ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECT OF CARBON NANOTUBES AND POLYANILINE ON THE PROPERTIES OF POLYACRYLONITRILE/CARBON NANOTUBES COMPOSITE NANOFIBERS

M.Sc. THESIS

OLCAY EREN

Department of Polymer Science of Technology

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JUNE 2015

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Olcay EREN
(515121025)

Department of Polymer Science of Technology

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Thesis Advisor: Prof. Dr. H. Ayşen Önen

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POLİAKRİLONİTRİL/KARBON NANOTÜP KOMPOZİT NANOLİF ÖZELLİKLERİ ÜZERİNE KARBON NANOTÜP VE POLİANİLİN ETKİSİ

YÜKSEK LİSANS TEZİ

Olcay EREN
(515121025)

Polimer Bilimi ve Teknolojisi Bölümü

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. H. Ayşen Önen

HAZİRAN 2015

Olcay EREN, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 515121025 successfully defended the **thesis** entitled "**EFFECT OF CARBON NANOTUBES AND POLYANILINE ON THE PROPERTIES OF POLYACRYLONITRILE/CARBON NANOTUBES COMPOSITE NANOFIBERS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. H. Ayşen Önen** ....
İstanbul Technical University

Jury Members : **Prof. Dr. Yüksel Güvenilir Avcıbaşı** ....
İstanbul Technical University

Doç. Dr. Vezir Kahraman ....
Marmara University

Date of Submission : 4 May 2015
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To my family,

FOREWORD

This study has been carried out in TEXFIB (Textile and Synthetic Fiber) Research Laboratory and POLMAG Laboratory (Polymeric Material Research Group) with the support of TUBITAK (project number 112M877), in Istanbul Technical University.

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May 2015

Olcay EREN
(Chemical Engineer)

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ABBREVIATIONS

ASTM **:** American Society for Testing and Materials
CNT **:** Carbon nanotubes
CSA **:** Campfor sulfonic acid
DMF **:** Dimethylformamide
DMSO **:** Dimethylsulfoxide
DSC **:** Differential Scanning Microscope
FT-IR **:** Fourier Transform Infrared Spectroscopy
KBr **:** Potassium Bromide
MWCNT **:** Multi walled carbon nanotubes
SEM **:** Scanning Electron Microscope
PAN **:** Polyacrylonitrile
PANI **:** Polyaniline
PTFE **:** Polytetrafluoroethylene
THF **:** Tetrahydrofuran
XRD **:** X-Ray Diffraction

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EFFECT OF CARBON NANOTUBES AND POLYANILINE ON THE PROPERTIES OF POLYACRYLONITRILE/CARBON NANOTUBES COMPOSITE NANOFIBERS

SUMMARY

PAN is the most widely used precursor for processing high performance fibers due to its combination of tensile and compressive properties as well as its high carbon yield. CNTs are ideal reinforcing materials for polymeric matrix. Some important interactions exist between PAN chains and CNTs and these ones lead to a higher orientation of PAN chains during the heating process. It was reported that the PAN macromolecular orientation increases with increasing CNT orientation in the polymer.

Some difficulties must be overcome before producing a homogenous dispersion of CNTs in a polymer matrix, including modification for CNTs and processing methods for fabrication CNTs/polymer composites. Modification for CNTs may be succeed by lots of methods including the use of surfactants and chemical functionalization which has been shown to be effective in improving dispersion because the functional groups on the CNTs surface counteract the van der Waals attractive forces between CNTs and then enhance interaction of the matrix phase. Pristine and functionalized CNTs can be dispersed in a lot of polymer matrix systems.

Among the conductive polymers, polyaniline (PANI) is widely used in polymer matrix to improve conductivity thanks to ıts low cost, ease of synthesis and good compability with other polymers.

Nanofibres can be prepared from a polymer solution utilizing electrospining. Electrospinning is one of tools for preparation of nanofibers and also ıt provides a straightforward and cost-effective approach to produce fibers from polymer solutions or melts having various diameters.

In this thesis, PAN-CNT and PAN-CNT-PANI composite fibers were produced. Characterization of composite nanofibers is made by FT-IR, DSC, XRD, SEM, tensile tester and conductivity meter. With the addion of PANI and CNT, tensile strength improved to 10.85 N/mm^2 from 8.64 N/mm^2. Also electrical conductivity and crystallization were improved with PANI and CNT.

POLİAKRİLONİTRİL/KARBON NANOTÜP KOMPOZİT NANOFİBER ÖZELLİKLERİ ÜZERİNE KARBON NANOTÜP VE POLİANİLİN ETKİSİ

ÖZET

Poliakrilonitril sentetik yarı kristalin organik polimerdir. Genel formülü $(C_3H_3N)_n$ şeklindedir. Çoğu solvent ve kimyasala karşı dayanıklıdır. Akrilonitril polimerinden serbest radikal polimerizasyonu ile üretilir. Anyonik polimerizasyonla da üretilebilir. Yüksek moleküler ağırlıklı poliakrilonitril ile karbon fiber üretimi yapılır.

Karbon nanotüpler tek katmanlı veya çok katmanlı olabilirler. Çapları 1 nm ile 100 nm arasında değişebilir. Boyları ise 0.1 lm'den itibaren başlayarak farklılık gösterir. Çok katmanlı veya tek katmanlı yapılarına göre çeşitli özellikler gösterirler. Genellikle tek katmanlı karbon nanotüpler daha spesifik ve ideal mekanik özellikler gösterirler. Fakat yüksek üretim maliyetlerinden dolayı çok katmanlı karbon nanotüpler terch edilir. Mükemmel özelliklerine rağmen, güçlü Van der Waals kuvvetleri yüzünden karbon nanotüpler kolaylıkla aglomere yapı oluşturabilirler. Bu zayıf kimyasal uyumu ugulamalarını kısıtlar. Bu nedenle karbon nanotüpler çeşitli kimyasal yöntemlerle fonksiyonlandırılırlar.Karboksil, hidroksil ve amino grupşarın yardımıyla karbon nanotüplerin solventler içerisindeki çözünürlüğü ve dispersiyonu gelişir.

İletken polimerler ise elektormanyetik kalkanlama, biyosensörler, enerji depolama cihazları gibi birçok alanda kullanılır. İletken polimerler arasında polianilin ucuz maliyeti, kolay sentezi ve diğer polimerlerle iyi uygunluk göstermesi bakımından polimerik matrikslerde iletkenlik sağlamak için kullanılan polimerlerden biridir. Fakat polianilin zor çözünebilen ve işlenmesi zor olan bir polimerdir. Bu nedenle çeşitli kimyasallar ile birlikte kullanılarak işlenebilirliği arttırılır.

PAN özelliklerinden dolayı yüksek performanslı lif üretimi için kullanılan önemli polimerlerden biridir. Karbon nanotüpler ise polimerik matriks için ideal güçlendirici materyallerdendir. PAN zincirleri ve CNT arasındaki etkileşimler sayesinde, polimer matris içinde CNT oryantasyonunun artmasıyla PAN makromoleküler oryantasyonunun arttığı bildirilmiştir. CNT yüzeyindeki fonksiyonel grupların CNT'ler arasındaki çekici van der Waals kuvvetlerini etkisizleştirmesinden dolayı dispersiyonu geliştirmede etkili olan işlenmemiş ve fonksiyonlanmış CNT'ler birçok polimer matris içinde disperse olabilirler.

Nanolifler elektrospining kullanılarak, polimer çözeltisinden hazırlanabilir. Bu metotla, polimer çözeltisi iğne ucu ile metal toplayıcı arasına yüksek voltaj uygulanarak, içerisine CNT gömülü şekilde nanolif oluşur.

Bu çalışmada PAN-CNT ve PAN-CNT-PANI kompozit lifleri elektrospining tekniği ile üretilmiştir. Liflerin karakterizasyonu FT-IR, SEM, DSC, XRD, mukavemet cihazı ve iletkenlik cihazıyla yapılmıştır.

Deneysel kısımda ilk olarak CNT/PAN kompozitleri üzerine çalışılmıştır. Kolaylıkla aglomere olabilen karbon nanotüpler için en uygun çalışma yüzdesini belirleyebilmek için % 0,5'ten başlayarak sırasıyla 1, 3, 5, 7 ve 10 yüzde oranlarında CNT ilavesi ile PAN lifleri hazırlanmıştır. Mukavemet sonuçlarına göre yapılan değerlendirmelerde en uygun çalışma yüzdesi %1 ve %3 CNT ilavelerinde görülmüştür. Bu değerlerden sonra yüksek miktarda gözlenen aglomere yapılardan dolayı mekanik özellikler düşme göstermiştir.

Diğer bir taraftan CNT disperse yöntemi incelenmiştir. Ultrasonik banyo, ultrasonik homojenizer ve mekanik homojenizer ile yapılan çeşitli deneyler sonucu üretilen nanoliflerin mukavemet sonuçları değerlendirildiğinde en iyi sonucun karbon nanotüplerin önce 10 dk ultrasonik homojenizer ile disperse edilmesi daha sonra ise 45 dk ultrasonik banyoda kalması ile elde edildiği gözlemlenmiştir. Bundan sonraki proseslerde CNT dispersiyonu için kullanılan yöntem olarak bu kullanılmıştır.

Bu bölümde son olarak ise hazır alınan plazma yöntemiyle karboksil ve amin grup bağlanmış karbon nanotüplerin etkisi incelenmiştir. Mukavemet sonuçlarına bakıldığında yapısındaki nitril grupları sayesinde amin grup bağlı karbon nanotüplerin PAN matrik içerisinde daha iyi uyum gösterdiği ve saf PAN lifine göre mukavemeti geliştirdiği görülmüştür.

Fonksiyonel grubun etkisi incelendikten sonra ikinci adımda amaç asit muamelsei yöntemiyle karbon nanotüpleri fonksiyonlandırmak ve etkilerini incelemektir. Karbon nanotüplere ilk olarak sülfürik asit/hidroklorik asit yardımıyla muamelesiyle karboksil grup bağlanır. Hidroksil ve amin grubu bağlama işlemi bu karboksil grup bağlanmış karbon nanotüpleri üzerinden yapılır. Hidroksil grup için etilen glikol, amin grup için izoforon diamine kullanılır. FT-IR sonuçlarıyla karbon nanotüplere fonksiyonel grup bağlama işleminin başarıyla gerçekleştirildiği görüldükten sonra bu karbon nanotüpler ile CNT/PAN nanolifleri hazırlanır ve mukavemet, iletkenlik, ısıl ve morfolojik bakımdan nanoliflere etkileri incelenir. Nanoliflerin çap sonuçları incelendiğinde fonksiyonlandırma ile çap değerlerinin azalma gösterdiği görülmüştür. Mukavemet sonuçlarında ise, amin grup bağlı karbon nanotüpleri ile hazırlanan kompozitlerin 2.24 N/mm^2 ile en iyi değeri vermiştir. İletkenlik ve kristalinite de saf PAN lifine göre gelişme göstermiştir. Fakat karboksil, amin ve hidroksil grup bağlı karbon nanotüpler arasında iletkenlik bakımından çok farklılık görülmemiştir. Bu bölümdeki sonuçlardan elde edilen verilere göre amin grup başlı karbon nanotüpler ile çalışılmaya devam edilmiştir.

Üçüncü bölümde amin grup bağlı karbon nanotüpler ile saf, hiçbir grup bağlı olmayan karbon nanotüpleri üzerine çalışma yapılmıştır. %1 ve %3 oranında CNT ilavesi ile kompozitler hazırlanmıştır ve morfolojik, iletkenlik ve mukavemet bakımından sonuçlar incelenmiştir. Bu sonuçlar dahilinde %1ve %3 oranında amin bağlı karbon nanotüp en iyi sonucu verdiğinden dolayı PANI ile yapılacak kompozitlerde kullanılmaya karar verilmiştir.

Deneysel kısmın son bölümünde hem karbon nanotüp hem PANI aynı anda PAN matriksi içine katılıp, kompozit nanolif üretilmiş ve özellikleri incelenmiştir. PANI oranı %3 oranında tutulmuş, karbon nanotüp ise %1 ve %3 oranında çalışılmıştır. Saf PAN ve PANI liflerine göre karşılaştırma yapılarak sonuçlar değerlendirilmiştir.

%3 PANI ve %1 CNT katkısı ile mukavemet saf PAN lifine göre 8.64 N/mm^2'den 10.85 N/mm^2 'ye çıkmıştır. En iyi mukavemet bu değerlerde elde edilmiştir.

İletkenlik bakımından incelendiğinde nanolifler antistatik sınırına gelmiş ve saf PAN lifine göre gelişme göstermiştir.

Termal testlerden elde edilen verilere göre ise PANI etkisi ile ısıl bakımından da nanoliflerin gelişme gösteridiği gözlemlenmiştir. XRD sonuçlarına göre ise en iyi kristaliniteyi %3 PANI ve %1 CNT içeren numunenin gösterdiği bulunmuştur.

1. INTRODUCTION

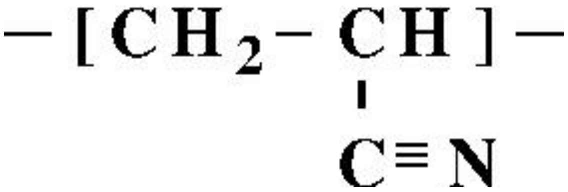
As it is known, polyacrylonitrile (PAN) is the one of the most important polymers which can have application areas in textiles, automotive industry, drug applications and implant materials in medical sector, and membranes etc. [1]. Polyaniline (PANI) is also an important polymer, for example, doped PANI has electrical conductivity property [2]. Thus, polymer composites including PANI can be employed in many areas such as antistatic textiles, electromagnetic shielding, filtration media, sensors and actuators, and radiation detectors [3-10]. Moreover, there are also many inorganic nanofillers available which are used to improve the properties of polymer matrix. Carbon nanotube (CNT) is one of the well-known nanofillers with desirable properties including good mechanical, electrical and thermal properties [11]. CNTs are generally functionalized with carboxyl or amine groups by treating with chemicals to provide better interfacial bonding between polymer matrix and CNTs [11,12].

In this study, both PANI and CNT were used to improve PAN composite nanofibers. Amount of loadings of PANI and CNT were examined. Also dispersion methods of CNTs and the effect of functionalized CNT were investigated. Performance and characteristic properties of composite nanofibers have been analyzed by tensile tester, electrical conductivity meter, FTIR, DSC, XRD, and SEM.

2. THEORETICAL PART

2.1 Polyacrylonitrile

Polyacrylonitrile is a synthetic, semicrystalline organic polymer resin, with the linear formula $(C_3H_3N)_n$ (Figure 2.1). PAN has a melting point of about 319 ^{o}C. It is thermoplastic, it does not melt under normal conditions. It degrades before melting [13,14]. it is a hard, rigid thermoplastic material that is resistant to most solvents and chemicals, slow to burn, and of low permeability to gases [15].



$$-[CH_2-\underset{\substack{| \\ C\equiv N}}{CH}]-$$

Figure 2.1 : Structure of PAN [16].

