ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECTS OF STABILIZATION ON PHYSICAL AND CHEMICAL PROPERTIES OF CARBON NANOFIBERS

M.Sc. THESIS

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Polymer Science and Technology

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NOVEMBER 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

STABİLİZASYON İŞLEMİNİN KARBON NANOELYAFIN FİZİKSEL VE KİMYASAL ÖZELLİKLERİNE ETKİLERİ

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KASIM 2012

Mustafa Edhem Kahraman, a **M.Sc** student of ITU **Graduate School of Polymer Science and Technology** student ID 515101019, successfully defended the **thesis** entitled "Effects of Stabilization on Chemical and Physical Properties of Carbon Nanofibers", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 26 MAY 2012
Date of Defense : 02 NOVEMBER 2012

This work has been carried out in conjunction with SANTEZ project number 00534.STZ.2010-1. The kind support of Turkish Ministry of Science, Industry and Technology and Commerce as well as Aksa Akrilik Kimya Sanayi A.S..

FOREWORD

This master study has been carried out at Istanbul Technical University, Institute of Science and Technology, Polymer Science & Engineering Program. In this study, carbon nanofibers are obtained by electrospinning, stabilization and carbonization processes, respectively. Nanofibers were characterized by different methods and conversion of PAN nanofibers into carbon nanofibers was observed. The carbon nanofiber production system is optimized and many researches may be done for carbon nanofiber applications refer to this master study.

Firstly, I would like to express my eternal gratitude to my supervisor, Prof. Dr. Ali DEMIR, for his expertise, understanding, support and opening up new horizons for me during my thesis study even in his busy schedule.

I tender my thanks to Aksa Akrilik Kimya Sanayi A.S. as they always allowed me to use their equipments and laboratories, supplied the materials necessary for carbon nanofiber production and financed the project. I also thank to Turkish Ministry of Science, Industry and Technology Commerce for financing the thesis study.

I would like to thank my partners Hasan Alper ONDUR and Aras MUTLU for giving me valuable advice and support always when needed.

Other important persons considering my thesis are Muzaffer Can IBAN, Ergin KOSA, Selda SEN, Onur AYAZ, Zehra YILDIZ, Timuçin BALKAN, Tuba TOPRAK, Mert Emre OZTOKSOY and Mehmet Tolga SATICI whom I like to give my special thanks to share their knowledge and the best available information for this study.

I would like to acknowledge TEMAG Group including Ismail BORAZAN, Salih GÜLŞEN, Yaşar Emre KIYAK, Onur ERDEN, Zarife DOGAN, Mahmut DIRICAN, Tuncay GUMUS and Cemile AKSU for their friendship and helping. It was a pleasure to be the same working area with them.

Finally, I express my heart-felt thanks to my father Yahya KAHRAMAN, my mother Tulay KAHRAMAN and of course my brother Salih Mehmet KAHRAMAN for the support they provided me through my entire life and in particular.

NOVEMBER 2012

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IMPORTANT REMARK:

This thesis work has been carried out within the following project:

SANTEZ Project Number: 00534.STZ.2010-1, entitled “Polimer Esaslı Karbon Nanolif Üretim Teknolojisisnin Geliştirilmesi” under the guidance of the Project Manager Prof. Dr. Ali Demir.

The project provided Research Student Scholarship and material attended to present all the results of this research work.

The data, figures as well as pictures included in this thesis have also been included in the interim as well as the final reports of the above mentioned projects and no citation has been reciprocally made.

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ABBREVIATIONS

AA : Acrylic Acid
Al_2O_3 : Alumina
AM : Acryloamide
CF : Carbon Fiber
CFs : Carbon Fibers
CNF : Carbon Nanofiber
CNFs : Carbon Nanofibers
CNT : Carbon Nanotube
CO : Carbon Monoxide
CO_2 : Carbon Dioxide
CVD : Chemical Vapor Deposition
DMF : Dimethyl Formamide
EDX : Energy Dispersive X-ray
FT-IR : Fourier Transform Infrared
H_2 : Hydrogen Gas
HCl : Hydrochloric Acid
HCN : Hydrogen Cyanide
He : Helium
HM : High Modulus Carbon Fibers
H_2O : Water
N_2 : Nitrogen Gas
NH_3 : Ammonia
NM : Nanometer
PA : Phosphoric Acid
PAA : Poly(amic acid)
PAN : Polyacrylonitrile
PEG : Poly(ethylene glycol)
PMDA : Pyromellitic dianhydride
PPV : Poly(*p*-phenylenevinylene)
RPM : Repeat Per Minute
SEM : Scanning Electron Microscope
SiO_2 : Silica
TEM : Transmission Electron Microscope
VGCF : Vapor Grown Carbon Fiber

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EFFECTS OF STABILIZATION ON PHYSICAL AND CHEMICAL PROPERTIES OF CARBON NANOFIBERS

SUMMARY

Carbon fibers (CFs) due to their high mechanical strengths and modulus, superior stiffness, excellent electrical and thermal conductivities, strong fatigue and corrosion resistance properties, have been started to gain attention by researchers in the last decades. PolyAcrylonitrile (PAN) with high carbon yield is the most popular polymer in CFs production. Electrospinning is a straightforward and cost-effective method to produce nanofibers. Heat treatments called stabilization and carbonization are carried out in order to manufacture carbon nanofibers (CNFs) from PAN nanofibers. Characterization methods, such as scanning electron microscope (SEM), Fourier Transform Infra Red (FT-IR), Electron Dispersive X-Ray (EDX), and mechanical analyses should be performed to understand the properties of CNFs.

It is difficult to produce CFs having diameters below 5 μm with traditional methods. CFs having nanoscale diameters could be obtained by both chemical vapor deposition (CVD) and from pitch, but due to its simplicity and cost-efficiency, popularity of electrospinning rapidly increases. Various polymers such as poly(vinyl alcohol) (PVA), poly(amic acid) (PAA), polyimide (PI), Poly(*p*-xylenetetrahydrothiophenium chloride) (PXTC) and poly(vinylidene fluoride) (PVDF) are experimented by researchers in order to obtain CNFs, but PAN is still the most widespread polymer in carbon nanofiber production because, it has a continuous carbon backbone and the nitrile groups are ideally placed for cyclization reaction to occur, producing a ladder polymer, believed to be the first stage towards the carbon structure of the final fiber.

Stabilization, consisted of four chemical reactions including cyclization, dehydrogenation, cross linking and oxidation, is the process that principally determines the final structure and mechanical properties of the carbon nanofibers. Stabilization is carried out under air atmosphere because oxygen is an important gas to initiate the mentioned reactions. After stabilization, PAN nanofibers are heated up to 900 – 1500 °C in an inert atmosphere (argon) to obtain CNFs. Stabilization is one of the most important processes in carbon nanofiber production because properties of final product are very relevant to process parameters.

In this work, the aim is to determine the effect of stabilization parameters on average fiber diameter, fiber morphology and properties of stabilized PAN and CNFs.

STABİLİZASYON İŞLEMİNİN KARBON NANOELYAFIN FİZİKSEL VE KİMYASAL ÖZELLİKLERİNE ETKİLERİ

ÖZET

Hızla gelişen kompozit malzemelerin ve teknik tekstillerin ana malzemesi olan karbon elyafı, üstün yorulma ve korozyon dayanımının yanı sıra yüksek mekanik özellikler ve modülüs, üstün sertlik, mükemmel elektrik ve termal iletkenlik özelliklerine sahiptir. Bu üstün özelliklerinden dolayı karbon lifleri özellikle katma değeri son derece yüksek yük taşıyan kompozitler ve gaz ve radyoaktif molekül filtrasyonu, statik elektrik giderimi gibi nitelikli tekstiller alanında çeşitli uygulama alanlarına sahiptir.

1997'den 2007 yılına kadar 10 yıl içerisinde dünya genelinde karbon elyaf kullanımı % 80 oranında artış göstermiştir. 1997 yılında 15 milyon kg olan karbon elyaf üretimi, 2002 yılında bu miktar 20 milyon kilograma yükselmiştir ve 2007 yılında 27 milyon kg seviyelerinde olması öngörülmüştür. 1980 yılından itibaren karbon elyaf maliyetleri düşüyor olmasına rağmen halen günümüzde orta seviyede modüle sahip karbon elyafının fiyatı 20 $/kg, yüksek modüllü, yüksek iletkenliğe karbon elyafları 3000 $/kg civarında satış fiyatına sahiptir.

Geleneksel karbon lifi yaygın olarak PoliAkrilonitril (PAN) polimeri esaslıdır ve lifler genellikle 5-10 μm arasında değişen çapa sahiptirler. Nanometre mertebesinde çapa sahip karbon elyafları üretilmesi için ilk önce kimyasal buhar biriktirme metodu (CVD) çalışılmıştır ancak söz konusu yöntem çok karmaşık fiziksel ve kimyasal işlemlerden oluşan bir yöntemdir. Böylece üretim maliyetlerini artmaktadır. Ayrıca CVD yöntemiyle kısa uzunlukta lifler üretilebilmektedir. Kısa uzunlukta liflerin varlığı daha sonraki işlemlerin uygulanmasında zorluklara yol açmaktadır. Katran bazlı liflerin mekanik özellikleri ve tekrar üretilebilirliği düşüktür. Yüksek modül ve mukavemet özelliklerine sahip mezofaz katran bazlı karbon elyaflar yüksek maliyetleri nedeniyle kendine geniş bir pazar yaratamamıştır. Nanometre boyutunda çapa sahip karbon lif üretmek için son yıllarda hızla gelişen elektrospinning tekniği üzerinde çalışılmaktadır. Bu yöntemle mikron altı ve nanometre boyutlarında çapı olan lifler basit ve ucuz bir şekilde üretilebilmektedir. Takip eden, stabilizasyon ve karbonizasyonu içeren termal işlemler, PAN nanolifleri istenen mikro yapı, elektrik, mekanik ve diğer özelliklere sahip karbon nanoliflere dönüştürür. Literatürde rapor edilen çalışmalarda karbon nanolifler rastgele serilmiş nanoliflerden üretilmektedir bu nedenle termal işlemler esnasından liflere bir gerilim uygulanamamaktadır. Termal işlemler sırasında, özellikle stabilizasyon aşamasında, liflere gerginlik uygulanması yüksek mekanik özelliklerin geliştirilmesinde önemlidir.

Karbon nanolifler, diğer tek boyutlu nano yapılı malzemeler gibi çok yüksek uzunluk çap oranına sahiptir. Karbon nanoelyaflar, filtre uygulamaları, süper kapasitörler, nanokompozitler, hidrojen depolama, pillerde katalizör desteği, optoelektronikler ve özellikle lityum iyon pillerde anot malzemesi olarak kullanılmakta ve geniş yelpazeye sahip uygulama alanına sahiptir. Günümüzde hibrit elektrik araçlarda

(HEV) kullanılmak üzere üretilen anot malzemesinin fiyatı 30-50 $/kg arasındadır. HEV üreticileri yüksek kapasiteli anot malzemesi için ekstra 120-150 $ daha ödeyebilmektedirler. Bu fiyat toplam lityum iyon pilin üretim maliyetinin % 4-5'lik bir kısmını oluşturmaktadır. Bu da karbon nanoliflerden mamül anot malzemesinin hitap ettiği ciddi bir pazarı teşkil etmektedir.

Bu çalışmada, PAN polimerinden elektrospinning yöntemi ile örümcek ağı formunda nanolif ağının yanı sıra birbirine paralel nanolif demetleri elde edilmiş ve bu akrilik nanolif ağları gerilme altında stabilize (200 – 250 ℃ arasında) edilip karbonize (900 – 1500℃ arasında) edilmiştir. Eğer stabilizasyon işlemi, gerginlik olmaksızın yapılırsa, ortaya çıkan karbon nanolif mekanik olarak zayıf olmaktadır. Her iki tip nanolif ağları gerginlik altında ısıl işlemlere tabi tutulmuştur.

Örümcek ağı formundaki nanolif ağı cam bir taşıyıcıya sıkıca sarılarak oksidatif stabilizasyon işleminde gergi altında sırasında ısıl işleme tabi tutulmuştur. Takip eden karbonizasyon işleminde gerilim uygulanmadan 900-1500 ̊C arasında kontrollu olarak sıcaklık uygulanmtır. Paralel olarak üretilmiş nanolif demeti ise iki ucu silindirlere bağlanarak gergin bir şekilde ısıl işleme tabi tutulmuş, ısıl işlem boyunca gerginlik boyutsal çekmeyi engelleme yoluyla yapılmıştır. Neticede bu yolla paralelizasyonun ve mekanik özelliklerin geliştiği de gözlemlenmiştir.

Elektrospining işlemiyle nanolif üretimi için aşağıdaki tambur ve disk tipi olmak üzere iki tip toplayıcı kullanılmıştır. Tambur tipi olan topraklanmış, yaklaşık 500 gram ağırlığında, 28 cm genişliğinde, 6 cm çapa ve sadece 3,2 m/saniye hızla dönebilen toplayıcı yapısal özelliklerinden ötürü örümcek ağı formunda olan nanolif ağının toplanması için kullanılmıştır. Örümcek ağı formunda nanolif elde edilmesinin nedeni elektrospining işleminin çok hızlı gerçekleşmesidir. Öte yandan oryantasyon çalışmaları için PoliEtilen(PE) kütükten kesilerek elde edilmiş 2,5 cm et kalınlığına sahip, 15 cm çapa sahip ve 24 m/saniye hızla çalışabilen disk tipi toplayıcı kullanılmıştır. Hafif olması nedeniyle daha yüksek hızlarda çalışılabilmektedir. Toplayıcının altına simetrik olarak yerleştirilen 2 adet medikal iğnenin ucunda biriken polimer çözeltisine yüksek voltaj uygulanarak elektrospining işlemi gerçekleştirilmiştir.

Karbonizasyon işleminden önce, PAN nanoliflerini karbonizasyon işlemi esnasında uygulanacak oldukça yüksek sıcaklıklara dayanıklı hale getirmek amacıyla nispeten düşük sıcaklılarda yapılan (200-250 °C) stabilizasyon işlemi uygulanmıştır. Stabilizasyon işlemi oryante edilmiş ve örümcek ağı formundaki farkı nanoliflere gergi uygulama şekillerine göre farklı şekillerde uygulanmıştır. Örümcek ağı formundaki PAN nanolif ağı cam plaka üzerine yerleştirilerek stabilizasyon işlemine tabii tutulmuştur. Isıl işlem farklı reçelere göre yapılmış, stabilizasyon sıcaklığının ve bekleme süresinin nanolif üzerindeki etkileri incelenmiştir. Stabilisazyon işlemi oksijen içeriğinin ağırlıkça % 10 olacak şekilde optimize edilmiştir. Ayrıca 220 ℃'de süre artışının numunenin renk değişimine olan etkisi gözlemlenmiştir. 24 m/saniye çevresel hız kullanılarak toplanmış nanolif demeti iki ucundan sabitlenerek ısıl işleme maruz bırakılmıştır. Boyutsal olarak çekmeye karşı uygulanan gerdirme işleminde mekanik ve morfolojik özellikler açısından kazanımlar elde edilmiştir. Stabilizasyon sonucunda nanoliflerin paralelizasyonun arttığı gözlemlenmiştir. Bu yöntem kullanılarak farklı reçetelerin tatbikiyle stabilizasyon üzerinde çalışılmıştır. Ayrıca gerginliğin etkisininde anlaşılması için 2 kademeli germe işlemi uygulanmıştır. Birincisi; ısıl işlemden önce nanolif demetinin 2 metal silindir arasına sıkıca yerleştirilmesi, ikincisi; nanolif demetinin 2 metal silindir arasına %20

oranında sarkıtılarak yerleştirilmesi. Bu iki işlem neticesinde üretilen nanoliflerin mekanik özelliklerinin de farklı olduğu olduğu gözlemlenmiştir.

Üretilen nanolif numunelerinin karbonizasyonunda ise 900 – 1500℃ (100℃'lik artışlarla) arası sıcaklıklarda çalışılmıştır. Stabilize edilmiş nanolif ağlarının karbonizasyondan sonra göstermiş olduğu kimyasal ve fiziksel değişimler incelenmiştir.

Karbon nanolif üretiminin gerekli görülen her aşamasında karakterizasyon işlemi yapılmıştır. Elektrospining, stabilizasyon ve karbonizasyon sonucunda; lif morfolojisi, paralelizasyonu ve çapının ölçülmesinde taramalı elektron mikroskobu (SEM) kullanılmıştır. Isıl işlemler sonucunda gerçekleşmesi beklenen kimyasal değişimlerin tespiti için Fourier Dönünüşümlü Kızıl Ötesi (FI-IR) spektroskopisi rol almıştır. Stabilizasyon işleminin oksijen kontentinin miktarının ölçülmesi yoluyla optimize edilmesi ve sıcaklık artışının karbon nanolifin karbon kontentine olan etkisini incelemek için Enerji Dağılımlı X-Ray spektroskopisi (EDX) kullanılmıştır. Stabilizasyon sonrasında, elektrospining işlemindeki paralelizasyon çalışmaları ve stabilizasyon esnasındaki gergi vermenin mekanik özelliklere olan etkisini anlamak için mekanik analizlerden faydalanılarak elastik modulus üzerinde çalışılmıştır. Ayrıca stabilizasyon işlemi sırasında pirolizin gerçekleşip gerçeklemediğinin ve artan sıcaklığın ağırlık kaybına etkisinin tespit edilmesi için oksidatif stabilizasyona maruz bırakılmış PoliAkrilonitril'ten mamül nanolif ağının ağırlıkça değişimi hassas terazi kullanılarak tespit edilmiştir.

1. INTRODUCTION

Due to their high mechanical strength – weight ratio, superior stiffness, excellent electrical and thermal conductivities, and strong fatigue and corrosion resistance, CFs have been became the main material for developing composite materials [1-8, 70, 85]. They are used for reinforcement of metals, ceramics, polymers and carbon. Nature of polymer and ceramics are non-conductive. Adding CFs to non-conductive matrix makes them not only electrically conductive but also mechanically strong and thermally conductive [8, 10, 19, 20].

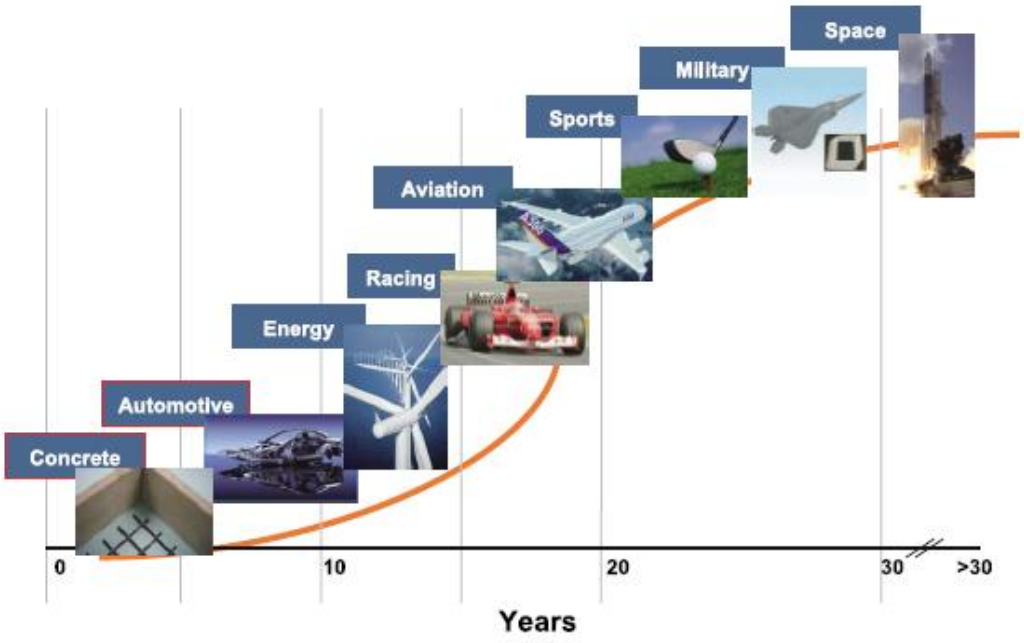


Figure 1.1 : Maturity of carbon fiber market [79]

Hence, CFs have widespread applications in the fields of high value added composite materials for spacecrafts, high temperature gas and radioactive molecular filtration media and electrically conductive textiles and other industrial applications (figure 1.1). CF is a very expensive material due to the raw material prices are directly connected with crude oil prices and energy costs (110 $/barrel in 2012 and 140 $/ barrel in 2008)[28]. The cost structure of carbon fibers is dominated by the precursor

cost with close to 50 % (table 1.1). Maturation of production technology will decrease the energy requirement. The second position is held by energy necessity because of high temperature heat treatments such as carbonization and graphitization [79].

Table 1.1 : Cost share of carbon fiber's items [79]

Items	Cost Share (%)
PAN Precursor	45
Energy	20
Staff	10
Maintenance	8
Chemical Processes	8
Others	9

Traditionally CFs are based on Polyacrilonitrile (PAN) and are of varying diameters in the range of 5 – 10 μm. In order to produce carbon fibers with diameters in the range of 100 – 300 nm (nanometer), the electrospinning techniques have been recently used. By the techniques, fibers with sub-micron diameters can be produced economically and efficiently. With the following stabilization and carbonization processes, PAN nanofibers are converted into CNFs with required nano-structure. Due to their unique properties, carbon nanofibers have many potential applicaitons in different fields of commercial interests such as eneregy storage, filtration and mechanical applications [65, 67-75].

2. CARBON FIBERS

Carbon fibers refer to fibers which are at least 92 wt.% carbon in composition [8]. The fine structure of carbon fibers consists of basic structural units of turbostratic carbon planes [9]. There are van der walls bonding between the layers, so carbon layers can easily slide with respect to on another. Due to the difference between the in-plane and out-of-plane bonding, carbon fiber has a higher Young's modulus parallel to the plane than perpendicular to the plane [8].

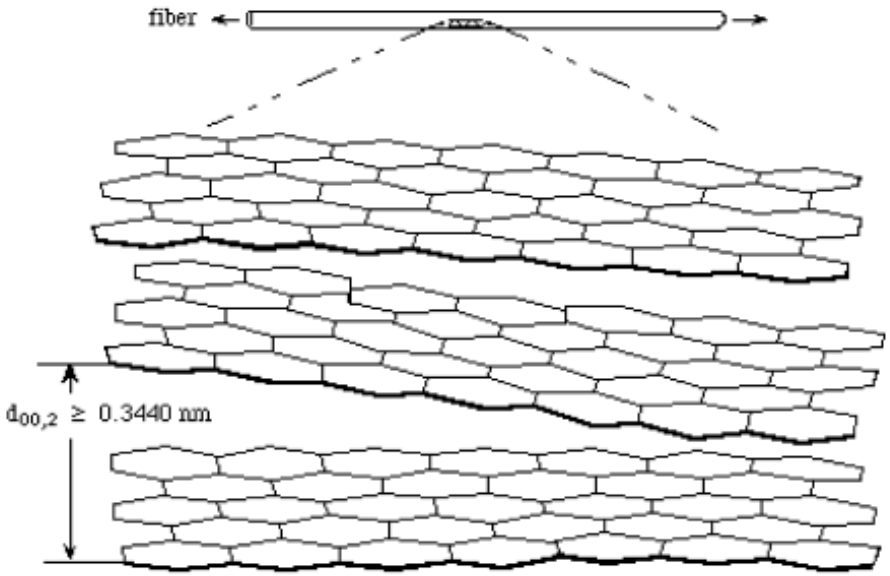


Figure 2.1 : Turbostratic plane of carbon fiber[11]

Production of PAN based carbon fibers can be achieved into four or five steps:

- Polymerization of Polyacrylonitrile
- Spinning of fibers
- Stabilization
- Carbonization
- Graphitization (optional)

Graphitization can be applied while the fibers are under tension, for improving preferred orientation of carbon fiber. Higher graphitization temperature results the greater the preferred orientation [8].

Commercial continues carbon fibers are in the tows form, which contains 1000 – 12000 fibers per tow. They may be sized and the sizing improves the handle ability and may enhance between the fibers and certain matrices when the fibers are used in composites [9].

For carbon fiber production, PAN is mostly used due to the fact that PAN has the high carbon yield, containing 68 % carbon atoms, and acceptable tensile properties. Another reason of suitability of PAN is that weight loss at 1000 ˚C in helium is very low compared to other precursor such as cellulose and pitch as shown in table 2.1 [10]. Furthermore, PAN fibers have a higher degree of molecular orientation than other precursors.

Table 2.1 : Weight loss (%) of precursor fibers at 1000 ˚C [10]

Precurson Fibers	Weight Loss (%)
Pitch	30
PAN preoxidized	38
PAN	60, 67
Saran	74
Rayon	88
Ramie	91

2.1 Polyacrylonitrile (PAN) Based Carbon Fiber

PAN is polymerized from acrylonitrile (AN) by commonly used initiators, such as peroxides and azo compounds through the addition type polymerization. Solution polymerization is preferred to be conducted in a PAN solvent so that PAN solution can be used as a fiber spinning dope directly [10, 57].

