-CNT, brown: CNT3-0.02% aa-PF-CNT+SDBS

Table 3 shows fiber fineness, tenacity and elongation-at-break.

Table 3. Physical properties of fiber samples (0-5)

Fiber Sample	Fiber Fineness, dtex	Tenacity, cN/tex	Elongation at break, %
0-Undoped PAN	4.00	23.34	26.24
1-0.2%PF-CNT+SDS	3.89	20.33	22.77
2-0.2%PF-CNT+Triton-X	3.89	19.92	21.20
3-0.4% PF-CNT+SDS	Very little amount of fiber could be obtained.		
4-1.0% PF-CNT+SDS	3.60	16.37	20.12
5-0.2%PF-CNT	3.85	23.59	27.69

0.4%CNT+SDS doped sample was an unsuccessful trial. The finest fiber was fiber4 with 1.0%PF-CNT+SDS. Similar fineness values were obtained for similar additive ratios of fiber1, fiber2 and fiber5. However, tenacity seemed to decrease respectively from fiber0 to fiber4. Lower tenacity values were obtained from surfactant doped fibers. Additional dispersing agents (surfactants in our study), while aiding uniform suspension of CNTs in liquid form, became impurity in fiber production negatively affecting physical properties. Surface active agents modify surfaces of CNTs connecting from its hydrophobic tail to CNTs and turning hydrophilic head to polar solvents by non-covalent way. As a result, they cannot be removed in fiber spinning process and prevent orientation of PF-CNTs. Comparing to all of them, PF-CNT doped fiber, plasma modification alone, has the highest tenacity and elongation. Low frequency air plasma modification was sufficient to obtain effective dispersion and it did not affect mechanical properties. In this case, we can conclude that plasma functionalization alone gives the best dispersion results and no other additives are needed for uniform dispersion. However, there were no increase in the strength values, because in our study as spun fibers were used having no further drawing process and the doping ratio was not sufficient to increase tenacity. Drawing process in fiber spinning influences the evolution of subsequent properties during production. For this reason, the strength values may increase, if more effective ultrasound mixing or additional fiber drawing process is applied [4, 5, 8, 13, 14, 29].

LOI test results of Fiber 0, Fiber 4 and Fiber 5 are given in Table 4. Standard PAN fiber, fiber having PF-CNT alone and the highest strength and fiber having the highest PF-CNT content were compared in terms of flammability property.

Table 4. LOI test results of fiber samples

Fiber Samples	**LOI Values (%)**
PAN Fiber	18.2
Fiber with 0.2%PF-CNT	18.2
Fiber 1.0% PF-CNT + SDS	18.2

CNTs in polymers enhance burning properties especially forming barrier between fire and material, however in our study, there is no difference between the LOI results of different fibers. [7]. They might be insufficient to enhance burning property of PAN fiber. In the work of Patel et al. in 2012 they concluded optimal loading for single-walled CNTs was found to be 1.0% and multi-walled CNTs was found to be 0.5%. Besides, in the study of Wen et al. in 2020, with small amounts as 1% and 3% and 5%, carbon black was found to be more effective than CNTs in development of flame retardancy [7, 30, 31]. Fiber surface resistance values are given in Table 5.

Table 5. Surface electrical resistances of fibers

Fiber Samples	**Surface Electrical Resistance (Ω)**
Fiber0-Standard PAN fiber	$1.02x10^{11}$
CNT3-0.02% aa PF-CNT doped fiber	$1.50x10^{11}$
Fiber1-0.2% PF-CNT+SDS doped fiber	$2.77x10^{10}$
Fiber2-0.2% PF-CNT+Triton-X doped fiber	$1.15x10^{11}$
Fiber3-0.4% PF-CNT+SDS doped fiber	$1.07x10^{11}$
Fiber4-1.0% PF-CNT+SDS doped fiber	$1.58x10^{11}$
Fiber5-0.2% PF-CNT doped fiber	$6.60x10^{10}$

PAN fibers have high electrical resistance. In this test, standard PAN showed a value of $1.02x10^{11}$ Ω. fiber1 and fiber5 showed surface resistances approximately five times lower than the others. These fibers showed more uniform distribution than the other fibers, as seen in optical microscope images (Figure 9) and physical properties (Table 3). PAN/CNT composite film and electrospun fibers showed electrical properties similar to our fibers [2, 32]. Amount of the SDS adsorbed on the surface of CNTs are lower than the amount of the Triton-X100 because of the negative charge of hydrophilic groups of SDS. Besides, anionic surfactant SDS can only be adsorbed on CNT surfaces via hydrophobic interaction, while nonionic surfactant Triton-X100 interact with the CNT surface via hydrophobic and $\pi - \pi$ stacking forces. Head of SDS molecule has negative charge like marginal negative surface charge of carbon clusters and this prevents all SDS to get adsorbed via hydrophobic interaction. Therefore, its poor adsorption affinity results in the presence of free carbon nanoparticles in the medium at all times. This may make current easier to pass via CNTs inside the fiber [4, 13, 33, 34].

4. CONCLUSIONS

The conclusions of the study are as follows: High quality CNTs were obtained at determined production conditions with low defect density and high crystallinity. These pristine CNTs stayed as agglomerates in dimethylacetamide and fiber production was impossible. Among anionic and nonionic surfactants after plasma treatment, anionic surfactant sodium dodecilsulfate was better than nonionic Triton-X100 for distribution of CNTs in PAN spinning solution. SDS was better in smaller amounts but increase in the amount (and thus residual amount in the fiber) worsened the mechanical, electrical properties. Plasma alone conditions, i.e. low frequency air plasma was found to be the best functionalization technique for distribution of CNTs in PAN fiber wet spinning solution. No other additives were needed for uniform distribution. 30W-50min low frequency air plasma alone was sufficient to disperse CNTs uniformly in wet spinning solution of PAN fiber. Enhanced results may be obtained by future studies adding higher amount of plasma functionalized CNTs in the fiber solution to get lower electrical surface resistance. More effective ultrasound mixing and additional fiber drawing process may be applied for higher strength values.

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