All commercial methods of production of PAN are based on free radical polymerization of Acrylonitrile (AN). Most of the cases, small amount of other vinyl comonomers are also used (1-10%) along with AN depending on the final application. Anionic polymerization also can be used for synthesizing PAN. For textile applications, molecular weight in the range of 40,000 to 70,000 is used. For producing carbon fiber higher molecular weight is desired.

2.1.1 Applications of PAN

Polyacrylonitrile is major precursor for the production of carbon fiber. PAN is first thermally oxidized in air at 230 degrees to form an oxidized PAN fiber and then carbonized above 1000 degrees in inert atmosphere to make carbon fibers found in a variety of both high-tech and common daily applications such as civil and military aircraft primary and secondary structures, missiles, solid propellant rocket motors, pressure vessels, fishing rods, tennis rackets, badminton rackets and high-tech bicycles [13].

It is a versatile polymer used to produce large variety of products including ultra filtration membranes, hollow fibers for reverse osmosis, fibers for textiles, oxidized PAN fibers. Also most polyacrylonitrile acrylic which is a common substitute for wool in clothing and home furnishings [13,15].

Its homopolymers can be used as fibers in hot gas filtration systems, outdoor awnings, sails for yachts, and fiber-reinforced concrete while ıts copolymers can be used as fibers to make knitted clothing like socks and sweaters, as well as outdoor products like tents and similar items.

PAN has properties involving low density, thermal stability, high strength and modulus of elasticity. These unique properties have made PAN an essential polymer in high tech.

Its high tensile strength and tensile modulus are established by fiber sizing, coatings, production processes, and PAN's fiber chemistry. Its mechanical properties derived are important in composite structures for military and commercial aircraft [13].

2.2 Carbon Nanotubes

2.2.1 Introduction to CNTs

As reported by Iijima in 1990, carbon nanotubes (CNTs) are the ideal materials for reinforcing polymer materials because of their high structural, mechanical, chemical, thermal and electrical performance [11,17]. Carbon nanotubes can be single or multiwalled. They may have diameters from 1 nm to 100 nm, and lengths from 0.1 lm to several mm. Both multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) (Figure 2.2) possessing tubular nanostructures and unique quantum and promising mechanical properties have been widely considered as attractive candidates for important composition hybrids for fabricating novel materials with desirable properties. Generally, SWNTs exhibit simpler structures and are easily controllable as regards diameter during fabrication as compared with MWNTs. But high cost of SWNTs restricts its commercialization hence generally MWCNTs can be used [18,19].

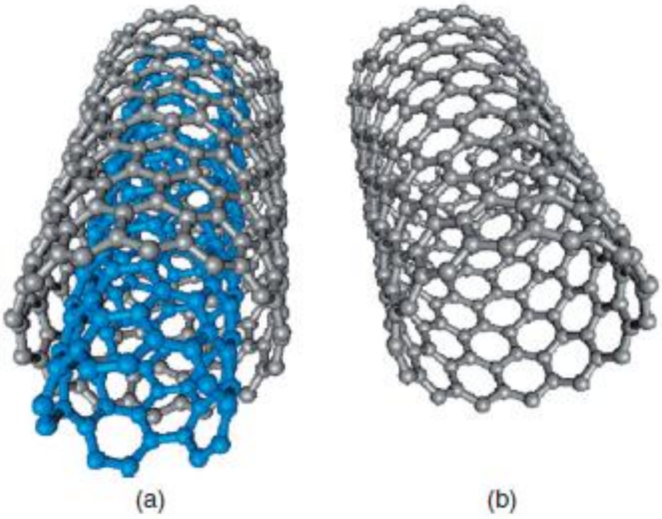


Figure 2.2 : a) MWCNTs b) SWCNTs [20].

Despite its excellent properties, because of the strong intrinsic Van der Waals forces, CNTs tend to aggregate and entangle together spontaneously. The poor chemical compatibility greatly limits their applications. To overcome from this problem, the chemical functionalization of CNTs is of fundamental importance. With various process (acid treatment etc.) CNTs can be functionalized (Figure 2.3). Introduction of functional groups, such as carboxyl and amino groups, not only can improve CNTs solubility in various solvents, but also are useful for the further chemical link with other compounds, such as biomolecules, inorganic compounds and polymers, and the CNTs self-assembly into devices structures [21].

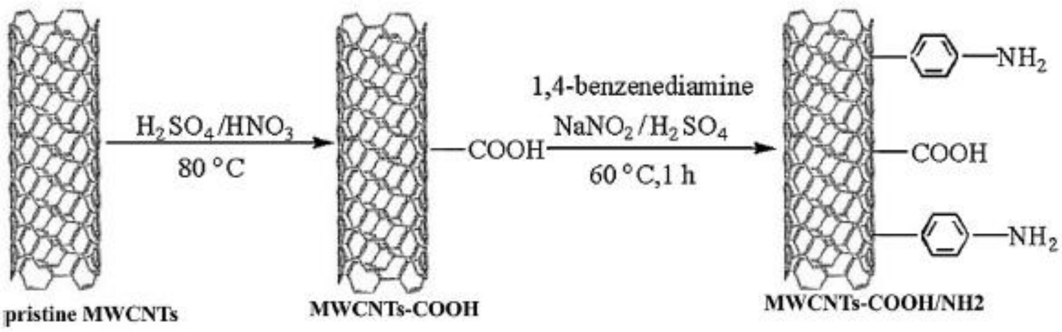


Figure 2.3 : Functionalization of CNTs with carboxyl or amine groups.

Several approachs are developed to functionalize CNTs. These approaches include defect functionalization, covalent functionalization of the sidewalls, noncovalent exohedral functionalization, for example, formation of supramolecular adducts with surfactants or polymers, and endohedral functionalization (Figure 2.4) [22].

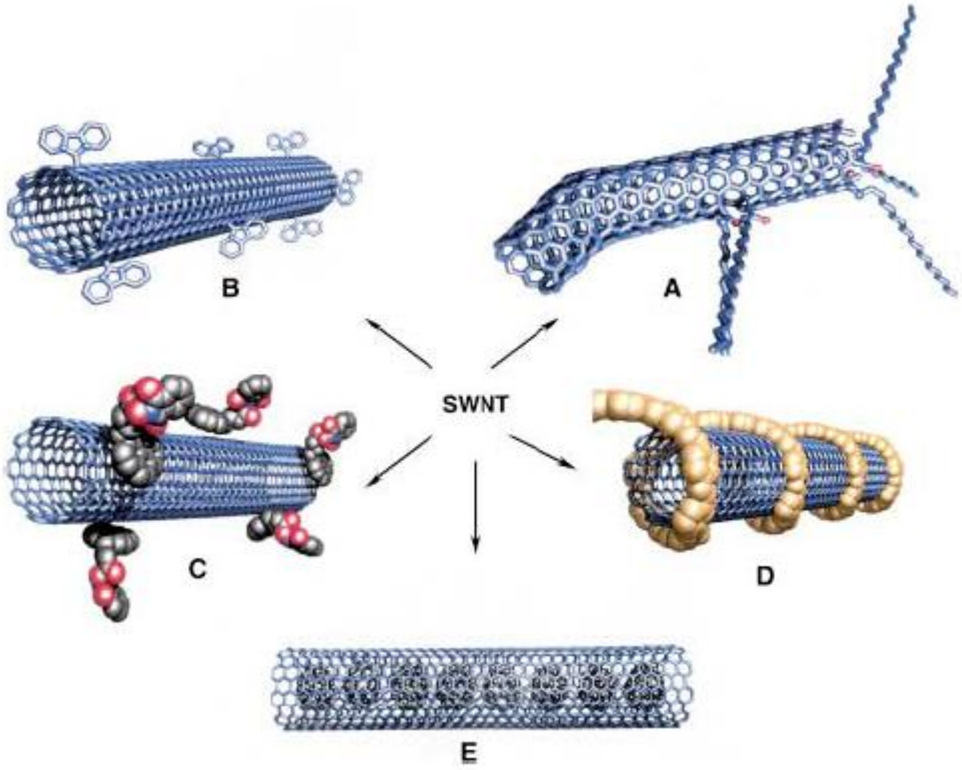


Figure 2.4 : Functionalization possibilities a) defect group functionalization b)covalent sidewall functionalization c) non-covalent exohedral functionalization with surfactans d) non-covalent exohedral functionalization with polymers e)endohedral functionalization [22].

2.2.2 Properties of CNTs

The chemical bonding of CNTs is composed entirely of sp^2 carbon– carbon bonds. This bonding structure – stronger than the sp^3 bonds found in diamond – provides CNTs with extremely high mechanical properties. It is well known that the mechanical properties of CNTs exceed those of any existing materials. Although there is no consensus on the exact mechanical properties of CNTs, theoretical and experimental results have shown unusual mechanical properties of CNTs with Young’s modulus as high as 1.2 TPa and tensile strength of 50–200 GPa. These make CNTs the strongest and stiffest materials on earth. In addition to the exceptional mechanical properties associated with CNTs, they also possess other useful physical properties and it is clear that CNTs have many advantages over other carbon materials in terms of electrical and thermal properties. These properties offer CNTs great potential for wide applications in field emission, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibers, catalyst supports, biological applications, air and water filtration, ceramics and so on [23].

2.3 Polyaniline (PANI)

Conductive polymers have exhibited developing potential for use in many areas with the early work of MacDiarmid, Shirakawa and Heeger [24]. Conductive polymers and their composites have been studied enthusiastically because of their potential applications in the electromagnetic interference shielding, radiation detector, information storage, energy storage devices, sensors, biosensors, membranes, and so on. Polyaniline (PANI) is one of the most promising conducting polymers due to its straightforward polymerization and excellent chemical stability combined with relatively high levels of conductivity, good combination of properties, environmental stability, low cost of raw material, ease of synthesis, and good compatibility with polymer supports [25,26]. However, PANI is insoluble, infusible and almost non-processable, which retard its potential applications. In order to improve the processability of PANI, a large number of methods have been studied, of which the most widely adopted strategy is to dope PANI with organic acids with long alkyl chain such as camphor sulfuric acid (CSA) or dodecylbenzene sulfonic acid (DBSA). The bulk non-polar tail renders the polyanilines in conducting form to be soluble in some ordinary organic solvent such as m-cresol, chloroform and xylene. Therefore, such doped PANI can be solution processed together with common insulating polymers in proper solvent [27].

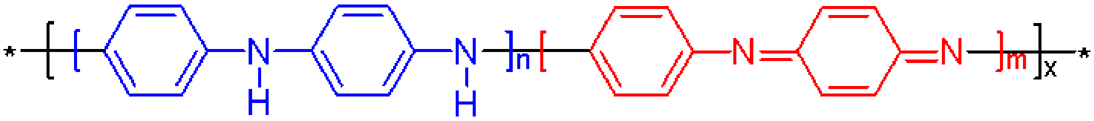


Figure 2.5 : Structure of PANI.

Polyaniline polymerized from the inexpensive aniline monomer and it can be found in one of three idealized oxidation states: leucoemeraldine, emeraldine and (per)nigraniline. PANI is especially attractive because it is relatively inexpensive, has three disctinc oxidation states with different colors and has an acid/base doping response. This latter property makes PANI an attractive for acid/base chemical vapor sensors, supercapacitors and biosensors [28].

2.4 PAN-CNT-PANI Composite Nanofibers

Researchers are highly interested in the development of high-quality multifunctional materials such as the advanced nanostructured composites. The key factor is represented by the suitable choice of the appropriate synthetic polymers and fillers. Carbon nanotubes are excellent filler to reinforce polymer composites. Due to strong π-π interaction between functionalized carbon nanotubes surface and nitrile group of PAN matrix, better adhesion is formed and it improves the thermal and mechanical properties [29]. Also conductive polymer PANI can be used to improve electrical properties of PAN which has a insulator behaviour in nanofiber form.

Several authors have studied about CNT-PAN and PAN-PANI composite nanofibers. There are various studies related to composite PAN nanofiber with only CNTs. However there are very limited studies carried out on PAN composite nanofiber together with PANI.

Qiao et al. observed an increase in diameter and better modulus and tensile strength by the addition of carbon nanotubes [30]. Kyung Park et al. investigated the effect of functional groups of carbon nanotubes and pointed out that enthalpy of composites with the functional carbon nanotubes increased compared to pure PAN fibers [31]. Wang et al. pointed out the improved mechanical properties using functionalized carbon nanotubes [29].

3. EXPERIMENTAL PART

3.1 Equipments

In this study, Polyacrylonitrile fibers reinforced with carbon nanotubes and polyaniline were produced with electrospininng. In the electrospinning system, the composite polymer solution which is loaded into a syringe was purged to the needle tip by the syringe pump. A positive voltage was applied to the rotating drum collector that is covered by aluminum foil. The negative voltage from high-voltage power supply was connected to the needle tip. Because of high electric field, solution is drawn from needle tip into nonwoven mat covered on the aluminum foil on rotating drum and it is collected in nanofiber web form.

On electrospinning system, the feeding rate of the polymer solutions was 1 mL/h with 15 kV electrospinning voltages and the distance between the needle tip and collector was 10 cm.

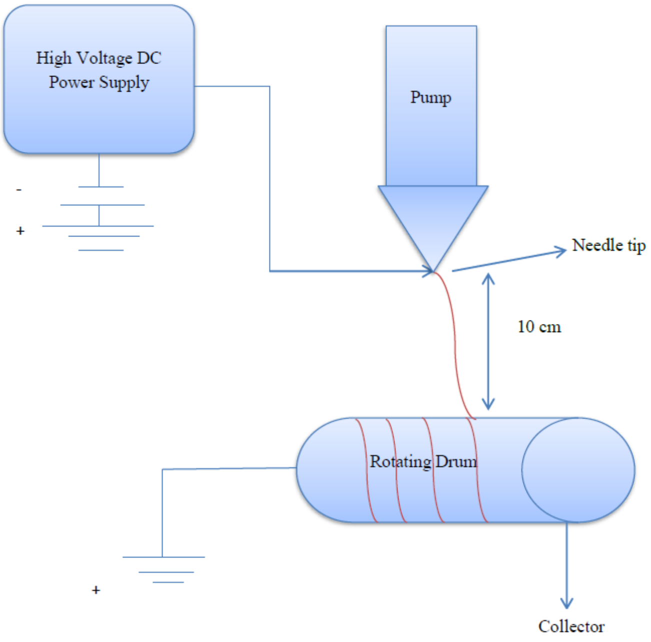


Figure 3.1 : Scheme of electrospininng system.

Tensile tester was used for the evaluation of mechanical properties. Tensile strength, breaking elongation and modulus of the webs were obtained with a 100N load cell at a crosshead speed of 20 mm/min At least 7 measurements were done to obtain average value of mechanical properties of nanofiber web. The gauge length, the length of nanofibers and the width of nanofiber was 15 mm, 50 mm, 5 mm, respectively.