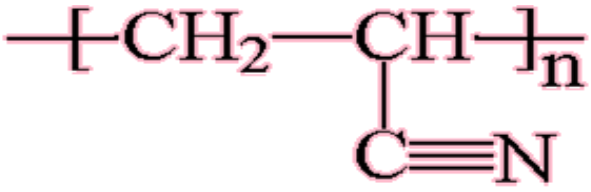


Figure 2.2 : Polyacrylonitrile (PAN) [1]

One of the reasons of obtaining poor quality carbon fiber is PAN homopolymer usage. Processability of PAN homopolymer is limited due to their hydrogen bonding in the structure. Therefore, 5 – 10 % of a comonomer added [9, 10].

Table 2.2 : Comonomers [10]

Comonomer	**Chemical Structures**
Acrylic acid (AA)	CH_2=CHCOOH
Methacrylic acid (MAA)	CH_2=C(CH_3)COOH
Itaconic acid (IA)	CH_2=C(COOH)CH_2COOH
Methacrylate (MA)	CH_2=CHCOOHCH_3
Acrylamide (AM)	CH_2=CH$CONH_2$

Various comonomers such as vinyl comonomers having acidic groups (acrylic acid, metacrylic acid, itaconic acid), esters (metacrylate, acrylamide ammonium salts of vinyl compounds (quaternary ammonium salts of amino ethyl 2 methyl preponate) can be used for processibility [10]. The comonomer is a more bulky acrylic monomer, which diminishes the crystallinity of the PAN structure, thereby acting as an internal plasticizer and improving the drawability. Therefore, commercial PAN fibers are copolymers [9, 10].

PAN should have these properties to be a good candidate for carbon fiber production;

- High molecular weight (~10^5),
- A molecular weight distribution corresponding to a polydispersity ratio of 2-3 Mw/Mn,
- Minimum moleculary defects [8]

The precursor fiber should have ;

- A fine denier (5-19 denier or 10-12 micrometer diameter),
- High strength and modulus,

- A broad exothermic peak due to nitrile group oligamerization during heating, and it should start at a lower temperature,
- High carbon yield (>50 %)
- Preferring of solution spinning eliminates PAN drying and re-dissolving processes for wet spinning [10].

2.1.1 Thermal analyses of P(AN-co-VAc)

In this study, industrial PAN (p(AN-co-VAc)(w/w:92/8 wt%)) is taken from AKSA Acrylic Chemical Co.,(M_w = 30000-40000 $gmol^{-1}$ and M_n = 100000-120000 $gmol^{-1}$). In order to understand thermal behaviour of p(AN-co-VAc), DSC (Differential Scanning Calorimetry) and TGA (Thermal Gravimetric Analysis) are used. According to DSC analysis, p(AN-co-VAc) display an exothermic peak at 318,68 ˚C. This peak is existing as the result of the nitrile gruops of PAN. The glass transition temperature is about 110 ˚C.

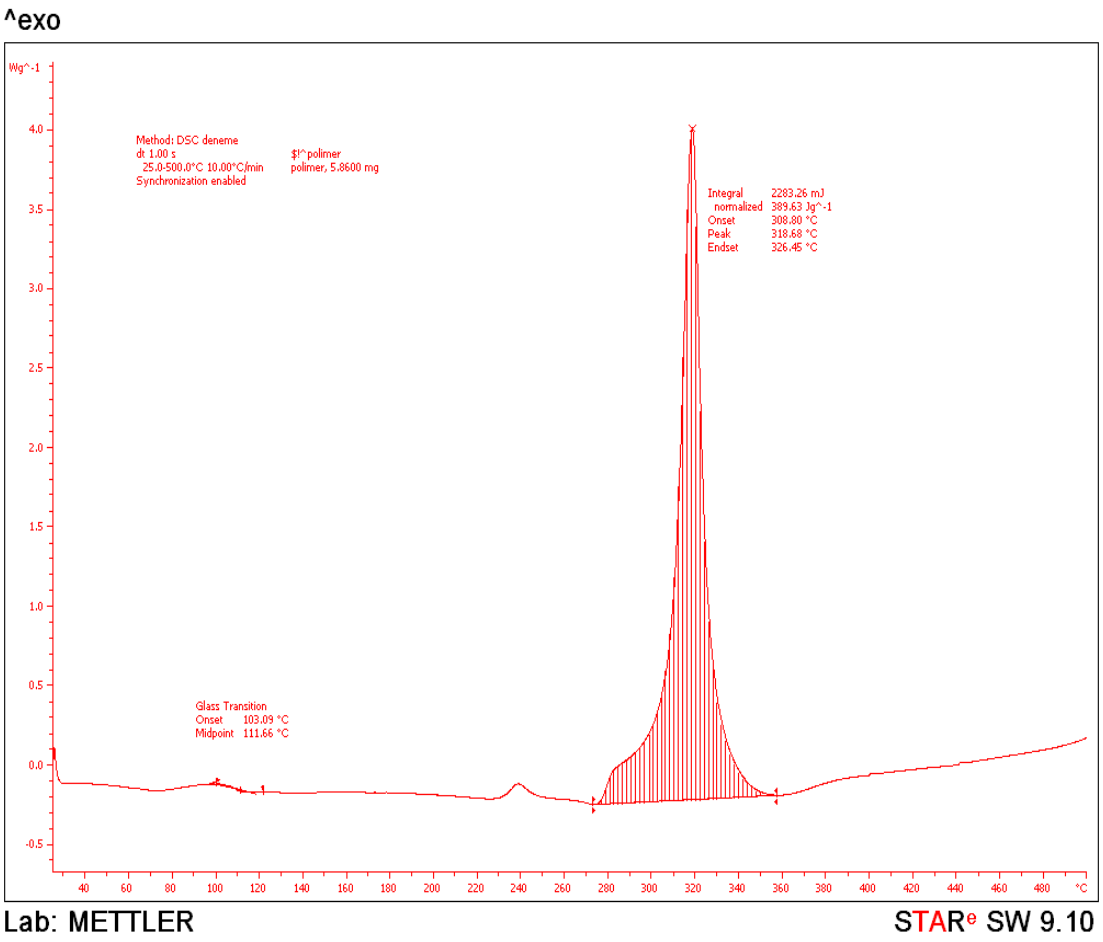


Figure 2.3 : DSC plot of p(AN-co-VAc)

By refer to TGA analysis, degredation is beginning about 240 ˚C than it is ending about 400 ˚C. 50% weight loss is determined at 570 ˚C. End of the measurement 34,37 % residue is accounted.

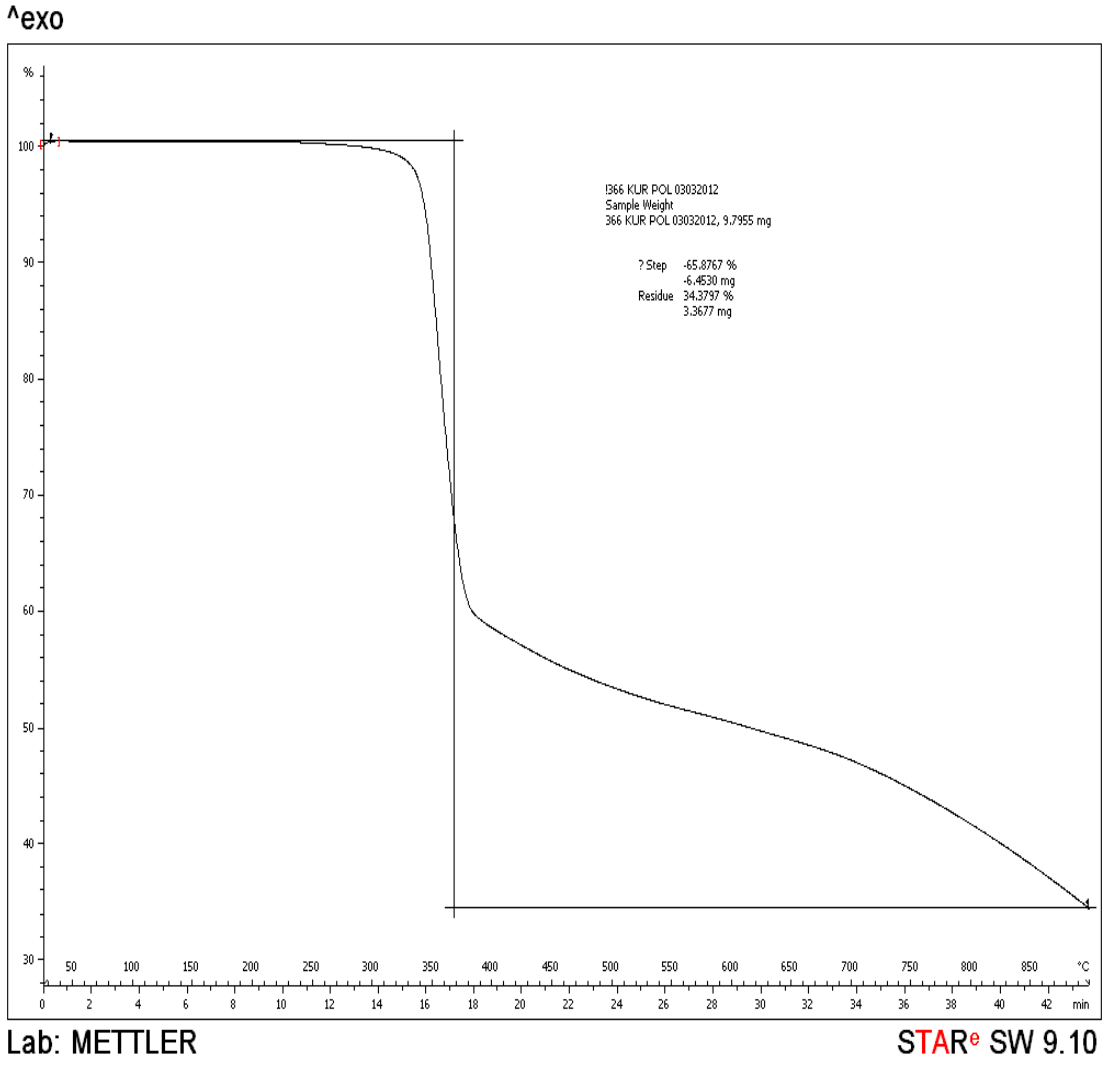


Figure 2.4 : TGA plot of p(AN-co-VAc)

2.1.2 Spinning of PAN

Polar nitrile groups of PAN lead to strong intermolecular interactions in the molecules. Because of strong intermolecular interaction, PAN has a high melting point and, it tends to degrade before the temperature reaches its melting point. Solution (wet) spinning appears to be the only proper choice for PAN precursor fiber spinning. There are many parameters, which are spinneret orifice diameters, doping, rate, take up velocity etc. These variations affect fiber drawability, molecular orientation of fiber, tensile strength etc. Strength of fiber especially depends upon the condition of coagulation bath and stretching parameters [8].

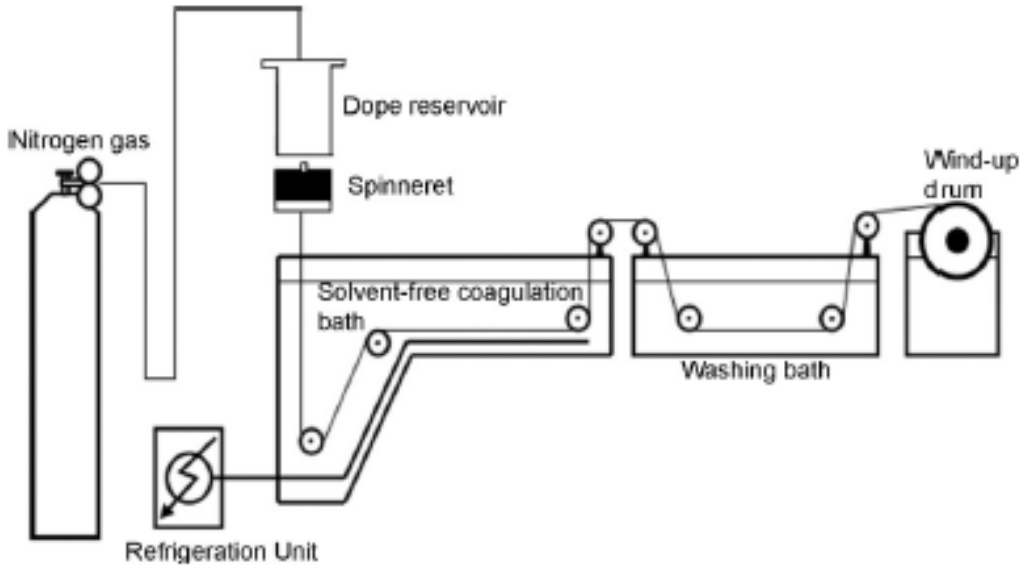


Figure 2.5 : Wet spinning [17]

2.1.3 Stabilization

Precursor fiber are heated in the 180 – 400 ˚C range in air or in an oxidizing atmosphere under tension for being thermally stable subsequent high temperature heat treatments (carbonization and graphitization).

In order to reduce stabilization time and obtain more uniform fiber properties, pre-stabilization treatments are suggested. This process obtains impregnation of PAN precursor fibers with solutions of persulfate, cobalt salts, a combination of a salt of iron (II) and hydrogen peroxide, acids, guanidine carbonate, dibutylindimethoxide, potassium permanganate and flame retarders or antioxidants [8].

The stabilization process play an important role in converting PAN fiber to an ladder type polymer that converts C≡N bonds to C=N bonds and to develop crosslink between molecules of PAN which tend to operate at high temperatures, with minimum volatilization of carbonaceous material [15].

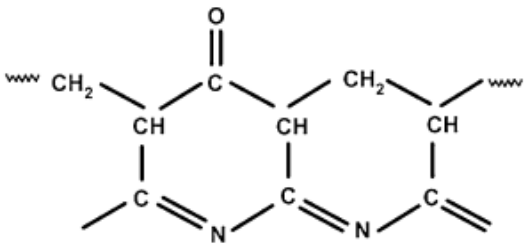


Figure 2.6 : Ladder PAN structure [15]

The thermal stability of the stabilized fibers are attributed to the formation of the ladder structure due to cyclization of the nitrile groups in acrylic molecule. Stabilization is the most decisive process to designate final properties of carbon fibers. Chemical structure changes occur during heat treatment that begins 180 ˚C. Stabilization is also responsible for the change in color of precursor fiber to yellow or dark brown [16].

Figure 2.7 : Stabilizaiton furnace and oxidized PAN fibers [18]

An oxidizing atmosphere is used because it results in a higher rate of cyclization, a higher carbon yield after subsequent carbonization and improved mechanical properties of resultant carbon fibers. Besides cyclization, dehydrogenation and three-dimensional cross-linking of the parallel molecule chains by oxygen bonds occurs during stabilization (Figure 2.6). The cross-links keep the chains straight and parallel to fiber axis, even without stress application [15].

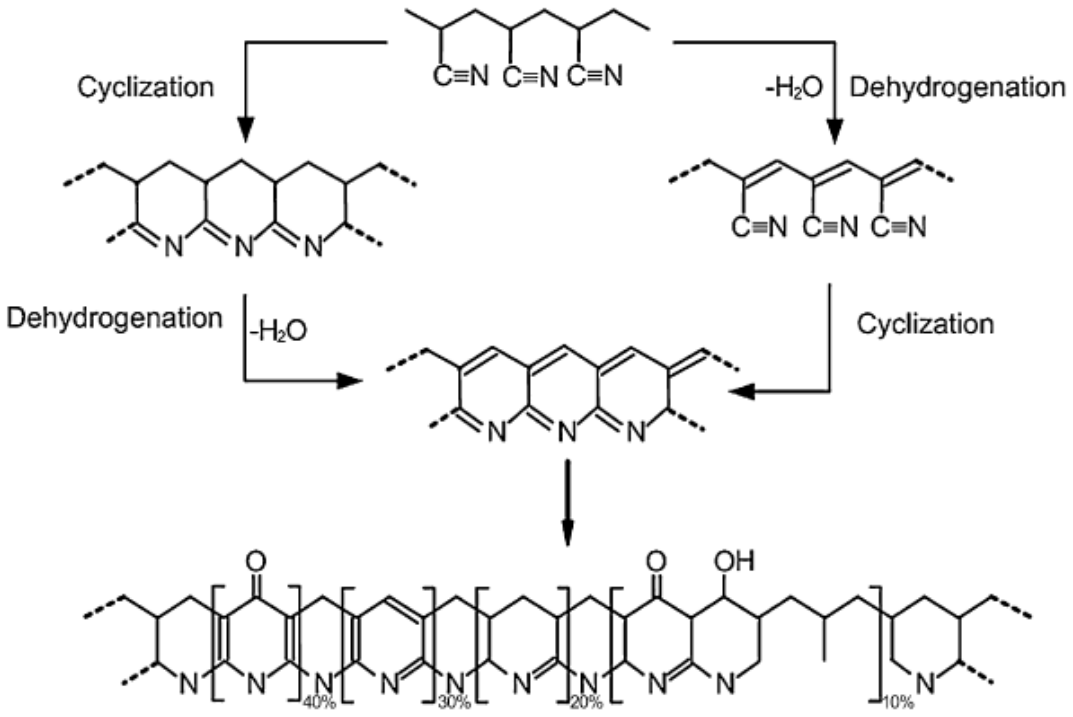


Figure 2.8 : Proposed chemistry of PAN stabilization [15]

Two important reactions occur during stabilization process, which can change the chemistry of PAN structure. They are dehydrogenation and cyclization reactions as illustrated in figure 2.6. Both are important to form ladder polymer structure, which was thermally stable and might be able to withstand high temperature during pyrolysis process. In addition, stabilization process also could be present in oxidation reaction that gives an insight about diffusion of oxygen through the reacting polymer [10].

Oxygen is an initiator for the formation of activated center for cyclization. Dehydrogenation is the formation of double bonds that stabilizes carbon chain and cyclization is the process by which the rings are formed. The dehydrogenation reactions have at least two elementary steps, with oxidation in the first step and elimination of water in the second [19]. Cyclization is the most important reaction in stabilization process. The reaction is necessary to hold molecules in fiber together and increases the stiffness [15].

If the stabilization temperature is too high, the fibers can overheat and fuse or even burn. However, if the temperature is too low, the reactions are slow and incomplete stabilization can be resulted, yielding poor carbon fiber properties [15].

2.1.3.1 Importance of tension for stabilizaiton

During stabilization, tension is applied to prevent shrinkage or cause elongation of the fiber, when fully relaxed by heating, shrink by about 25% due to the formation of nitrile conjugation cross-links between polymer chains [16]. It is crucial to apply tension particularly during stabilization in order to produce carbon fibers with high mechanical strength. If not, the final product of carbon fiber would be mechanically weak [14].

2.1.3.2 Aspects of stabilization

There are many methods to evaluate degree of stabilization process and to establish optimum conditions such as measuring O_2 content [50], determining oxidized fiber density [20], calculating water uptake of oxidized fiber [55], employ the aromatization index [19].

Amount of oxygen is determined by elementary analysis. 8-12 % of oxygen is considered as preferable value. Homopolymer PAN involves 0 % O_2, whilst an acrylonitrile copolymer is theoretically less than 3%. Maximum saturation value of O_2 is 20%, however the values more than 15 % resulted in carbon fibers with reduced mechanical properties and less than 5 % reduced the yield of carbonized fiber [50].

An increase in oxidized fiber density with longer stabilization times results in density to closer packing of molecular chains due to cyclization of the nitrile groups [20].

The water absorption of stabilized PAN fiber is calculated as follows:

$(W - W_o)$ x $100/W_o$

Where W is the weight after absorption and W_o the weight after drying for 2 hours at 120 ˚C. A value of 5-10 % is preferred; <3.5% will make poor carbon fiber and <15% will lower the carbonization yield [55].

Aromatization index (AI) is a measure of degree of oxidation.

$$AI = (((H_v - H_0) \times 100) / H_v)\%$$

Where Hv = exothermic heat of virgin PAN fiber, H_0 = exothermic heat of oxidized PAN fiber and an AI value of 60 % is preferred [19].

2.1.4 Carbonization

Stabilized PAN fibers are heated up to the range of 400 – 1500 ˚C in an inert atmosphere (generally nitrogen or argon gases) in order to obtain carbon fibers.

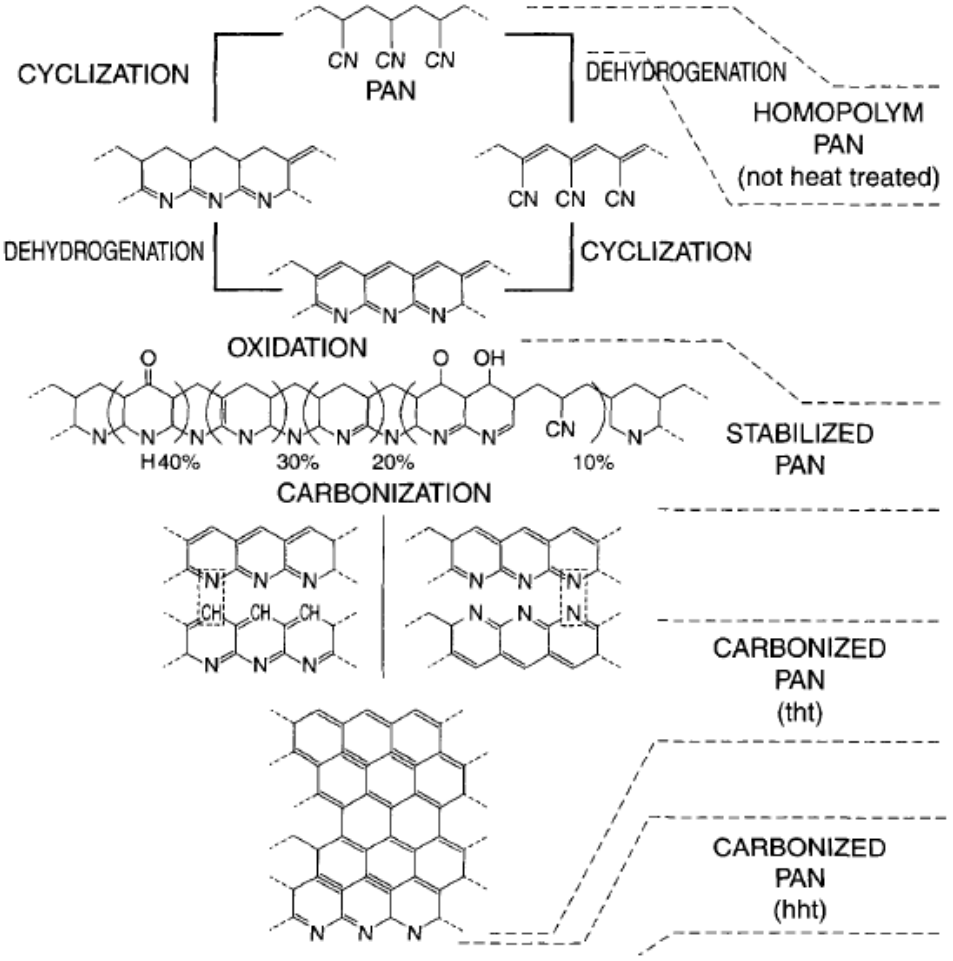


Figure 2.9 : PAN stabilization and subsequent carbonization [20]

Stress application is not a necessity during carbonization because after stabilization, backbone of PAN fibers has already consisted of carbon atoms completely. However, in the case of using rayon as a precursor, one oxygen atom per monomer unit is existed in the backbone, so it shows structural reorganization during carbonization [8]. During carbonization about 50 % of the weight of the fiber is lost by the effect of extracted gases such as H_2O, NH_3, HCN, CO, CO_2, N_2, and H_2 (Table 2.3). The volume of the gases evolved is 10^5 times the volume of the fibers [15]. The reason to use an inert gas atmosphere is to dilute the toxic waste gas in the gas extract system and to prevent ingress of atmospheric air [12].

Table 2.3 : Carbonization products of oxidized PAN [19]

Temperature °C	Observation	Interpretation
220	HCN evolved and O_2 chemically bonded	Ladder polymer formation and oxidation of polymer
260	Little change. No modulus increase	No chain scission
300	Large CO_2 and H_2O evolution, also CO, HCN and some nitriles. No modulus increase	CO_2 from –COOH groups in oxidized polymer. No cross-linking
400	CO_2, H_2O, CO, HCN and NH_3 evolved. Small evolution of C3 hydrocarbons and nitriles. Modulus increase	Cross-linking by intramolecular H_2O elimination
500	Increased H_2 evolution. Some NH_3 and HCN evolved. Modulus increase	Cross-linking by dehydrogenation
600	Reduced H_2 evolution. HCN and trace N_2	Cross-linking by dehydrogenation
700	N_2, HCN and H_2 evolution. Modulus increase	Cross-linking by dehydrogenation and evolution of N_2
800	Large increase in N_2. H_2 and HCN still evolved. Modulus increase	Cross-linking by evolution of N_2
900	Maximum evolution of N_2, some H_2, traces HCN. Modulus increase.	Cross-linking by N_2 elimination
1000	N_2 evolution decreases to about the same as at 800°C. Trace H_2 evolved. Modulus increase.	Cross-linking by N_2 elimination

2.1.5 Graphitizaiton

Graphitization, also called high temperature carbonization, is carried out between the temperatures 1500 – 3000 ˚C. An inert atmosphere is needed for graphitization too. Up to 2000 ˚C nitrogen can be used to create this atmosphere but above 2000 ˚C argon should be used because above this temperature, reaction between nitrogen and carbon forms cyanogens, which is toxic. Little amount of gas is evolved during graphitization. However, crystallite size is increased and preferred orientation is improved, so the fiber becomes more graphitic. Energy need of graphitization is very high so process cost increases. Thus, it is not usually preferred during carbon fiber production [19].

