ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF POLY(ACRYLONITRLE-co-VINYLACETATE-co-ITACONIC) ACID TERPOLYMER AS CARBON FIBER PRECURSOR

M.Sc. THESIS

Dilek SUADİYE

Polymer Science and Technology

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(515111006)

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Thesis Advisor: Prof. Dr. A. Sezai SARAÇ

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KARBON FİBER PREKÜRSOR OLARAK AKRİLONİTRİL-ko-VİNİL ASETAT-ko-İTAKONİK ASİT TERPOLİMERİNİN SENTEZ VE KARAKTERİZASYONU

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OCAK 2014

Dilek Suadiye, a **M.Sc.** student of ITU **Institute of Science Engineering and Technology** student ID **515111006**, successfully defended the **thesis** entitled "M.Sc. **THESIS TITLE SYNTHESIS AND CHARACTERIZATION OF POLYACRYLONITRLE-CO-VINYLACETATE-CO-ITACONIC ACID TERPOLYMER AS CARBON FIBER PRECURSOR**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

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December 2013

Dilek SUADİYE
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ABBREVIATIONS

AN	**:** Acrylonitrile
VAc	**:** Vinylacetate
IA	**:** Itaconic acid
P(AN-co-VAc)	: Poly(acrylonitrile-co-vinyl acetate)
P(AN-co-VAc-co-IA)	**:** Poly(acrylonitrile-co-vinylacetate-co-itaconic acid)
APS	**:** Amonium persulphate
DMF	**:** Dimethylformamide
η_{sp}	**:** Specific Viscosity
FTIR-ATR	**:** Fourier Transform Infrared Spectroscopy –Attanuated Total Reflectance
NMR	**:** Nuclear Magnetic Resonance
GPC	**:** Gel Permeation Chromatography
$\mathbf{M_n}$	**:** Number Avarage Molecular Weight
$\mathbf{M_w}$	**:** Weight Avarage Molecular Weight
DSC	**:** Differantial Scanning Calorimetry
TGA	**:** Thermal Gravimetric Analysis
SEM	**:** Scanning Electron Microscope
AFM	**:** Atomic Force Microscope

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SYNTHESIS AND CHARACTERIZATION OF POL(YACRYLONITRLE-co-VINYLACETATE-co-ITACONIC ACID) TERPOLYMER AS CARBON FIBER PRECURSOR

SUMMARY

Carbon fibers are an important area being studied in recent years.Carbon nanofibers have a variety of applicaiton areas such as defense, aeroscape, civil enginnering and etc. Nanaoscale materials have a great interest. Carbon nanomaterials such as carbon nanofibers, carbon nanotubes and carbon nanowires are intriguing subjects in last few decades. Carbon fiber precursors are mostly produce from PAN. Due to some problems at spinning, stabilization and processability PAN is preffered to be used as copolymers.

This study has two main objectivities. One of them is synthesis of poly(acrylonitrile-co-vinyl acetate-co-itaconic acid) terpolymers. The terpolymers had different comonomer composition and synthesized via solution polymerization technique with amonnium per sulphate. The solvent used in the polymerization was the mixture of dimethyl formamide and disilled water. In the first part of this study five terpoymers are synthesized and dried in the oven under the vacuum. Main purpose of this part of the study is to mention the spectroscopic, thermal and chromatographic properties of the terpolymers according to the itaconic acid monomer feed ratio for each polymers composition. The synthesized terpolymers were characterized in detail by several methods. Viscosity of the terpolymers are measured by Obbelohde Viscosimeter. Molecular weight of the terpoymers are determined by Gel Permeation Chromatography . Spectroscopic analysis of terpolymers were done by Fourier Transform Infrared Spectroscopy–Attanuated Total Reflectance and Nuclear Magnetic Resonance Spectroscopy. Thermal analysis of the poymers were determined by Thermal Gravimetric Analysis and Differantial Scanning Calorimetry methods. The spectroscopic study done by FTIR-ATR shows that the absorbance ratios of C=O specific peak to absorbance of C≡N peak is increasing with the increasing fed of initial itaconic acid comonomer. NMR results have an agreement with the litarature. The signals obtained from NMR spectrum shows the -CH proton of AN were observed at 3.25 – 3.09 ppm. The other peak at 5.13 ppm is due to –CH proton of VAc. The carboxylic proton signals of IA are shown around 6.3-7.8 ppm. Morphologic analysis used to determine fiber characteristic for the synthesized polymers. The change of the varage fiber diameters of nanofibers are obtained from SEM wtih the composition of the monomer feed ratios are discussed. It is realized that the avarage fiber diameters are decreasing with the increasing itaconic acid monomer feed ratio. The specific viscosity values for each terpolymer monomer feeding composition show that, the specific viscosities are decrasing with increment of the initial itaconic acid monomer feed ratios similar to decrease of the avarage fiber diameters obtained from SEM.

In the second part of the study it was aimed to produce nanofibers via electrospinning technique and obtaining oxidized and carbonized nanofibers of the terpoymers. The terpolymer with different monomer feed composition were electrospun and the obtained nanofibers were oxidized at six different oxidation temperatures varying from 200°C to 325 °C. It is observed that the color of the nanofiber mat is changing from white at room temperature to golden yellow, orange than to the dark brown with the increasing oxidation temperature about 300 °C that is attributed to the stabilization reactions existing. Fourier Transform Infrared Spectroscopy –Attanuated Total Reflectance in detail, characterizes the oxidized nanofibers spectroscopically. The decrease at the absorbance of C≡N is related to the conversion of C≡N peaks to -C=N peaks. The absrobance change of the specific C≡N of acylonitrile unit and =C−H of the bending peak in saturated ring is proportioned. The nanofibers also are characterized morphologically by Scanning Electron Microscope method.The oxidized nanofiber was carbonized at 1100°C for 2.5 hours. After the carbonization process nanofiber mat became totally black. Oxidized and carbonized nanofibers were compared with original electrospun nanofibers of terpolymers according to their spectroscopic and morphologic properties.

KARBON FİBER PREKÜRSOR OLARAK AKRİLONİTRİL-ko-VİNİL ASETAT-ko-İTAKONİK ASİT TERPOLİMERİNİN SENTEZ VE KARAKTERİZASYONU

ÖZET

Nanoboyutlu malzeme üretimi büyük ilgi görmektedir. Karbon fiber, karbon nanotüp gibi nanoboyutlu malzemeler son elli yılın yaygın olarak çalışılan bir alanı olmuştur. Karbon fiber son yıllarda büyük gelişme gösteren bir çalışma alanıdır. Karbon nanfiberler endüstride geniş bir uygulama alanına sahiptir. Bu alanlardan bazıları savunma sanayi, havacılık uygulamaları, inşaat sektörü vb. alanlardır. Karbon fiber malzemelerin üretiminde çoğunlukla PAN kullanılmaktadır. PAN, akrilonitril monomerinin uygun koşullarda polimerleştirilmesiyle elde edilir. PAN kopolimerleri olatak kullanımı yaygın olarak görülmektedir. Karbon fiber üretiminde PAN'dan karbon fiber oluşturmak için izlenen termal oksidasyon yöntemini kolaylaştırmak için bazı asidik monomerler kullanılmaktıdır. Bu monomerlere örnek olarak itaconic acid ve akrilik asit verilebilir.