Fourier transform infrared absorption (FTIR) spectra for composite nanowebs and carbon nanotubes were collected with Thermo Scientific Nicolet IS10 spectrometer. The scanning ranged from 4000 to 400 cm^{-1} with a signal resolution of 4 cm^{-1}. In all cases, 16 interferograms of a sample were averaged. ATR method was used to collect the IR spectra for composite nanofibers and pristine CNT, -COOH and –OH functionalized CNTs. KBr pellet method was used to collect the IR spectrum of amine functionalized CNTs.

The morphology and the surface structure of composite nanofiber samples were investigated by SEM Carl Zeiss EVO MA10. The samples were coated with gold to prevent the charging effects during scanning. The SEM were applied at 5 kV voltage. Image J Software was used to calculate the diameters of nanofibers from SEM photomicrographs. At least 50 measurements were done to obtain average fiber diameter.

DSC Q10 (temperature range between 20-400 ˚C) was used for thermal analysis at a heating rate of 20 ˚C/min, under nitrogen atmosphere.

Wide-angle X-ray diffraction traces were obtained using a Bruker® AXS D8 Advance X-ray diffractometer system using nickel filtered CuK$_\alpha$ radiation (λ, 0.15406 nm) and voltage and current settings of 40 kV and 40 mA, respectively. Counting was carried out at 10 steps per degree. The observed equatorial X-ray scattering data was collected in reflection mode in the 5-40º 2θ range. X-ray data-curve fitting developed by Hindeleh et al. has been applied [32]. Apparent X-ray crystallinity is based on the ratio of the integrated intensity under the resolved peaks to the integrated intensity of the total scatter under the experimental trace [33].

Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ) with two circular probe with four wire system was used for the measurement of the resistance of composite nanofibers. The integrated thickness meter was used to measure the thickness of the samples. At least 7 measurements were done to obtain average value of electrical conductivity and thickness of nanofiber web. Volume conductivity of the samples in S/cm were calculated according to equation 1 as indicated in ASTM standards [34,35]. Volume resistance values were measured and the conductivity of the composite nanofibers in S/cm were calculated by using equation 1.

$$\gamma_v = t/(AxR_v) \tag{1}$$

where:

R_v = volume resistance, Ω,

A = area of the electrodes, cm^2 and

t = distance between the electrodes, cm.

Variation analyses were done with t tests or ANOVA test in the 95 % confidence interval to see whether the differences between the average values important or not.

3.2 The Effect of Modified CNTs and Processing Parameters on the Properties of CNT/PAN Composite Nanofibers

In this part, plasma modified CNTs containing amino and carboxyl (NH_2 and COOH) functional groups instead of CNTs modified by an acid treatment method were used to observe functional group effect. Also the effect of dispersion method for homogenization of CNTs in polymer matrix was studied. In addition to ultrasonic homogenizer which is widely used for dispersing CNTs in polymer matrix, mechanical homogenizer and ultrasonic bath are also used to evaluate the effect of preparation method on final composite product. The amount of CNT has been changed as 0, 0.5, 1, 3, 5, 7 and 10 wt% to observe the effect of loading on properties of PAN-CNT composite nanofibers.

3.2.1 Materials and Methods

PAN possessed a molecular weight of 150.000 g/mol was purchased from Sigma Aldrich. DMF from Merck was used as solvent. MWCNTs as pristine (diameter 10-20 nm, length 10-30 μm) and plasma modified CNTs with NH_2 and with COOH functional groups (diameter 13-18 nm, length 3-30 μm) were supplied by cheaptube.

PAN (with 7 wt% PAN concentration) was dissolved in the stable suspension of MWCNT in DMF (with different CNT loading such as 0.5, 1, 3, 5, 7, 10 wt %).

To investigate the effect of dispersion method on mechanical properties, ultrasonic bath, ultrasonic homogenizer and mechanic homogenizer were used. For ultrasonic bath dispersion method; CNT/DMF stable solution was dispersed for 10 minutes with ultrasonic homogenizer and then for 45 minutes with ultrasonic bath. After the addition of PAN, solution was stirred at 60 ˚C by magnetic stirring. For ultrasonic homogenizer dispersion method and mechanic homogenizer method, prior to the addition of PAN, CNT/DMF solution was only dispersed for 2 hours with ultrasonic homogenizer and mechanic homogenizer (4000 rpm) separately. After then PAN was added and stirred at 60 ˚C by magnetic stirring. The last method is to use ultrasonic homogenizer for CNT/PAN/DMF solution, i.e., ultrasonic homogenizer was used to disperse CNT/DMF solution for 2 hours and then PAN was added into CNT/DMF solution and processed by ultrasonic homogenizer for 30 minutes.

On electrospinning system, the feeding rate of the polymer solutions was 1 mL/h with 15 kV electrospinning voltage and the distance between the needle tip and collector was 10 cm.

3.2.2 Results and Discussion

Figure 3.2 shows the photos of nanofibers which were produced with electrospinning on the spunlace nonwoven. As the amount of carbon nanotubes are increased the colour of the nanofibers become darker.

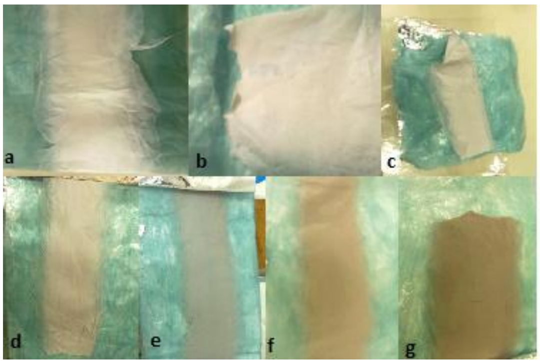


Figure 3.2 : Picture of nanofibers a) 100% PAN nanofiber b) 0,5% CNT loading PAN composite nanofiber. c) 1% CNT loading PAN composite nanofiber d) 3% CNT loading PAN composite nanofiber e) 5% CNT loading PAN composite nanofiber f) 7% CNT loading PAN composite nanofiber.g) 10% CNT loading PAN composite nanofiber.

Morphology of the nanofibers

Figure 3.3 and Figure 3.4 show the SEM images of PAN nanofiber and PAN/CNT composite nanofibers. The surface morphology of the pristine PAN nanofiber and the 1% CNT loaded nanofiber is smooth and straight. The surface of composite PAN nanofiber with 10 % CNT becomes rougher with an increase in the concentration of MWCNTs. It indicates the existence of agglomeration and the existence some amount of CNTs which are near to fiber surface. Also the bead formation was observed at 10 % CNT loaded nanofiber due to less dispersion and agglomeration of CNTs at high concentration. Beads areas act as stress concentration points which affect the mechanical properties [36].

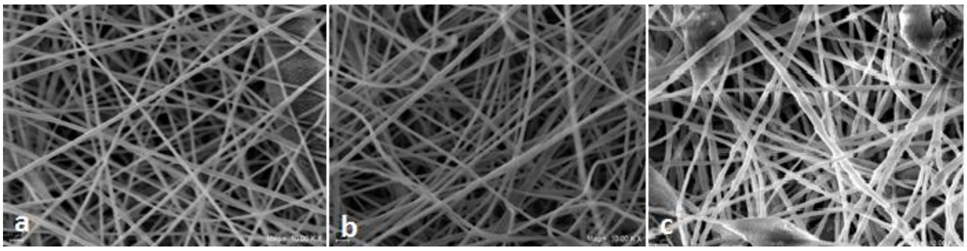


Figure 3.3 : SEM images of a) PAN nanofibers, b) CNT/PAN nanofiber containing 1% carbon nanotubes, c) CNT/PAN nanofiber containing 10 % carbon nanotubes.

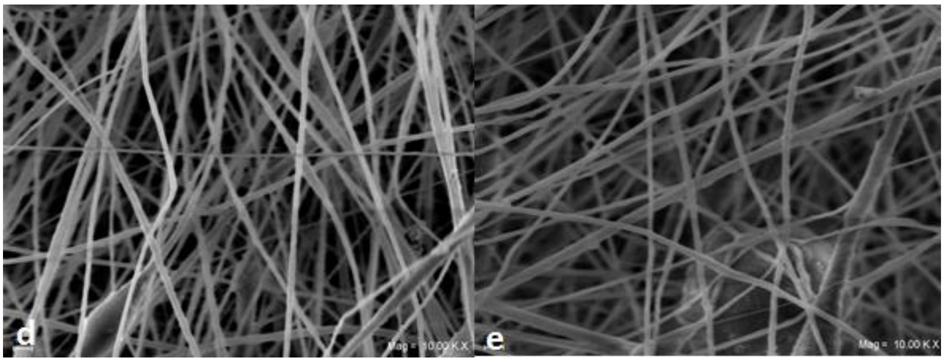


Figure 3.4 : SEM images of d) plasma modified COOH functional CNT/PAN nanofiber, b) plasma modified NH2 functionalized CNT/PAN nanofiber.

The diameters of PAN nanofiber and CNT loaded PAN composite nanofibers are given in Table 3.1. As seen on from the Table 3.1, the diameter of the nanofibers increased with an increase in the concentration of CNT. This behavior depends on the increasing viscosity of the system with the increasing amount of filler. As known an increase of viscosity results to an increase of nanofiber’s diameter.

The plasma modified CNT-PAN composite nanofibers containing COOH and NH_2 functional groups have nanofiber diameters as 331 and 337 nm, respectively. As seen from the Table 3.1, all 1% CNT loaded nanofiber have lower diameters than pure PAN nanofiber. This may be due to an increase of conductivity of nanofiber due to the presence of CNT.

The difference in diameter for plasma modified NH_2 functional CNT/PAN nanofiber and plasma modified COOH functional CNT/PAN nanofiber is insignificant according to statistical t test (95% level and two sided).

Table 3.1: The diameters of composite nanofibers.

PAN nanofiber (nm)	**1% CNT loaded PAN/CNT nanofiber (nm)**	**10% CNT loaded PAN/CNT nanofiber (nm)**	**PAN/CNT with plasma modified COOH (1% loaded) (nm)**	**PAN/CNT with plasma modified NH_2 (1% loaded) (nm)**
342±149.3	322±80	417±160	331±94.8	337±126.5

As it is well known, the effect of nano fillers on the mechanical behavior of composite polymers is some different than that of with fiber filler. Fiber fillers can carry the load which leads to an increase in the strength of the composite polymer. Nano filler has more intense interaction with the polymer matrix because of their large surface area. Nano fillers interfere with polymer chain movement (blockage effect), this may result with an increase in the strength of composite because of the decrease of the molecular mobility. Some nano fillers can also take the load and thus, it can transfer the stress away from the polymer matrix [37].

Table 3.2 shows the mechanical properties of PAN/CNT nanofibers loaded with different CNT amounts. The incorporation of a small quantity of CNTs (1%) improved the mechanical properties of PAN nanofibers (improvement approximately 20%) thanks to nanoreinforcing effect of CNTs. But 0,5 % CNT loaded composite nanofiber shows lower values of tensile strength compared to PAN nanofiber. In non-homogenous dispersion of nanotubes in polymer matrix, the nanotube can be considered as stress concentration point in nanofiber structure [36]. 1% CNT loaded composite nanofibers exhibited higher tensile strength values. Good dispersion and good interfacial interaction provides the best mechanical properties. 1% CNT loaded PAN/CNT nanofiber has the best mechanical properties in terms of tensile strength and modulus in comparison with the other composite nanofiber webs. The tensile strength and the strain of composite nanofiber decrease with an increase of CNT. This may be because of an increase of non-homogenous distribution and agglomeration of CNTs and the formation of voids at high concentration of filler. Addition of CNT into polymer matrix results in an increase of modulus of polymer composite nanofiber compared to 100% PAN nanofiber, because of decrease of mobility of polymer (nano filler interfering the polymer chain movement (blockage effect) [37]. The increase in elastic modulus is usually related to an increase in polymer chain orientation along the fiber axis. It was reported that the PAN macromolecular orientation increases with increasing CNT orientation in the polymer and CNT presence results in higher crystalline size in the polymer and thanks to interactions existing between PAN chains and CNTs [30,38]. It is highly possible that CNTs may be aligned along the nanofiber axis direction which may in turn increase the alignment of PAN/CNT composite structure. After all, the elastic modulus of CNT is much higher than that of pure PAN. Availability of CNT results in the decrease of strain of polymer composite nanofiber compared to 100 % PAN nanofiber. This may be explained with two different mechanisms. The reasons may be in such a way that, it may result from the weakness of polymer composite with high CNT loading such as 10% CNT and a decrease in polymer chain movement at optimal loading such as 1% CNT.

Table 3.2 : The effect of loading on properties of PAN/CNT nanofibers.

	Tensile Strength (N/mm^2)	**Tensile Strain (%)**	**Modulus (N/mm^2)**
PAN nanofiber	1.47±0.24	18.25±2.55	12.01±4.4
0.5% CNT loaded PAN/CNT nanofiber	1.32±0.25	12.13±2.3	16.72±4.9
1% CNT loaded PAN/CNT nanofiber	1.75±0.46	14.15±1.83	14.22±13.6
3% CNT loaded PAN/CNT nanofiber	1.51±0.3	15.54±2.4	14.20±4.0
5% CNT loaded PAN/CNT nanofiber	1.22±0.3	13.52±2.4	14.06±7.5
7% CNT loaded PAN/CNT nanofiber	1.00±0.2	10.30±2.3	18.43±5.4
10% CNT loaded PAN/CNT nanofiber	0.80±0.3	9.45±1.5	14.87±4.6

In Table 3.3 and Table 3.4, the effect of functional group of CNT on tensile properties has been given and the effect of dispersion method on tensile properties has been given, respectively. Tensile strength of plasma modified NH_2 and COOH functional groups containing CNTs-PAN nanofibers are 1,97 N/mm^2 and 1,45 N/mm^2 respectively. NH_2 functionalized CNT provides improvement on the strength of PAN polymer matrix. However, COOH functionalized CNT could not provide such improvement in strength, while providing more stiff structure. This may be due to the fact that NH_2 functionalized CNT is well along the fiber axis and the plasma modified NH_2 functional CNTs have better interfacial bonding than the plasma modified COOH functional CNTs in PAN matrix [39].

Table 3.3 : The effect of plasma modified NH_2 and COOH functional CNTs on tensile properties.

	Tensile Strength N/mm^2	**Tensile Strain %**	**Modulus (N/mm^2)**
PAN/CNT with NH_2 (%1 CNT loaded)	1.97±0.5	14.83±2.9	21.54±6.44
PAN/CNT with COOH (1% CNT loaded)	1.45±0.3	11.68±3.2	18.98±4.7

The difference between plasma modified NH_2 functional CNTs/PAN nanofibers and plasma modified COOH functional CNTs/PAN nanofibers is insignificant for modulus values according to t test (95%, two sided) statistical analysis. But it is significant for tensile strength and strain according to t test (95%, two sided) statistical analysis.