2.2 Properties of Carbon Fiber

According to structures and treatment conditions of carbon fiber, they shows different properties, but there are some important common features which are high tensile strength and modulus, high thermal conductivity, low electrical resistivity, chemical stability, low density, low thermal expansion coefficient excellent creep resistance [12]. Carbon fibers have great thermal and electrical conductivity because of parallel alignment of graphene layers along the fiber axis and high content of delocalized π electrons. The coefficient of thermal conductivity of carbon fibers

varies between the ranges of 21-125 W/mK, which is similar to that of metals. Thermal conductivity of high modulus mesophase pitch carbon fibers may increase above 500 W/mK at room temperature. Carbon fibers treated at relatively high temperatures, about 2500 ˚C, have electrical conductivity similar to the metals have [21]. Modulus of carbon fibers are directly affected by the crystallinity and alignment of the crystals along the fiber axis. The higher crystallinity and better alignment of crystals result higher modulus carbon fibers [12]. PAN-based carbon fibers consisting of smaller turbostratic crystallites are expected to have better tensile strength [22]. There are weak van der Waals bonds between the graphene layers and their fibrillar structure. Thus, carbon fibers have low compressive strength. The compressive strength of mesophase pitch carbon fibers is relative lower than that of PAN-based carbon fibers [12].

3. CARBON NANOFIBERS

PAN has been used as the principal precursor and associated with different modifications in processing such as the use of additives, oxidative stabilization of as-spun PAN fibers at a low temperature and stretching during stabilization and carbonization [23]. In order to obtain nanofibers, electrospinning is carried out. Electrospinning has been used to produce nanofibers of various polymers with diameters from a few tens of nanometers to a few micrometers in different forms such as nonwoven webs, yarns, etc. [24]. Then thermal treatments calling as stabilization and carbonization are applied to the nanofibers. Oxidative stabilization is essential step for several reactions which are cyclizaiton, oxidation, dehydrogenation, aromatization etc. [10] Stabilized PAN nanofibers are carbonized at >800 ˚C in an inert atmosphere such as argon, nitrogen, helium etc.

3.1 Electrospinning

Electrospinning has been regarded as the most effective and versatile technology to produce nanofibers with controlled fiber morphology, dimension and functional components from various polymeric materials [29]. A schematic diagram to interpret electrospinning of polymer nanofibers is shown in fig. 3.1. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process, a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibers [25].

Most of the nanofibers are non-woven form, which can be useful for small number of applications such as filtration, tissue scaffolds, and implant coating film, and wound dressing [25]. Alignment is very important property for textile applications and several researchers focused on production of aligned nanofibers in order to improve mechanical, electrical and optical properties.

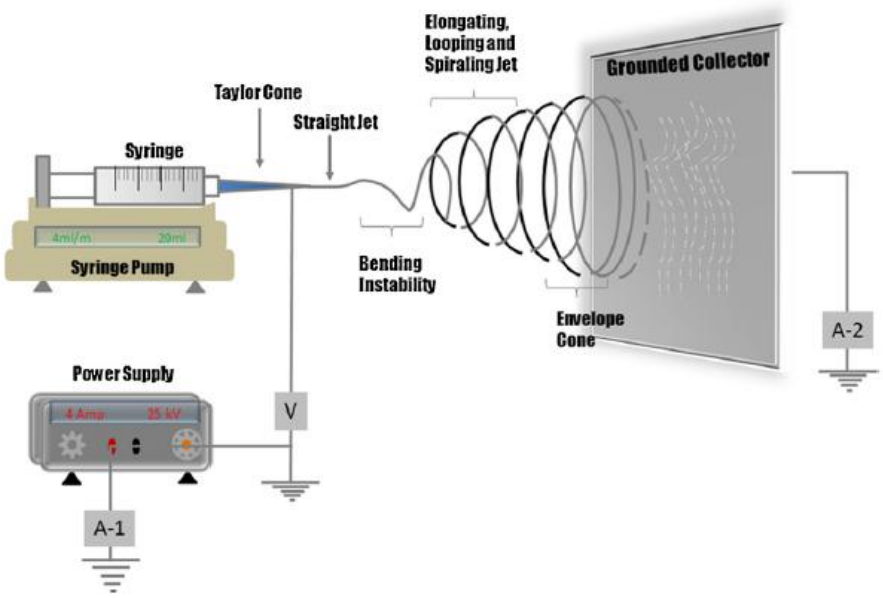


Figure 3.1 : Principal illustration of electrospining [26]

Rotating cylinder collector is used to parallelize nanofibers. Collector is working at a very high speed up to thousands of rpm (repeat per minute). When the collector rotates at a high surface speed such as 8 m/sec. fibers start to align along the rotating axis [29]. This speed can be defined as alignment speed. If surface speed of the collector is slower than alignment speed, randomly deposited fibers will be collected. On the other hand, there must be a limit rotating speed above which continuous fibers cannot be collected since the over fast take-up speed will break the fiber jet. [27].

Figure 3.2 : Multi-Frame type collector [25]

It is also possible to produce aligned nanofibers by manipulation of electric field. Two split parallel flat plates connected with grounded electrode, a frame or multi frame-shaped collector (figure 3.2) [25]. High degree of alignment can be achieved by this method. However, length and thickness of these nanofibers are limited. Most

of the early studies focused on non-twist nanofiber bundles. Twisting can be inserted by a post-electrospining process and now continuous yarns can be produce directly from an electrospinning process [30].

According to form of final products, nanofiber alignment studies can be classified as following:

- Short Nanofiber Bundles
- Short Nanofiber Yarn
- Continuous Nanofiber Bundles
- Continuous Nanofiber Yarns [29].

Table 3.1 : Short Nanofiber Bundles

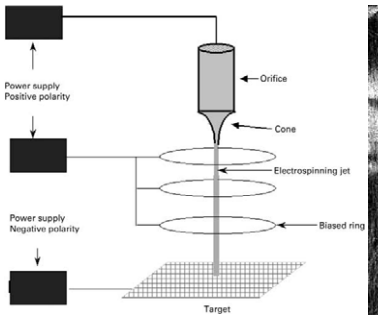
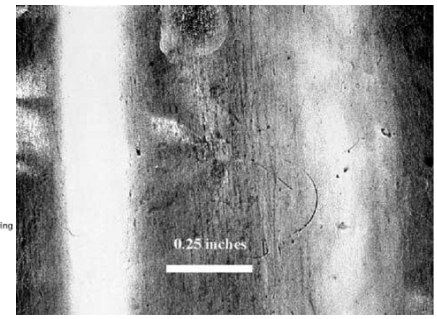
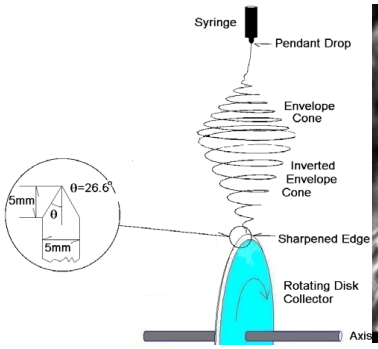
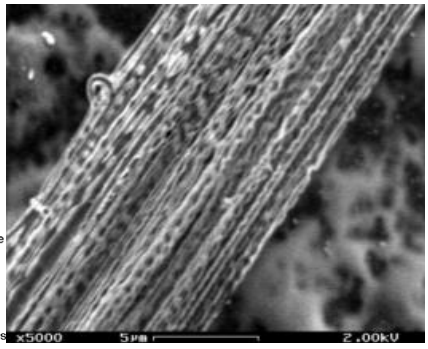
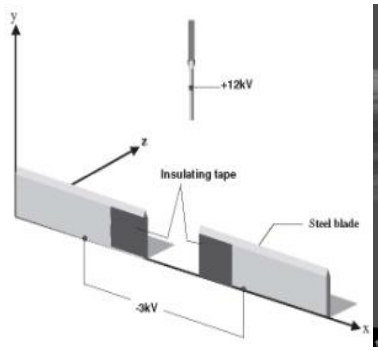
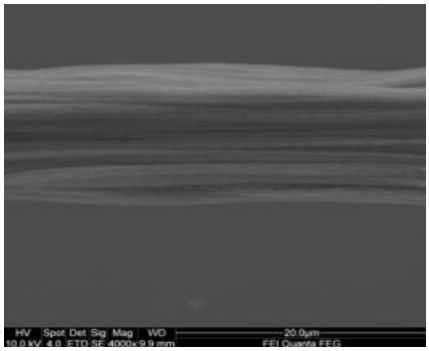
Set Up	Morphology	Explanation
		Jet was stabilized by placing a series of charged rings in the electrospinning zone and the rings were charged to have the same polarity to the spinneret; PEO [31].
		Electric field is concentrated on the tapered wheel which rotates for fiber alignment. The collector has a limited fiber deposition area; PEO[32].
		Gap collector using sharp blades for concentration of electric field; PCL[33].

Table 3.2 : Short Nanofiber Yarns

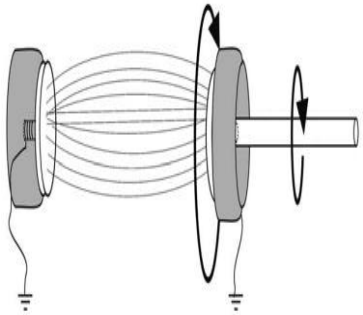
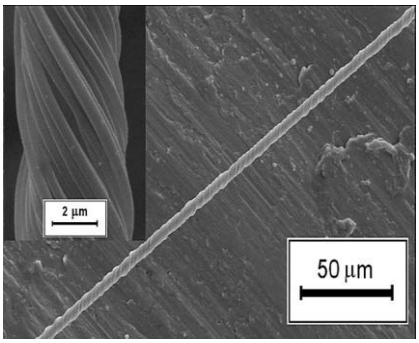
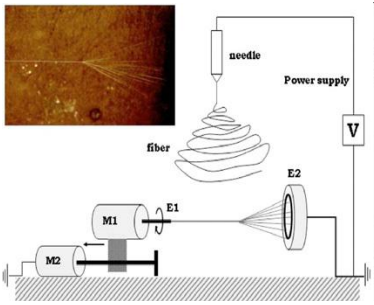
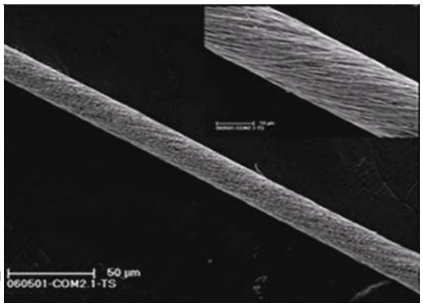
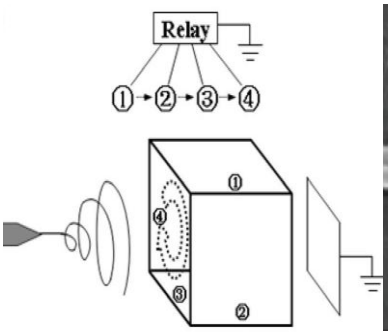
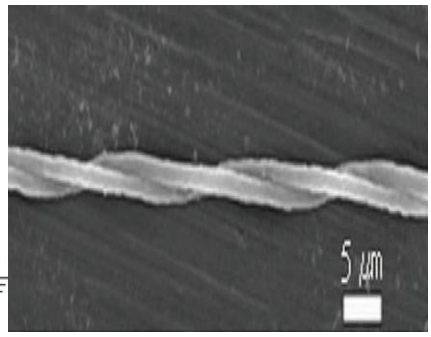
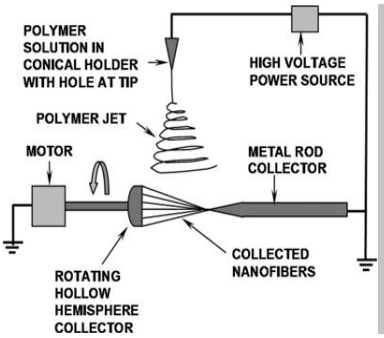
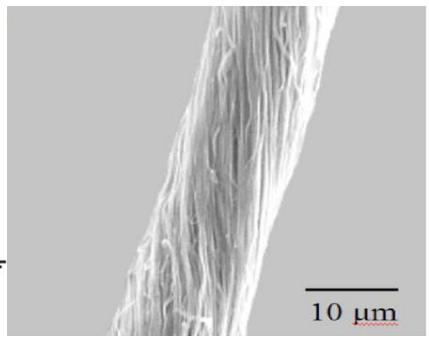
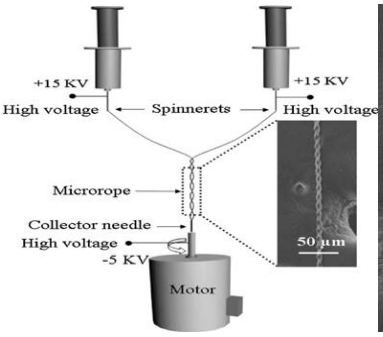
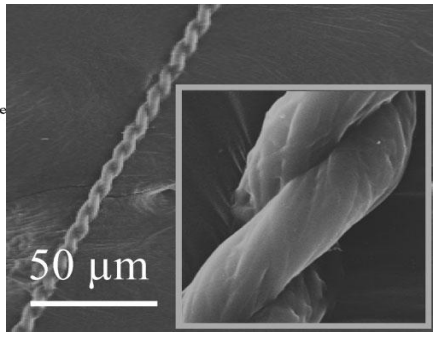
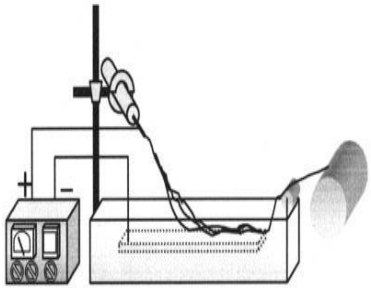
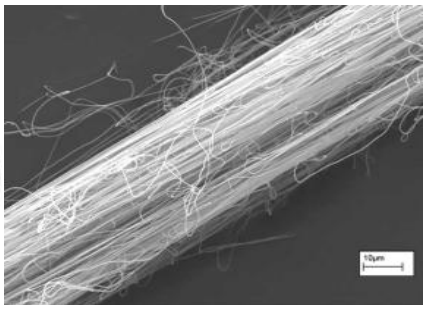
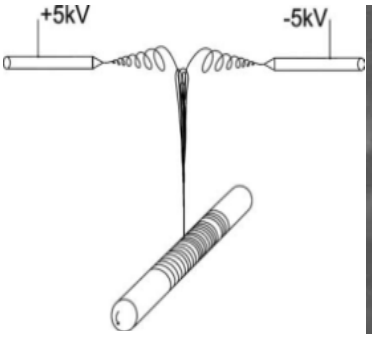
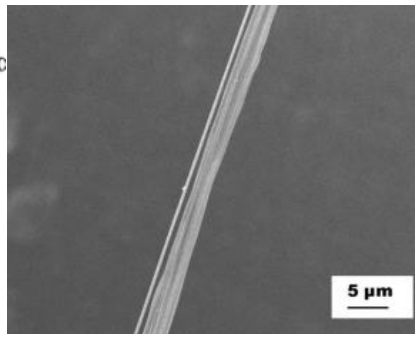
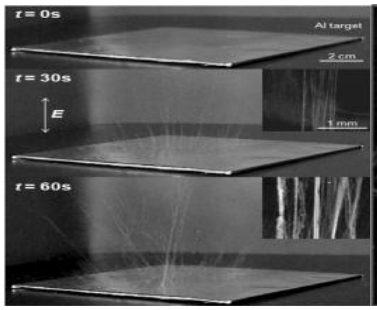
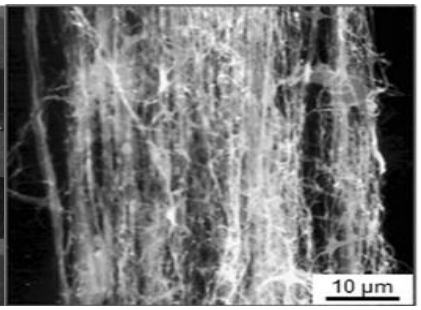
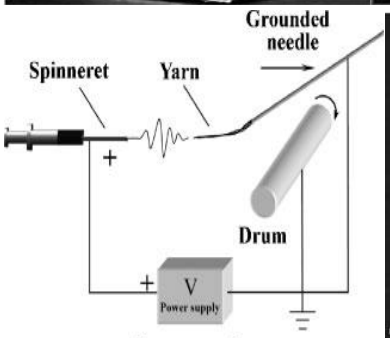
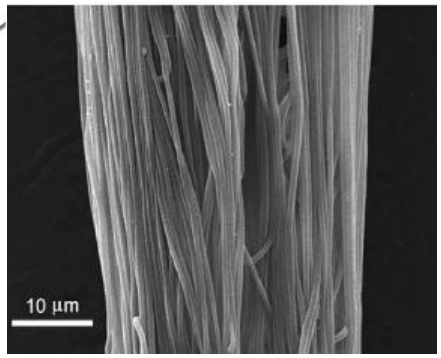
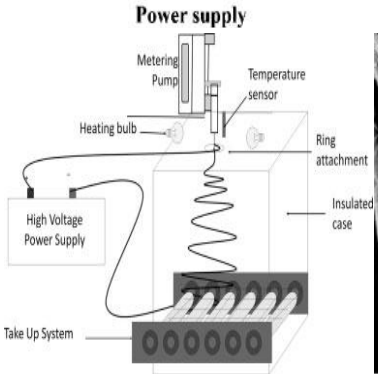
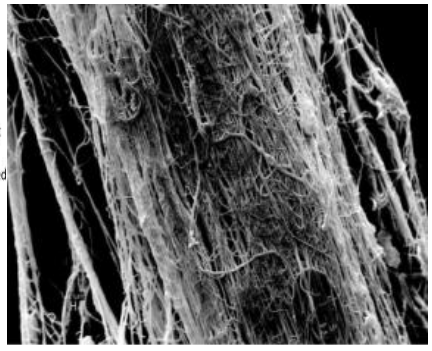
Set Up	Morphology	Explanation
		Aligned nanofibers were collected between the electrodes (gap collector) and twisted by rotating one electrodes; PCL [34].
		Aligned nanofibers collected by twisting needle electrode; PMMA/MWNTs [35].
		Nanofibers were twisted by electric field using an auxiliary polygon electrode; PEO[36].
		(Gap collector) aligned NFs twisted by rotating the round electrode; ZnO, NiO[37].
		Helical ropes were prepared with two needle spinnerets and one rotating needle collector; PVP [38].

Table 3.3 : Continuous Nanofiber Bundles

Set Up	Morphology	Explanation
		Flexible fiber web in liquid was withdrawn into fiber bundles; PCL, PVDF, PAN, PVAc [50]
		Nanofibers electrospun from opposite charged spinneret attract each other to form bundles; PVA; PVP [41, 42, 43].
		Conductive fiber induces self-bundling; PPV [44].
		Needle collector induced self-bundling of nanofibers; PHBV[45].
		Ring induced self bundling of nanofibers; PAN[46].

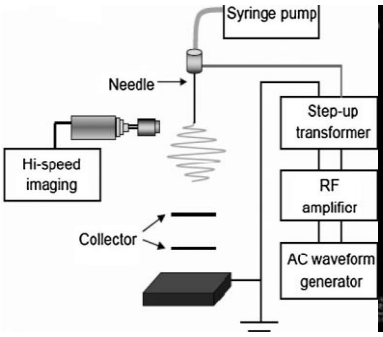
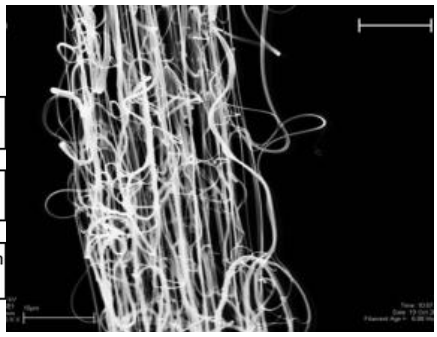
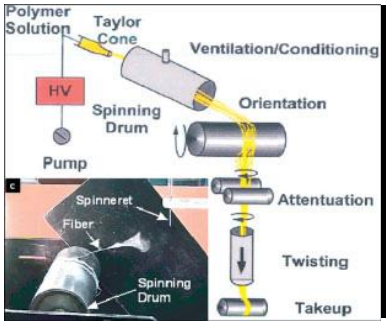
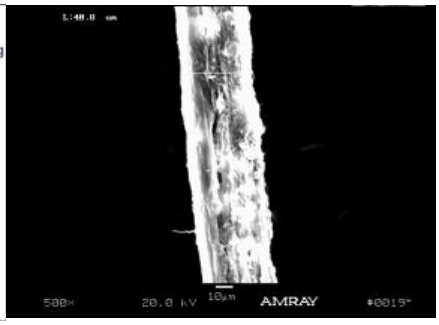
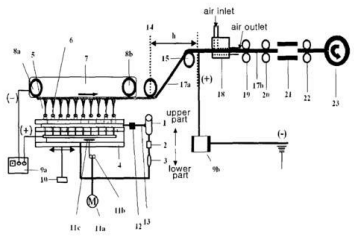
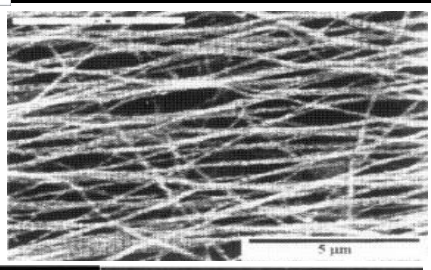
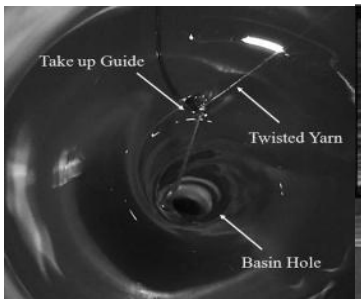
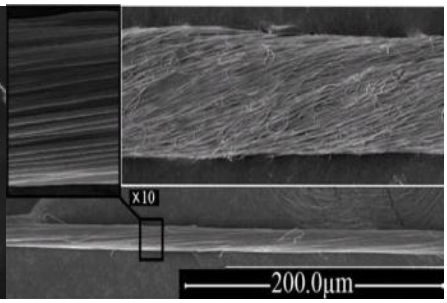
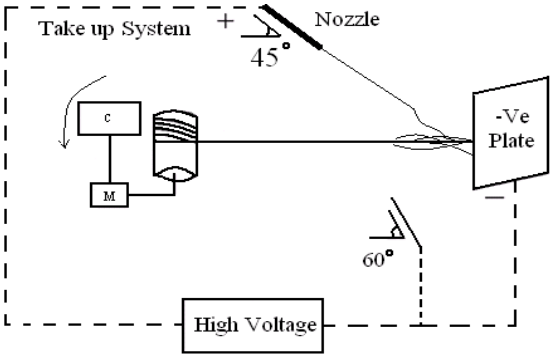
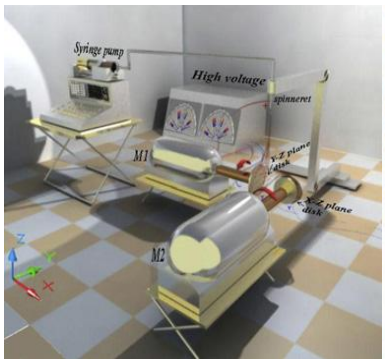
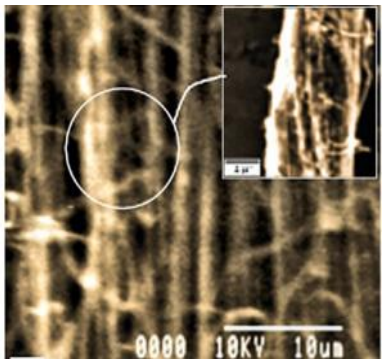
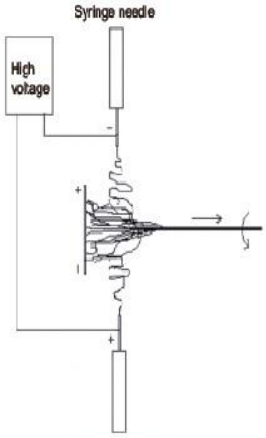
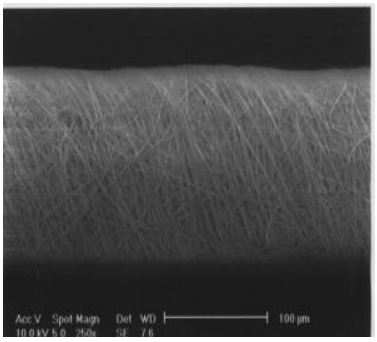
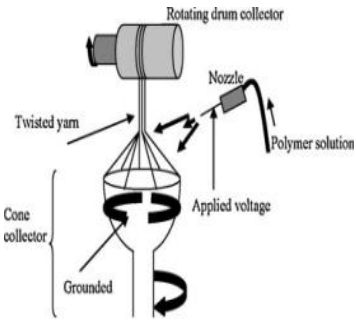
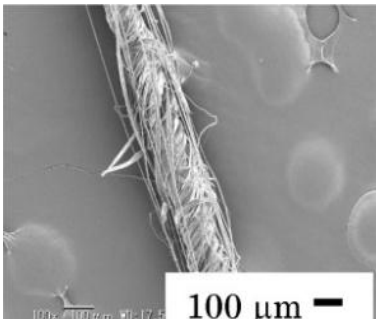
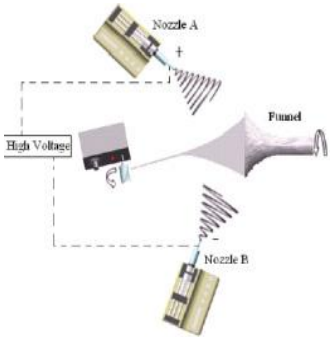
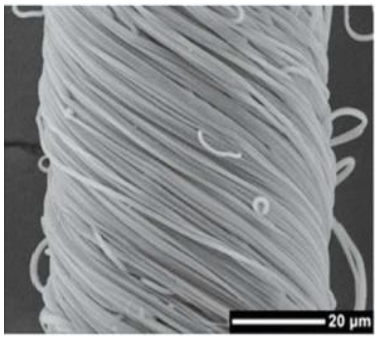
Set Up	Morphology	Explanation
		AC induced self-bundling of nanofibers; PVP [47].