Yürütülen bu çalışmada akrilonitrili farklı bileşimlerde iki monomer kullanarak polimerleştirmek ve elde edilen polimerlerden karbon fiber prekürsor özellikli sonuç ürünü elde etmek amaçlanmıştır. Çalışma iki kısımdan oluşmaktadır. İlk kısımda akrilonitril (AN) monomerinin farklı oranlarda vinil asetat (VAc) ve itakonik asit (IA) ile polimerleştirilmesi ve elde edilen polimerlerin karakterize edilmesi amaçlanmıştır. IA monomerinin toplam monomerlerin besleme oranlarında %1 ile %5 arasında değişen oranlarda besleyerek beş farklı terpolimer elde edilmiştir. Polimerizasyon su ile DMF karışımının kullanıldığı ortamda ger.çekleştirilmiştir. oluşmaktadır. Bütün polimer örneklerinin santezinde başlatıcı olarak aynı miktarda amonyum persülfat (APS) kullanılmıştır. Amonyum persülfat eşit 30ml distile edilmiş su içerisinde çözülerek sisteme damla damla beslenmiştir. Polimerizasyon sonucunda yüksek verim ile farklı monomer besleme oranları ile sentelenmiş beş terpolimer elde edilmiştir. Terpolimerlerin verimi %90 ile %95 arasında değişine yüksek oranlarda yapılmştır. Elde edilen polimerler spektroskobik olarak Fourier transform infrared spectroscopy – attanuated total reflectance (FTIR-ATR) ve Nükleer Manyetik Rezonans (NMR) yöntemleri ile analiz edilmiştir. Polimerlerin viskozite ölçümleri Ubbelohde viskozimetresi ile tayin edilmiştir. Elde edilen sonuçlar artan itakonik asit besleme oranıyla birlikte spesifik viskozitede düşme olduğunu göstermiştir. GPC analizleri ile ağırlık ortalama molekül ağırlıkları tespit edilmiştir. Artan itakonik asit monomer besleme oranıyla birlikte polimerlerin ağırlık ortalama molekül ağırlığında 580.400 g/mol den 415.850 g/mol' e doğru bir düşme tespit edilmiştir. FTIR-ATR sonuçlarında polimer zincirindeki IA veVAc monomer ünitelerine ait -C=O spesifik piki ile akrilonitrile (AN) ait spesifik -C≡N pikinin değişen absrobansları oranlanmıştır. Oranların itakonik asit besleme miktarıyla birlikte artış göstermesi polimer bileşiminde itakonik asit miktarının arttığını

göstermiştir. ^{1}H- NMR sonuçlarında AN'in -CH protonu of 3.25 – 3.09 ppm aralığında gözlenmiştir. Bir diğer pik ise 5.13 ppm aralığında VAc'nin –CH protonuna aittir. IA'nın hidroksilik protonları ise 6.3-7.8 ppm civarında gözlenmiştir. Elde edilen sonuçlar literatür ile uyum içerisindedir ve yapıya katılan komonomerlerin varlığını göstermektedir.

Terpolimer örneklerinin termal özellikleri Termal Gravimetrik Analiz (TGA) ve Diferansiyel Taramalı Kalorimetri (DSC) metotları ayrıntılı olarak incelenmiştir. Termal gravimetrik analiz yöntemi ile malzemenin yüksek sıcaklık değerlerindeki davranışı irdelenmiştir. Analizler 0° C ila 800° C sıcaklık aralığında azot (N_2) varlığında ve 90 ml/dk azot besleme hızında yapılmıştır. Bütün örnekler için ısıtma hızı 20° C/dk şeklindedir. Analiz sonuçlarında yüksek sıcaklık değerlerinde beslenen polimer miktarının kütlece %35 oranında yanmadan sistemde kaldığı belirlenmiştir.

Çalışmanın ikinci aşamasında ise elde edilen polimerlerin DMF içerisindeki çözeltilerinden elektrospining metoduyla nanofiber elde edilmesi amaçlanmıştır. Yapılan bazı denemeler ardından elektrospining ile istenilen nanofiberlerin eldesi için uygun parametreler tespit edilmiştir. Elektrospining parametreleri olarak 17 kV, 20 cm ve 0,8 ml/sa. seçilmiştir. Elektrospining ile elde edilen nanofiberlerin morfolojik özellikleri Taramalı Elektron Mikroskobu (SEM) ve Atomik Kuvvet Mikroskobu (AFM) yöntemleri ile incelenmiştir. Taramalı elektron mikroskobundan elde edilen sonuçlarda artan itakonik asit besleme oranıyla birlikte polimerlerin ortalama fiber çaplarında 350 nm civarından 200 nm civarına bir düşüş olduğu gözlenmiştir. Atomik kuvvet mikroskobunda elde edilen analiz sonuçlarında elektrospinle elde edilmiş nanofiber matındaki fiber varlığı görüntülenmiştir.

Sentezlenen terpolimerlerden karbon fiber prekürsor elde edilmesi aşamalarında nanofiber matına karbon fiber eldesi aşamaları uygulanarak denemeler gerçekleştirilmiştir. Elde edilen nanofiberlerin farklı sıcaklıklarda okside edilmiş nanofiberlerinin eldesi amaçlanmıştır. Nanofiber matına ilk olarak termel oksidasyon işlemleri uygulanmıştır. Termel oksidasyon aşamasında 200° C ila 325° C arasında değişen sıcaklarda tüm terpolimer örnekleri için hava ortamında ve 2.5° C/dk ısıtma hızında ısıl işlem uygulanmıştır. Uygulanan ısıl işlemin ardından elde edilen nanofiber matlarının renginde orijinal halde beyaz olan renkten uygulanan ısı değerinin artışıyla birlikte sarımsı renkten açık kahveye, ardından koyu kahve renklerine doğru bir değişim olduğu gözlenmiştir. Termal oksidatif stabilizasyon sonucunda fiberlerin yapısında oluşacak değişikliklerin spektroskopik ve morfolojik değişimleri incelenmiştir. Okside nanoliflerin spektroskobik analizi FTIR-ATR ile gerçekleştirilmiştir. Analiz sonucunda elde edilen spektrumlarda akrilonitrilin spesifik C≡N grubuna ait pikin absorbansında azalma görülmüştür. Bu durum -C≡N grubunun halkalı yapı oluşturmaya giderek halka içerisinde –C=N grubu oluşturduğu şeklinde yorumlanmıştır. Ayrıca =C−H doymamış halka yapısına ait pikin absorbansında artış görülmesi halkalaşma reaksiyonlarının gerçekleştiğini göstermektedir. Spektrumun 1580−1620 cm^{-1} aralığında gözlenen geniş pikler of –C=N− , C=C and N−H gruplarını ve oksidasyon ve tautemerizasyonun bir parçası olarak dehidrojenasyonun gerçekleştiğini göstermektedir. Oksidasyonu tamamlanmış nanoliflerin SEM ile gerçekleştirilen morfolojik analizler gerçekleştirilmiştir. Okside edilmiş nanolif matlarına ait taramalı elektron mikroskobu görüntüleri ayrıntılı olarak incelenmiş ve oksidayon sıcaklığı atışı ile birlikte nanofiber çaplarında bariz bir artış veya azalış trendi oluşmadığı tespit edilmiştir. Elde edilen liflerin ortalama fiber çaplarının değişim aralığı belirlenmiştir.