To obtain best mechanical properties, it is necessary to find the best dispersion method. In this experiment, ultrasonic homogenizer, mechanical homogenizer and ultrasonic bath have been used in different ways to evaluate mechanical properties. As seen from Table 3.4, 10 minutes ultrasonic homogenizer application together with 45 minutes ultrasonic bath is the most suitable dispersion method in order to obtain higher strength values for composite material. The use of ultrasonic homogenizer nozzle degrades the polymer solution.

Table 3.4 : The effect of dispersion method on tensile properties of composite with 1% CNT.

	Tensile Strength (N/mm^2)	**Tensile Strain %**	**Modulus (N/mm^2)**
10 min Ultrasonic homogenizer+ 45 min ultrasonic bath	1.75±0.46	14.15±1.83	14.22±13.6
2 h. ult. homogenizer	1.4±0.42	11.22±2.6	17.78±4.6
2 hour ultrasonic homojenizer+30 min ult homogenizer together with PAN	0.36±0.1	11.61±4.7	6.58±2.2
2 hour mechanical homogenizer	0.93±0.2	9.63±1.9	15.09±5.1

Thermal Tests

The thermal properties like cyclization temperature (T_c) and enthalpy values of pure PAN and CNT/PAN composite nanofibers were examined by DSC at a heating rate of 20 ˚C/min under nitrogen. Throughout this process, a series of chemical reactions may occur which can provide the conversion of carbon-carbon (C=C) and (−C≡N) to (C=N) groups; and these reactions primarily include cyclization, dehydrogenation and oxidation. These reactions generated ladder-like molecular structures which make PAN fibers heat-resistant and infusible [31,40].

As seen from Figure 3.5 and Table 3.6, the cyclization temperature (T_c) increased with the increasing amount of carbon nanotubes. Pure PAN nanofiber's cyclization temperature is 310,96 ˚C while 10% loading CNT/PAN composite is 316,74 ˚C. That means that cyclization reactions occur at a higher temperature and more energy is needed.

As seen from Figure 3.6 and Table 3.6, plasma functional CNTs/PAN composite nanofibers show exothermic peaks at some different T_c value due to different thermo-chemical reaction caused by the presence of the functionalized CNTs. Plasma modified NH_2 functional CNT has better interfacial bonding in PAN matrix due to the presence of nitrile group in the PAN $(C_3H_3N)_n$. Amine-functionalised CNTs inhibits the mobility of the macromolecular chains [13]. Thus the value of enthalpy is somewhat higher than plasma modified COOH functional CNT/PAN nanofiber. More energy requirement with some lower T_c values comes out for plasma modified NH_2 functional CNT/PAN cyclization reactions. But both composite nanofibers have higher entalpy and Tc values than 100% PAN nanofiber which are caused by higher energy requirements and higher temperatures which are needed for cyclization reactions.

Table 3.5 : Cyclization temperatures and enthalpy values of nanofibers.

	Tc (˚C)	**ΔH (j/g)**
%100 PAN nanofiber	310.96	498
1% loaded CNT/PAN nanofiber	315.86	512
10% loaded CNT/PAN nanofiber	316.74	733.3

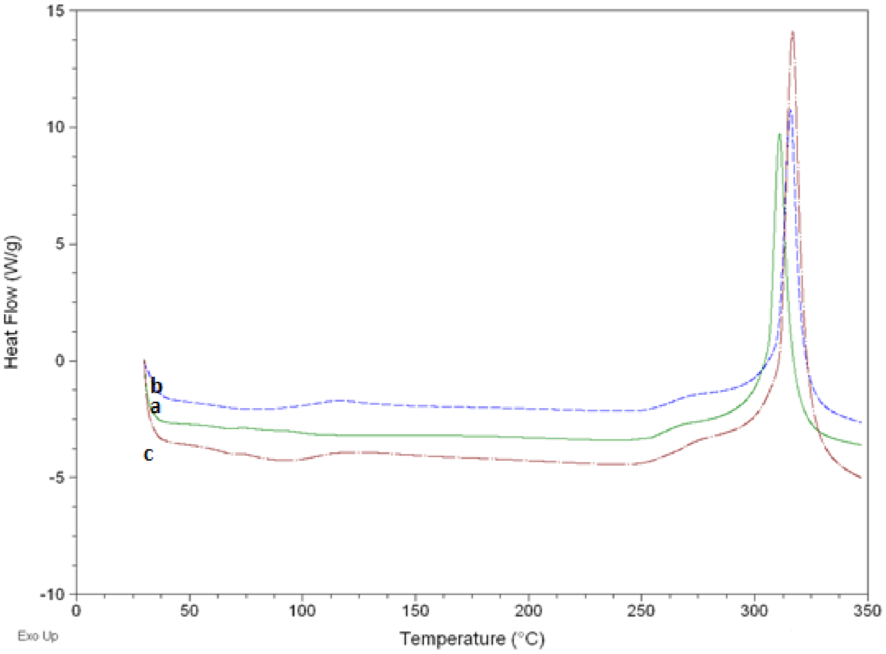


Figure 3.5 : DSC curves of electrospun nanofibers: a)100% PAN nanofiber b) 1% loaded CNT/PAN nanofiber c)10% loaded CNT/PAN nanofiber.

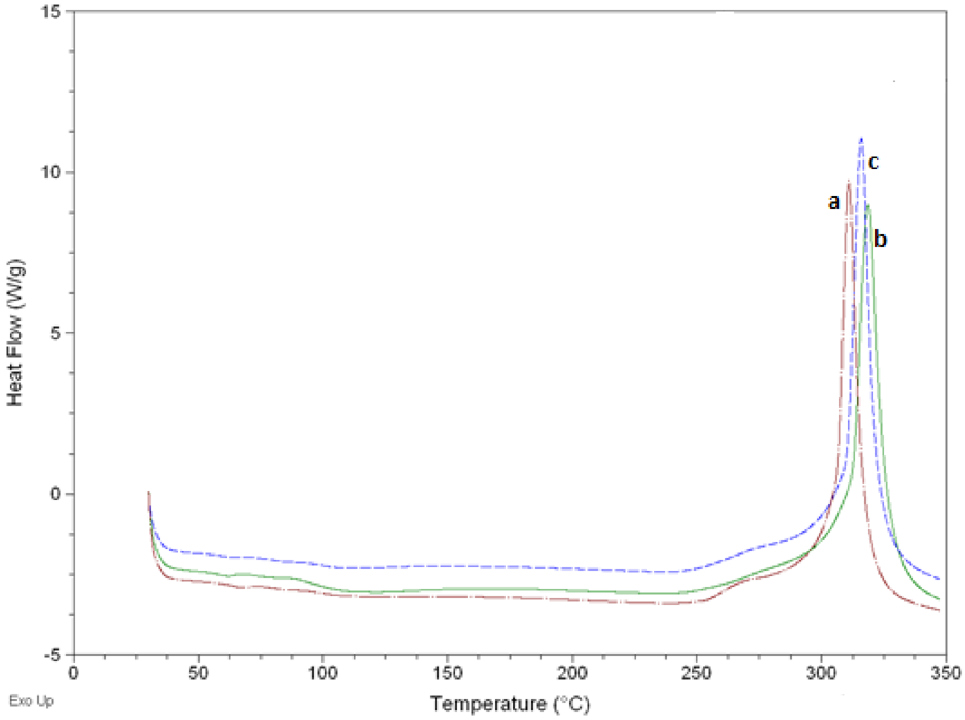


Figure 3.6 : DSC curves of functional CNT/PAN composite nanofibers a) 100% PAN nanofiber b) plasma COOH modified functional CNT/PAN nanofiber c) plasma NH_2 modified functional CNT/PAN nanofiber.

Table 3.6: Cyclization temperatures and the enthalpy values of nanofibers.

	Tc (˚C)	**ΔH (j/g)**
%100 PAN nanofiber	310.96	498
Plasma modified COOH CNT/PAN nanofiber	318.53	552
Plasma modified NH_2 CNT/PAN nanofiber	315.88	558

Electrical conductivity of composite nanofibers

The conductivity of composite nanofibers can be seen in Table 3.7. The presence of CNT provides conductive properties into PAN nanofiber which is normally an insulator. In this case, 3% CNT loaded nanocomposites which can be classified as a static dissipative material according to the conductivity tests results in higher conductivity than other loading [41]. However, different loading of CNT could not provide any distinct change on the electrical conductivity of polymer composite nanofiber. This may be due to unchanged network where polymer composite contains insulator polymer matrix, conductive CNT and insulator voids.

Table 3.7 : The conductivity of composite nanofibers at different loading.

	Conductivity (S/cm)
0,5% CNT loaded PAN/CNT nanofiber	$8.67*10^{-8}±3.48*10^{-8}$
1% CNT loaded PAN/CNT nanofiber	$6.87*10^{-8}±2.76*10^{-8}$
3% CNT loaded PAN/CNT nanofiber	$1.28*10^{-7}±4.57*10^{-8}$
5% CNT loaded PAN/CNT nanofiber	$9.96*10^{-8}±2.75*10^{-8}$
7% CNT loaded PAN/CNT nanofiber	$9.59*10^{-8}±5.19*10^{-8}$
10% CNT loaded PAN/CNT nanofiber	$8.33*10^{-8}±4.81*10^{-8}$

As seen from Table 3.8, the difference in conductivity is insignificant between plasma modified NH_2 and COOH functional CNT/PAN nanofiber according to statistical t test analysis (95% level, two sided).

Table 3.8: The conductivity of composite nanofibers.

	Conductivity (S/cm)
PAN/CNT with plasma modified NH_2 nanofiber (1% loaded)	$1.64*10^{-7}±6.83*10^{-8}$
PAN/CNT with plasma modified COOH nanofiber (1% loaded)	$1.08*10^{-7}±5.02*10^{-8}$

3.2.3 Conclusions

From the present studies,

- It has been seen that ultrasonic bath method is the most suitable dispersion method to obtain higher tensile strength of composite material.
- 10 % CNT loaded PAN composite nanofiber has the highest diameter among the others. 1 wt% CNT loaded PAN among the other CNT loadings is the best one in terms of mechanical properties.
- Plasma modified NH_2 functional CNT loaded nanofibers have better mechanical properties than plasma modified COOH functional CNT loaded nanofiber.

- From the thermal tests, it has been seen that with the availability of CNT, cyclization reactions occur at a higher temperature with higher energy.
- The electrical conductivity of PAN polymer matrix increases in the presence of CNT.

3.3 Synthesis of Functionalized MWCNTs and the Effect Functionalized Carbon Nanotubes (MWCNT) On The Properties Of Polyacrylonitrile-Carbon Nanotube Composite Nanofiber Web

In the present study, carbon nanotubes were functionalized and the effects of functionalized CNTs on the properties of PAN composite nanofiber were investigated.

3.3.1 Materials and Methods

PAN possessing a molecular weight of 150.000 g/mol was purchased from Sigma Aldrich. Multiwall carbon nanotube (MWCNT) as pristine MWCNT (diameter 60-100 nm, length 5-15 µm) were purchased from NTP China. Concentrated (98%) sulfuric acid (H_2SO_4), concentrated (65%) nitric acid (HNO_3), sodium nitrite ($NaNO_2$), thionyl chloride ($SOCI_2$) and ethylene glycol were purchased from Merck. Isophorone diamine, Tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) and NaOH were also used. All the chemicals were used as received without further purification.

Synthesis of MWCNT-COOH: Gao et al.'s method was used to synthesize carboxyl functionalized carbon nanotubes [42]. Carboxyl-functionalized multiwalled carbon nanotubes MWCNT-COOH is prepared by oxidation of pristine MWCNTs with a concentrated H_2SO_4/HNO_3 (3:1 by volume) mixture. Into a flask equipped with a condenser, pristine MWCNTs (3 g), HNO_3 (65%, 25 mL), and H_2SO_4 (98%, 75 mL) were added with vigorous stirring. Before the reaction, flask was immersed in an ultrasonic bath (40 kHz) for 10 min. Then mixture was stirred for 100 min under reflux (the oil bath temperature was increased gradually from 90 to 133 °C). Aqueous NaOH were used to collect and treat to evolved brown gas. After cooling to room temperature, the reaction mixture was diluted with deionized water and then vacuum-filtered through a filter paper (Whatman 0,45 µm PTFE filter). The solid was dispersed in water and filtered again, and then water was used to wash the filter cake several times. The dispersion, filtering, and washing steps were repeated until the pH of the filtrate reached 7 (at least four cycles were required). The filtered solid dried under vacuum for 24 h at 60 °C, giving 1,8 g of MWCNT-COOH.

Synthesis of MWCNT-OH: Gao et al.'s method was used to synthesize hydroxyl functionalize carbon nanotubes [42]. The as-prepared MWNT-COOH (0,2 g) was reacted with excess neat thionyl chloride ($SOCl_2$) (50 mL, 0.685 mol) for 24 h under reflux (the temperature of oil bath was 65-70 °C). After the reaction, the mixture was washed with THF (Tetrahydrofuran) and filtered. In this section, acyl chloride-functionalized MWCNTs was obtained (MWNT-COCl). The as-produced MWCNT-COCl was immediately reacted without further purification with glycol (50 mL, 0.9 mol) for 48 h at 120 °C. Hydroxyl-functionalized MWCNTs (MWCNT-OH) (0,05 g) were obtained by repeated filtration and washing with the deionized water.

Synthesis of MWCNT-NH_2: Zhao et al.'s amino functionalization method was used to synthesize amine functionalized carbon nanotubes [21]. MWCNTs-COOH (200 mg) were mixed with $NaNO_2$ (580 mg) and isophorone diamine (0,5 ml). Concentrated H_2SO_4 (0.36 ml) and 10 ml DMF was added. Then the mixture was stirred and heated for 1 h at 60 °C. The mixture was cooled to room temperature, then DMF was added and the mixture was filtered with a PTFE membrane (0.45 µm pore size). The solid was sonicated in DMF and filtered again, and the process was repeated until the DMF was colorless after sonication. The sample was then dried at 60 °C overnight under vacuum. 0,014 g MWCNT-NH_2 was obtained.

Preparation of PAN/MWCNT composite nanofibers: f-CNT (functional CNT)/DMF stable solution was dispersed for 10 min with ultrasonic homogenizer and then for 45 min with ultrasonic bath. PAN (with 7 wt% PAN concentration) was dissolved in the stable suspension of MWCNT in DMF. The ratio of CNT to PAN is 1%. After the addition of PAN, solution was stirred at 60 ˚C, 400 rpm for 1.5 hour by magnetic stirring. Then the solution was fed into electrospinnig system in order to produce nanofiber web.