Table 3.4 : Continuous Nanofiber Yarns

Set Up	Morphology	Explanation
		Twisting of nanofibers with a special setup; PAN,PLA [48].
		Manually drawing and twisting nanofibers electrospun from a multineedle setup; Polyurethane [49].
		Nanofibers twisted due to rotation of liquid water; polymer (Helix angel 19.76°) [51, 52]
		Nanofiber stream redirected and twisted by a twist winder; PAN [53].

Set Up	Morphology	Explanation
		Nanofibers twisted by rotating the left disk and then taken up by the right disk; Nylon6/MWNT [54].
		Nanofibers produced from two oppositely charged spinneret and twisted by using a electronic twister; PAN [56]
		Fiber web was twisted by an earthed rotating funnel; PLLA [58]
		Nanofiber yarns were directly produced from an un-earthed fibrous cone formed on a rotating funnel; PVDF-HFP, PCL, PAN, PS (twist angle up to 0 - 61°) [59].

3.2 Stabilization

Stabilization is very crucial step for conversion of PAN precursor nanofibers to carbon nanofibers. The oxidative stabilization is an essential step, in which several reactions i.e., cyclization, dehydrogenation, aromatization, oxidation and cross-

linking reactions are involved [24]. Stabilization conditions can be change for different type of precursor materials.

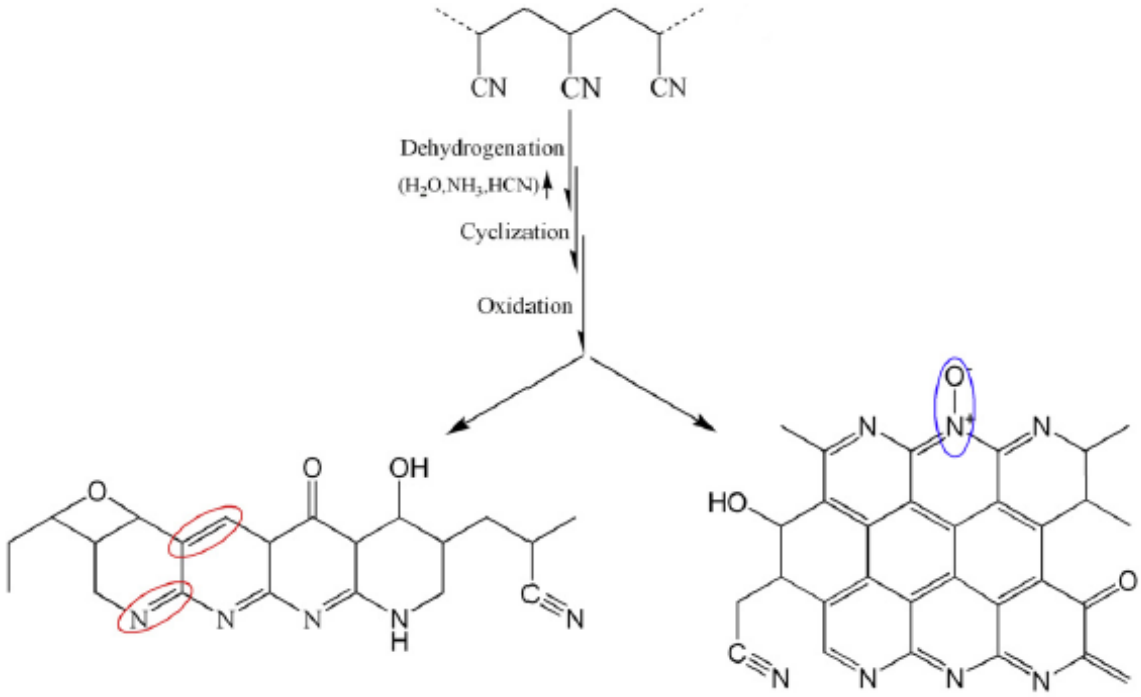


Figure 3.3 : Stabilization of PAN nanofibers [24]

Mechanical properties of electrospun nanofibers need to be improved because of limited crystallinity and orientation during the jet spinning [62]. During the stabilization, PAN nanofibers should be stretched to improve the molecular orientation and the degree of crystallinity to enhance the mechanical properties of nanofibers. Several attempts were tried to apply stretching forces to PAN nanofibers as following:

- Tightly wrapping of PAN nanofiber web onto ceramic or glass rods to thermal treatments, thus tension existed in the individual nanofibers during stabilization [60]
- Confining of PAN nanofiber web on a graphite sheet before stabilization [61]
- Hot stretching by weighing [62].

First two methods are based on preventing shrinkage during heat treatment. Other method is carried out for applying more stretching to improve the crystallinity and molecular orientation.

3.3 Carbonization

Stabilized PAN nanofibers are heat up to 800 – 2000 ˚C in an inert atmosphere (nitrogen, argon or helium) to produce carbon nanofibers. Carbonization process over 1500 ˚C is called high temperature carbonization or graphitization. Using nitrogen at high temperature (>1500 ˚C) can be damage for chemical and physical structure of carbon nanofibers. Hence argon or helium are preferred as inert atmosphere at high temperatures (>1500 ˚C). Carbonization is also important production step because this process affects directly properties of final product. Therefore, final carbonization temperature, heating rate, duration of carbonization process should be accurately regulated [64-72].

3.4 Properties

Carbon nanofibers have high mechanical properties, acceptable thermal and electrical conductivities, good hydrogen storage and nanoscale diameters which make them favorable for many applications such as filtration, energy etc.

3.4.1 Mechanical properties

The amount, size and distribution of structural defects such as surface defects, bulk defects and structural inhomogeneity, macromolecular orientation and crystalline structure, morphological and structural homogeneity and diameters of fibers are the parameters that determine the mechanical properties of carbon fibers [80].

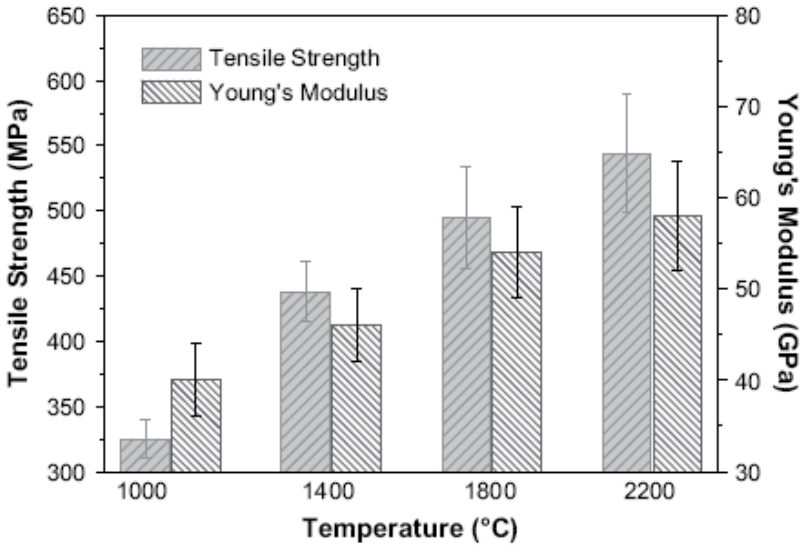


Figure 3.4 : Mechanical properties of electrospun carbon nanofibers [60]

In 2009, Zhou et al [60] demonstrated both Young's modulus and tensile strength of carbon nanofibers carbonized at 1000, 1400, 1800 and 2200 ˚C.

According to their test method [66], Young's modulus and tensile strength of carbonized nanofiber bundles at 1000 ˚C were measured 40 GPa and 325 MPa, respectively. At 2200 ˚C, Young's modulus and tensile strength were increased to 58 GPa and 548 MPa. Young's modulus and tensile strength were improved by increase of carbonization temperature. In 2011, Salman et al [63] are determined mechanical properties of a single carbon nanofiber carbonized at 800, 1100, 1400, 1700 ˚C. According to their test method, Young's modulus of individual carbon nanofiber carbonized at 800 ˚C was calculated 80 GPa, and tensile strength was calculated 1.85 GPa. At 1700 ˚C, Young's modulus and tensile strength were determined as 191 and 2.05 GPa respectively.

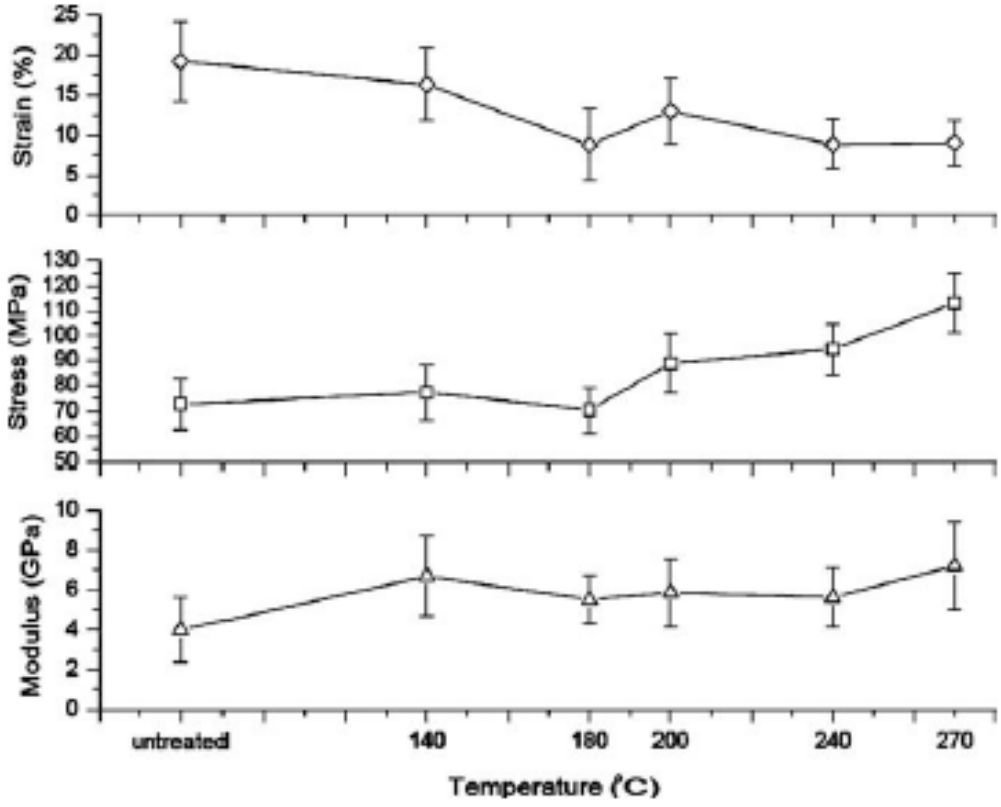


Figure 3.5 : Stress, strain and initial modulus of prepared PAN nanofiber bundles versus treatment temperature.

Ravandi and Sadrjahani [66] demonstrated mechanical properties of heat treated PAN nanofibers. The stress-strain behaviors and the initial modulus, tenacity and extension were measured as a function of temperature. Tenacity values increases

gradually from 72.5 to 113 MPa at 25 - 270 ˚C, respectively. The extension values followed an inverse trend; it decreased from 19.2 to 9% with increasing temperature from 25 to 270 ˚C, respectively. The most value of modulus was obtained 7.2 GPa for treated nanofibers at 270 ˚C in comparing with the modulus of 4.1 GPa for untreated nanofibers.

3.4.2 Electrical conductivity

Electrical conductivity of carbonaceous materials is important for application such as super capacitors, lithium ion batteries and catalyst supports.

Wu et al [24] observed the effect of stabilization temperature and duration time on electrical conductivity. In order to analyze influence of stabilization temperature and duration time, stabilized nanofibers were carbonized at 1000 ˚C.

When stabilization temperature increase from 250 to 280 ˚C, electrical conductivity of the 1000 ˚C carbonized nanfiber powders increased from 4.7 to 12.9 Scm^{-1}. The holding time gave a positive effect also. Electrical conductivity of carbonized nanofiber powders of the sample stabilized 280 ˚C/2h was 20.2 S cm^{-1}, which has 56% higher than that of 280 ˚C/1h.

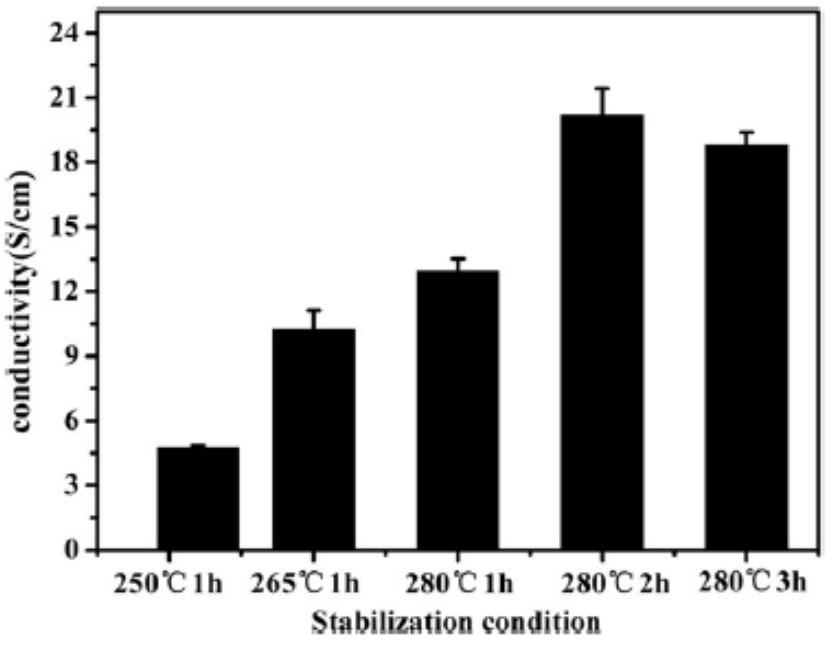


Figure 3.6 : Electrical conductivity of 1000 ˚C carbonized PAN nanofiber powders[24]

In 2009, Zhou et al. [60] observed the effects of carbonization temperature and orientation on electrical conductivity. The electrical conductivities of the nanofiber bundles carbonized at 1000, 1400, 1800 and 2200 ˚C were measured in both parallel and perpendicular to bundle axis. The nanofiber bundle carbonized at 1000 ˚C had electrical conductivities of 180 Scm^{-1} in parallel direction and 7.7 Scm^{-1} in the perpendicular direction. It means the discrepancy of electrical conductivities in the two directions was 20 times.

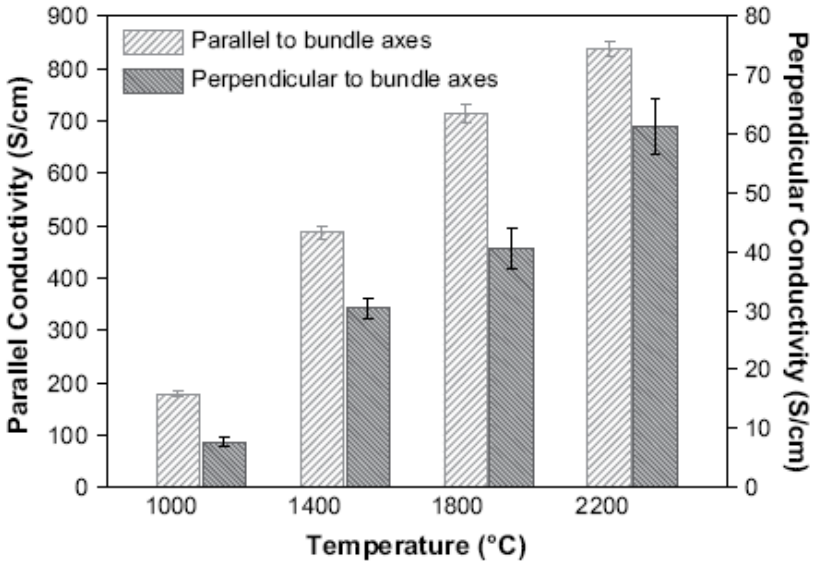


Figure 3.7 : Electrical conductivities of electrospon carbon nanofiber bundles in both parallel and perpendicular directions

3.4.3 Elementary analysis

XPS is one of the most effective methods in characterizing chemical structure and elemental composition on the surface of PAN nanofibers after stabilization and carbonization.

Table 3.5 : Element concentration obtained from XPS for the PAN precursor nanofibers, stabilized and carbonized nanofibers [24]

Element	Atomic concentration (%)				
	PAN fiber	250 °C/1 h	265 °C/1 h	280 °C/1 h	1000 °C carbonized fiber
C_{1s}	68.0	61.5	61.2	56.4	85.6
N_{1s}	28.8	28.2	24.8	21.4	4.90
O_{1s}	3.20	10.3	14.0	22.1	9.50

In 2012, M. Wu et al [24] determined carbon, oxygen and nitrogen contents of precursor, stabilized and oxidized nanofibers. According to their measurements, they reported that the oxygen concentration was the highest for 280 ˚C/1 h stabilized PAN fibers, indicating more oxygen-bearing groups were formed at this stabilization condition.

3.4.4 Surface area

Surface area of carbon nanofibers is also an important property for many applications such as lithium ion batteries. Carbon nanofibers and its composites can be a good candidate as an anode material. The surface area value of carbon nanofibers is very relevant with energy capacity of lithium ion batteries.

Ji and Zhang [67] observed effect of additives in carbon nanofiber precursor on surface area of carbon nanofibers. They used PLLA to produce porous CNF. It was clearly understood that surface area of PLLA added carbon nanofibers are larger than other precursor, which do not have PLLA inside, after carbonization.

Table 3.6 : Some of the structural properties of PAN and PAN/PLLA (9:1) nanofibers [67]

	SSA[a] ($m^2\ g^{-1}$)	TPV[b] ($cm^3\ g^{-1}$)	V^c_{meso} ($cm^3\ g^{-1}$)	V^d_{micro} ($cm^3\ g^{-1}$)
Nonporous CNFs	33.9	—	—	—
Porous CNFs	235	0.114	0.028	0.086

In their other study [68], results (table 3.8) show that the BET specific surface area of carbon nanofibers increase with increase of $ZnCl_2$ content in PAN/$ZnCl_2$. 438 m2g-1 was measured as largest value for specific surface area.

Kim et al [69] observed 815,6 m^2g^{-1} of surface area for palladium coated carbon nanofibers.

Table 3.7 : Specific surface area of ZnCl2 added carbon nanofibers[68]

$ZnCl_2$ (%)	SSA[a] ($m^2\ g^{-1}$)
0	31.6
5	69.5
10	332.8
15	438.0

3.4.5 Other properties

Hydrogen is becoming popular with the chance to use it as an environmentally friendly fuel for transportation and suitable materials for its storage is the subject of current researches. Besides carbon nanotubes active carbon, active carbon fiber and graphite powder can be considered as suitable materials for hydrogen storage [69].

Carbon fibers can be used in a variety of thermal control applications because of their relatively high thermal conductivities [77]. Mahanta et al. [78] produced carbon nanofibers with a maximum thermal conductivity of 157 W/m-K but stated that they would generate carbon fibers having thermal conductivity over 500 W/m-K with some configuration.

3.4.6 Applications

Due to their unique properties, carbon nanofibers have many potential applications in different fields of commercial interests such as energy storage, filtration and mechanical applications. Carbon nanofibers can be used their own as well as they can be used as composites with other polymer or can be added into some materials in order to change or improve properties of materials.

Many attempts have been made to produce PAN-based carbon nanofibers of high surface area for applications as super capacitors, lithium ion batteries and hydrogen storage etc. They are intensely investigated as backup energy storage systems, since they carry high power and have long lifecycles.

Hydrogen is a promising energy alternative to fossil fuels because it is renewable and pollution-free. Microporous materials are promising as components for hydrogen storage applications. Kim et al [69] observed that the specific surface area of the palladium coated carbon nanofibers were 815,6 m^2g^{-1}. Reversible hydrogen adsorption capacity was determined to be 0.35 wt% at 298 K 0.1 MPa.

Carbonized and activated electrospun PAN fibers are attractive for super capacitor electrodes. In 2010, Barranco et al [70] produced activated carbon nanofibers as a good candidate for super capacitor electrodes because of their good cycle life.

Thanks to high energy density and long cycle life Lithium-ion batteries (LIBs) used in cell phone, camera, mp3, laptop so on. as an energy source. Although it

theoretically displays very high capacity performance, they have not been improved entirely. Anode material of LIBs that is state of art could not meet a need.

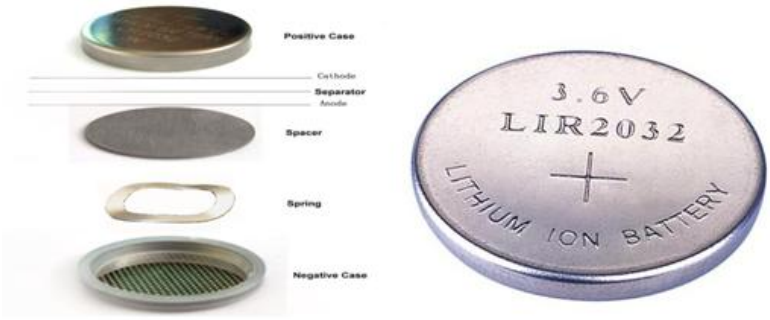


Figure 3.8 : Exploded view of lithium ion battery

Anode is the most important part of lithium ion battery in determining capacity. Lithium ion storage capacity of anode determines lifetime of battery. Also lithium ion storage capacity is related to surface area and composition of anode. Degradation of anode caused by chemical reaction in battery occurs during electrochemical cycling. During the using of lithium ion battery, lifetime is shortened as result of degradation [74-75]. For example although pure Sn and silicon used in negative electrode have theorical capacity of 992 $mAhg^{-1}$ and 4200 $mAhg^{-1}$ (theorical capacity of conventional graphite anode is 372 $mAhg^{-1}$) could not be used effectively in practical because of the fact that it consumes rapidly while electrochemical cycle [71-73]. Therefore, lifetime is not stable and fails rapidly.

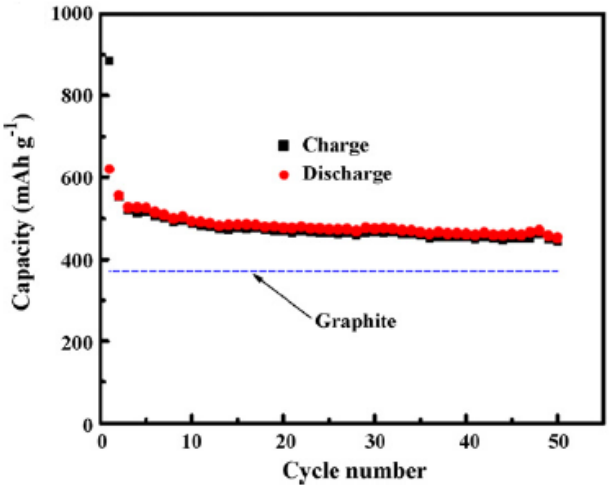


Figure 3.9 : Charge-discharge curve of PAN-based carbon nanofibers used as anode electrode in lithium ion battery [74]

Carbon nanofibers (CNFs) have very large surface area for storing of lithium ions. This situation makes it possible to have higher capacity in a cycle. Chemical resistance of carbon nanofibers is also very high. Lifetime is more stable than conventional anodes due to chemical resistance of CNFs. CNFs are an electrical conductive material, and have thin structure. Using thin material is shortened diffusion distance of lithium ions. They have high carbon purity (> 90 wt.%), and they can used as anode without any binder and conductive filler.