Elde edilen oksidasyonu tamamlanmış nanoliflerin Fourier transform infrared spectroscopy –attanuated total reflectance (FTIR-ATR) ile analizlerinin elde edilen sonuçlar ile - C≡N pikinde değişimin belirgin değişimini gösteren 225° C deki I2

(AN/VAc/IA; 89/9/2) kodlu terpoliimer seçilerek karbonizasyonu amaçlanmıştır. 225 ° C 2de okside edilmiş nanofibers matının karbonizasyonu yüksek sıcaklık fırınında, azot gazı ortamında, 1100° C de ve 2.5 saat süresince gerçekleştirilmiştir. Sonuç ürünü olarak elde edilen karbonize edilmiş nanfiber matının renginin açık kahve tonlarından tamamen siyah renge dönüştüğü gözlenmiştir. Karbonize edilmiş nanofiber matlarının spektroskobik analizleri FTIR-ATR cihazı ile gerçekleştirilmiştir. Analiz sonuçları ile elde edilen spektrumlardan sıcaklık değişimi ile akrilonitrilin spesifik piklerindeki değişim irdelenmiştir. Yüksek sıcaklıklarındaki karbonizasyon aşamasının ardından akrilonitrile ait -C≡N pikinin tamamen yok olduğu gözlenmiştir. Karbonize edilmiş nanofiber matlarının morfolojik analizleri taramalı elektron mikroskobu ile gerçekleştirlmiştir. Taramalı elektron mikroskobundan elde edilen görüntülerden nanofiber yapısının korunduğu gözlemlenmiştir.

1.INTRODUCTION

Acrylonitrile and acrylonitrile based polymers are widely used as carbon and graphite fiber precursors [1]. Polyacrylonitrile (PAN) is one of the mostly used polymer at making carbon fiber precursors [2]. PAN fibers are manufactured are consisted of at least 85% by weight of acrylonitrile units. The remaining 15% of the fiber are consisted of neutral or ionic comonomers which are composed with acrylonitrile to improve the fibers properties [3]. PAN homopolymers have some problems of being hardly processed and having poor stabilization and spinnability. Due to its characteristic acrylonitrile is preferred to copolmerized with some comonomers having acidic groups [2-4]. Acidic comonomers like acrylic acid(AA), methacrylic acid(MA), methyl methacrylate(MMA) and itaconic acid(IA) are used as comonomers to improve the stabilization of the PAN copolymers that is an important parameter for carbon fibers [4]. The comonomers having acidic groups can facilitate the cyclization of nitrile groups during the heat treatment reactions of the PAN precorsors [5]. Neutral comonomers like vinyl acetate(VAc) and methyl acrylate (MA) are used to modify the solubilty of PAN copolymers into spinning solvents, to enhance the rate of the diffusion of dyes into PAN fiber and to modify the morphology of the PAN fibers. The composition of PAN fibers that are used to produce carbon fiber precursors usually contain 5-10% neutral comonomer, 0-5 % acidic and ionic comonomers and the remaining percentage of the composition in consisited of acrylonitrile units [3]. With the incorporation of such as comonomers to PAN reduces the cyclization temperature and relax heat release [4]. Therefore, the selection of the appropriate comonomer or comonomers is too important.

Some of commercial precursors used in the industry are known to be synthesized with a third comonomer for example MA addition to AN and IA. The terpolymer usually used to adjust the dope characteristic and to increase the quality of the obtained fiber with high tensile strength. The terpolymer is also used to modify the thermal caharacteristic of the fiber to get good-quality carbon fiber [6].

Controlled thermally treatment in several steps produces metamorphosis of PAN-based textile fibers into carbon fibers. These important steps at carbon fiber production is named as oxidation and carbonization. In the stabilization ,that is also called oxidation step, the fibers are heated at 200-300°C for 5-10 hours in the presence of air. The intermolecular cyclization C≡N groups of the AN units and the intermolecular crosslinking reactions makes the polymer containing AN units is converted from a linear structure into the ladder structure. The process is believed to occur intra- and inter-molecularly. In order to obtain required yield and requested quality of stabilized fiber the operation temperature and the amount of the oxygen during the process are important parameters. The next step of carbon fiber production is the carbonization step in which the stabilized fibers are heated in an inert atmosphere at a temperature above 1000°C for a few hours. At this process the non-carbon elements are removed and 97% of carbon content is aimed to be obtained from the material [7].

Carbon fibers can be produced in two different ways which are the pyrolysis of fibers spun from an organic precursor (PAN or alternatively pitch) and using chemical vapor deposition method. Electrospinng of fibers from polymer solution is a cost-effective way of fiber production. Electrospun fibers sustain huge alongation and thinning with a strain rate of ~ 1000 s^{-1}. The orientation and the degree of the crystallinty of the electrospun fibers are high [8].

Carbon fibers are sideboards that used to be adapted greatly at aeroscape, defense areas, automobiles, civil engineering and composite materials due to their characteristic [4,7,9]. It has a growing section of the industry which is being to be developed with so many studies.

Itaconic acid and vinylacetate are two comonomers that respectively have excellent caharacteristic to be composed with acrylonitrile in order two synthesize terpolymer as carbon fiber precursors. Vinyl acetate is commonly used in the industry that has a widespread copolymer with acrylonitrile in fiber production. Itaconis acid an unique molecular structure with two carboxylic acid groups which is frequently studied by many reseachers in oreder to be copolymerized with acrylonitrlie for carbon fiber production.

In this study, in order to obtain good-quality carbon fibers VAc and IA comonomers are used with AN to synthesize terpolymers. Five different terpolymers are havingdifferent composition of comonomers are synthesized with the same procedure and charactarized particularly according to their spectroscopic, chromatographic, thermal and morphologic properties. The terpolymers are electrospun to obtain nanofibers. The obtained nanofibers are oxidized and carbonized to obtain carbon fiber precursors. The oxidized and carbonized fibers are characterized with spectroscopic and morphologic methods.

2.THEORETICAL PART

2.1. Acrylonitrile and Acrylonitrile Copolymers

Acrylonitrile(AN) and acrylonitrile based polymers are effectively used in the industry at producing acrylic fibers.

Acrylonitrile can be synthesized in three different methods. The mostly used one of these methods is the production according to the Sohio process which proceeds from propylene and ammonia as it is shown at **Figure 2.1.** Different methods are only due to the applied catalysts and the reaction sequence.

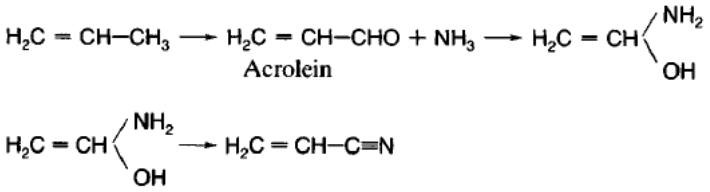


Figure 2. 1: Sohio process which proceeds from propylene and ammonia.

Another process used at acylonitrile production is the two phase process starts with ethylene oxide and hydrogen cyanide and then leads via ethylene cyanhydrin. The reaction mechanism is shown in **Figure 2.2.**

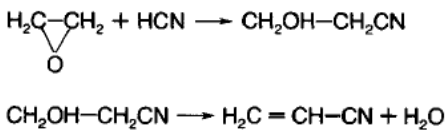


Figure 2. 2: Reaction mechanism of acrylonitrile synthesis from ethylene oxide and hydrogen cyanide.

As mentioned by by *O. Bayer* and *P. Kuntz* one other synthesis process of acrylonitrile is direct addition of hydrogen cyanide to acetylene The reaction mechanism is shown in **Figure 2.3.**

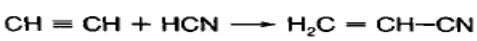


Figure 2. 3: The reaction with addition of prussic acid to acetylene.

Acrylonitrile and acrylnitrile based copolymers are widely used in many applications like plastics, syntethic fibers, rubbers and so many composites [1]. Polyacylonitrile (PAN) is one of the mostly used polymer in manufacturing of syntethic fibers [10].