3.3.2 Results and Discussion

Analysis of Infrared Spectroscopy

FT-IR spectroscopy was used to monitor the presence of surface functional groups at each step in the chemical functionalization. To characterize the surface modification of MWCNT-COOH, carbon nanotubes were dispersed in THF. Figure 3.7 shows the comparision of the FT-IR spectra of pristine carbon nanotubes and carboxyl functionalized carbon nanotubes. Compared with the spectra of pristine MWCNTs, a new peak around 1724 cm^{-1} appears in the spectrum of MWCNTs-COOH and can be assigned to carbonyl (-C=O) stretching of the carboxylic acid (-COOH) group. The peak at 3424 cm^{-1} can be assigned to OH stretching vibrations of the carboxylic acid group. The IR peak located at 1648 cm^{-1} appearing as a medium intensity band in Figure 3.7 is due to C=C stretching vibration indicating the graphitic structure of MWCNTs [21]. There appears a new band in the spectrum of carboxyl functionalized CNT at 1120 cm^{-1} due to C–O stretching vibration occurring in alcohols probably formed during the purification step [12]. The bands at 1034 cm^{-1}, appearing as a shoulder and 1184 cm^{-1} band appearing as a stronger peak in the COOH-functionalized CNT spectrum are also due to the C-O vibration [21,43]. Additionally, there are strong peaks at 2927 and 2855 cm^{-1} due to asymmetrical and symmetrical methylene (CH_2) stretching vibrations [21].

These results suggest that carboxylic acid groups have been successfully introduced onto the MWCNT surfaces [11].

In Figure 3.8, the IR peaks of hydroxyl (OH) functionalized carbon nanotubes can be seen. A broad peak at 3401 cm^{-1} shows that hydroxyl (-OH) group on the carboxyl functionalized carbon nanotubes expanded because of -OH functionalization.

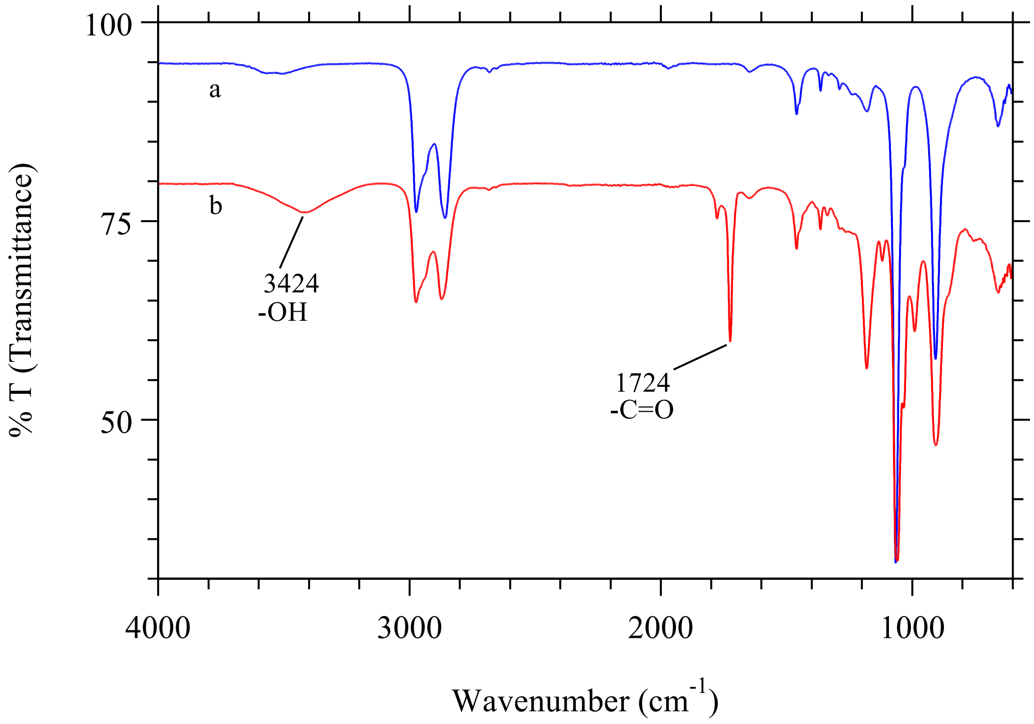


Figure 3.7 : FT-IR spectra of (a) pristine MWCNT; (b) MWCNT-COOH.

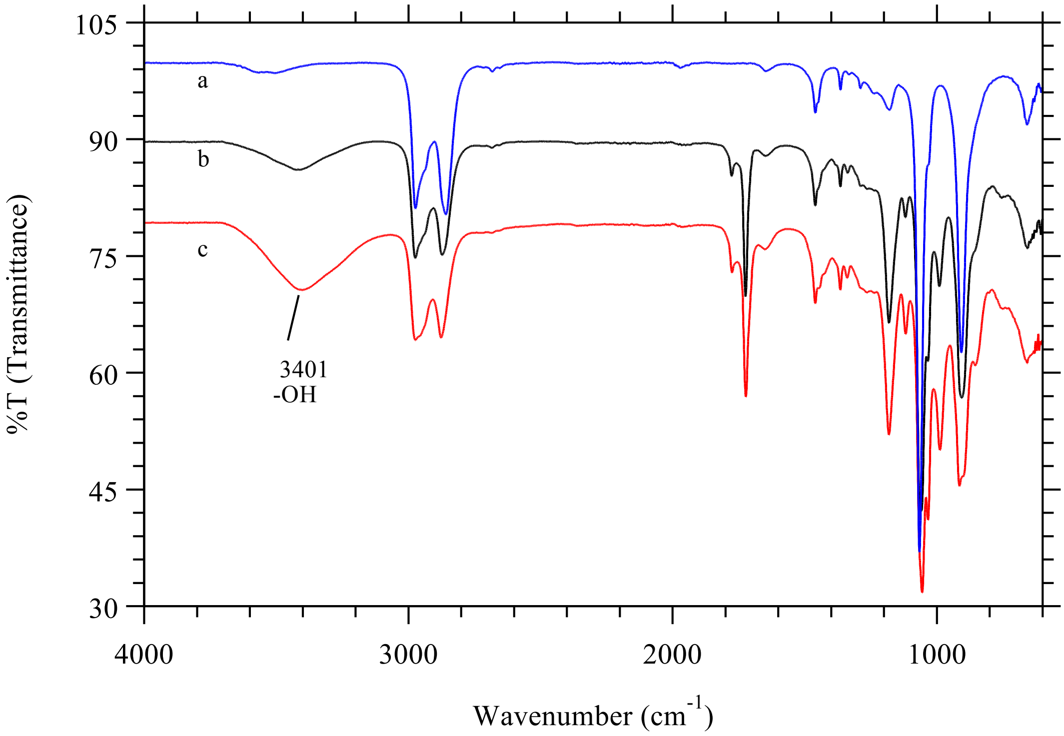


Figure 3.8 : FT-IR Spectra of (a) pristine MWCNT; (b) MWCNT-COOH; (c) MWCNT-OH.

To characterize the amine functionalized carbon nanotubes, KBr pellets were prepared and used during the collection of IR spectra. Fourier transform infrared (FT-IR) spectra were recorded with a KBr pellet ranging from 4000 to 400 cm^{-1}. In Figure 3.9, Peak positions of functionalized carbon nanotubes can be seen. In comparison with pristine MWCNTs, it can be seen that a few new peaks appeared in the spectra of MWCNTs/NH_2. The IR peaks in the 3500-3400 cm^{-1} region can be attributed to –OH and N-H stretching vibrations [21]. The peak at 1632 cm^{-1} can be assigned to C=C stretching of carbon nanotube structure and C=O stretching of amide (-NH-C=O) structure. The peaks at 1547 cm^{-1} and 1139 cm^{-1} are attributed to C-NH, C=N and C-C stretching vibrations, respectively. From the amide structure, N-C=O stretching at 621 cm^{-1} is obtained [44].

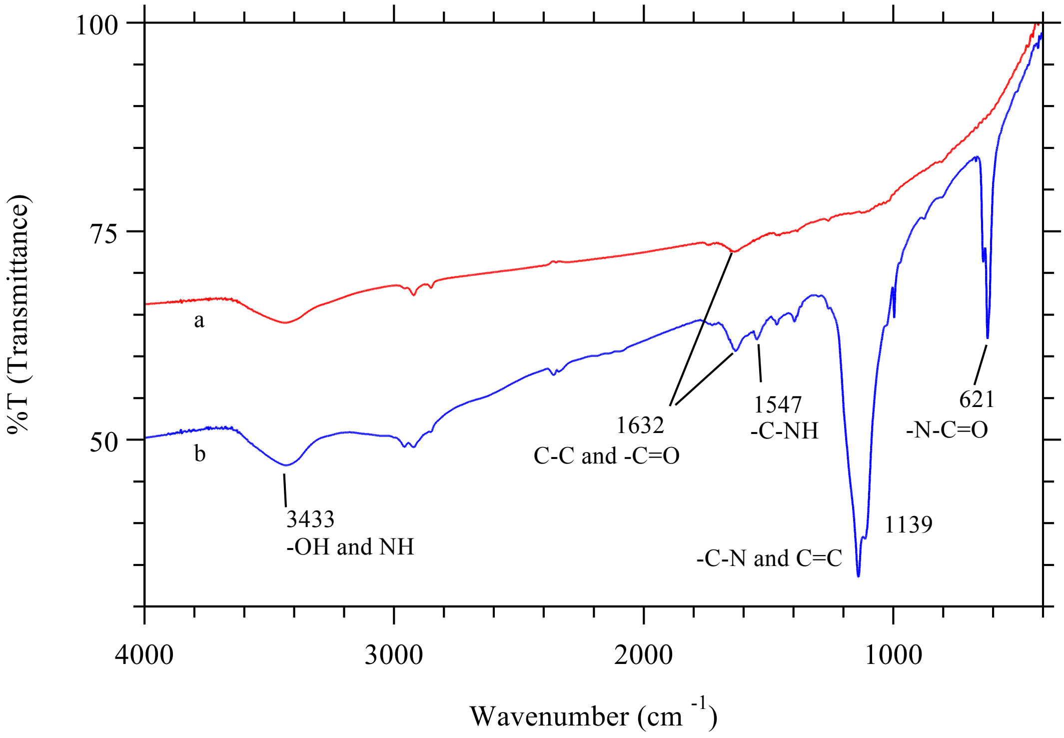


Figure 3.9 : FT-IR spectra of a) pristine CNT b) MWCNT/NH_2.

Analysis of morphological properties of the nanofibers

The diameters of CNT/PAN composite nanofibers obtained from SEM observations are presented in Table 3.9. The nanofibers containing functionalized CNTs generally are found to have lower diameter values than that of the pristine CNT. This is probably due to better dispersion of CNT in polymer solution arising from the presence of functional groups. While the diameter of the nanofiber containing CNT-NH_2 is similar to that of CNT-COOH, the diameter of the nanofiber containing CNT-OH is similar to pristine CNT. Presence of CNT result to an increase of diameter of pure PAN nanofiber due to additional filler effect.

When statistical analyses (F test) has been carried out , it has been seen that these differences are not statistically significant according to F test with 95% significant.

Table 3.9 : Diameters of nanofibers level.

Sample	Diameter (nm)
Pure PAN (100%)	312±35.25
1% CNT (pristine)/PAN nanofiber	343±64.87
1% CNT-COOH/PAN nanofiber	321±115
1% CNT-OH/PAN nanofiber	340±48
1% CNT-NH_2/PAN nanofiber	328±66

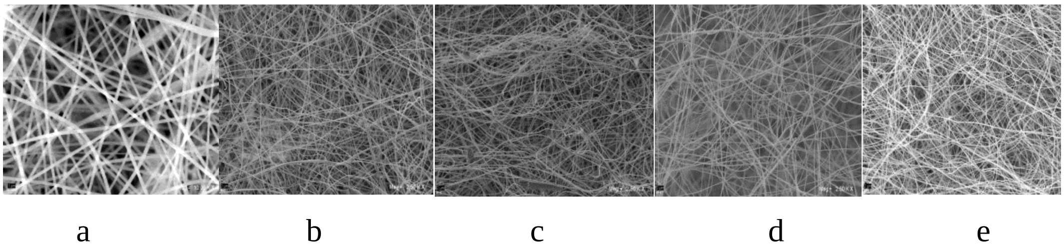


Figure 3.10 : SEM images of a) pure PAN(100%) b) 1% CNT /PAN nanofiber c) 1% CNT-COOH/PAN nanofiber d) 1% CNT-OH /PAN nanofiber e) 1% CNT-NH_2 /PAN nanofiber.

Analysis of Mechanical Properties

As can be seen from Table 3.10, all the CNTs with functional groups provided more strength than that of the pristine CNT due to good dispersibility of MWCNTs [45]. However, CNTs containing amine functional groups resulted in slightly more strength and modulus than that of the pristine CNTs in comparison to other CNTs containing COOH and OH functional groups. This can be attributed to amine group's better interfacial bonding and less agglomeration tendency in PAN matrix due to the presence of nitrile group in the PAN $(C_3H_3N)_n$ [12,46].

While PAN composite nanofiber with amine functionalized CNT has slightly higher E modulus than that of pristine CNT, PAN composite nanofiber with COOH and OH functionalized CNT has slightly lower E modulus than that of pristine CNT. While strength differences between CNT with functional groups and pristine CNT are not statistically significant, the difference between pure PAN and PAN with CNT is statistically significant according to F test with 95% significant level. The differences on modulus between the sample with amine functionalized CNT and samples with other functional group is also significant according to F test with 95% significant level.

Table 3.10 : Tensile properties of PAN/CNT nanofibers.

Sample	**Tensile Strength (N/mm^2)**	**Tensile Strain (%)**	**Modulus (N/mm^2)**
100% PAN	1.47±0.24	18.25±2	12.01±4.4
1% CNT (pristine)/PAN nanofiber	2.18±0.3	12.63±2	19.5±6.7
1% CNT-COOH/PAN nanofiber	2.25±0.3	17.28±2	14.5±6.3
1% CNT-OH/PAN nanofiber	2.25±0.1	15±2.9	14.8±8
1% CNT-NH_2/PAN nanofiber	2.41±0.7	14.32±3	22.8±6.7

Electrical Conductivity of Composite Nanofiber

It has been reported that MWCNTs possess a high aspect ratio and p-bonds and that the electrons are normally transferred through the p-bond of CNT [47]. The results presented in Table 3.11 show that the incorporation of 1% CNT significantly improved the electrical conductivity of composite PAN nanofiber web in comparison to insulator pure PAN nanofiber. The composite polymer became antistatic material due to its electrical conductivity value. The results further confirm that the functionalization of nanotubes seem to have insignificant effect on the values of conductivity of CNTs with different functional groups. However, the electical conductivity values were found to vary between 1.9×10^{-7} and 2.6×10^{-7} S/cm compared to insulator PAN (10^{-12} S/cm [48]).

Table 3.11 : The electrical conductivity of composite nanofibers at different different functional group.