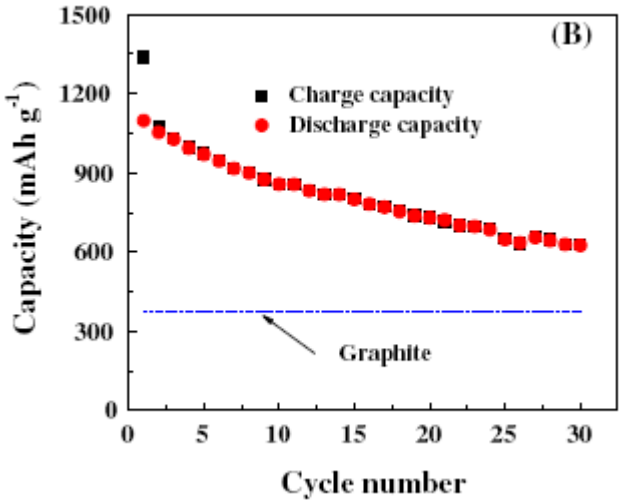


Figure 3.10 : Charge-discharge curve of PAN-based carbon/Si nanofibers used as anode electrode in lithium ion battery [76]

In 2009, Ji and Zhang [76] prepared a lithium ion battery by using carbon/Si composite nanofibers as anode material. The resultant anodes exhibit good electrochemical performance such as a large discharge capacity of 1100 mAh^{-1} at a high current density of 200 mAg^{-1}.

4. EXPERIMENTAL

Purpose of experimental part was fabricating oriented and unoriented carbon nanofiber webs with optimum experimental parameters including electrospinning, especially stabilization and carbonization processes, and producing appropriate samples for analyzing effects of stabilization on physical and chemical properties of carbon nanofibers. Parameters used in production process arranged with extensive literature researches.

4.1 Production

Main difference between carbon fiber and carbon nanofiber production is fiber obtaining method as shown in figure 4.1. In carbon nanofiber production, electrospinning is performed to produce nanoscale fibers. Then thermal treatments calling as stabilization and carbonization are implemented to fabricate CNFs. All the production steps are carried out in TEMAG laboratory (Textile Machinery Research and Development Laboratory), Istanbul Technical University.

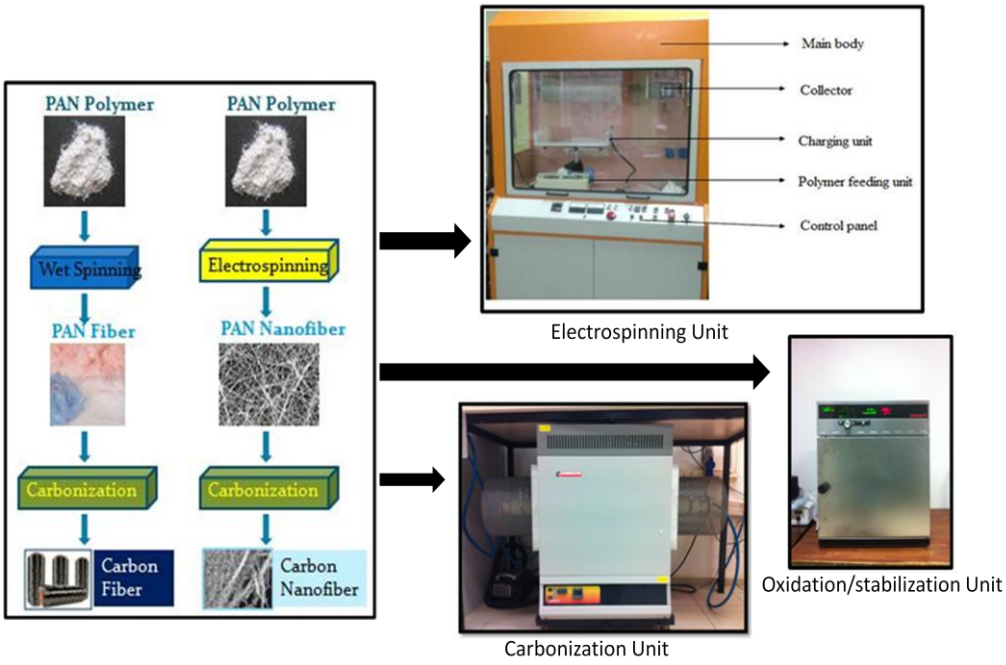


Figure 4.1 : Carbon fiber and carbon nanofiber production

4.1.1 Electrospinning

Firstly, precursor nanofibers were produced via electrospinning. PAN copolymer, constituted of acrylonitrile (CH2CHCN) monomer and vinyl acetate ($CH_3COOCH=CH_2$), was used in the experiments. The average molecular weight of PAN copolymer varies between 120000 – 150000 g/mol. In order to prepare electrospinning solution, PAN was dissolved in high purity (99.9 %) DMF. Both PAN copolymer and DMF were taken from Aksa Acrylic Chemical Industrial Company, Yalova. GAMMA High Voltage Power Supply that is capable of creating high voltage between 0-100 kV generates high voltage. ORIENTAL Motor was utilized in order to provide the rotational motion of the collector.

A rotor mechanism was installed to increase the rotational speed of the collector. A rotational surface speed up to 24 m/sec was carried out by this configuration. A linear actuator was employed to supply the axial motion of the collector. Solution was fed to the nozzle by the help of SK-5001 Syringe Pump. The pump could adjust solution flow rates varying between 0-100 ml/h. Drum and disc types of collectors, illustrated in figure 4.2 and 4.3, were used for electrospinning experiments.

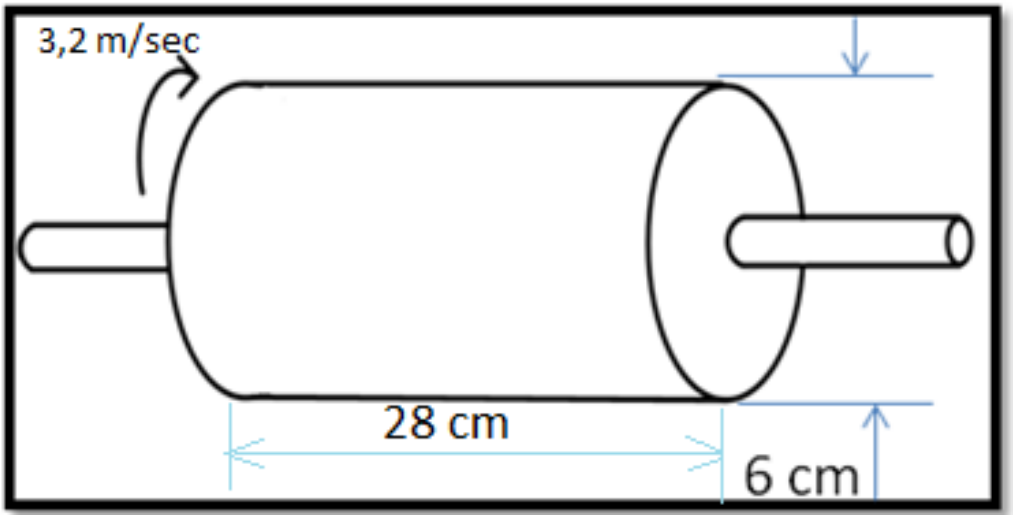


Figure 4.2 : Drum type rotational collector

Drum type rotational collector, illustrated in figure 4.2, was employed for fabrication of unoriented PAN nanofibers. Structural properties of the collector are 570 gr of weight, 28 cm of width and 6 cm of diameters. Due to heavy structure of collector, vibration occurred during the electrospinning process and oriented nanofiber production couldn't achieved efficiently. Surface speed of drum type collector could be increased only to 3.2 m/sec. Parallelization of nanofibers couldn't achieve by

using drum type rotational collector. Results of electrospining by using drum type collector, sheet-like spider web non-woven unoritented nanofiber webs were produced. In order to prevent machinery breakdown resulted from vibrations, disc type collector, illustrated in figure 4.3, was designed.

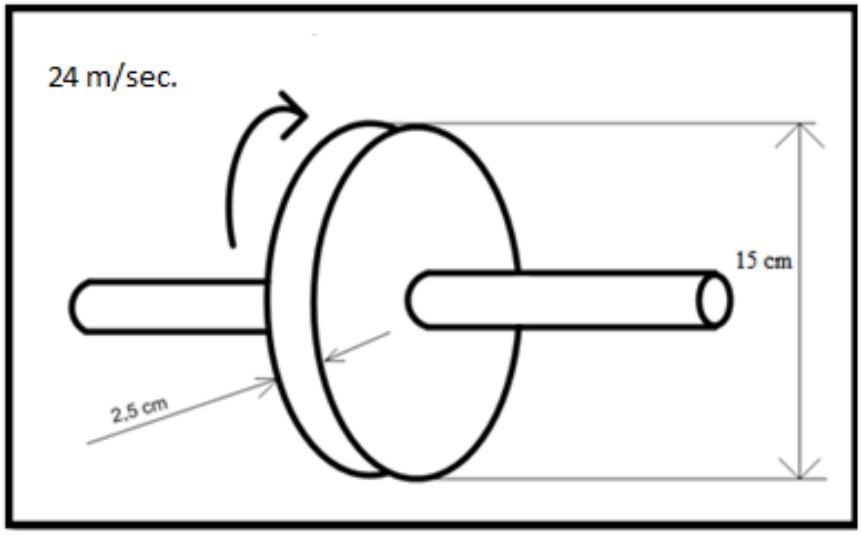


Figure 4.3 : Disc type rotational collector

Disc type rotational collector was used for production of oriented PAN nanofibers. Structural properties of disc type rotational collector are 80 gram of weight, 2.5 cm width and 15 cm diameters. Surface speed of disc type collector can be increased up to 24 m/sec. Disadvantages of drum type collector are prohibited by using disc type collector. PAN nanofiber bundles (figure 4.4) were produced at end of the process by working with disc type collector. In addition, parallelization of nanofibers was achieved.

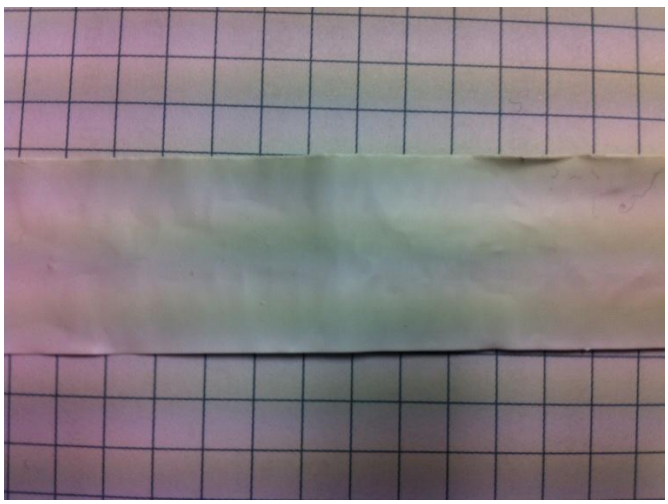


Figure 4.4 : PAN nanofiber bundle

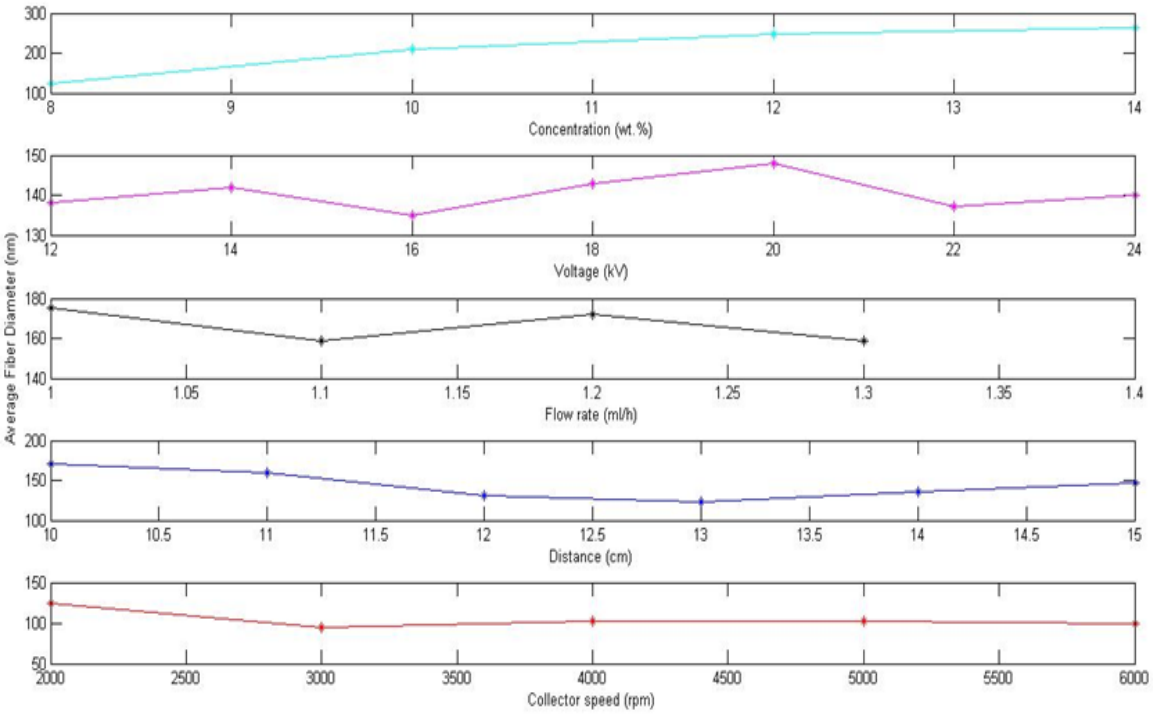


Figure 4.5 : Effect of concentration, voltage, flow rate, distance and collector speed on average fiber diameter [80]

In order to fabricate thinner PAN nanofibers, Mutlu A. in 2011 has been studied on PAN/DMF concentration, voltage, and distance parameters for same PAN copolymer polymer precursor**.** According to his study, 8 % of PAN/DMF concentrations, 20 kV of high voltage, 13 cm of distance are determined in order to produce the thinnest PAN based nanofibers, which has 140 nm of average fiber diameter [80]. In this study, these parameters except for collector speed are used for electrospinning process. In addition, collector type was modified. Surface speed was increased up to 24 m/sec to produce oriented nanofibers. Therefore, parameters for fabricating unoriented and oriented nanofibers, illustrating in table 4.1, are implemented.

Table 4.1 : Parameters for Oriented and Unoriented PAN Nanofiber

	Flow Rate (ml/h)	Collector Type	Surface Speed (m/sec)
Oriented PAN Nanofibers	0,2	Disc	24
Unoriented PAN Nanofibers	1	Drum	3,2

4.1.2 Stabilization

After electrospinning, for withstanding in proportion to high temperature, which is necessary for carbonization process, stabilization (oxidation) should be applied to the PAN nanofibers. The stabilization process was performed in TEMAG, ISTANBUL. MEMMERT UFE 400 oven (Figure 4.6) was used for stabilization in this step.

Figure 4.6 : MEMMERT UFE 400 oven

Stabilization is implemented with two different ways for unoriented and oriented nanofibers. Unoriented nanofibers are peeled off the aluminum foil. Then, it is wrapped around a glassy plate in order to provide required tension during stabilization. Because unorinented nanofibers have spider web structure, there were not effective methods for tension mechanism.

Oriented PAN nanofibers were stabilized by applying effective tension during the stabilization. In order to perform an effective tension to nanofibers, oriented nanofiber bundles were produced and an effective tension was applied by using designed tension mechanism shown in figure 4.7.

In this mechanism, a metallic rod is assembled to metallic wheels for preventing ribbon-like electrospun nanofiber webs contact any surface in oven (MEMMERT UFE 400) while performing stabilization. Two points of samples are wrapped around metallic rods. Samples are held around them easily, because of electrostatic forces occuring between nanofiber and metallic rod.

Table 4.2 : Stabilization experiments to analyze ultimate stabilization temperature and holding time for unoriented PAN nanofibers

Ultimate Stabilization Temperature (°C)	Holding Time (hours)
220	2
220	4
220	6
220	8
220	10
230	2
230	4
230	6
230	8
230	10
240	2
240	4
240	6
240	8
240	10
250	2
250	4
250	6
250	8
250	10

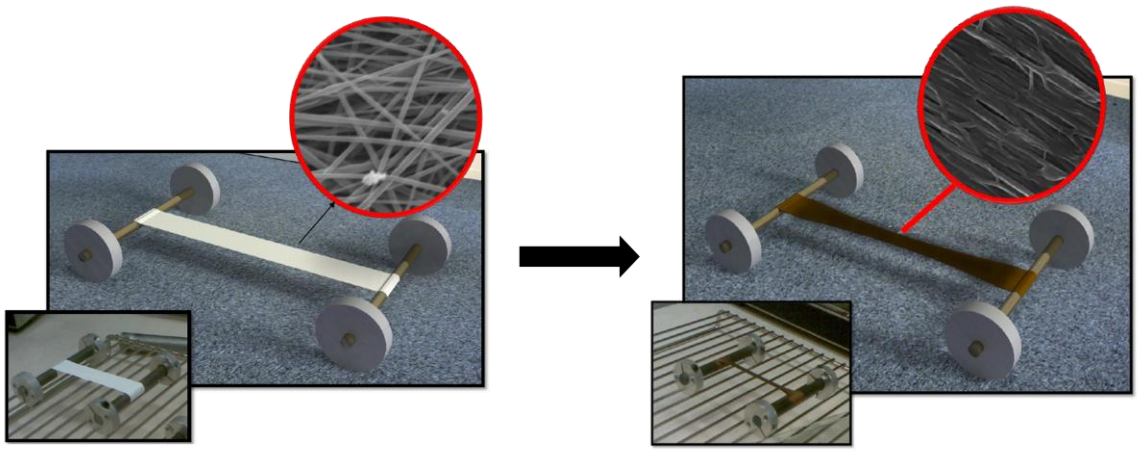


Figure 4.7 : Tension mechanism for electrospun PAN nanofiber bundles

Then probable mobilization existing from shrinkage during heat treatment is blocked by fixing metallic rods to grids. Required tension is applied to the PAN nanofiber bundles to opposite direction of shrinkage. Various stabilization recipes are exerted for realizing the effect of stabilization conditions. Stabilization is carried out in air atmosphere because oxygen is very important gas to initiate the reactions, which make nanofiber web durable during carbonization process. In order to examine effect of temperature, holding time and heat rate, new recipies (table 4.3) are designed as follow:

Table 4.3 : Stabilization recipes for electrospun PAN nanofiber bundles (*heat rate is examined for 1,2,3,4,5 ^{o}C/min at 250 ^{o}C and 30 minutes pending time)

	15 min	30 min	1 H	2 H	4 H	6 H	8 H	14 H
200 °C		+						
220 °C		+						
230 °C		+	+	+	+			
240 °C		+	+	+	+	+		
250 °C	+	+*	+	+	+	+	+	+

Effect of heat rate is also examined between 1 and 5 ˚C/min at 250 ˚C for 0,5 hours to oriented electrospun PAN nanofiber bundles. The oxidized samples should be characterized with different methods, such as Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and Energy-disperse X-ray spectroscopy (EDX) to conceive whether the nanoweb is properly stabilized or not. The results of analyses will be shown in characterization part.

4.1.3 Carbonization

Final step of carbon nanofiber production is carbonization. Carbonization process is carried out in TEMAG ITU. Carbolite Eurotherm 2132 (Figure 4.8) is employed for this process. In order to prevent undesirable reactions during carbonization, an inert atmosphere is created by using argon gas. Argon is fed to the tube with 0.8 l/h flow rate. Oxidized samples are put in alumina boat to prevent the samples flit. Then the boat is located at the center of the tube of the carbonization furnace. No tension is applied during carbonization process. Carbonization is performed at different ultimate temperatures between 900 – 1500 ˚C. Stabilized samples heat up from room temperature to 200 ˚C with 10 ˚C/min of heat rate. Then 5 ˚C/min heat rate is applied

until 600 ˚C and samples are heated up to ultimate temperature with 3 ˚C/min. After ultimate temperature, it is cooled with 10 ˚C/min heat rate to room temperature. One of the examples of carbonization recipes performed 1500 ˚C ultimate carbonization temperature is illustrated at figure 4.3.

Figure 4.8 : Carbolite Eurotherm 2132

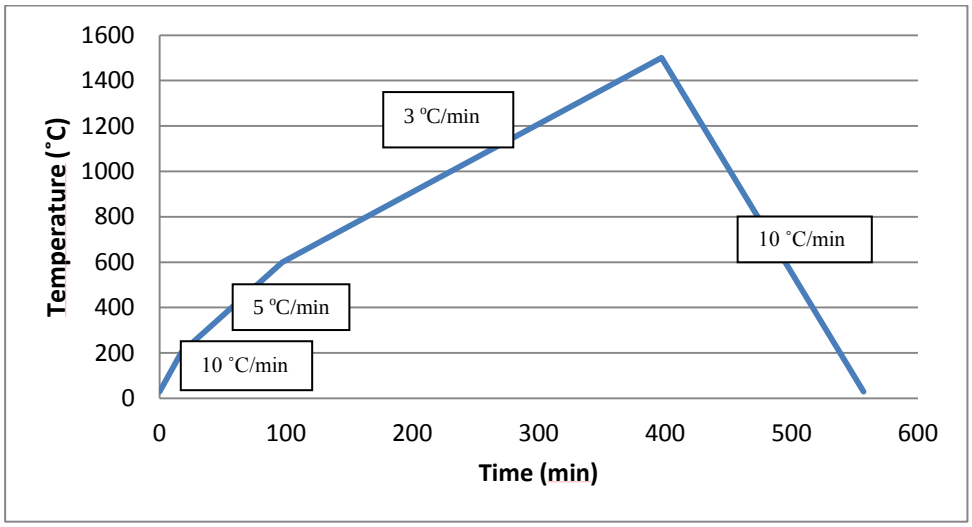


Figure 4.9 : One of the example of carbonizaiton recipe

Various ultimate carbonization temperatures that are 1000, 1100, 1200, 1300, 1400 and 1500 ˚C are performed for realizing effect of temperature on fiber properties. Dimensional and color changes are detected resulting from stabilization and carbonization. Color of electrospun PAN nanofibers turn into brown and black.

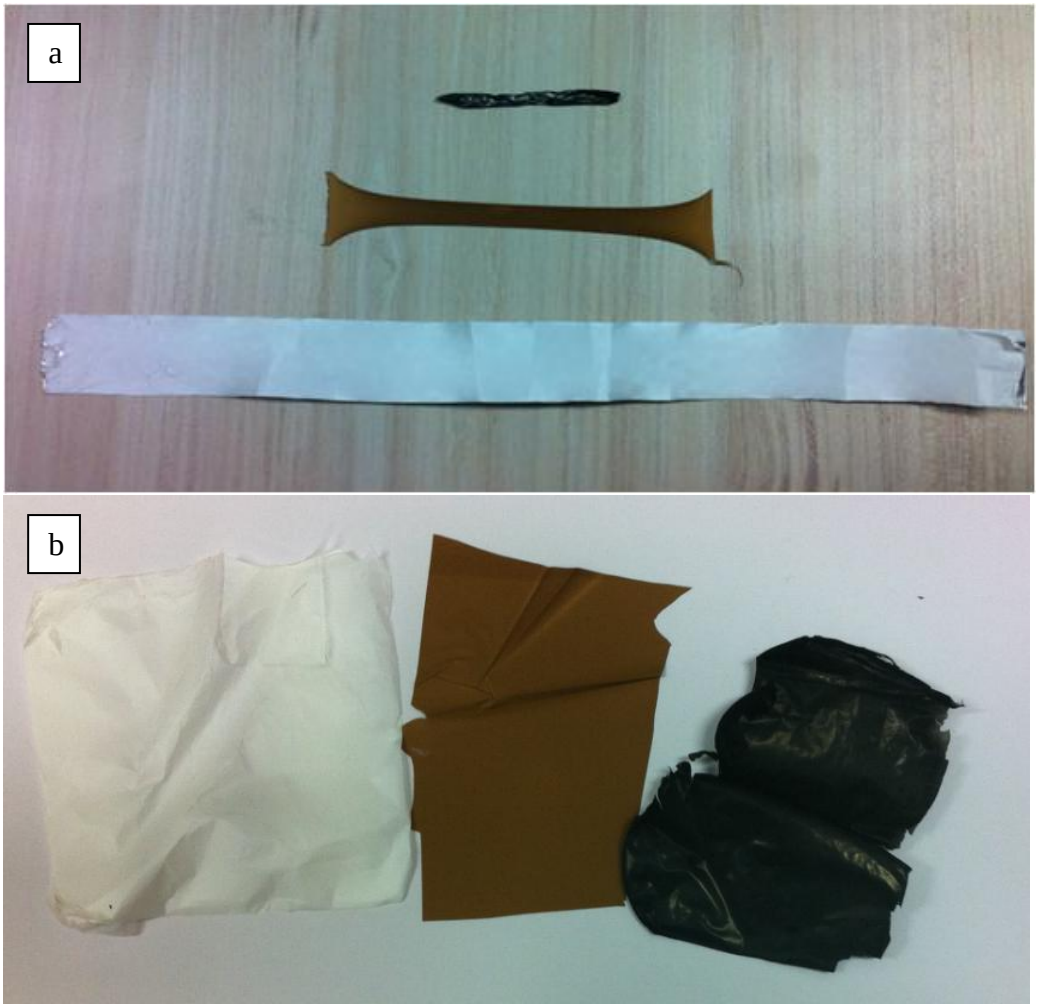


Figure 4.10 : Color conversion of (a) oriented and (b) unoriented PAN nanofibers

5. RESULTS AND DISCUSSION

Effects of electrospinning, especially stabilization and carbonization parameters on physical and chemical properties of nanofiber webs are the issues of this thesis. Collector type and surface speed are eletrospinning parameters. Heat rate, ultimate temperature, pending time and tension mechanism are variable for stabilization. Ultimate temperature is also versatile during carbonization prosess. SEM, FT-IR, EDX and mechanical analyses, are the methods to characterize the samples on each required steps of production. Using SEM is very useful method to understand change of nano scale diameter of nanofibers during the carbon nanofibers production. Characterization method such as FT-IR and EDX are useful to realize the conversion of PAN nanofibers into carbon nanofibers. Furthermore, mechanical properties are determined to investigate the suitability of carbon nanofibers webs for different applications.