The homopolymer, PAN, is rarely used in fiber manufacturing because of the difficulty to spin and dye. Acrylonitrile homopolymer's flow temperature is higher than its decomposition temperature. The decrease at the glass transition temperature and melting point of acrylonitrile is the important point to use it in industrial applications. In order to solve this problem copolymerization of acrylonitrile with one or two comonomers such as methacrylates, styrene and vinyl acetate is commonly used [11]. All commercial acrylic fibers are made from acrylonitrile is incorporated with at least one other monomer. The neutral comonomers most such as MA (methacrylic acid) and VA (vinyl acetate) to increase the solubility of the polymer in spinning solvents, modify the fiber morphology, and improve the rate of diffusion of dyes into the fiber. Sulfonated monomers, such as sodium styrene sulfonate (SSS), sodium methallyl sulfonate (SMAS), and sodium sulfophenyl methallyl ether (SPME) are used to provide dye sites or to provide a hydrophilic component in water-reversible crimp bicomponent fibers. Halogenated monomers, usually vinylidene chloride, vinyl bromide, and vinyl chloride, impart flame resistance to fibers used in the home furnishings, awning, and sleepwear markets [12]. Acidic comonomers such as AA (acrylic acid), IA (itaconic acid) are incorparated not only to improve the hygroscopicity but also to help the cyclization of the nitrile groups of AN to form ladder structure **(Figure 2.4**) polymer during the stabilization of the acrylic fibers [10].

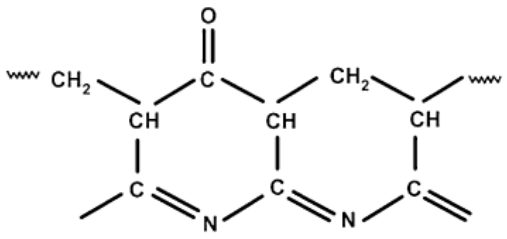


Figure 2. 4: Ladder PAN structure [13].

PAN and PAN based copolymers are synthesized by free radical polymerization and commercially three general methods are used well-known named as solution, suspension and emulsion polymerization methods. In commercial practice solution and particularly suspension polymerization methods are the most commonly used methods.

used in manufacturing of acrylic fibers. Solution polymerization has an advantage of being directly modified into spinning dope for fiber formation.

2.2. Electrospining Method for Producing PAN-based Nanofibers

Electrospining is a significant method that is used to produce nanofibers of polymers. At the process, a non-woven nanfiber mat is obtained by elongating the polymeric fluid under an electric field onto a collector [14].

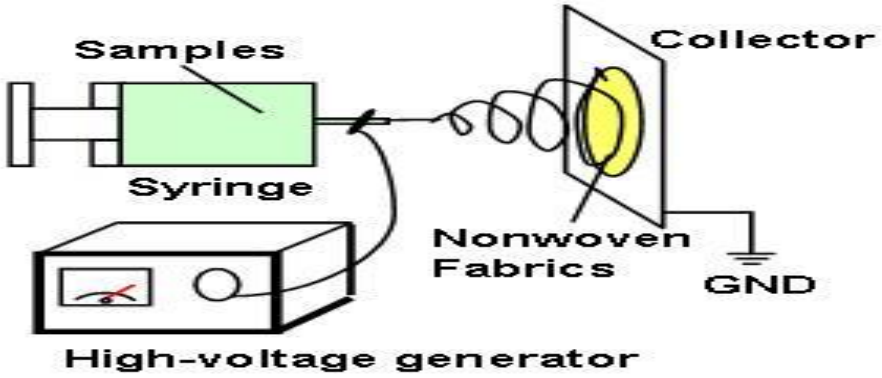


Figure 2. 5: Electrospining setup.

Polymeric fluid is hold in a syringe is ejected from a orifice under the applied high voltage in the form of a polymer solution jet. There is the developed droplet at the tip of the needle is distorted by an electrostatic force creating a conic shape called Taylor cone. As the flow continuous, the properties of the fluid is going to be stabilized due to the repulsion between the charges which rarefies the deformation. The stabilized jet hits the collector emerging in fibers with nanoscale diameters [15-16]. The morphology and diameter of the obtained nanofibers are depends on the solution and process parameters. Solution parameters are consisting of the soluiton viscosity, conductivity and concentration. Process parameters can be explained in the topics such as the applied voltage, flow rate of the solution, the distance betweem the tip of the needle and the collector and the diameter of the needle [16].

Electrospining technique has a common attention in recent years because of facilatating the fabrication of the nanofibrous materials and determining the versatility [17]. Nanofibrous structure of the fibers obtained via the electrospinning method provides many applications areas to bu used such as filtration, catalysis, electronics, fuel cells, sensors and tissue engineering due to their great specialities of having high

value of open porosity combined with significant specific surface area and axial strength and being very flexible [16].

By the usage of the electrospinning method serves variety of polymer solutions or melts, composites and sol–gel ceramics have been successfully electrospun into nanoscale, or ultrafine fibers. Electrospinning method is not commonly used in the industry at present but there is an enormous progress for improving the related equipment and processes.

Nanofibers obtained via electrospining method are used in many fields, such as catalysis, scaffolds for tissue engineering, drug delivery systems, antibacterial agents, super-paramagnetic field-responsive materials, filtration, wound dressings, and so on. Also electrospun nanofibers have potential application areas such asenergy generation, defense and security, biotechnology and environmental engineering, and healthcare [18].

Nanofiber mats have submicron fiber size and high interconnecting pore networks that appealing more interest on this issue. Electrospinning process is the most cost-effective way to produce nanofiber mats and a simple approach to fabricate fiber mats with diameters of the fibers ranging from the submicrometer size to the nanometer range. Carbon nanofiber mats can be prepared by stabilizing and then carbonizing a precursor electrospun organic nanofiber mat, such as polyacrylonitrile (PAN) nanofiber mats. When the fiber diameter decreases from micron to nanoscale level, the heat treatment process should be carefully adjusted to control the defects in the nanofibers [19].

2.3. PAN-based Carbon Fibers

Carbon fibers are the fibers that have at least %92 wt% carbon in their composition. Carbon fibers can have crystalline, amorphous or partly amorphous structure [20]. Carbon fibers are very important in the industry due to their wide range of applicational areas such as aviation, aerospace, defense areas, civil enginnering and other new induatrial areas [4,21,22]. Carbon fibers is becoming a significant area of high technology such as aeroscape industry and defense application areas due to properties of resisting against high temperature and chemical and environmental effects [6]. This properties lead to develop the high-strain and high-performance carbon fibers [22].

Polyacrylonitrile (PAN) based precursors are the mostly used precursor at production of carbon fibers [2,6,9,15,21,23,24]. 90% of the produced carbon fibers are obtained from PAN. The rest of the production is made from phenolic, rayon or pitch fibers. PAN fibers are more expensive than rayon fibers but due to the high yield of production of carbon fiber from PAN fiber, which is twice that of rayon, PAN precursor is preferred. Pitch carbon fibers have poorer strength and non-reproducibility of their properties. So, PAN is the most appropriate precursor for obtaining high-performance carbon fibers [22].

Due to its unique and well-known chracateristic PAN is an important precursor used for carbon fiber applications [25]. Among the precursors PAN-based precursors are the most suitable materials for carbon fiber production [6]. A high-quality PAN procures most of the necessities of having high molecular weight distribution, appropriate molecular weight distribution, high tacticity and high purity to obtain high-quality carbon fibers [25]. The properties of the obtained carbon fibers can be developed by increasing the molecular weight of the precursor [6]. Carbon fibers made from PAN precursor have some other specialities of high tensile strength and Young's modulus, high heat resistance and low density [21]. However, PAN homopolymer has been hardly used owing to its poor stabilization and spinnability [2,4]. Due to these properties PAN is mostly incorporated with a certain amount of acidic comonomer such as acrylic acid (AA), methacrylic acid(MA) and itaconic acid to produce high performence carbon fibers [2,4,15]. It is especially aimed to improve the solubility and spinnability of the polymer for enhancing the stabilization that is the critical point of obtaining high-performance carbon fiber [4].