Sample	Conductivity (S/cm)
100% PAN	10^{-12}
1 % CNT (pristine)/PAN nanofiber	$1.92*10^{-7}\pm5.88*10^{-8}$
1 % CNT-COOH/PAN nanofiber	$1.99*10^{-7}\pm3.29*10^{-8}$
1 % CNT-OH/PAN nanofiber	$2.27*10^{-7}\pm7.31*10^{-8}$
1 % CNT-NH_2/PAN nanofiber	$2.60*10^{-7}\pm7.64*10^{-8}$

Analysis of X-ray Diffraction Results

Crystallinity values of composite samples containing functionalized CNTs varied between 16.2 and 23.6 % (Table 3.12, Figure 3.10). While composite nanofiber containing NH_2 functional groups has similar crystallinity (22.7%) to that of pristine PAN (22.6%), the others have a lower crystallinity than that of PAN containing pristine CNT and the lowest one is belong to PAN structure containing CNTs with COOH functional group. It is a common experience in polymer science that the introduction of bulky side groups almost always disrupts the crystalline structure. The side groups (OH, COOH, NH_2) attached to CNT allows the formation of bonds with acrylonitrile (AN) units of PAN polymer chains which in turn, in most cases, cause the whole PAN-CNT composite chains to unable to pack efficiently. This, also, in turn cause the reduction of the degree of order [49]. Since the concentration of pristine and functionalized CNT is only 1%, the net effect on crystallinity is not expected to be too high. The lowest crystallinity is found to be 16.2% which is due to the bulky nature of COOH functionalized CNTs causing decrystallization via disruption of order.

Table 3.12 : X-ray diffraction results of nanofibers.

Sample	Degree of Order (%) PAN	PAN (100) (°2θ)	CNT (002) (°2θ)	PAN (110) (°2θ)
%100 PAN	22.6	16.70	29.20	-
%1 CNT(pristine) / PAN	23.6	17.2	26.5 Broad	29.2 Broad
(%1) CNT-COOH/ PAN	16.2	17.0	26.5 Broad	29.2 Broad
(%1) CNT-OH/ PAN	19.1	17.2	26.5	29.2
(%1) CNT- NH_2/ PAN	22.7	16.9	26.5	29.2

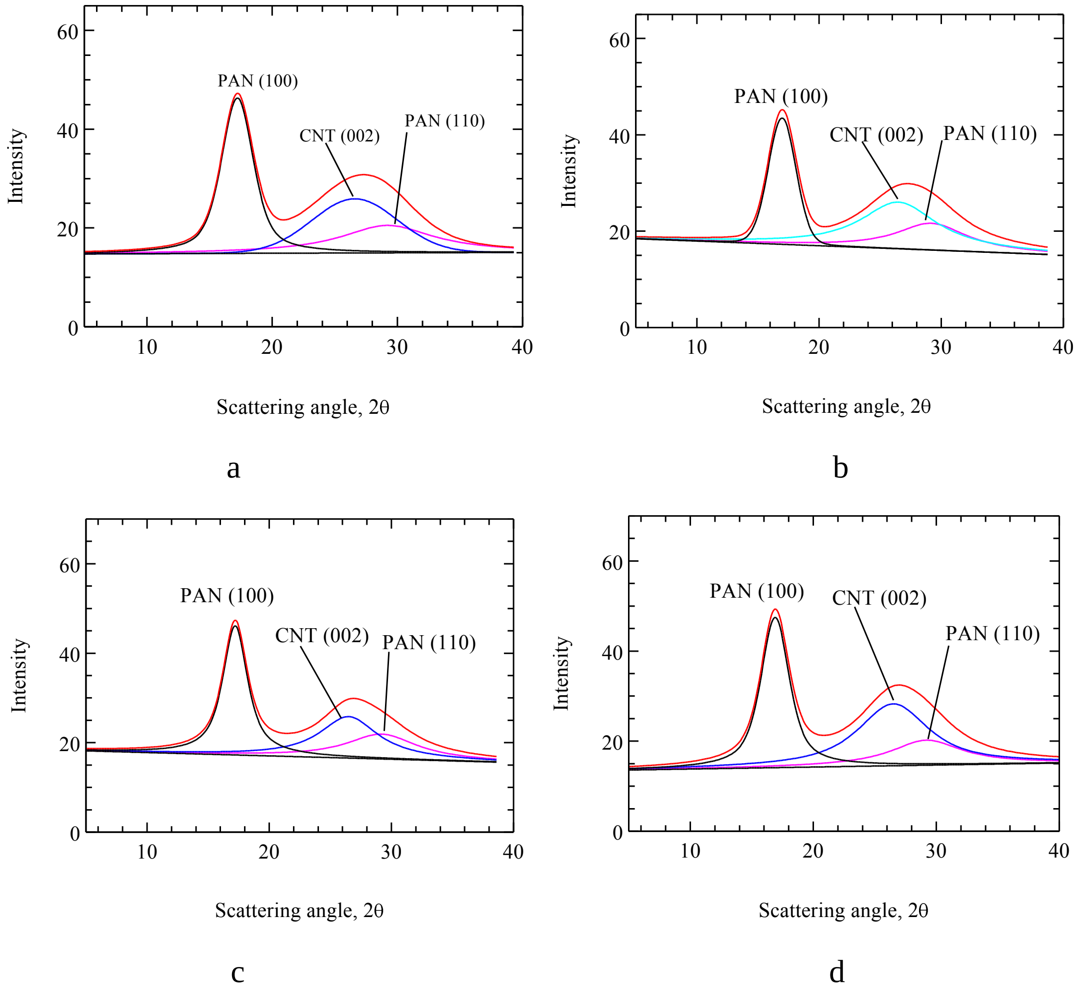


Figure 3.11 : Curve fitting of X-ray diffraction trace of electrospun, a) PAN nanofibers containing 1% CNT; b) PAN nanofibers containing 1% CNT-COOH; c) PAN nanofibers containing 1% CNT-OH; d) PAN nanofibers containing 1% CNT- NH_2.

Thermal Analysis

Entalphy values of composite nanofibers with functionalized CNTs are decreased compared to pristine carbon nanotube/PAN nanofiber and the lowest one is belong to amine functionalized CNT. As mentioned before X-ray diffraction studies showed that the crystallinity of PAN-CNTs with COOH functional groups was lower than that of the pure PAN structure. The decrease on the enthalpy of composite nanofibers may also be due to easy formation of free radicals on the nitrile groups and the subsequent recombination between the intramolecular radicals [31].

Samples with functionalized CNT have generally a higher cyclization temperature than sample with pristine CNT except for the CNT with COOH group.

It is suggested that the cyclization of nitrile groups of PAN chains proceed via ionic and free radical reaction mechanisms (Figure 3.12) [31]. The cyclization of nitrile groups of pure PAN initiated through a free radical mechanism is considered to occur as the result of inter or intramolecular jumping of free radicals. Free radicals seem to be allowed to accept hydrogen atoms as a result of dehydrogenation reactions during the thermal treatment (i.e. during DSC scanning) from nearby chain molecules and consequently they propogate along the chain direction [31].

The ionic reaction of PAN chains is suggested to require an acid such as carboxylic acid or acrylic acid [31]. The acid molecules such as carboxylic acid make a nucleaphilic attack on the carbon atom of nearby nitrile group and cause it to cyclize. As a result, DSC thermograms show the exothermic peaks being located in different temperatures as a result of different reaction rates and reaction mechanisms [31].

It seems that the cyclization of nitrile groups can be initiated at a higher temperature through an only free radical mechanism [31].

Table 3.13 : Cyclization temperatures and enthalpy values of nanofibers.

	Tc (˚C)	ΔH (J/g)
Pure PAN (100%)	314.8	483.8
1% CNT (pristine)/PAN nanofiber	317.4	296.3
1% CNT-COOH/PAN nanofiber	313.1	270.9
1% CNT-OH/PAN nanofiber	320.8	266.9
1% CNT-NH$_2$/PAN nanofiber	321.0	221.9

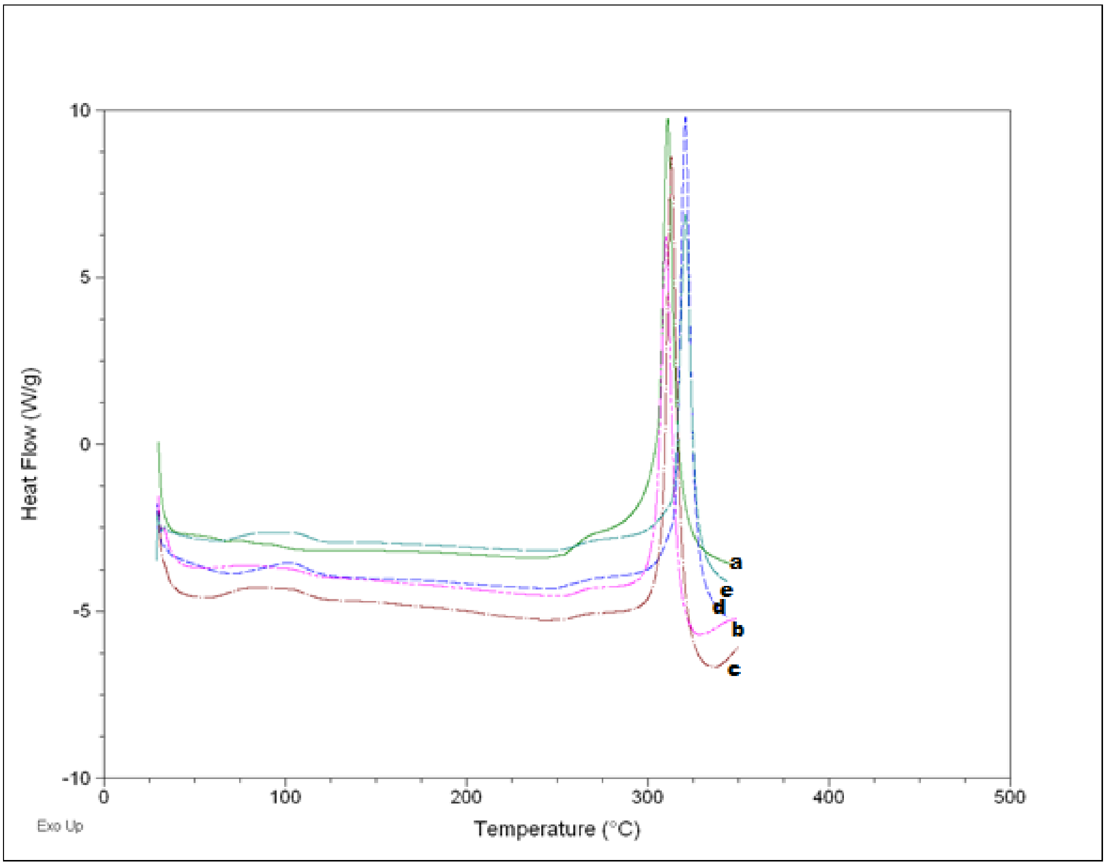


Figure 3.12 : DSC curves of electrospun nanofibers: a)Pure PAN nanofiber b) CNT(pristine)/PAN nanofiber c) CNT-COOH/PAN Nanofiber d) CNT-OH/PAN nanofiber e) CNT-NH$_2$/PAN nanofiber.

3.3.3 Conclusions

Several important results have been concluded as following

- While diameter of nanofiber containing CNT-NH$_2$ is similar to that of CNT-COOH, the diameter of nanofiber containing CNT-OH is similar to pristine CNT. Nanofiber containing functionalized CNT generally has less diameter than that containing pristine CNT.

- All CNTs with functional groups provided more strength than pristine CNT. However, CNT with amine functional group provided slightly more strength and modulus than that of CNT with other functional group (COOH and OH).
- While composite nanofiber containing NH_2 functional groups has similar crystallinity to that of pristine CNT and it has highest crystallinity value, the others have a lower crystallinity than that of pristine CNT and the lowest one is belong to CNT with COOH functional group.
- Functionalization of nanotubes did not affect the conductivity significantly. Insulating PAN became semi conductive material capability with static electric dischargability due to the use of pristine and functionalized CNTs (10^{-7} S/cm)
- Entalphy values of composite nanofibers with functionalized CNT ($COOH, OH, NH_2$) are decreased in comparison to pristine carbon nanotube/PAN nanofiber and the lowest value one is belong to amine functionalized CNT.
- The PAN samples containing functionalized CNTs have generally higher cyclization temperature than the PAN samples containing pristine CNT except for CNT with COOH group.

3.4 The Effect of Amine Functionalized Carbon Nanotubes on the Properties of CNT/PAN Composite Nanofibers

In this study, the effect of NH_2 functional group of CNT and the different CNT loading on properties of Polyacrylonitrile-Carbon nanotube composite nanofiber has been studied.

3.4.1 Materials and Methods

PAN possessed a molecular weight of 150.000 g/mol was purchased from Sigma Aldrich. MWCNTs (NTP, from China) as pristine MWCNT (diameter 60-100 nm, length 5-15 μm). N,N-dimethylformamide (DMF) as solvent.

Preparation of Composite Nanofibers

As prepared amine functional CNTs from Zhao et al.’s amino functionalization method, were used. 1 and 3 wt% f-CNT/DMF and p-CNT/DMF solution was dispersed with ultrasonic homogenizer for 10 minutes and then processed with ultrasonic bath for 45 minutes. PAN (with 7 wt% PAN concentration) was dissolved in the stable suspension of MWCNT in DMF. After the addition of PAN, solution was stirred at 60 ˚C by magnetic stirring. Then the solution was feeded into electrospinning system in order to produce nanofiber web.

3.4.2 Results and Discussion

The Morphology of Composite Nanofibers

The SEM images of PAN/CNT composite nanofibers can be seen in Fig 3.13. The surface morphology of the 1% CNT loaded nanofiber is smooth and straight. With the 3% CNT loading, some agglomerations occur. Also the bead formation was observed at 3% CNT loaded nanofiber due to less dispersion and agglomeration of CNTs at high concentration.

Beads areas act as stress concentration points which affect the mechanical properties [36].

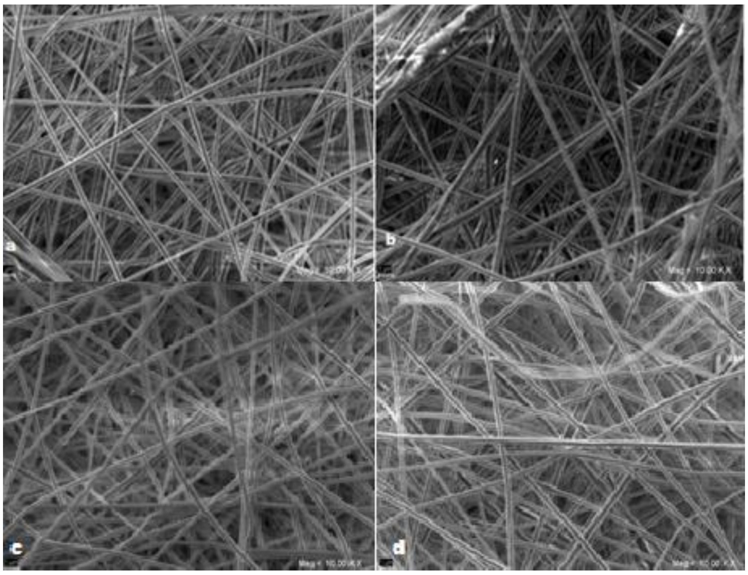


Figure 3.13 : SEM images of a) 1% CNT loaded PAN/CNT nanofiber b) 3% CNT loaded PAN/CNT nanofiber c) 1% CNT-NH_2 loaded PAN/CNT nanofiber d) 3% CNT-NH_2 loaded PAN/CNT nanofiber.