5.1 Scanning Electron Microscope (SEM)

Figure 5.1 : Carl Zeiss EVO/MA10 Scannning Electron Microscopy

Scanning Electron Microscope (SEM) is a type of electron microscope, which images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make the sample producing signals. The signals can give information about the morphology and the composition of the material [2]. Carl Zeiss EVO 10 (Figure 5.1) is used for SEM analysis.

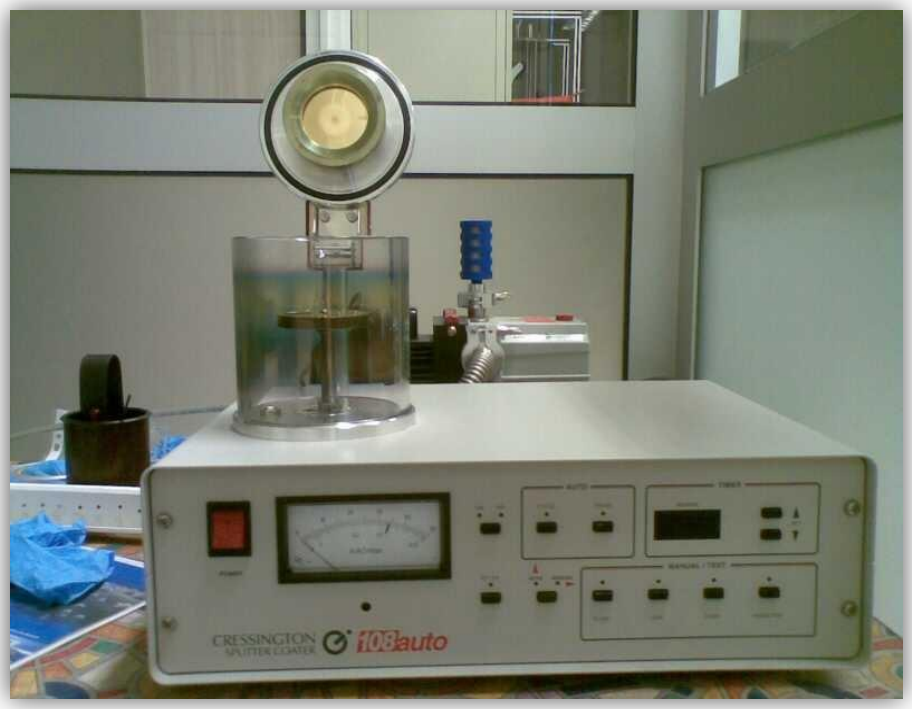


Figure 5.2 : Cressington Sputter Coater 108 Auto

The samples were first sputtered with gold (Cressington sputter coater 108 Auto, Cressington Scientific Instruments Ltd, England) in Argon for 20 sec. before analyzing them under high voltage (20kV) during scanning. The SEM produces images by hitting the samples with a high-energy electron beam. The electrons interact with the atoms in the sample giving information about surface topography and other properties [3].

5.1.1 Electrospinning

Mutlu A. determined optimum production procedure in order to fabricate PAN based nanofibers that has 140 nm of average fiber diameter. According to his work, 1 ml/h of flow rate, 13 cm of distance, 20 kV of voltage are chosen as appropriate conditions [80]. In this study, collector types and their effects examined to improve

nanofiber alignment for electrospinning. Alignment is very important specialty for textile applications. Many physical specialties such as mechanical, electrical, opaque etc. depend on fiber alignment.

Nanofibers fabricated by drum type collector with 3.2 m/sec surface speed were not fully-parallelized as shown figure 5.3A. As increasing rotational speed by using disc type collector, which has 24 m/sec surface speed, improves fiber alignment as shown figure 5.3b. Improving alignment on nanofibers provide effective and controlled tension possible during stabilization.

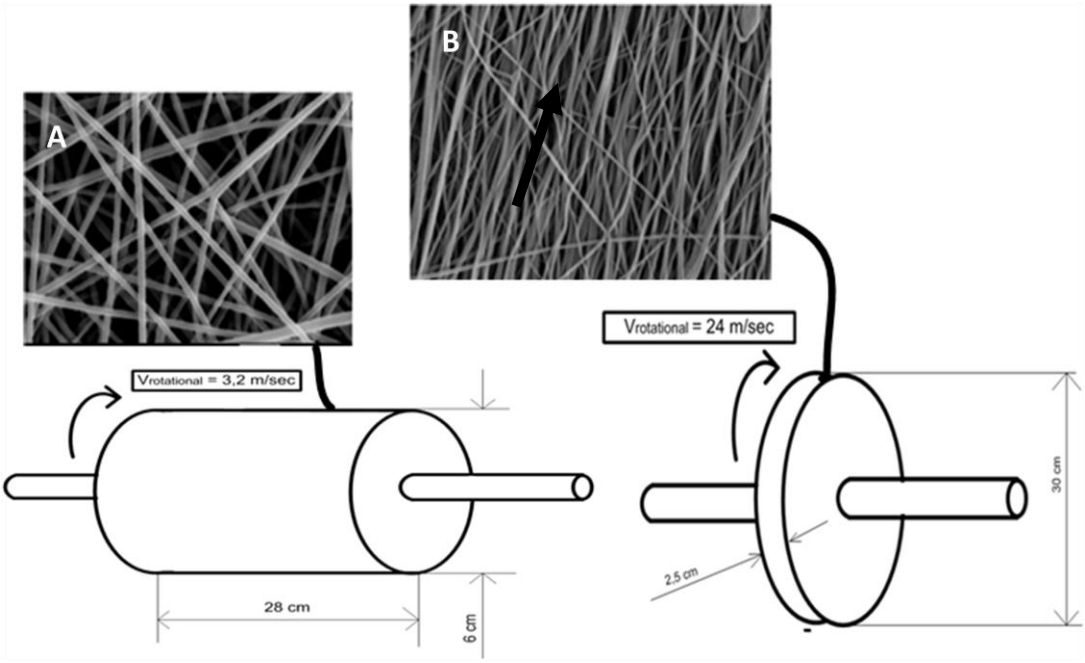


Figure 5.3 : Effect of rotational speed on nanofiber aligment A) PAN nanofibers (15.00 kX) produced with using drum type collector B) PAN nanofibers (10.00 kX) produced with using disc type collector

5.1.2 Stabilization

Effect of stabilization ultimate temperatures, holding times and heat rates on nanofiber diameters are evaluated for both oriented and unoriented nanofibers. By the help of SEM images, average fiber diameters are calculated by measurement at least 50 different points. Firstly, stabilization is achieved for oriented nanofibers with and without stretching at 200, 210, 220, 230, 240 and 250 ˚C ultimate oxidation temperature and for 0.25, 0.5, 2, 4, 6 and 8 hours holding time. In order to understand effect of temperature, samples oxidized for 0.5 hours at different temperatures. On the other hand, samples are heated up to 250 ˚C for different holding time to realize effect of holding times.

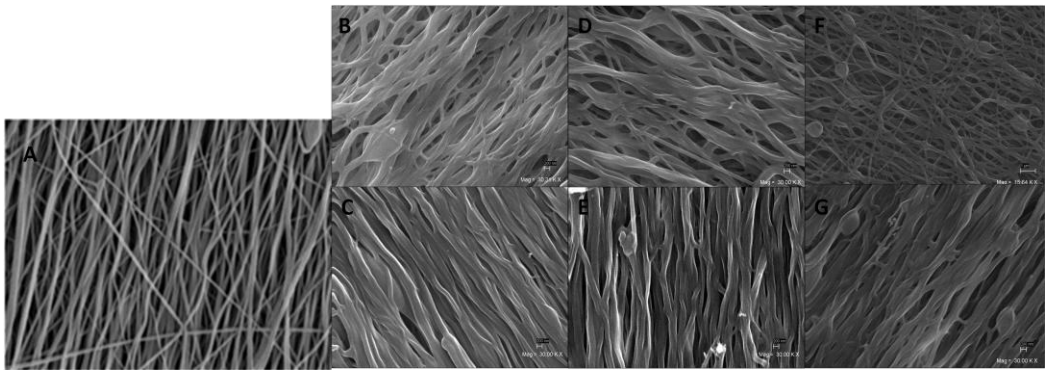


Figure 5.4 : A)Precursor nanofibers, B) 220 ˚C-30 min, no stretching, C)220 ˚C-30 min, with stretching, D)220 ˚C-60 min, no stretching, E) 220 ˚C-60 min, with stretching, F)220 ˚C-120 min, no stretching, G)220 ˚C-120 min with stretching

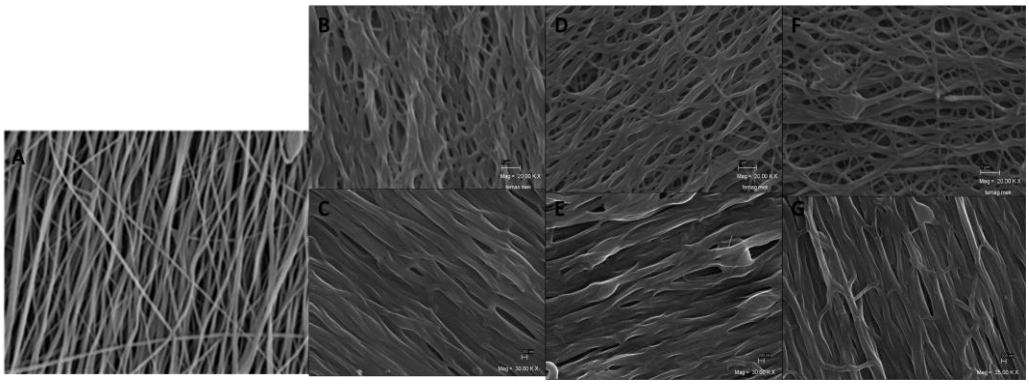


Figure 5.5 : A)Precursor nanofiber, B) 250 ^{o}C-30 min, no stretching, C)250 ^{o}C-30 min, with stretching, D)250 ^{o}C-60 min, no stretching, E) 250 ^{o}C-60 min, with stretching, F)250 ^{o}C-120 min, no stretching, G)250 ^{o}C-120 min with stretching

Average fiber diameter of no stretching applied oriented samples oxidized at different ultimate temperatures is calculated as 238, 227, 220, 209, 193 and 185 nm respectively. Effect of ultimate temperatures is measured as 195, 191, 183, 180, 181 and 185 nm for stretching applied oxidized nanofibers. Moreover as increase of temperature and holding time, oxidized nanofiber diameters reduce.

Unoriented nanofibers are also oxidized at 220, 230, 240, 250 ˚C and for 2, 4, 6, 8, 10 hours. Because unoriented nanofibers have spider web non–woven structure, stretching could not performed efficiently.

Average fiber diameters are detected 196, 182, 179, 178 and 174 nm respectively at 200, 220, 230, 240, 250 ˚C with 1 ˚C/min. for 2 hours. Figure 5.7 shows SEM images of oxidized PAN nanofibers manufactured in order to evaluate the effect of temperature on average fiber diameter. Heat rate is also important parameter in

stabilization process. Samples were oxidized with at 250 ˚C for 2 hours as they heated to this temperature from room temperature by 1, 2, 3, 4, 5 ˚C/min heat rates. According to SEM images increment of average fiber diameter is noticed and measured 152, 163, 165, 170 and 204 nm respectively for 1, 2, 3, 4, 5 ˚C/min heat rates.

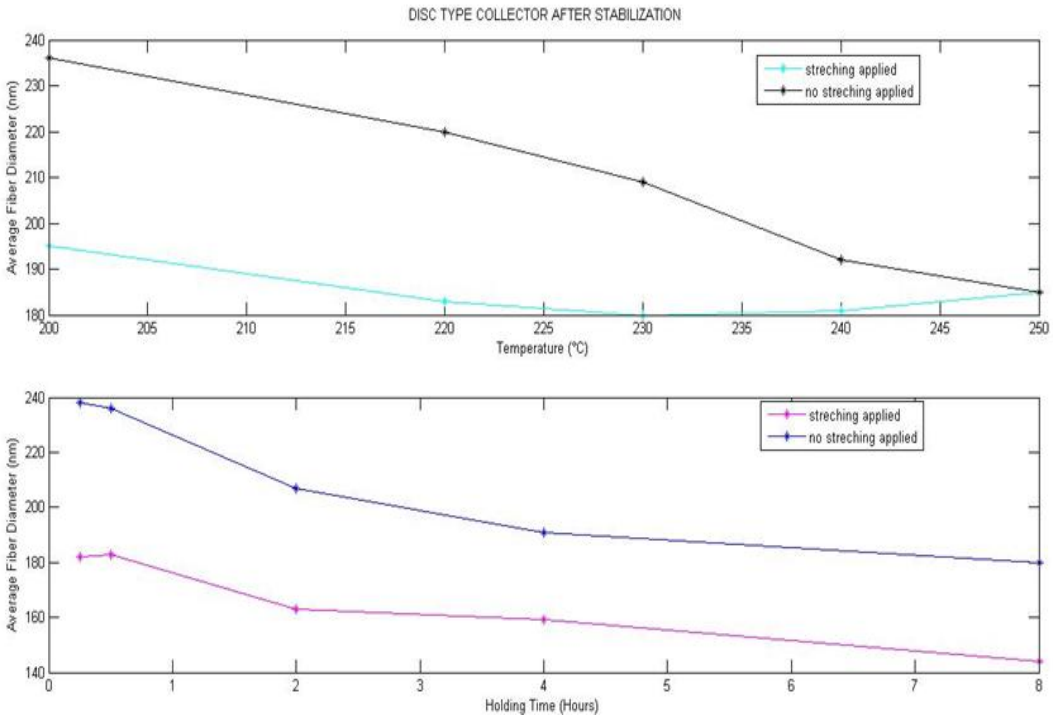


Figure 5.6 : Comparison of average fiber diameters of stretching applied and no stretching applied nanofibers at different holding times and temperatures

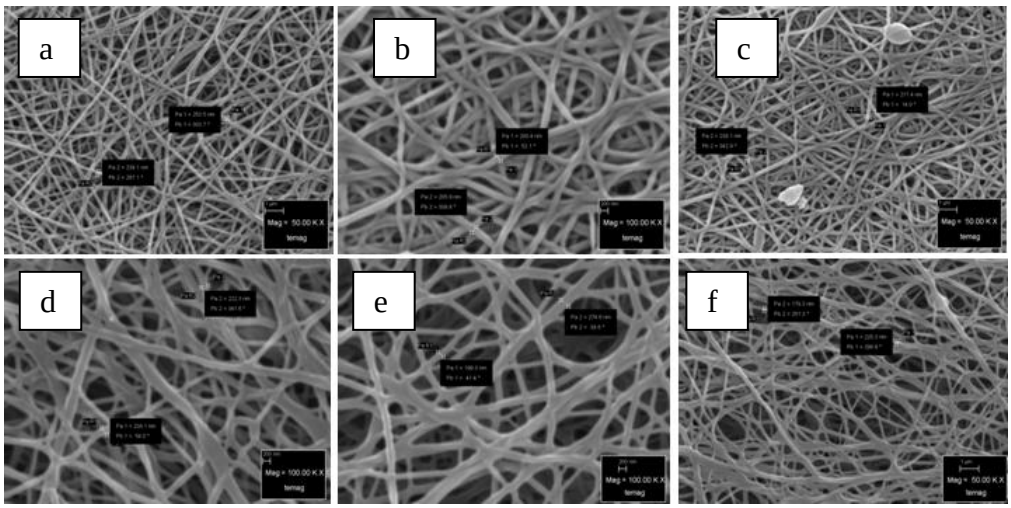


Figure 5.7 : Oxidized unoriented PAN nanofibers at different ultimmate temperature (a)200 ˚C – 2 hours, (b)220 ˚C – 2 hours , (c)230 ˚C – 2 hours ,(d)240 ˚C – 2 hours ,(e)250 ˚C – 2 hours, and (f)250 ˚C – 4 hours

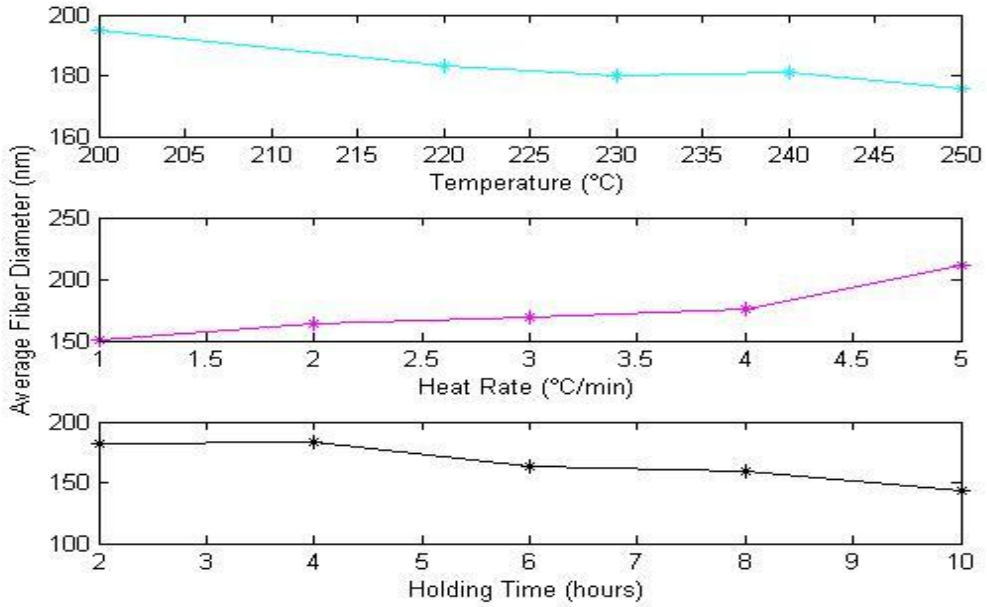


Figure 5.8 : Effect of ultimate stabilization temperature, heat rate and holding time on average fiber diameter

Holding time is defined as the time which PAN nanofibers are continued to stabilization process at their ultimate temperature. Besides ultimate temperature and heat rate, holding time also affects average fiber diameters. 181, 183, 164, 157 and 144 nm average fiber diameters are measured for 2, 4, 6, 8 and 10 hours of holding time at 250 ˚C and with 1 ˚C/min of heat rate.

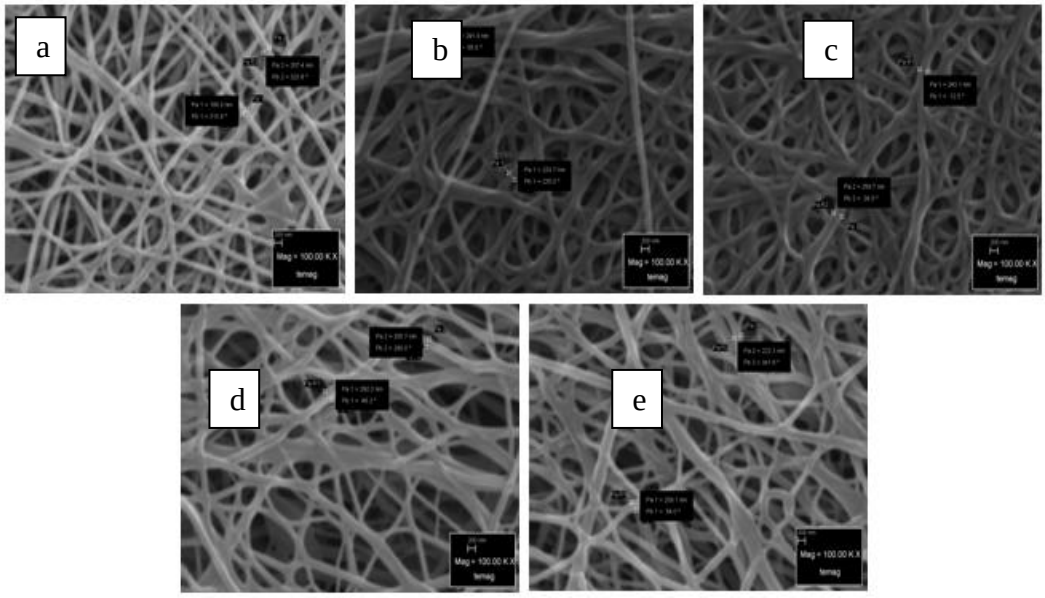


Figure 5.9 : Oxidized PAN nanofibers for different pending time (a)250 ˚C – 2 hours, (b)250 ˚C – 4 hours, (c)250 ˚C – 6 hours, (d)250 ˚C – 8 hours, (e) 250 ˚C – 10 hours

5.1.3 Carbonization

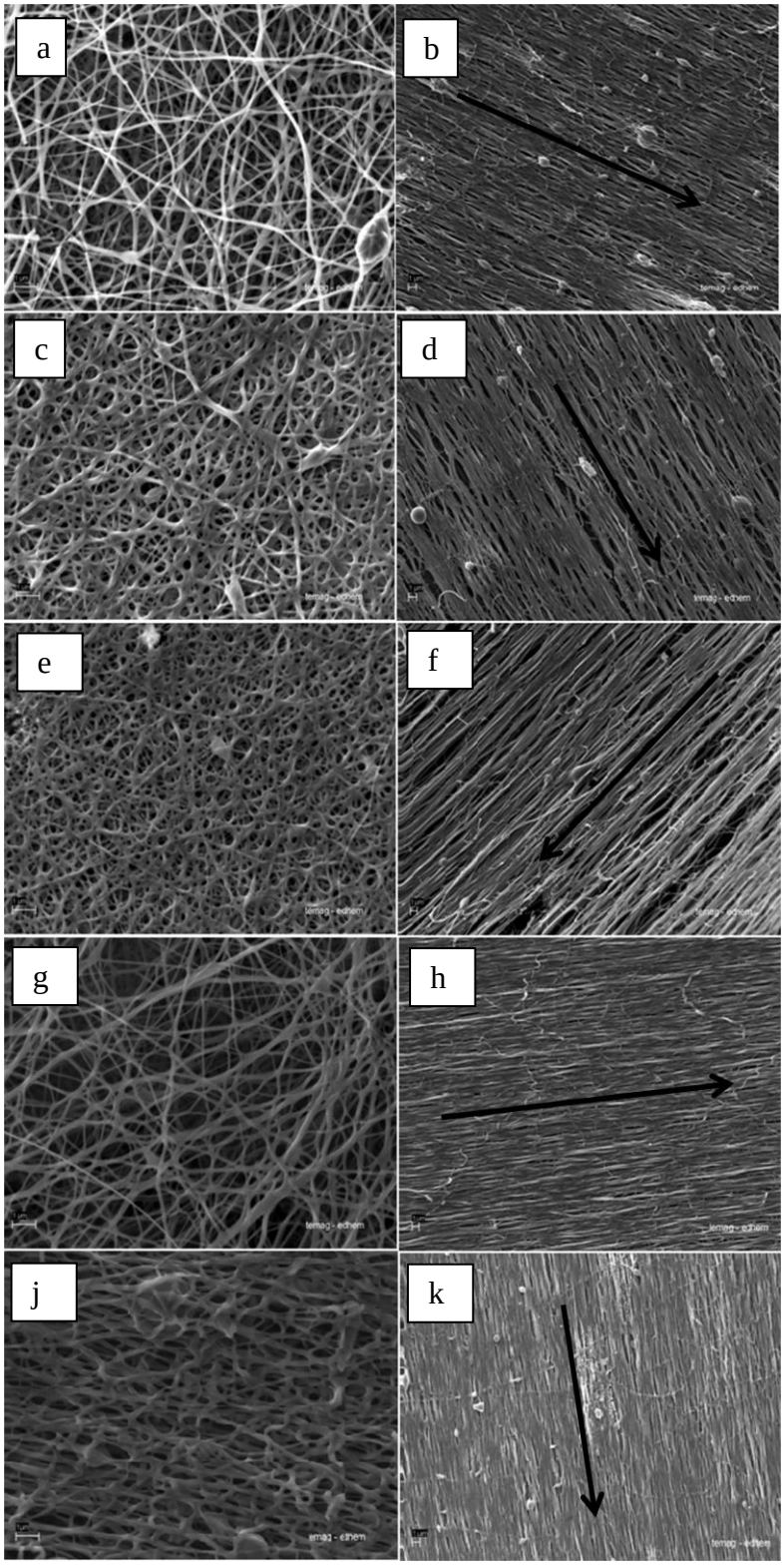


Figure 5.10 : SEM images of samples to observe the temperature and orientation effects (a)1100 ˚C unoriented, (b)1100 ˚C oriented, (c)1200 ˚C unoriented, (d)1200 ˚C oriented, (e) 1300 ˚C unoriented, (f)1300 ˚C oriented, (g) 1400 ˚C unoriented, (h) 1400 ˚C oriented, (j) 1500 ˚C unoriented, (k) 1500 ˚C oriented

Carbonization is the last step of carbon nanofiber production. In order to examine effect of carbonization temperature and stabilization methods on carbon nanofiber properties, the samples are produced at 1100, 1200, 1300, 1400 and 1500 ˚C. Different carbonization temperatures are applied to the samples oxidized at 250 ˚C, for 0,5 hours and by 1 ˚C/min. Furthermore, carbonization is performed for both oriented and unoriented nanofibers. Parallelization of nanofibers is detected as shown in figure 5.10. Average fiber diameters of carbon nanofibers are also measured as illustrated at figure 5.11. Decrease of average fiber diameters is apparently realized after carbonization process. As increase of process temperature, nanofiber diameter decreases unsurprisingly.