2.4. Oxidation and Carbonization Treatment of PAN-based Polymers

An important step of converting PAN fibers into carbon fiber is the stabilization PAN fibers are by heat in the presence of air or oxygen-containing atmosphere at temperature range 200°C to 300°C for one or more hour. The stabilized fiber has a ladder polymer form with this process. [22,24]. After this process the fibers can be hetaed up to the carbonization temperatures between ~1000 and 1300 °C [23]. The white colored PAN fibers turn to golden yellow, orange, then tan-brown and finally black through the oxidation process [26].

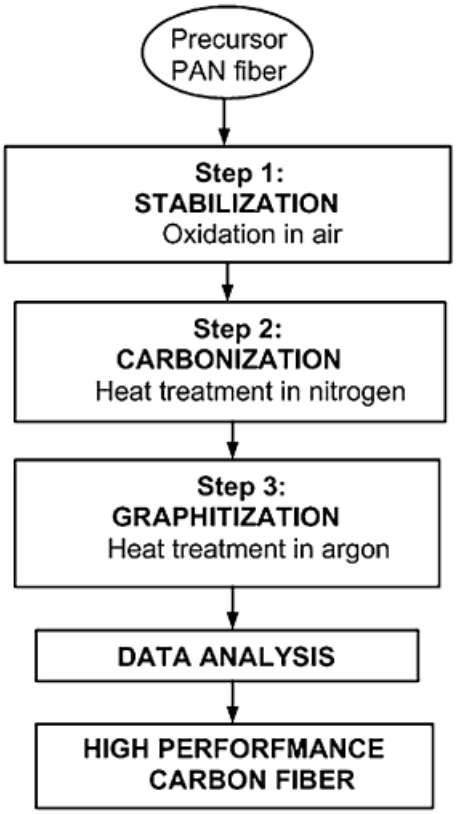


Figure 2. 6: The steps of producing carbon fiber from PAN fibers [13].

PAN fiber precursor are converted into carbon fiber by the heat treatment process. Currently 90% of all commercial carbon or graphite fibers are produced by the thermal conversion of a PAN precursor. The successful

conversion of PAN to high strength, high modulus fibers depend in part upon the understanding of the oxidative and thermal treatment. The three steps for the conversion of precursor of PAN-based fiber to carbon, which are as follows. As listed by Liu et al. [27];

i. Oxidative stabilization, which forms ladder structure to enable them to undergo processing at higher temperatures.

ii. Carbonization at high temperature, (<1600 °C) to keep out noncarbon atoms.

iii. Graphitization step Further heat up to 2000 °C to improve the orientation of the basal planes and the stiffness of fibers.

Many studies has been related to the stabilization of PAN during 1950s and 1960s. It has been taken 40 years to understand the modern belief of stabilization reaction is

that the nitrile groups of PAN undergoes a cyclization reaction as shown in **Figure 2.7** [32]. The reaction steps involved in the formation of stabilized PAN (fibres) have been studied and confirmed by several authors [3, 8, 28-31]. The schematic indication of the thermal degradation of PAN homopolymer is shown in the **Figure 2.7**.

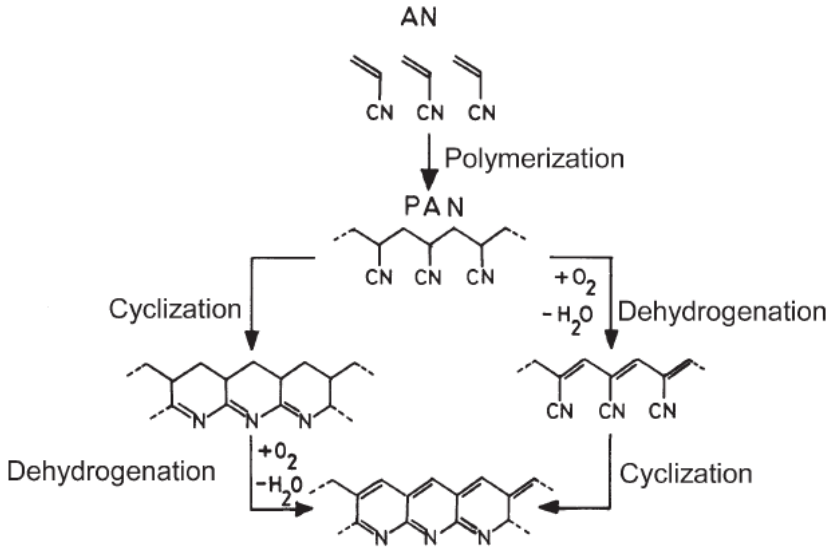


Figure 2. 7: Mechanistic pathways for the thermal degradation of PAN.

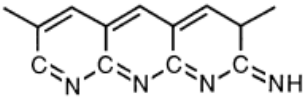
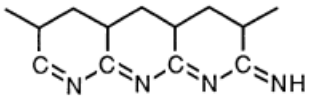
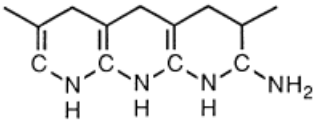
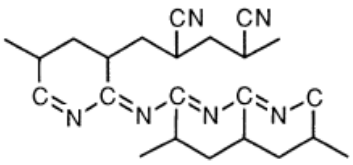
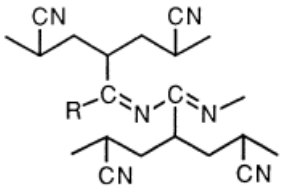
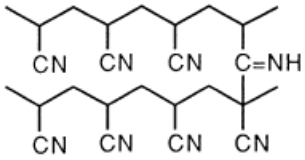
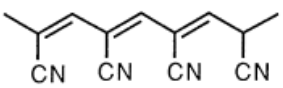
In some previous researches the reactions of the C≡N group of PAN was indicated briefly. As mentioned by Bashir and Dalton et.al., there are various schemes and studies shows the stabilization and cyclization of PAN during the oxidation process [23,24]. All the reactions occured at oxidation step stated in detail at the literature are given in **Table 2.1**

As given in details in the **Table 2.1** the reactions of PAN during stabilization was firstly indicated by Houtz [33] stating the formation of a heteroaromatic, cyclic structure Grassie et al. [34] Burlant [35] and Parsons LaCombe [36] was stated the cyclic polyimine structure referred to as ‘‘ladder polymer” and later researches has done by Coleman and Petcavich [37] Fochler et al. [38]. Xue et al. [39] explained the sustained tautomerization to a polyenamine structure and isomerization and further reactions.

It has also been suggested by Grassie and Hay [40], Olive [41] and Schurz [42] that various types of intermolecular crosslinking reaction that may ocurduring the stabilization reactions.

The possible dehydrogenation that may result in conjugated polyenes is suggested by Berline et. al. [43] Fester [44].

Table 2. 1: Stabilization reaction schemes reported in the literature [23,24].