Diameters of composite nanofibers can be seen at Table 3.14. 1% CNT loaded PAN/CNT nanofiber's diameter is 338 nm while 3% CNT loaded PAN/CNT nanofiber's diameter is 343 nm. An increase in the concentration of carbon nanotubes increases the viscosity. Increased viscosity enlarges the diameter of nanofibers. But with the functionalization of carbon nanotubes, diameters of nanofibers decrease compared to pristine carbon nanotubes/PAN nanofibers. It may be due to an increase of conductivity of the solution that leads to accelerating the jet [48].

Table 3.14 : Diameters of Composite Nanofibers.

1% CNT loaded PAN/CNT nanofiber (nm)	**1% CNT-NH_2 loaded PAN/CNT nanofiber (nm)**	**3% CNT loaded PAN/CNT nanofiber (nm)**	**3% CNT-NH_2 loaded PAN/CNT nanofiber (nm)**
338	333	343	308

Mechanical Properties of Composite Nanofibers

In Table 3.15, mechanical properties of pristine and functional carbon nanotube/PAN composite nanofibers can be seen. With the 3% loading of carbon nanotube, tensile strength decreases, this may be due to an increase of agglomeration and beads in the structure. Also amine functional group improves the mechanical properties thanks to amine group's better interfacial bonding in PAN matrix due to the presence of nitrile group in the PAN $(C_3H_3N)_n$ [12].

Table 3.15 : Mechanical Properties of Composite Nanofibers.

	Tensile Strength	**Tensile Strain**	**Modulus**
	(N/mm^2)	(%)	(N/mm^2)
1% CNT loaded PAN/CNT nanofiber	2.18±0.3	12.63±1.7	19.53±6.7
1%CNT-NH_2 loaded PAN/CNT nanofiber	2.41±0.7	14.32±3	22.83±6.7
3% CNT loaded PAN/CNT nanofiber	1.7±0.3	12.65±1.8	9.09±3.5
3% CNT-NH_2 loaded PAN/CNT nanofiber	2±0.4	16.23±3.5	9.52±4.4

Conductivity of Composite Nanofibers

Normally, PAN has insulating behavior in solutions and nanofibers. It is reinforced with nanofiller or other polymers to improve conductivity. As seen in Table 3.16, 1 and 3 % CNT loaded PAN nanofiber demonstrate 2.6×10^{-7} S/cm and 1.63×10^{-7} S/cm respectively. But functional group on the surface of carbon nanotube did not show significant changes. Thanks to good dispersion, polymeric layer is formed around the CNTs and it ensulates them. Thus, due to inhibition of formation conductive network in the polymer, conductivity does not improve much [12].

Table 3.16 : Conductivity of Composite Nanofibers.

	Conductivity (S/cm)
CNT/PAN nanofiber (%1)	$1.92*10^{-7}±5.88*10^{-8}$
CNT-NH$_2$/PAN nanofiber (%1)	$2.6x10^{-7}±7.64x10^{-7}$
CNT/PAN nanofiber (%3)	$1.63x10^{-7}±4.69x10^{-8}$
CNT-NH$_2$/PAN nanofiber (%3)	$1.56x10^{-7}±9.27x10^{-8}$

3.4.3 Conclusions

- Polyacrylonitrile nanofibers reinforced with amine functionalized carbon nanotubes has been prepared by electrospinning.
- Diameters of nanofibers increased with the increasing viscosity. 1 % carbon nanotubes loaded nanofibers showed the best mechanical properties. It indicates that some agglomerations occur at high amounts of carbon nanotubes and nanofiber’s mechanical properties reduced.
- Carbon nanotubes also improved the conductivity of ınsultor PAN nanofibers.
- While an increase in the concentration of carbon nanotubes increases the diameter of nanofiber, functionalization of CNT results to decrease of diameter of nanofiber.

3.5 The effect of PANI and Amine Functionalized CNTs on the Properties of PAN nanofibers

In this last experiment, the effects of both PANI and CNT-NH$_2$ were investigated.

3.5.1 Materials and Methods

Polyacrylonitrile (PAN) possessed a molecular weight of 150.000 g/mol was purchased from Sigma Aldrich. MWCNTs as pristine MWCNT (diameter 60-100 nm, length 5-15 µm) was purchased from NTP (China). Polyaniline (PANI) possessed molecular weight of 65.000 g/mol was purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO) was used as solvent. Camphor sulfuric acid (CSA) was purchased from Sigma Aldrich.

Preparation of solutions

Campforsulfonic acid (dopant) and polyaniline (equivalent molar ratio PANI:campforsulfonic acid (CSA) = 1:2) were added to DMSO and mixed with magnetic stirrer at 40˚C, 300 rpm for 2 days. The solution was filtered with Sartorius Stedim filter paper and amine functionalized carbon nanotubes added in the solution. CNT-NH_2/PANI/DMSO solution was dispersed for 10 min with ultrasonic homogenizer (BandelinSonopuls HD 2070, probe type: KE76) and then for 45 min with ultrasonic bath. PAN (7 wt% PAN concentration) was dissolved in the stable suspension of CNT-NH_2/PANI in DMSO. Then solutions were fed to electrospinning system. The concentration of PANI with respect to the weight of PAN was 3 %.

Table 3.17 : List of the samples produced.

Samples produced	PAN	CNT-NH_2	PANI
PAN-DMSOnanofiber	presence	-	-
PAN/PANI (3%)-DMSO nanofiber	presence	-	3%
(1%) CNT-NH_2/PAN/ DMSO nanofiber	presence	1%	-
(3%) CNT-NH_2/PAN/ DMSO nanofiber	presence	3%	-
(1%) CNT-NH_2/PAN/PANI/DMSO nanofiber	presence	1%	3%
(3%) CNT-NH_2/PAN/PANI/DMSO nanofiber	presence	3%	3%

3.5.2 Results and Discussion

Analysis of morphological properties of the nanofiber web

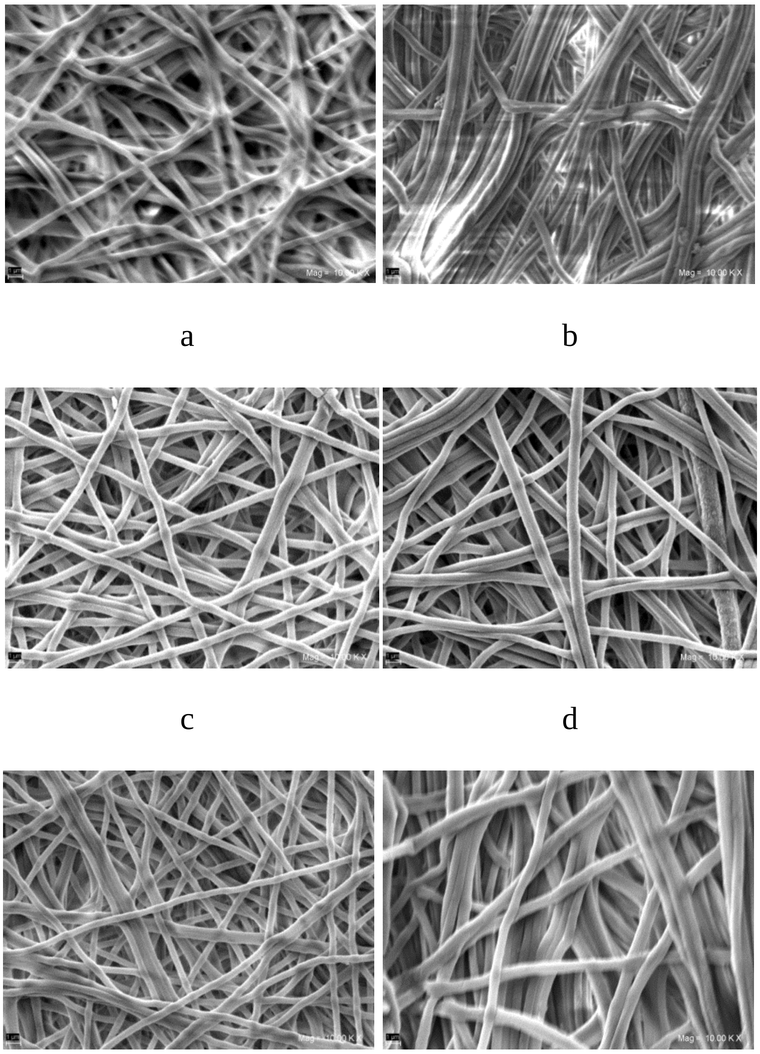
There are several mechanism that can affect the final diameter of nanofiber. Conductive filler particles have an influence on the conductivity of the solution and this may promote two phenomena having opposite effects on fiber formation and diameter [50]. They may either increase flow rate, which can lead to larger fibres [51] or increase net charge density, which suppresses the Rayleigh instability and enhances the whipping instability, leading to the formation of bead-free and smaller fiber diameter [48, 52]. An increase of filler will also results to an increase of diameter due to agglomeration and an increase of material. Thus, the diameter of the nanofibers depends on which the phenomena is dominant.

The diameters of composite nanofibers obtained from SEM observations can be seen in Table 3.18 (Figure 3.13). Pure PAN nanofiber's diameter is 515 nm. The diameter increases because of presence of CNT and PANI filler. The effect of PANI on an increase of diameter is higher than that's of CNT.

According to statistical analysis (F tests, 95% significant level), it has been seen that differences between the diameter of PAN-DMSO nanofiber and PAN/PANI composite nanofiber and also 3% CNT-NH_2/PAN/PANI composite nanofiber are significant at 0.05 significance level. However, the differences between PAN-DMSO nanofiber and PAN with 1% and 3% CNT-NH_2 are not significant for 95% significant level.

Table 3.18 : Diameters of composite nanofibers.

Sample	Diameter (nm)
PAN-DMSO nanofiber	515±72.1
PAN/PANI (3%)-DMSO nanofiber	575±86.2
(1%) CNT-NH_2/PAN/ DMSO nanofiber	536±91.1
(3%) CNT-NH_2/PAN/ DMSO nanofiber	531±74.3
(1%) CNT-NH_2/PAN/PANI/DMSO nanofiber	556±77.8
(3%) CNT-NH_2/PAN/PANI/DMSO nanofiber	719±122.2



a b

c d

e f

Figure 3.14 : SEM images of composite nanofibers a-PAN/DMSO nanofiber, b)PAN/PANI(%3)/DMSO nanofiber, c-(%1) CNT-NH_2/PAN/ DMSO nanofiber, d- (%3) CNT-NH_2/PAN/ DMSO nanofiber, e- (%1) CNT-NH_2/PAN/PANI/DMSO nanofiber, f-(%3) CNT-NH_2/PAN/PANI/DMSO nanofiber.

IR analysis

Infrared spectrum of composite nanofibers has been carried out to observe atomical vibrations. Figure 3.15 shows the IR spectra of PAN/DMSO, PAN/CNT-NH_2/DMSO and PAN/PANI/CNT-NH_2/DMSO nanofibers, respectively.

In figure 3.14 PAN/DMSO spectrum can be seen. Peaks at 1450 and 750 cm^{-1} are –CH_2 vibrations. The characteristic peak –CN, from PAN is at 2200 cm^{-1}. All other samples contain polyacrylonitrile have the same peak. The peak at 1600 cm^{-1} can be assigned to C=C stretching of carbon nanotube structure and C=O stretching of amide (-NH-C=O) structure [44].

Peak at 1490 cm^{-1} is attributed to polyaniline's benzenoid (N-B-N) vibrations.The strechings at 1140 ve 1302 cm^{-1} can be attributed to C-N and N=Q=N quinoid vibraitons, respectively [53].The increased peak in the 3200-3500 cm^{-1} region can be attributed to the effect of PANI which is the free imin (-NH) groups of PANI around 3390 cm^{-1} and aromatic C-H stretching around 3280 cm^{-1} [21].

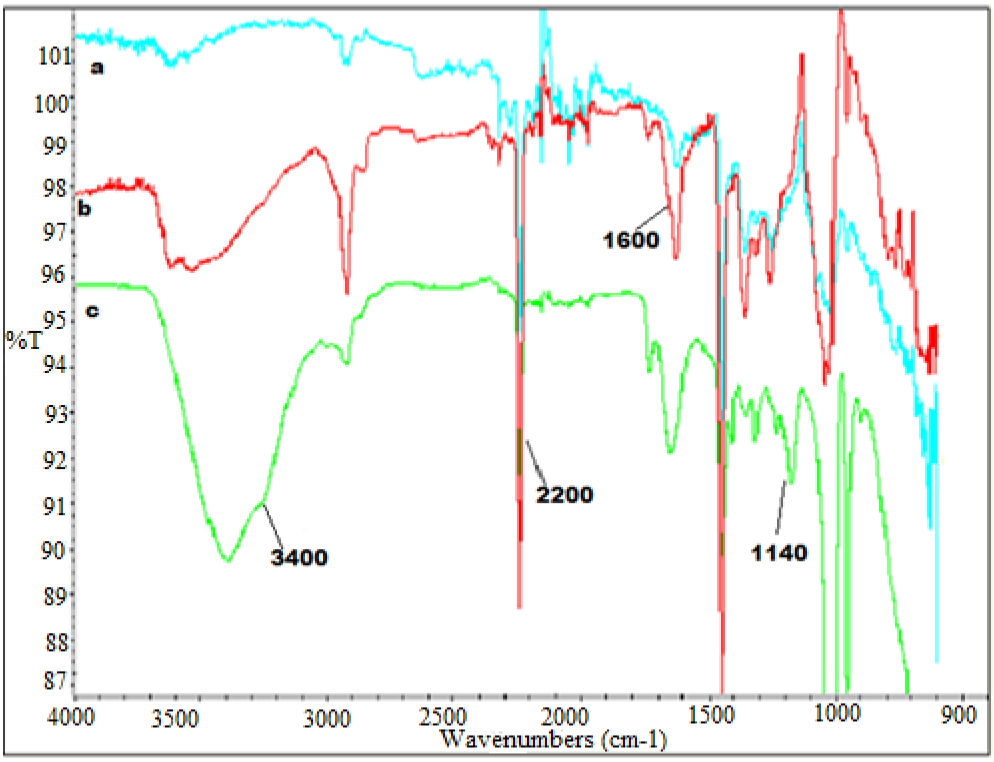


Figure 3.15 : FTIR spectra of nanofibers a)PAN/DMSO b)PAN/CNT-NH$_2$/DMSO c)PAN/PANI/CNT-NH$_2$/DMSO.