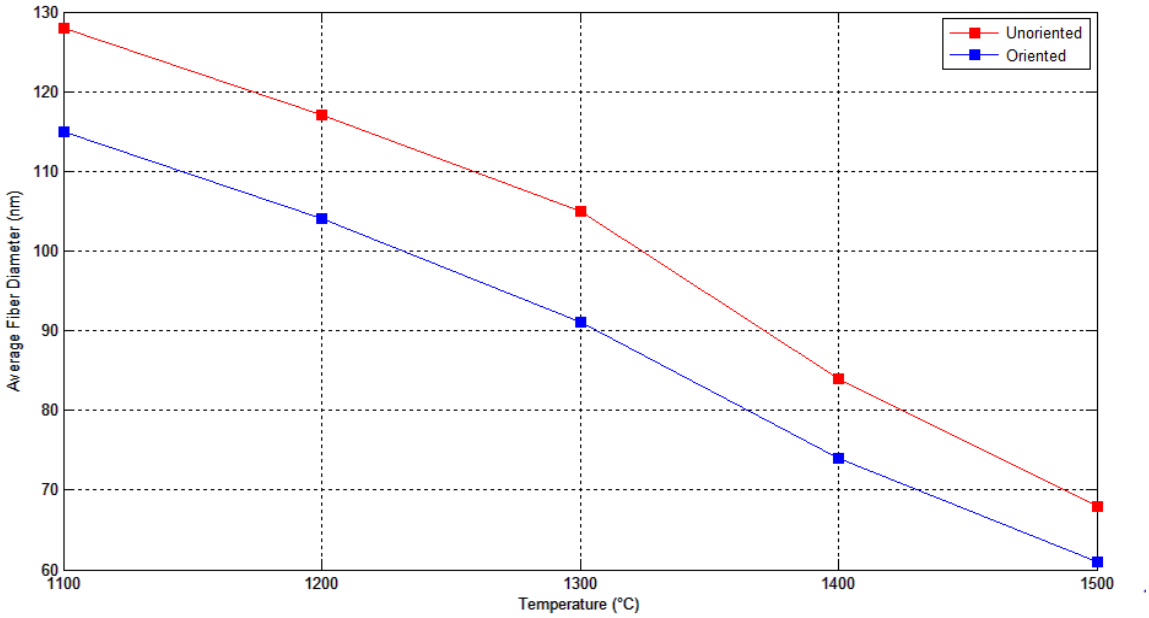


Figure 5.11 : Effect of carbonization temperature on average fiber dimaters

Average fiber diameters of unoriented carbon nanofibers are measered as 128, 117, 104, 96, 84 and 68 nm by increase of carbonization temperature. 114, 105, 91, 74 and 61 nm of average fiber diameters are calculated by increase of carbonization temperature for oriented carbon nanofibers. It is clearly understood from SEM images that the applications, which parallelize nanofibers during electrospinning and stabilization, results decrease in average fiber diameters after carbonization. In addition, average fiber diameters expectedly reduce by increment of process temperature.

5.2 Energy – Dispersive X-Ray Spectroscopy (EDX)

In order to find chemical composition of a material, Energy–dispersive X-ray spectroscopy (EDX) is one of the useful methods. An energy–dispersive (EDX) detector is used to separate the characteristic x-rays of different elements into an energy spectrum, and EDX system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. Energy peaks correspond to the various elements in the sample [4].

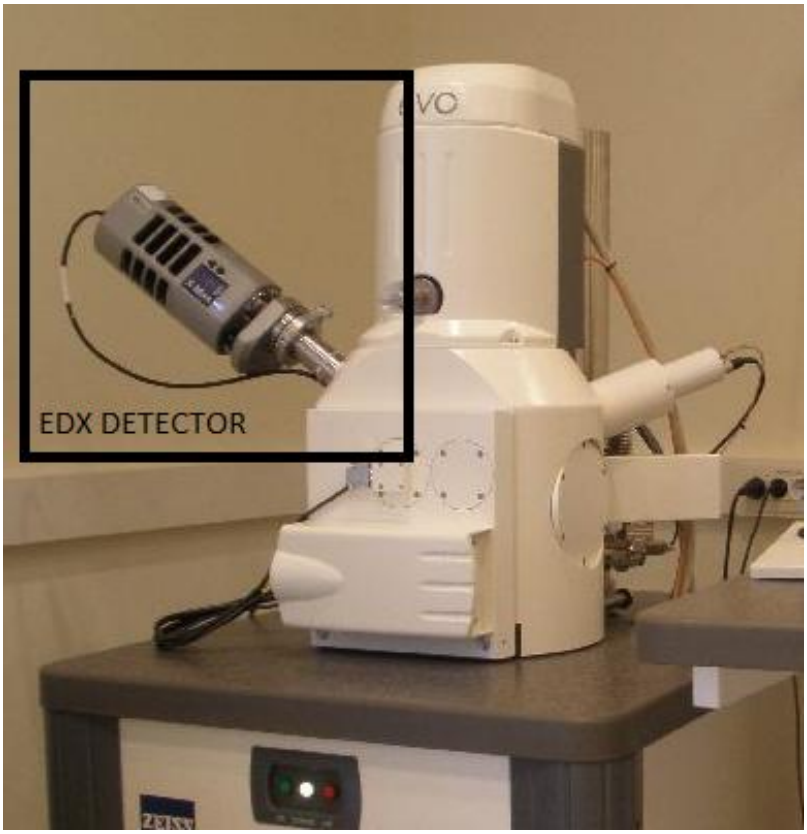


Figure 5.12 : EDX detector

EDX detectors are usually integrated to scanning electron microscopy. In this work, oxygen content is calculated to optimize stabilization step. Moreover, effect of carbonization temperature is realized by carbon content measurements.

5.2.1 Stabilization

In order to oxidize PAN based fiber appropriately, oxygen content of sample must be between 5 – 15 % wt. More than 15 % wt. of oxygen content results with reduced carbon fiber properties. If the samples have a oxygen content value less than 5 % wt., it results with reduced yield of carbonized fiber [6].

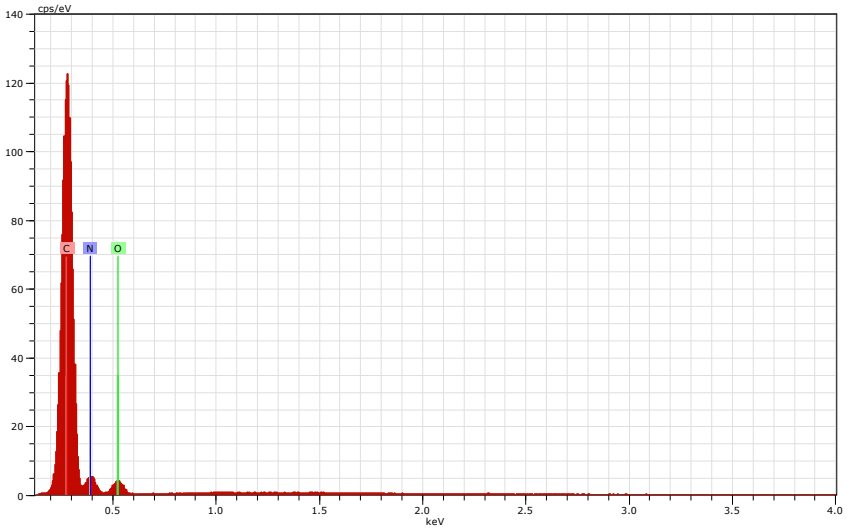


Figure 5.13 : EDX analysis for Oxydized PAN nanofiber web at 250 ˚C for 0,5 hours

PAN nanofibers are stabilized between 220 – 250 ˚C for 0,5, 2 and 4 hours and oxygen content is measured by EDX at 5 different points for each sample. Oxygen contents are 5.96, 8.51, 9.53, 10.10, 16.46 and 17.81 wt. % at 220, 230, 240 and 250 ˚C for 0.5, 2 and 4 hours, respectively.

Table 5.1 : EDX analysis for stabilizaiton

Stabilization Temperature (˚C)	Holding Time (hours)	Heat Rate (˚C/min)	Oxygen Content (wt. %)
220	0,5	1	5,96
230	0,5	1	8,51
240	0,5	1	9,53
250	**0,5**	**1**	**10,10**
250	2	1	15,46
250	4	1	17,81

Although oxygen content has appropriate value at 220 ˚C for 0.5 hours; as can be seen by help of SEM images from figure 5.14 nanofiber formation could not implement after carbonization at 1200 ˚C. Furthermore, there are powder-like discontinues residue by using the stabilization recipe of at 250 ˚C for 4 hours which has 17.81 wt.% oxygen content after carbonization at 1200 ˚C. All in all it is decided to apply stabilization process at 250 ˚C for 0,5 hours in order to have 10 wt. % which is the optimum point for oxidation.

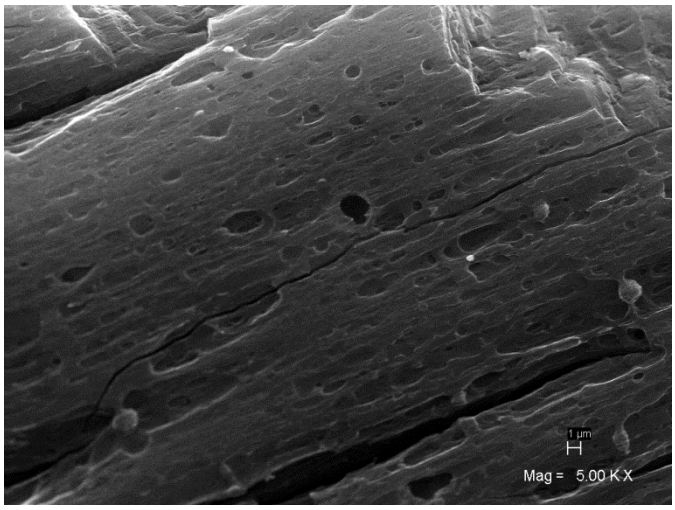


Figure 5.14 : SEM image of carbonized (at 1200 ˚C) nanofibers which have 5,96 wt. % of oxygen content after stabilization

5.2.2 Carbonization

Carbon content of carbon nanofibers are also examined by using EDX detector. According to measurements, 80.89, 90.15, 89,90, 90.24, 91.17, 91.78 and 93.08 wt.% are detected for 900, 1000, 1100, 1200, 1300, 1400 and 1500 ˚C, unsurprisingly. It is expectedly observed as increase of carbonization temperatures, carbon content also accrues.

Table 5.2 : EDX analysis for carbonization

Carbonizaiton Temperatures (˚C)	Carbon Contents (wt. %)
900	80,89
1000	90,15
1100	89,90
1200	90,24
1300	91,17
1400	91,78
1500	93,08

5.3 Mechanical Analyses

E (Elastic modulus) is the slope of the line in this region where stress (σ) is proportional to strain (ε) and is called the "Modulus of Elasticity" or "Young's Modulus". The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. If a specimen is loaded within this

linear region, the material will return to its exact same condition if the load is removed.

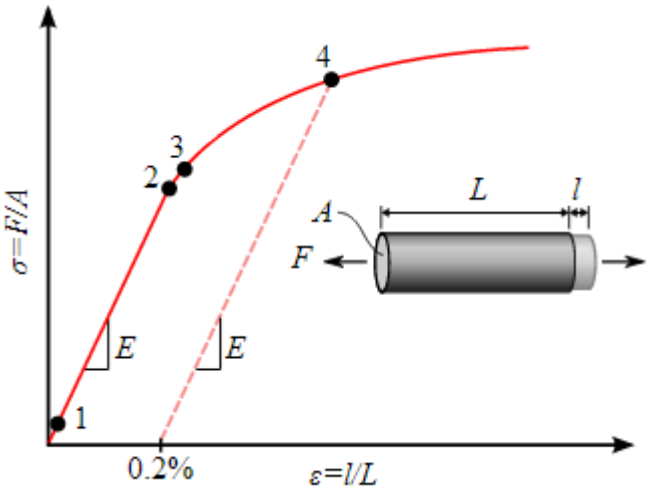


Figure 5.15 : Stress – strain curve [13]

5.3.1 Effect of orientation to mechanical properties of stabilized PAN nanofibers

DMA and instron were utilized in order to prove the alignment of nanofibers after stabilization. Stabilizaiton is applied at 250 ˚C for 0.5 hours and with 1 ˚C/min. Samples were prepared parallel and perpendicular to nanofiber collection directons (figure 5.17). As can be seen from figure 5.18. sample of the parallel to the collection direction has higher Young's modulus value while sample of the perpendicular to the collection direction.

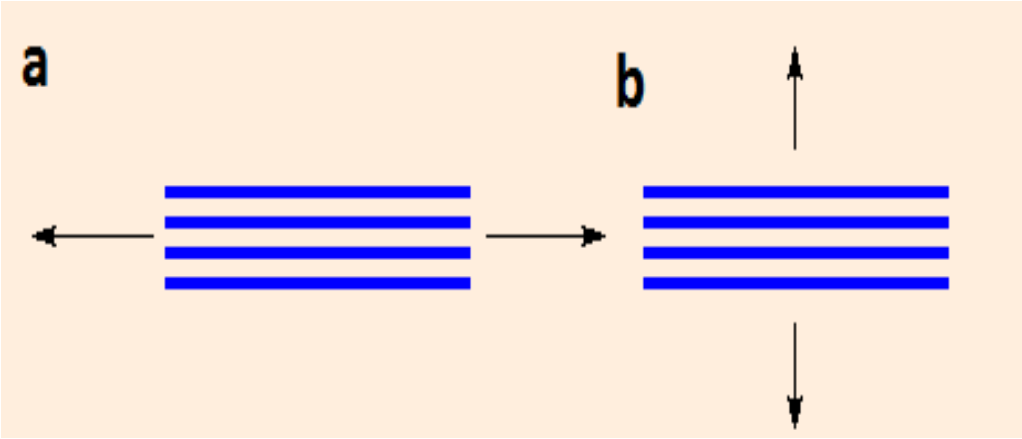


Figure 5.16 : (A) nanofibers are strong when they are pulled in the finer direction, (B) They are weak at right angles to the nanofiber direction

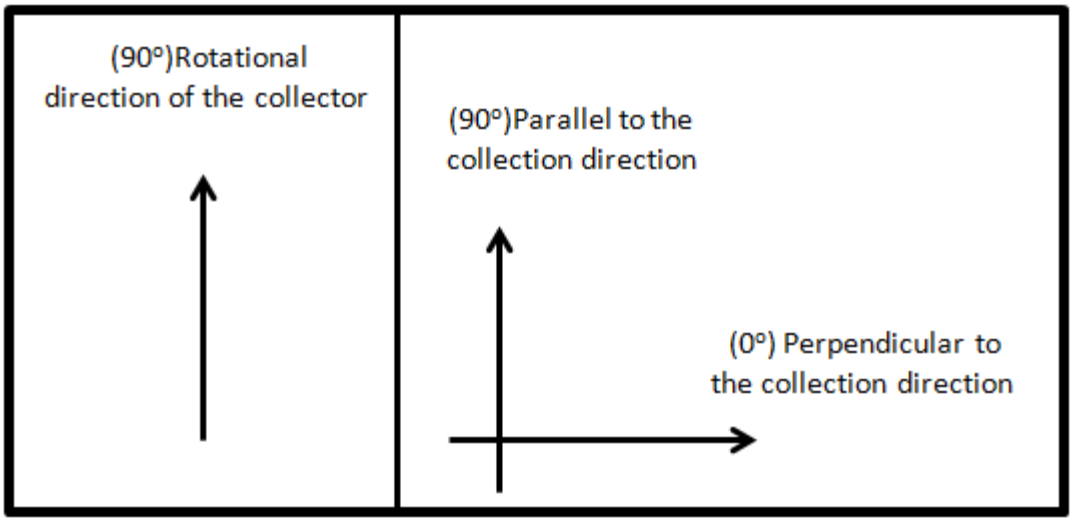


Figure 5.17 : Sample preparation for anayzing effect of orientation

Young's modulus of the sample, perpendicular to the collection direction, is 0,90 GPa while the Young's modulus of the sample, parallel to the collection direction, is 1.36 GPa. The samples produced for evaluating effect of orientataion on Young's modulus are stabilized at 220 ˚C for 0,5 hours.

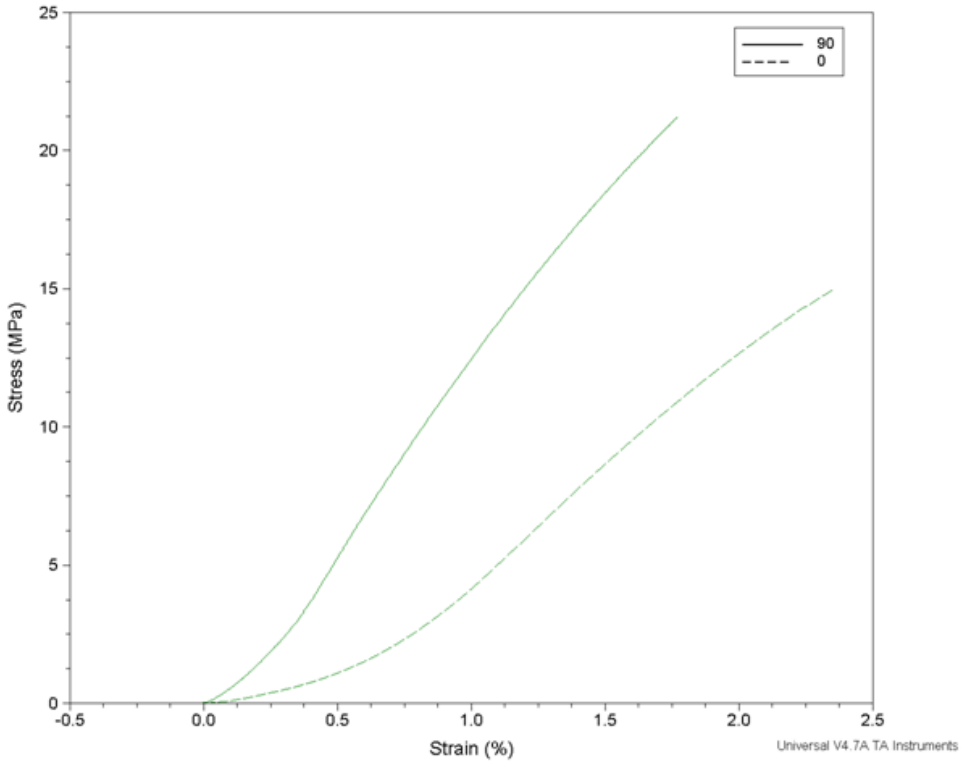


Figure 5.18 : DMA analysis with 0^{o} and 90^{o} to collector direction

5.3.2 Effect of stretching on Young's modulus of stabilized PAN nanofibers

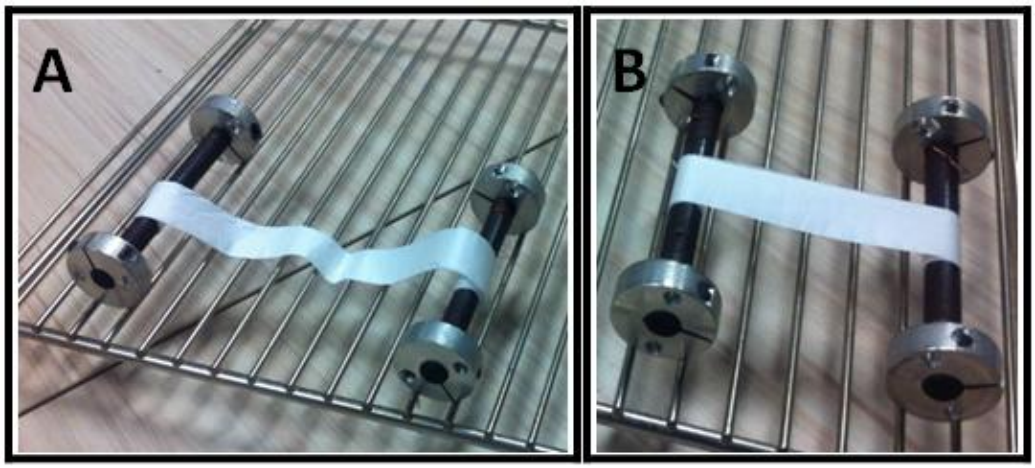


Figure 5.19 : Strecthing set up for different tension amount

In order to realize effects of stretching on Young's Modulus of stabilized PAN nanofibers, stretching mechanisms were prepared (figure 5.19) at different tension amount. 16 cm of PAN nanofiber bundle placed into 13.5 cm gap in a loose form while 7 cm of PAN nanofiber bundle layered into 7 cm gap tightly. Metal rods are fixed in order to prevent mobilization. After the stabilization, Young's modulus were determined.

Table 5.3 : Young's Modulus of Stabilized Nanofibers

Samples	Young's Modulus [Gpa]
0^o	0,95
90^o	1,31
placed loosely	1,71
placed tightly	3,90

Young's modulus measured for tightly placed nanofibers approximently 2.3 times higher than loosely placed naofibers. It means that amount of stretching during heat treatment is very important to designate mechanical properties of carbon nanofibers.

5.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infrared light is varied (monochromatic), the infrared light is through an interferometer. After passing through the sample, the measured signal is

the interferogram. Performing a Fourier diagram on this signal data results in a spectrum identical to that from dispersive infrared spectroscopy [6]

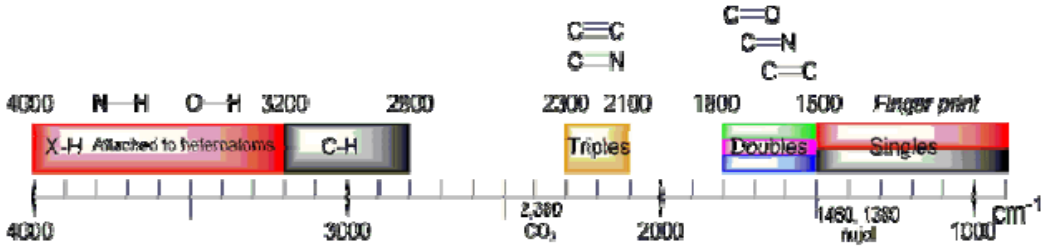


Figure 5.20 : Characteristic IR absorption frequencies of functional groups

The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. A transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample [7].