		Structure	**Reference**
1	Heteroaromatic cyclic structure		Houtz [33]
2	Polyimine cyclic structure (ladder polymer)		Grassie et al. [34] Burlant [35]and Parsons LaCombe [36
3	Polyenamine cyclic structure		Coleman and Petcavich [37] Fochler et al. [38] Xue et al. [39]
4	Propagation crosslink		Grassie and Hay [40]
5	Intermolecular nitrile crosslink		Olive´ and Olive´ [13]
6	Azomethine crosslink		Schurz [41]
7	Conjugated polyene		Berline et. al. [43] Fester [44]

Due to the some difficulities PAN precursor are preffered to be used as copolymers. Acidic comonomers suc as itaconic acid and acrylic acid are used as comonomers of PAN to facilitate the cyclization reactions during the oxidation process.

It has been claimed that the initiation of cyclization in the presence of an acidic comonomer takes place by an ionic mechanism. The mechanism given below is expected during the heat treatment of PAN with an acidic comonomer.

At the first step of the nucleophilic attack on a nitrile group by $–COO^-$ followed by the cyclization of isotactic sequences along the polymer chain as shown in **Figure 2.8.** The carbonyl group further helps in the acidic comonomer helps crosslinking of the chains through dehydrogenation reactions in the subsequent carbonization step [45].

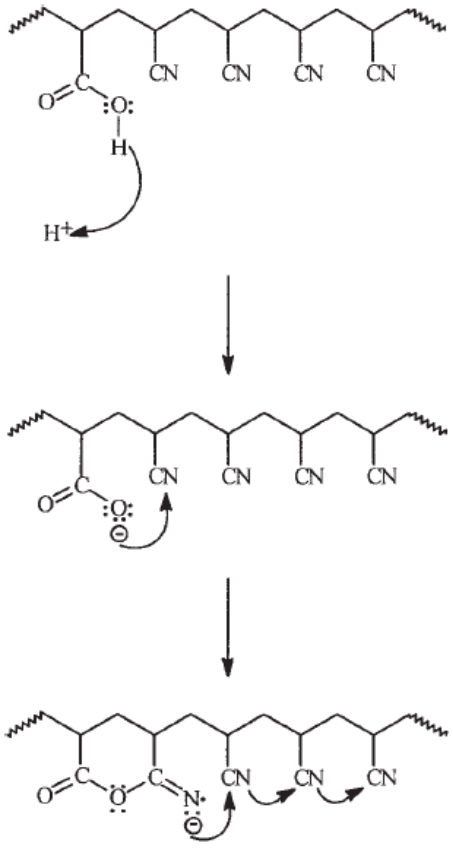


Figure 2. 8: Cyclization initiation through nucleophilic attack on a nitrile group by a $–COO^-$ group.

At the following steps ot thermal oxidative stabilization rearrangement of the structures to give enamine– imine equilibrium is expected as shown in **Figure 2.9** and this is followed by oxidation as shown in **Figure 2.10.**

Figure 2. 9: Rearrangement of the imine to enamine.

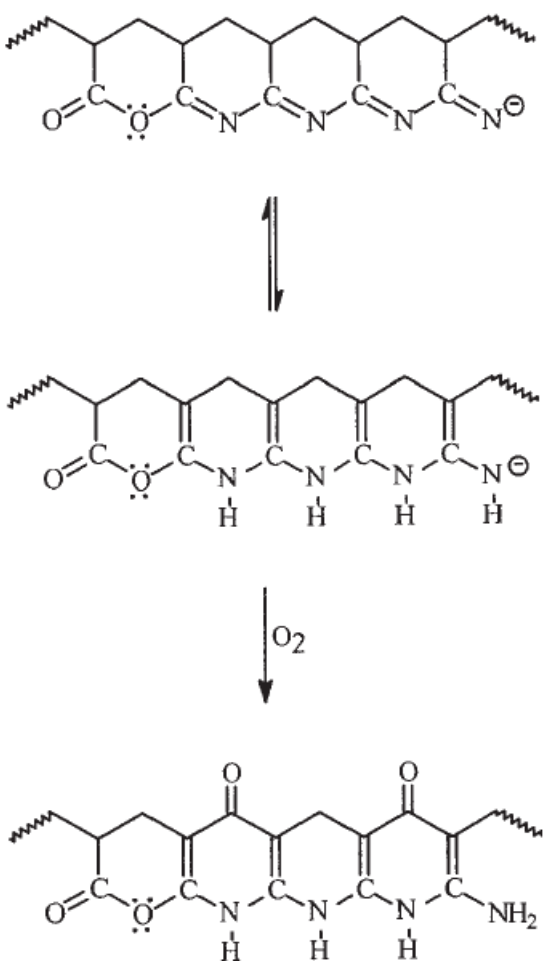
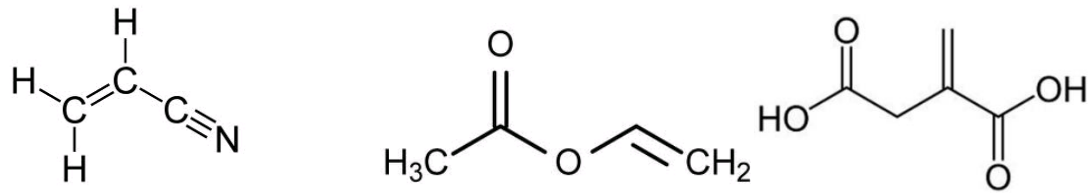


Figure 2. 10: Rearrangement and oxidative reactions of the tetrahydropyridine structure.

3. EXPERIMENTAL PART

3.1.Materials

Acrylonitrile (99.5>%) and Vinylacetate (99.5 %) was provided by the AKSA Acrylic Chemistry Company. Itaconic acid (99.5>%) was obtained from Sigma Aldrich. Ammoniumpersulfate (APS), (99.5>%), dimethylformamide (DMF) and ethanol were provided from Sigma Aldrich.



Acrylonitrile **Vinyl acetate** **Itaconic acid**

Figure 3. 1: The molecular formulas of the acrylonitrile, vinyl acetate and itaconic acid monomers.

3.2. Equipments and Analysis

3.2.1. Viscosity measurements

Viscosity measurements are used to determine the molecular weight of a polymer by correlating the polymer size with the viscosity. A pure solvent under laminar flow experiences a shear rate gradient due to frictional forces at the walls of the capillary. As a polymer particle in solution flows through the capillary it experiences different shear rates depending on its size. The result is in an increase in drag and therefore an increase in the viscosity of the solution. The viscosity is therefore related to the size. The relative viscosity, η_{rel}, of the polymer solution is given by the ratio of the solution viscosity, η, to the solvent viscosity, η_o.

$$\eta_{rel} = \eta / \eta_0 \qquad \textbf{Equation 3.1}$$

The specific viscosity , η_{sp}, is the relative viscosity minus one.

$$\eta_{sp} = \eta_{rel} - 1$$ **Equation 3.2**

The intrinsic viscosity, [η], is the zero concentration limit of the specific viscosity divided by the concentration [46].

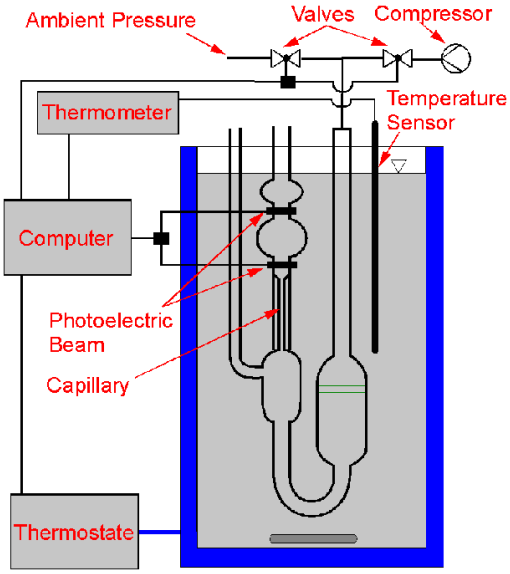


Figure 3. 2: Experimental setup of viscosity measurements.