Analysis of Mechanical Properties

Mechanial properties of nanofibers can be seen in Table 3.19. Increased nanofiller may results to an increase of agglomeration leading to degradation of mechanical and other properties of composite product [54]. However, higher breaking strength was obtained by composite nanofiber with 1% CNT and 3% PANI. However, when statistical ANOVA analyses (F test) has been carried out, it has been seen that there are no statistically significant strength differences between the samples except for (3%) CNT-NH$_2$/PAN/PANI-DMSO.

Table 3.19 : Mechanical properties of composite nanofibers.

Sample	Tensile Strength (N/mm^2)	Tensile Strain(%)	E-modulus (N/mm^2)
PAN-DMSO	8.64±3.1	9.0±2.7	10.6±36.5
PAN/PANI (3%)-DMSO	8.61±1.1	73.4±5.2	59.2±17.1
(1%)CNT-NH_2/PAN-DMSO	8.99±2.0	9.7±2.7	38.2±17.8
(3%) CNT-NH_2/PAN-DMSO	9.35±1.2	14±2.4	95.7±36.0
(1%) CNT-NH_2/PAN/PANI-DMSO	10.85±3.1	14.17±5.12	87.3±33.1
(3%) CNT-NH_2/PAN/PANI-DMSO	5.76±1.7	65.4±11.5	41.8±14.0

Electrical conductivity of composite nanofibers

Polyacrylonitrile is insulator material with the 10^{-12} S/cm conductivity value [48]. With the addition of conductive filler such as CNT and conductive polymer such as PANI results to an increase of electrical conductivity of composite nanofiber (Table 3.20). Thus composite material became an antistatic material with 10^{-8} S/cm [55].

As seen from Table 3.20, an increase of conductive filler did not increase the conductivity. This may be due to the agglomeration and void around the filler which destroy the network leading decrease of conductivity [54].

From the statistical analyses, differences between 3% CNT-NH_2/PANI/PAN/DMSO and others are significant according to F test with 95% significant level.

Table 3.20 : Electrical conductivity of nanofibers.

Sample	Conductivity (S/cm)
PAN/PANI(%3)/DMSO	$3.08*10^{-8}±8.1*10^{-9}$
1%CNT-NH_2/PAN/DMSO	$2.80*10^{-8}±3.9*10^{-9}$
3% CNT-NH_2/PAN/DMSO	$2.10*10^{-8}±7.8*10^{-9}$
1% CNT-NH_2/PANI/PAN/DMSO	$3.07*10^{-8}±1.1*10^{-8}$
3% CNT-NH_2/PANI/PAN/DMSO	$3.89*10^{-9}±1.2*10^{-9}$

Analysis of X-ray Diffraction Results

As seen from Table 3.21, crystallinity of PAN increases with presence of PANI and CNT. The crystallinity of composite nanofiber with both of CNT and PANI is higher than that’s of 100%PAN and PAN with CNT and PAN with PANI . Due to the atactic nature of PAN polymer chains, three dimensional structure can not be formed and only a two-dimensional network of chains can be developed. Wide-angle X-ray diffraction patterns of oriented PAN-based micro-sized and nano-sized fibers show the presence of highly oriented two-dimensional order perpendicular to the fiber axis and the absence of peridicity along the fiber axis direction.

A typical equatiorial X-ray diffraction trace of PAN nanofibers shows two well-defined and sharp and one diffuse equatorial reflections with d-spacings of 0.529 nm, 0.306 nm, and 0.34 nm, respectively. These reflections happen to have the scattering angles of 16.7, 26.7 and 29.2˚ 2θ.

Table 3.21 : XRD results of composite nanofibers.

Sample	**Degree of Order (%) PAN**	**PAN (100) (°2θ)**	**PAN Disordered (°2θ)**	**PAN (110) (°2θ)**	**CNT (002)**	**PANİ Peak-1 (°2θ)**	**PANİ Peak-2 (°2θ)**	**PANİ Peak-3 (°2θ)**
PAN-DMSO	11.3	16.70	26.60	29.20	-	-	-	-
PAN/PANI(3%)/DMSO	23.8	16.97	26.66	29.3	-	15.1 (broad)	20.0 (broad)	24.0 (broad)
(1%) CNT-NH$_2$/PAN/ DMSO	21.5	17.04	-	29.2	26.5	-	-	-
1% CNT-NH$_2$/PANI/PAN/DMSO	25.5	16.97	-	29.2	26.5	15.1 (broad)	20.0 (broad)	24.0 (broad)

Figures 3.16 shows the equatorial X-ray diffraction traces of pure and functionalized polyacrylonitrile nanofibers. Qualitative examination of equatorial X-ray diffraction trace of pure PAN shown in Figure 3.15 shows two prominent reflections with d-spacings of 0.529 and 0.306 nm which can be indexed as (100) and (110) reflections of hexagonal unit cell [49] with basal plane dimensions of a=b=0.6 nm. There is an additional reflection located at 2θ=26.66 attributed to disordered phase incorporated in the curve fitting (Figure 3.16).

Sample in Table 3.21 contain 3% polyaniline (PANI), it is expected that the reflections from PANI should show their presence. According to the published literature as-synthesized PANI always exhibit EB-1 (Emeraldine Base-1) form[56]. EB-1 form of PANI is reported to result from deprotonation of emeraldine hydrochloride, which is claimed to be the result of a common polymerization method

[56.] EB-2 type of PANI is obtained from the extraction in the presence of several organic solvents including THF, NMP or DMSO.

PANI in the form of emeraldine hydrochloride, obtained directly from the synthesis is denoted as ES-1, whereas the emeraldine hydrochloride obtained by protonation of EB-2 is known as ES-2. The X-ray diffraction patterns of ES-1 and ES-2 are reported to be very different from each other.

It is also interesting to note that EB-1 samples extracted by THF or NMP, as is the case with the present case, exhibit the diffraction profiles typical of EB-2 form of PANI. EB-1 type structure shows typical diffraction peaks at 15, 20 and 24˚ 2θ. The diffraction trace of EB-2 structure is characterized by a predominating intensity near 19˚ 2θ. The other reflections located at 15 and 23˚ 2θ are less intense. It is clear from the information provided from the published literature that the samples examined in the present investigation possess EB-1 structure.

During the curve fitting stage, the curve fitting of X-ray diffraction traces of the samples containing both PAN and PANI structures was carried out by introducing diffraction peaks located at 15, 20 and 24˚ 2θ. These diffraction peaks correspond to the PANI EB-1 structure. The peak positions of the PANI EB-1 structure were fixed at 15, 20 and 24˚ 2θ for the sake of comparison. As far as the structure of PANI chains are concerned, the breadth of the PANI peaks are found to be broad and represent highly disordered structure. Broad nature of PANI peaks indicate that the structure is highly amorphous in comparison to ordered PAN chain structure.

In the case of samples containing NH_2-functionalized CNT curve fitting was introduced with an additional diffraction peak at 26.5˚ 2θ due to 002 diffraction peak of graphite.

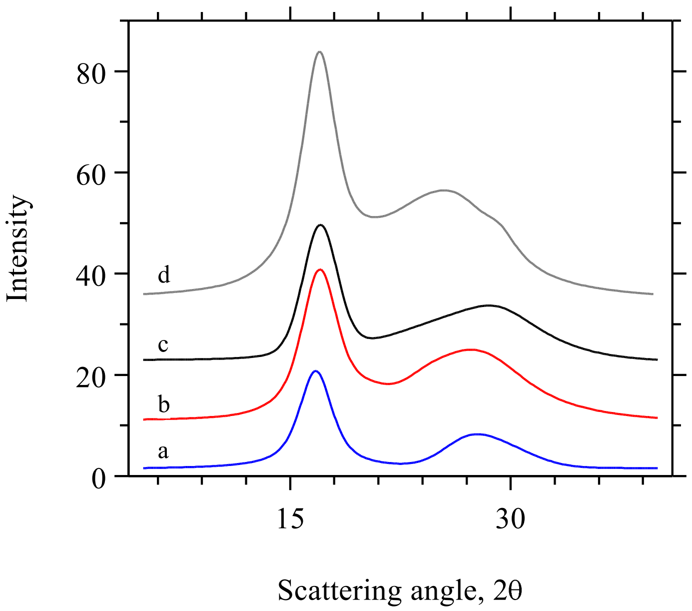


Figure 3.16 : Curve fitting of X-ray diffraction trace of electrospun pure PAN-DMSO nanofibers (a) in the presence of (b) 3% PANi; (c) 1% CNT-NH_2; (d) 3% PANi + 1% CNT-NH_2.

Thermal analysis

DSC results of composite nanofibers are in Table 3.22 (Figure 3.17). Addition of polyaniline into PAN results to an increase of cyclization temperature and decrease of entalphy. While CNT has a tendency to increase the both of cyclization temperature and enthalpy. This may be explained by the decrease of molecular movement. However, (3%) CNT-NH_2/PAN/PANI/DMSO nanofiber shows the lower values, this may be due to an increase of agglomerations and voids with an increase of filler.

Table 3.22 : Cyclization temperatures and enthalpy values of nanofibers.

	Tc (˚C)	**ΔH (j/g)**
PAN-DMSO nanofiber	303.4	437.7
PAN/PANI (%3)-DMSO nanofiber	330.62	293.2
(1%) CNT-NH_2/PAN/ DMSO nanofiber	318.84	411.8
(3%) CNT-NH_2/PAN/ DMSO nanofiber	323.61	468.0
(1%) CNT-NH_2/PAN/PANI/DMSO nanofiber	323.25	516.2
(3%) CNT-NH_2/PAN/PANI/DMSO nanofiber	304.32	349.7

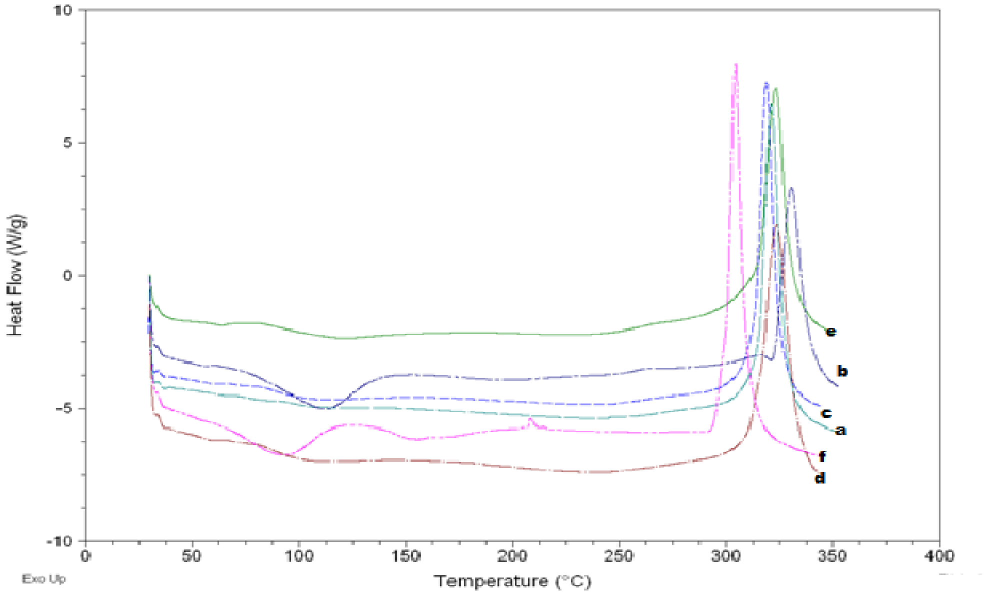


Figure 3.17 : DSC curves of electrospun nanofibers a-PAN/DMSO nanofiber, b)PAN/PANI(%3)/DMSO nanofiber, c-(%1) CNT-NH_2/PAN/ DMSO nanofiber, d- (%3) CNT-NH_2/PAN/ DMSO nanofiber, e- (%1) CNT-NH_2/PAN/PANI/DMSOnanofiber, f-(%3) CNT-NH_2/PAN/PANI/DMSO nanofiber.

3.5.3 Conclusions

Following results have been concluded;

- The diameter of nanofiber increases because of presence of CNT and PANI filler. However, the effect of PANI on an increase of diameter is higher than that's of CNT.
- Increased nanofiller may results to an increase of agglomeration leading to degradation of mechanical and other properties of composite product. However, higher breaking strength was obtained by composite nanofiber with 1% CNT and 3% PANI. The improvement of breaking strength compared to 100%PAN nanofiber was around 25% .
- Insulator PAN became antistatic material with use of CNT and PANI. An increase of conductive filler did not increase the conductivity. This may be due to the agglomeration and void around the filler which destroy the network leading decrease of conductivity

- Crystallinity of PAN increases with presence of PANI and CNT. The crystallinity of composite nanofiber with both of CNT and PANI is higher than that’s of 100%PAN nanofiber and nanofiber with PAN, CNT and nanofiber with PAN, PANI .
- Additon of polyaniline into PAN results to an increase of cyclization temperature and decrease of entalphy. While CNT has a tendency to increase the both of cyclization temperature and enthalpy. PAN with 3% CNT and 3% PANI has a lowest cyclization temperature and entalphy.

4. CONCLUSIONS

The aim of this study is to produce PAN composite nanofibers reinforced with CNTs and PANI to obtain better mechanical, thermal and conductive properties. Composite nanofibers were produced by electrospinnig technique. Firstly, dispersion of CNTs and optimum loading amounts for CNTs were investigated. 1% and 3% CNT amounts for PAN nanofibers have been chosen. Also, with the addition of CNT, mechanical and electrical properties have been improved.

To obtain better dispersion, carbon nanotubes were functionalized with acid treatment as –COOH, -OH and $–NH_2$. Amine functionalized CNTs have shown the best mechanical properties.

The best mechanical properties were obtained when 1% CNT-NH_2 and %3 PANI were employed together to prepare composite nanofibers. In this case composite material became antistatic and much higher conductivity values were recorded compared to pure PAN. The thermal stability and crystallinity of the composite material was also improved in comparision with pure PAN.

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CURRICULUM VITAE

Name Surname: Olcay EREN

Place and Date of Birth: 31.10. 1990 Kadıköy

E-Mail: olcayeren90@gmail.com

EDUCATION

B.Sc.: Yıldız Technical University – Chemical Engineering (2008-2012)

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

Nuray Ucar, **Olcay Eren,** Aysen Onen et al., “The Effect Of Polyanılıne And Amıne Functıonalızed Carbon Nanotubes On The Propertıes Of Composite Nanofıber Web”, Textile and Apperal, 24(3), 2014

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