5.4.1 Stabilizaiton

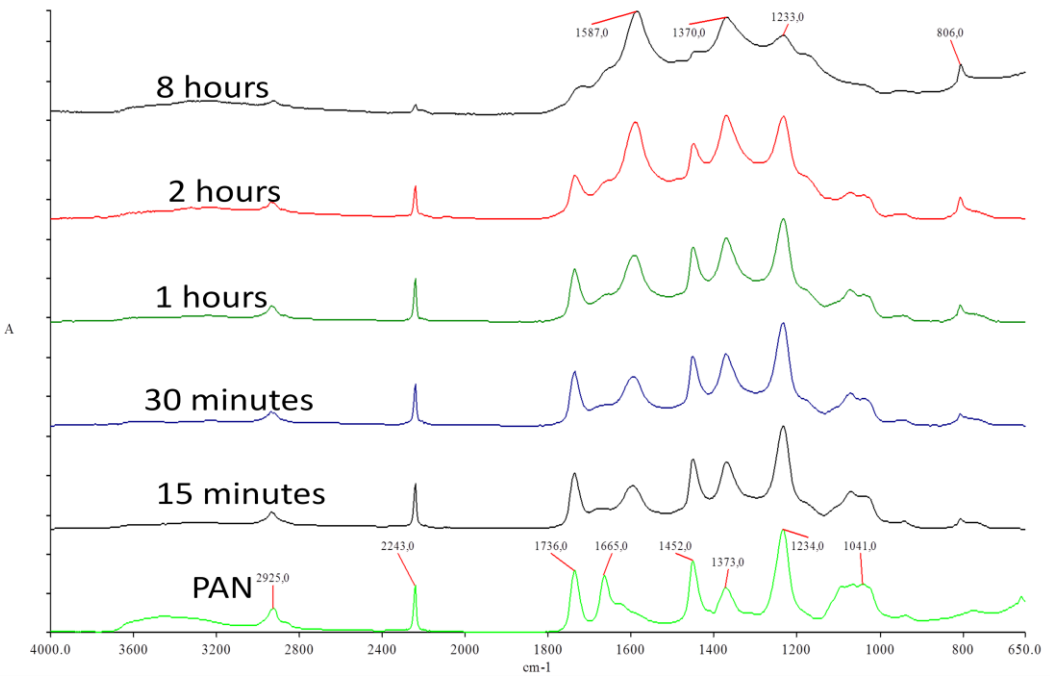


Figure 5.21 : FT-IR analysis of conversion of bands after stabilization at 250 ^{o}C for different holding times

Conversion of chemical structure after stabilization was observed by using FT-IR and success of the processes was questionized. According to FT-IR analysis, vibrations of C≡N bonds give peaks at 2243 cm^{-1}. A reduce of the intensity at this wave number after stabilization means that C≡N groups have started to disappear. Moreover, intensity of aliphatic C–H groups, which give peaks at 1453 cm^{-1} and 2932 cm-1 wave number, decrease unsurprisingly during stabilization. On the other hand, the sharp peak, which appear after stabilization at 1588 cm^{-1} wave number, shows a mix of C=N, C=C and N=H groups. These bonds are the result of cyclization, crass linking and dehydrogenation during stabilization. As can be seen in figure 5.21 and 5.22 intensity of C≡N and C–H bonds are reducing as increment of holding time and temperature. On the other hand peaks of C=N, C=C and N=H groups are increasing as expectedly.

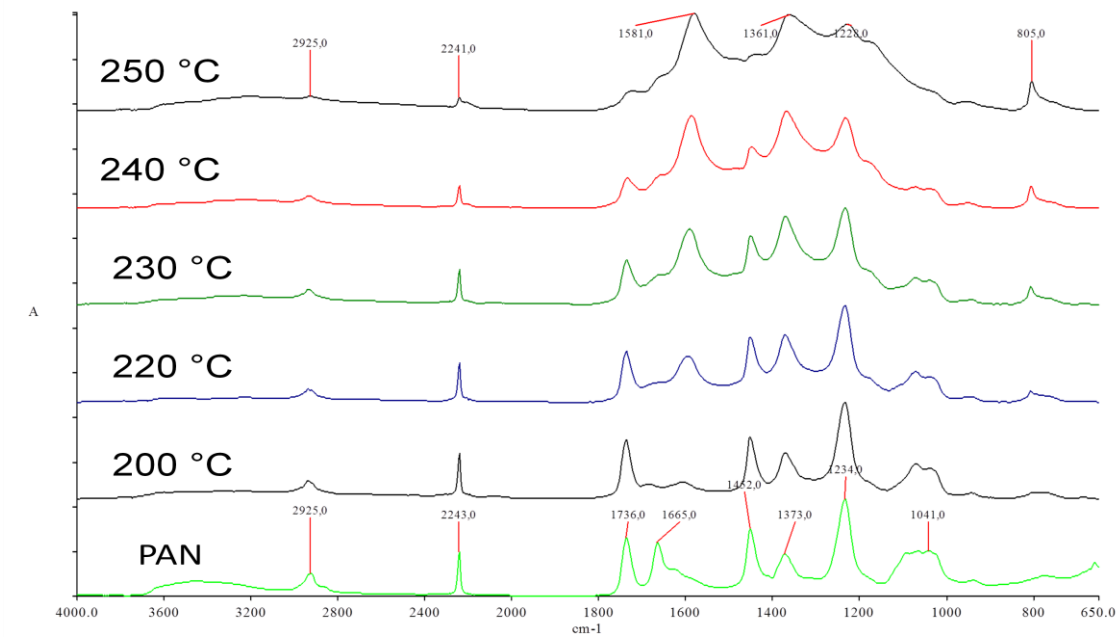


Figure 5.22 : FT-IR analysis of conversion of bands after stabilization for 30 minutes at different temperatures

5.5 Weight Loss

In order to prove existing pyrolysis reaction during stabilization, average weight loss is also determined. Weight of PAN nanofibers are measured before and after stabilization. Three piece of PAN nanofiber webs are taken for each experiment. After heat treatment, average weight loss wt. percentage is calculated for each

recipes figured out on table 5.4. As unsurprisingly, 8.22, 15.05, 17.94, 18.37 wt. % of average weight loss are calculated at 220, 230, 240, 250 ˚C, for 0,5 hours. Therefore, increase in stabilization temperature results increase in average weight loss.

Table 5.4 : Effect of temperature on average weight loss for stabilization

Stabilization Temperature (˚C)	Holding Time (hours)	Average Weight Loss (%)
220	0,5	8,22
230	0,5	15,05
240	0,5	17,94
250	0,5	18,37

6. CONCLUSIONS AND RECOMMENDATIONS

In this study, unoriented and partially aligned, oriented PAN nanofibers were electrospun from PAN/DMF solution for producing carbon nanofibers. Alignment of PAN nanofibers are improved by increase of collector surface speed up to 24 m/sec. Aligned nanofiber bundles were stabilized between 200 – 250 ˚C under stress by preventing dimensional shrinkage. On the other hand, unoriented PAN nanofibers were fabricated by drum type collector with 3,2 m/sec. surface speed. Stabilization was carried out on a glassy plate between 200 -250 ˚C. Then they were carbonized between 900 – 1500 ˚C under argon gas for creating inert atmosphere.

Surface speed of collector was the variable for electrospinning. Ultimate temperature, pending time, heat rate, stretching mechanisms were the paremeters to evaluate effect of stabilization on carbon nanofibers. Carbonization temperature was an important factor on carbonization process.

Samples were characterized by SEM, EDX, FT-IR. Moreover, mechanical properties and weight loss percentage were determined.

According to SEM images, increasing of rotational collector surface speed improves nanofiber alignment. Preventing shrinkage during stabilization also improves parallelization of nanofibers. It is clearly understood that increase in ultimate temperature and pending time and applying tension results decrease in avarage fiber diameter. Increase in heat rate from 1 to 5 ˚C/min results increase in average fiber diameter. Compared to electrospun and stabilized nanofibers, carbon nanofibers have significantly thinner fiber diameters. It is also observed that icrease in carbonization temperature slightly decrease average fiber diameter.

Refer to EDX analysis by evaluating amount of oxygen after stabilizaiton, the optimum process condition is decided as at 250 ˚C and for 0,5 hours. It is obviously understood that increase in carbonization temperature results increase amount of carbon in structure.

Conversion of bonds after stabilization was as it was expected with respect of FT-IR. Intensities of C≡N and aliphatic C-H bonds have decreased while that of C=N and C=C have increased by increase in temperature and pending time.

According to mechanical analysis, it was experimentally observed that Young's Modulus of stabilized nanofibers on alignment direction was higher than perpendicular to alignment direction. Furthermore, as increase of stretching rate, in stabilization, improves young's modulus.

In addition, weight loss was more when ultimate temperature of process is higher after stabilization.

The tension applied nanofiber nanofiber bundles can be used as a promising precursor for production high performance carbon nanofiber composite. According to all the analyses, it has been undersood that stabilization is the most decisive and the key process for carbon nanofiber production. The mechanical properties can be developed by studying on electrospinning conditions and tension mechanism. Refer to this study, further academic studies and applications of carbon nanofibers and enhancing the properties would be done.

REFERENCES

[1] < http://www.pslc.ws/macrog/kidsmac/polyac.htm>, accessed at 14.10.2012

[2] **Matsumoto, T.,** 1985: Mesophase pitch and its carbon fibers, *Pure&Applied Chemistry*, **57**(11), 1553-1562.

[3] **Lewis, I.C., McHenry, E.R. and Singer, L.S.,** 1976. Process for producing carbon fibers from mesophase pitch, *United States Patent,* No: 3976729 dated 24.08.1976.

[4] <http://serc.carleton.edu/research_education/geochemsheets/eds.html>, accessed at 22.08.2012

[5]<http://www.ehu.es/p200_content/en/contenidos/informacion/laspea/en_laspea/equipamiento.html>, accessed at 22.08.2012

[6] <http://www.thefullwiki.org/Infra-red_spectroscopy>, accessed at 25.08.2012

[7] **Baker, R.T.K.,** 1990: Electron microscopy studies of the catalytic growth of carbon filaments, in *Carbon Fiber Filaments and Composites,* edited by Figueiredo, J.L., Bernardo, C.A., Baker, R.T.K. and Hüttinger, K.J., Kluwer Academic, Dordrecht, 405-439.

[8] **Chung, D.D.L.,** 1994: Carbon fiber composites, Butterworth-Heinemann, Washington, 13-78.

[9] **Marilyn, M.L. and Kumar, S.,** 2005: The Processing, Properties, and Structure of Carbon Fibers, *Journal of the Minerals, Metals and Materials,* **57**(3), 52-58.

[10] **Gupta, A.K., Paliwal D.K. and Bajaj P.,** 1991: Acrylic Precursors for Carbon Fibers, *Journal of Macromoleculer Science*, **31**(1), 1-89.

[11] **Cato, A. D. and Edie D.D.,** 2003: Flow Behaviour of Mesophase Pitch, *Carbon,* **41**(7), 1411-1417.

[12] **Xiaosong, H.,** 2009: Fabrication and Properties of Carbon Fibers**,** *Materials,* **4**(2), 2369-2403.

[13]<http://upload.wikimedia.org/wikipedia/commons/8/8e/Metal_yield.svg>, accessed at 07.10.2012

[14] **Morgan, P.,** 2005: Carbon fibers and their composites, CRC Press Inc., Boca Raton, Florida, 121-267, 269-376, 951-1042.

[15] **Rahaman, M.S.A., Ismail, A.F. and Mustafa, A.,** 2007: A review of heat treatment on polyacrylonitrile fiber, *Polymer Degredation and Stability*, **92**(8), 1421-1432.

[16] **Freidlander, H.N., Peebles, L.H., Brandrup, J. and Kirby J.R.,** 1968: On the Chromophore of Polyacrylonitrile VI. Mechnism of Color Formation in Polyacrylonitrile, *Macromolecules*, **1**(1), 79-86.

[17] **Yosuf, N. and Ismail, A.F.,** 2012: Polyacrylonitrile/acrylamide-based carbon fibers prepared using a solvent-free coagulation process: Fiber properties and its structure evolution during stabilization and carbonization, *Polymer Engineering and Science*, **52**(2), 360-366.

[18]<http://www.despatch.com/carbon_fiber.aspx#&panel1-5> accessed at 21.07.2012

[19] **Morgan, P.,** 2005: Carbon fibers and their composites, CRC Press Inc., BocaRaton, Florida, 121-267, 269-376, 951-1042.

[20] **Takaku, A., Hashimoto, T., Miyoshi, T.,** 1985: Tensile properties of carbon fibers from acrylic fibers stabilized under isothermal conditions, *Journal of Applied Polymer Science*, **30**(4), 1565-1571.

[21] **Huang, X.,** 2009: Fabrication and properties of carbon fibers, *Materials*, **2**(4), 2369-2403.

[22] **Lafdi, K. and Wright, M.A.,** 1998: Carbon fibers, in *Handbook of Composites (2nd edition),* edited by Peters, S.T., Chapman&Hall, London, 169-201.

[23] **Inagaki, M., Yang, Y. and Kang, F.,** 2012: Carbon Nanofibers Prepared via Electrospinning, *Advanced Materials*, **24**(19), 2547-2566.

[24] **Wu, M.,Wang, Q., Li, K. and Wu, Y.,** 2012, Optimization of stabilization conditions for electrospun polyacrylonitrile nanofibers, *Polymer Degradation and Stability*, **97**(8), 1511-1519

[25] **Huang, Z.M., Zhang, Y.Z., Kotaki, M. and Ramakrishna, S.,** 2003: A review on polymer nanofibers by electrospinning and their applications in nanocomposites, *Composites Science and Technology*, **63**(15), 2223-2253.

[26] **Nataraj, S.K., Yang, K.S. and Aminabhavi, T.M.,** 2012: Polyacrylonitrile-based nanofibers-Astateof the art review, *Progress in Polymer Science*, 37(3), 487-513.

[27] **Matthews, J.A., Wnek, G.E., Simpson, D.G. and Bowlin G.L.,** 2002: Electrospinning of Collagen Nanofibers, *Biomacromolecules*, **3**(2), 232–238

[28] <http://www.oil-price.net/>, accessed at 21.03.2012.

[29] **Ali, U., Zhou, Y., Wang, X. and Lin, T.,** 2011: Electrospinning of Continuous Nanofiber Bundles and Twisted Nanofiber Yarns, "*Nanofibers-Production, Properties and Functional Applications" Edited by Tong Lin*,153-174.

[30] **Afifi, A.M., Nakano, S., Yamane, H. and Kimura, Y.,** 2010: Electrospinning of Continuous Aligning Yarns with a 'Funnel' Target, *Macromolecular Materials and Engineering*, **295**(7), 660-665.

[31] **Dietzel, J. M., Kleinmeyer, J. D., Hirvonen, J. K. and Becktan, N. C.,** 2001: Controlled deposition of electrospun poly(ethylene oxide) fibers, *Polymer*, **42**(19), 8163-8170.

[32] **Theron, A., Zussman, E. and Yarin, A. L.** 2001: Electrostatic field-assisted alignment of electrospun nanofibres. *Nanotechnology*, **12**(3), 384-390.

[33] **Teo, W. E. and Ramakrishna, S.,** 2005: Electrospun fibre bundle made of aligned nanofibres over two fixed points, *Nanotechnology*, **16**(9), 1878-1884.

[34] **Dalton, P. D., Klee, D. and Maller, M.,** 2005: Electrospinning with dual collection rings. *Polymer*, **46**(3), 611-614.

[35] **Liu, C. K., Sun, R. J., Lai, K., Sun, C. Q. and Wang, Y. W.**, 2008: Preparation of short submicronfiber yarn by an annular collector through electrospinning, *Materials Letters*, **62**(29), 4467-4469.

[36] **Gu, B. K., Shin, M. K., Sohn, K. W., Kim, S. I., Kim, S. J., Kim, S. K., Lee, H. and Park, J. S.,** 2007: Direct fabrication of twisted nanofibers by electrospinning, *Applied Physics Letters*, **90**(26), 263902.

[37] **Lotus, A. F., Bender, E. T., Evans, E. A., Ramsier, R. D., Reneker, D. H. and Chase, G. G.,** 2008: Electrical, structural, and chemical properties of semiconducting metal oxide nanofiber yarns, *Journal of Applied Physics*, **103**(2), 24910.

[38] **Chang, G. and Shen, J.** n.d: Fabrication of micro ropes via bi-electrospinning with a rotating needle collector. *Macromolecular Rapid Communications***, 31**(24), 2151-2154.

[39] **Khil, M. S., Bhattarai, S. R., Kim, H. Y., Kim, S. Z. and Lee, K. H.,** 2005: Novel fabricated matrix via electrospinning for tissue engineering, *Journal of Biomedical Materials, Research - Part B Applied Biomaterials*, **72B**(1), 117-124.

[40] **Smit, E., Buttner, U. and Sanderson, R. D.,** 2005: Continuous yarns from electrospun fibers, *Polymer*, **46**(8), 2419-2423.

[41] **Pan, H., Li, L., Hu, L. and Cui, X.,** 2006: Continuous aligned polymer fibers produced by a modified electrospinning method, *Polymer*, **47**(4), 4901-4904.

[42] **Li, L., Zhang, P., Liu, R. and Guo, S. M.,** 2011: Preparation of fibrous Ni-coated-YSZ anodes for solid oxide fuel cells. *Journal of Power Sources*, **196**(3), 1242-1247.

[43] **Yao, C., Li, X. and Song, T.,** 2009: Preparation and characterization of zein and zein/poly-Llactide nanofiber yarns, *Journal of Applied Polymer Science*, **114**(4), 2079-2086.

[44] **Okuzaki, H., Takahashi, T., Hara, Y. and Yan, H**., 2008: Uniaxially aligned carbon nanofibers derived from electrospun precursor yarns, *Journal of Polymer Science, Part B: Polymer Physics*, **46**(3), 305-310.

[45] **Wang, X., Zhang, K., Zhu, M., Hsiao, B. S. and Chu, B**., 2008: Enhanced Mechanical Performance of Self-Bundled Electrospun Fiber Yarns via Post-Treatments, *Macromolecular Rapid Communications*, **29**(10), 826-831.

[46] **Mondal, A., Borah, R., Mukherjee, A., Basu, S., Jassal, M. and Agrawal, A. K.** 2008: Electrospun self-assembled nanofiber yarns, *Journal of Applied Polymer Science*, **110**(1), 603-607.

[47] **Maheshwari, S. and Chang, H.C.,** 2009: Assembly of Multi-Stranded Nanofiber Threads through AC Electrospinning, *Advanced Materials*, **21**(3), 349-354.

[48] **Ko, F., Gogotsi, Y., Ali, A., Naguib, N., Ye, H., Yang, G. L., Li, C. and Willis, P.,** 2003: Electrospinning of Continuous Carbon Nanotube-Filled Nanofiber Yarns, *Advanced Materials*, **15**(14), 1161-1165.

[49] **Kim, H.Y., GIL, M.S., JUNG, Y.H., Kim, H.J., Lee, B.S.,** 2008. Process of preparing continuous filament composed of nano fiber, *United States Patent*, No: 7354546 B2 dated: 04.08.2008.

[50] **Saito, K., and Ogawa, H.,** 1978, Process for producing carbon fibers, Toho Beslon Co, *United States Patent*, No: 4069297 dated: Jan 1978.

[51] **Teo, W. E., Gopal, R., Ramaseshan, R., Fujihara, K. and Ramakrishna, S.** 2007: A dynamic liquid support system for continuous electrospun yarn fabrication, *Polymer*, **48**(12), 3400-3405.

[52] **Teo, W. E., Gopal, A., Yousefzadeh, M., Latifi, M., Teo, W.E., Amani, T.M., and Ramakrishna, S.,** 2011: Producing continuous twisted yarn from well-aligned nanofibers by water vortex, *Polymer Engineering and Science*, **51**(2), 323-329.

[53] **Dabirian, F., Hosseini, Y. and Ravandi, S. A. H.,** 2007: Manipulation of the electric field of electrospinning system to produce polyacrylonitrile nanofiber yarn, *Journal of the Textile Institute*, **98**(3), 237-241.

[54] **Buchko, C. J., Kozloff, K. M. and Martin, D. C.,** 2001: Surface characterization of porous, biocompatible protein polymer thin films, *Biomaterials*, **22**(11), 1289-1300.

[55] **Kinoshita, Y.,** 1977, High tensile strength, high Young's modulus carbon fiber having excellent internal structure homogeneity and process for producing same, *United States Patent*, No:4065549, 27.12.1977.

[56] **Dabirian, F. and Hosseini, S. A.,** 2009: Novel method for nanofibre yarn production using two differently charged nozzles, *Fibres and Textiles in Eastern Europe*, **17**(3), 45-47.

[57] <http://www.madehow.com/Volume-4/Carbon-Fiber.html#b>, accessed at 05.01.2011

[58] **Afifi, A. M., Nakano, S., Yamane, H. and Kimura, Y.,** 2010: Electrospinning of continuous aligning yarns with a "funnel" Target, *Macromolecular Materials and Engineering*, **295**(7), 660-665.

[59] **Ali, U., Zhou, Y., Wang, X. and Lin, T.,** 2011: Direct electrospinning of highly twisted, continuous nanofiber yarns, *Journal of the Textile Institute.*

[60**] Zhou, Z., Lai, C., Zhang, L., Qion, Y., Hou, H., Reneker, D.H., and Fong, H.,** 2009: Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanicalproperties, *Polymer*, **50**(13), 2999-2006.

[61] **Chen, F., Peng, X., Li, T., Chen, S., Wu, X.F. and Reneker D.H.,** 2008: Mechanical characterization of single high-strength electrospun polyimide nanofibers, *Journal of Physics D: Applied Physics*, **41**(2), 1-8.

[62] **Wo, S., Zhang, F., Yu, Y., Li, P., Yang, X., Lu, J. and Ryu, S,** 2008: Preparation of PAN-based carbon nanofibers by hot-stretching, *Composite Interfaces*, **15**(7-9), 671-677.

[63] **Arshoad, N.S., Naraghi, M. and Chasiotis, I.,** 2011: Strong carbon nanofibers from electrospun polyacrylonitrile, *Carbon*, **49**(5), 1710-1719.

[64] **Mataram, A., Ismail, A.F., Abdullah, M.S., Ng, B.C. and Matsuura, T.,** 2011: A Review Of Assembled Polyacrylonitrile-Based Carbon Nanofiber Prepared Electrospinning Process, *International Journal of Nanoscience*, **10**(3), 455-469.

[65]<http://www.sglgroup.com/cms/international/presslounge/news/2012/03/03222012_p.html?__locale=en>, accessed 09.23.2011

[66] **Ravandi, S.A.H. and Sadrjahani, M.,** 2012: Mechanical and structural characterizations of simultaneously aligned and heat treated PAN nanofibers, *Journal of Applied Polymer Science*, **124**(5), 3529-3547.

[67] Ji**, L. and Zhang, X.,** 2009: Fabrication of porous carbon nanofibers and their application as anode materials for rechargeable lithium-ion batteries, *Nanotechnology*, **20**(15), 155705.

[68] **Ji, L. and Zhang, X.,** 2009: Generation of activated carbon nanofibers from electrospun polyacrylonitrile-zinc chloride composites for use as anodes in lithium-ion batteries, *Electrochemistry Communications*, **11**(3), 684-587.

[69] **Kim, H., Lee, D. and Moon, J.,** 2011: Co-electrospun Pd-coated porous carbon nanofibers for hydrogen storage applications, International Journal of Hydrogen Energy, 36(5), 3566-3573.

[70] **Barranco, V., Lillo-Rodenas M.A., Linares-Solano A., Oya, A., Pico F., Ibañez, J., Agullo-Rueda, F., Amarilla, J.M. and Rojo J.M.,** 2010: Amorphous Carbon Nanofibers and Their Activated Carbon Nanofibers as Supercapacitor Electrodes, *The Journal of Physical Chemistry*, **144**(22), 10302-10307.

[71] **Ji, L. and Zhang, X.,** 2009: Fabrication of porous carbon/Si composite nanofibers as high-capacity battery electrodes, *Electrochemistry Communications*, **11**(6), 1146-1149.

[72] **Yu, Y., Gu, L., Whang, C., Dhanabalan, A., Aken, P.A.V. and Maier, V.,** 2009: Encapsulation of Sn@carbon Nanoparticles in Bamboo-like Hollow Carbon Nanofibers as an Anode Material in Lithium-Based Batteries, *Angewandte Chemie International Edition*, **48**(5), 6485-6489.

[73] **Yu, Y., Yang, Q., Teng, D., Yang, X. and Ryu, S.,** 2010: Reticular Sn nanoparticle-dispersed PAN-based carbon nanofibers for anode material in rechargeable lithium-ion batteries, *Electrochemistry Communications*, **12**(9), 1187-1190.

[74] **Ji, L., Yao, Y., Toprakci, O, Lin, Z., Liang, Y., Shi, Q., Medford, A.J., Millns, C.R. and Zhang, X.,** 2010: Fabrication of carbon nanofiber-driven electrodes from electrospun polyacrylonitrile/polypyrrole bicomponents for high-performance rechargeable lithium-ion batteries, *Journal of Power Sources,* **195**(7), 2050-20056.

[75] **Zou, L., Gan, L., Kang, F., Wang, M., Shen, W. and Huang, Z.,**2010: Sn/C non-woven film prepared by electrospinning as anode materials for lithium ion batteries, *Journal of Power Sources,* **195**(4), 1216-1220.

[76] **Ji, L. and Zhang, X.,** 2009: Fabrication of porous carbon/Si composite nanofibers as high-capacity battery electrodes, *Electrochemistry Communications,* **11**(6), 1146-1149.

[77] **Naito, K., Yang, J.M., Xu, Y. and Kagawa, Y.,** 2010: Enhancing the thermal conductivity of polyacrylonitrile and pitch-based carbon fibers by grafting carbon nanotubes on them, *Carbon,* **48**(6), 1849-1857.

[78] **Mahanta, N.K., Abramson, A.R., Lake, M.L., Burton, D.J., Chang, J.C., Mayer, H.K. and Ravine, J.L.,** 2010: Thermal conductivity of carbon nanofiber mats, *Carbon,* **48,** 4457-4465.

[79] **Frohs, W. and Jeager, H.,** 2011: Carbon Fibers and Composite Materials – Landscape Germany-, *TANSO*, **2011**(249), 174-178.

[80] **Mutlu, A.,** 2011, Development of Polymer Based Carbon Nanofiber Production Technology, MSc Thesis, Istanbul Technical University.

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