3.2.2. Gel permeation chromatography (GPC)

Gel Permeation Chromatography (GPC) method mostly known as size exclusion chromatography is used to seperate and determine the relative molecular weight of polymer samples. GPC is an important analysis method for both analytic and preparative work with a wide variety of solvents and polymers ranging from low to very high molecular weights. GPC is mostly used to characterize polymers by determinining the molecular weight distribution of them. GPC method improves the SEC especially used in characterization of copolymers at determination of the molecular weight by using differential refractive index (DRI) detector and also for getting compositional information by combining chromatograms from DRI and UV detectors [47].

In this study GPC was used to analyze the number avarage molecular weight and weight avarage molecular weight of the terpolymer samples. The obtained information was used to determine the molecular weight distribution of the samples. The analysis were realised at TUBİTAK MAM Institute of Chemistry by GPC Agilent 1100 Series.

3.2.3. Fourier transform infrared spectroscopy –attanuated total reflectance (FTIR-ATR)

Infrared spectroscopy is a commonly used method to investigate of polymer structure and the analysis of functional groups. IR spectrometers are used to study samples in the gaseous, liquid, and solid state, depending on the types of accessories used. IR has been used to characterize polymer blends, dynamics, surfaces, and interfaces, as well as chromatographic effluents and degradation products. It is capable of qualitative identification of the structure of unknown materials as well as the quantitative measurement of the components in a complex mixture [47].

In this study FTIR is used with the ATR accessories. It is used to investigate the structure of the synthesized homopolymer, copolymer and terpolymers. Quantitative measurements of the specific group of the polymer is indicated. Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal model FTIR-ATR is used at the studies.

3.2.4. Nuclear magnetic resonance (NMR) spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a very efficient method used to describe the structure and dynamic of polymers and compounds[1]. This methosd is mostly used to make structure analysis to identify the atom or atom groups in a molecule and the position of these groups to relative to each other. Chemical reaction rates can be studied with the time scale involved in NMR measurements. Some other measurments such as isomerism, internal relaxation, conformational analysis, and tautomerism can be done with this method.

Nuclear magnetic resonance spectroscopy is a form of absorption spectroscopy and concerns radio frequency (rf)-induced transitions between quantized energy states of nuclei that have been oriented by magnetic fields [47]. NMR spectroscopy has been proven to be one of the most important and reliable techniques forstudying polymer structure and copolymer composition [48].

In this study ^{1}H NMR method is used to describe the structure of the terpolymers. The conversion of hthe monomers and the reactivity ratios of the monomers are calculated. Agilent VNMRS 500 MHz Nuclear Magnetic Resonance Spectrometer is used at the measurements.

3.2.5. Thermal gravimetric analysis (TGA)

Thermal Gravimetric Analysis **(**TGA) is used to make quantitative measurements of any mass change caused by a transition or thermal degredation in the sample. TGA measures the change in mass due to dehydration, decomposition, or oxidation of a polymer with time and temperature. Due to the unique sequence of the physicochemical reaction occuring at specific temperature range and heat rate and being a fuction of molecular structure, thermogravimetric curves are specific for a given polymer or compound. TGA curves, data concerning the thermodynamics and kinetics of the various chemical reactions , reaction mechanisms and the intermediate and final reaction products are obtained. Other processes that can be studied by TGA are adsorption and desorption phenomena, reactions with purge gases, ash content analysis, quantitative determination of additives ,solid-state reaction composition of filled polymers, rates of evaporation,sublimation and at the estimation flame-retardancy of polymers [47].

The principle of thermogravimetric analysis is based on a thermobalance which describes an instrument and is shown in the **Figure 3.3** that continuously measures the weight changes of a substance at gradually varying temperatures [49].

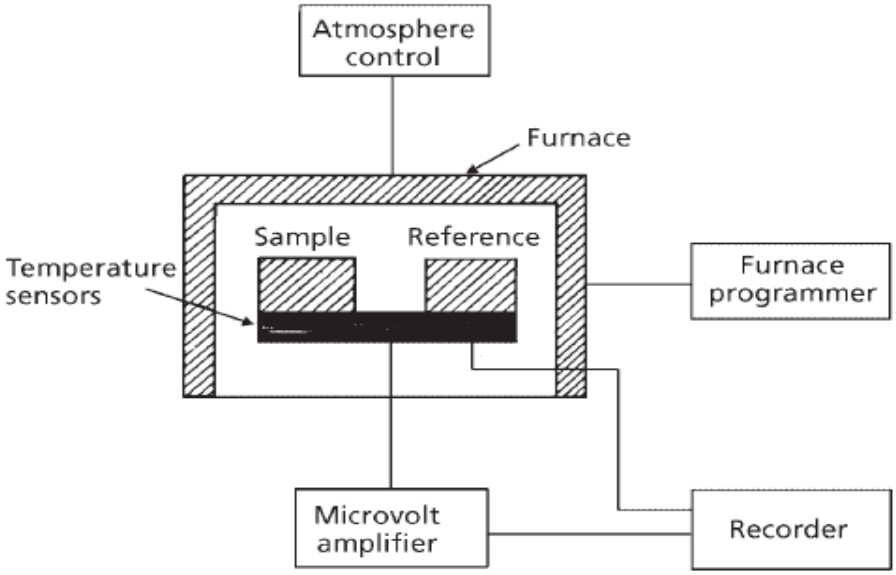


Figure 3. 3: Schematic diagram of TG apparatus.

In this study thermal gravimetric analysis is used to describe the thermal degradation and stability of the synthesized terpolymers. It is aimed to observe the polymers stability at wide temperature range varying from 0°C to 800°C. Thermal Analysis TGA Q50 model

thermal gravimetric analyzer is used to examine some thermal properties of the terpolymer samples.

3.2.6. Differantial scanning calorimetry (DSC)

Thermal analysis is a term DSC term is used by IUPAC for any apparatus used at measuring thermal power in a temparature scan irrespective of the mode of operation. In DSC mesaruments, the reference and the sample are heated in a furnace where in the temperature is altering with the time during the process. At the initial position the temperature diffrence between the reference and the sample is zero. The difference between the temperature of the reference and the sample is selected as a fuction of the furnace temperature. Due to the exchange of the heat wtih the surrounding environment, temperature difference between the reference and the sample is observed when a physical change occurs in the sample [50]. DSC-DTA curves show the physical or chemial change in the energy of the system under investigation. DSC method is used to measure the heat needed to preserve the same temperature in the sample against a reference material in the furnace. Enthalpy changes are observed due to the change of the state of the sample. There are many physical changes measured by DSC such as glass transition temperature (Tg) the crystallization temperature (Tc), the melt temperature (Tm), and the degradation or decomposition temperature (TD). Also, chemical changes due to polymerization reactions, degradation reactions, and other reactions affecting the sample can be mesaured by this method [47].

In this study DSC is used to determine the physical changes occuring in the synthesized terpolymers to characterize some thermal properties of them. DSC TA Q1000 is used at the measurements. The samples are heated from 0°C to 250°C with the heat rate of 10 °C/dk.

3.2.7. Atomic force microscopy (AFM)

In AFM setup a fine tip takes a part to measure surface morphology and properties through an interaction between the tip and surface. AFM uses a constant force maintained between the probe and sample while the probe is raster scanned (parallel lines) across the surface. By monitoring the motion of the probe as it is scanned across the surface, a three dimensional image of the surface is constructed. The atomic force microscope (AFM) is a method of synthesizing of the mechanical profilometer, using

mechanical springs to sense forces, and the STM (Scanning Tunneling Microscopy), using piezoelectric transducers for scanning [51].In this stduy atomic force microscope is used to monitor the surface of nanofiber mat and analyze the surface characteristic of it. Nanosurf Easysacn 2 model AFM is used at this study.

3.3. Copolymerization and Terpolymerization of Comonomers

Terpolymerization of acrylonitrile,vinylacetate and itaconic acid termonomers were made by free radical polymerization. The polymerization technique is solution polymerization technique. APS was used as initiator. The polymerization is accesed in a three necked flask. The total monomer feed was 10 g for all terpolymers, copolymers and homopolymer of PAN. The monomers were mixed in the three necked flask for 20 minutes. 0.8 g APS is dissolved in 30 ml of distilled water and added to the monomer mixture. The total mixture was 70 ml. The monomer feed ratios for terpolymers were 90:9:1, 89:9:2, 88:9:3, 87:9:4, 86:9:5 (AN:VAc:IA). The polymerizations were proceed at 60° C. The polymerization were completed generally in 3 hours. The synthesized polymer is washed with excess ethanol and distilled water. The filtered polymers are dried under the vacuum for 12 hours. The copolymers of AN:VAc and AN:IA were synthesized with the same process steps of the terpolymers. The monomer feed ratios of the copolymers were 85:15 (AN:VAc) and 85:15 (AN:IA). The PAN homopolymer was synthesized by the same process. The APS amounts were same for all polymerization processes.

Table 3. 1: Feed ratios of monomers, initiator amounts and polymerization time.

CODE	**AN (g)**	**VAc(g)**	**IA(g)**	**TIME (hour)**
I1	9	0.9	0.1	3:00
I2	8.9	0.9	0.2	3:00
I3	8.8	0.9	0.3	2:30
I4	8.7	0.9	0.4	1:45
I5	8.6	0.9	0.5	1:50
C2	8.5	1.5	0	3:00

4. RESULTS AND DISCUSSION

4.1. Characterization of P (AN-co-VAc-co-IA) Terpolymers

P(AN-co-VAC-co-IA) terpolymers are particularly characterized with several techniques. The viscosity values of the polymers are measured with Ubbelohde viscosimeter method. Molecular weight distribution of the polymers are measured with Gel Permeation Chromatography. Terpolymers are also spectroscopicly characterized by FTIR-ATR and NMR methods. FTIR analysis of P(AN-co-VAc-co-IA) terpolymers were performed with FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal). ^{1}H NMR spectroscopy of P(AN-co-VAc-co-IA) terpolymers in deuterated dimethyl sulfoxide (DMSO-d_6) was performed using a Agilent VNMRS 500 MHz spectrometer.

Thermal characterization of the terpolymers are made by DSC and TGA methods. Spinnability of the polymers are checked by electrospinning. The electrospun nanofibers are morphologically caharacterized by SEM and AFM. In addititon to this, the electrospun terpolymers are oxidized at different temperatures varying from 200°C to 325°C in order to observe the oxidation phenomena of the terpolymers. The oxidized and carbonized terpolymers are characterized spectroscopically by FTIR-ATR and morphologically by SEM and AFM.

4.1.1. Viscosity measurements

The specific viscosity measurements for the polymers were proceed. 0.1 g of each polymers were dissolved in 15 ml of DMF. The prepared solutions were stirred for 12 hours. Polymer solution is diluted by adding 2 ml of DMF for each time. The measurements were proceed for five different polymer concentration. The viscosity of the polymer solutions were measured with Ubbelohde viscometer replaced in temperature-controlled bath setup that is shown in **Figure 4.1.** The measurements are made at a stable temperature 30°C±1.

Figure 4. 1: The setup used for viscosity measurements consisting of Ubbelohde viscosimeter and temperature controlled water-bath.

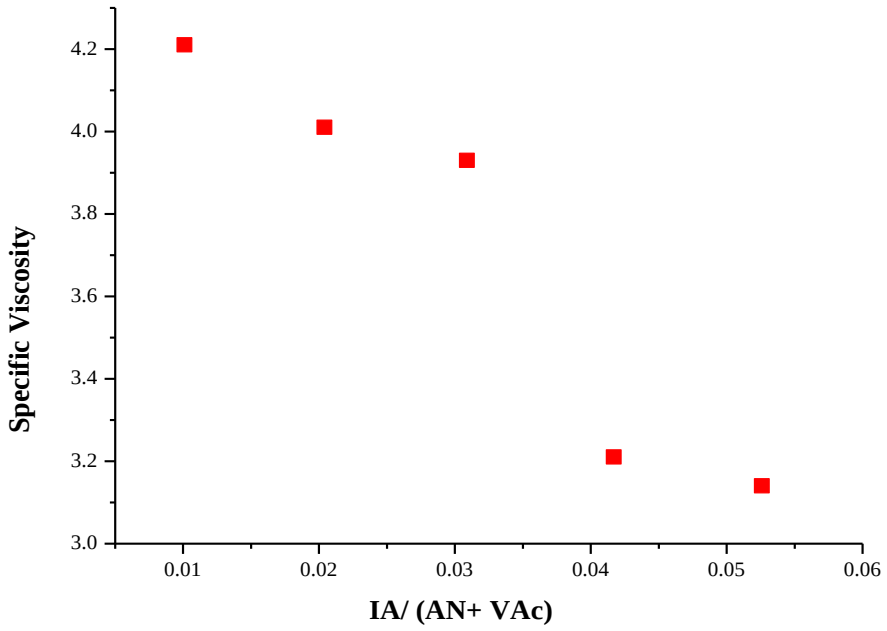


Figure 4. 2: The change of the specific viscosity value of the terpolymer with the initial monomer feed ratio.

It is observed from the graphs at the **Figure 4.2.** as the IA monomer feed ratio increases the specific viscosity of the terpolymer solutions have a trend of decreasing.

4.1.2. Gel permeation chromatography

The synthesized terpolymers molecular weights are measured with gel permeation chromotography method. DMF is used as the eluent at the measurements and the standard calibration was lineer poly(methly methacrylate) standard.

The composition of the monomer feed ratios ,the number average molecular weight (M_n), the weight average molecular weight (M_w) and polydispersity index (PDI) values for the polymers are given in the **Table 4.1.**

It is determined that terpolymers have high molecular weight distribution.

Table 4. 1: The percentage of the monomer feed ratios, the number avarage molecular weight (M_n), the weight average molecular weight (M_w) and polydispersity index (PDI) values.

Code	AN(%wt)	VAc(%wt)	IA(%wt)	M_n (g/mol)	M_w	PDI
I1	90	9	1	213,020	580,400	2.72
I2	89	9	2	152,210	486,470	3.20
I3	88	9	3	161,370	474,720	2.94
I4	87	9	4	135,900	426,240	3.14
I5	86	9	5	124840	415,850	3.33

4.1.3. Fourier transform infrared spectroscopy –attanuated total reflectance (FTIR-ATR)

The synthesized PAN homopolymer, P(AN-co-VAc) copolymer and P(AN-co-VAC-co-IA) terpolymers are characterized spectroscopically by FTIR-ATR. The spectrums of each terpolymer, P(AN-co-VAc) copolymer and PAN homopolymer were shown at **Figure 4.3.**

The -C≡N streching peak of acrylonitrile unit of the polymer chain is observed at 2243 cm^{-1} . The absorption bands of 2937 cm^{-1} and 1455 cm^{-1} is attributed to -CH_2 streching and bending peaks. The peak at 1358 cm^{-1} is related to –CH peak of acrylonitrile units [2].

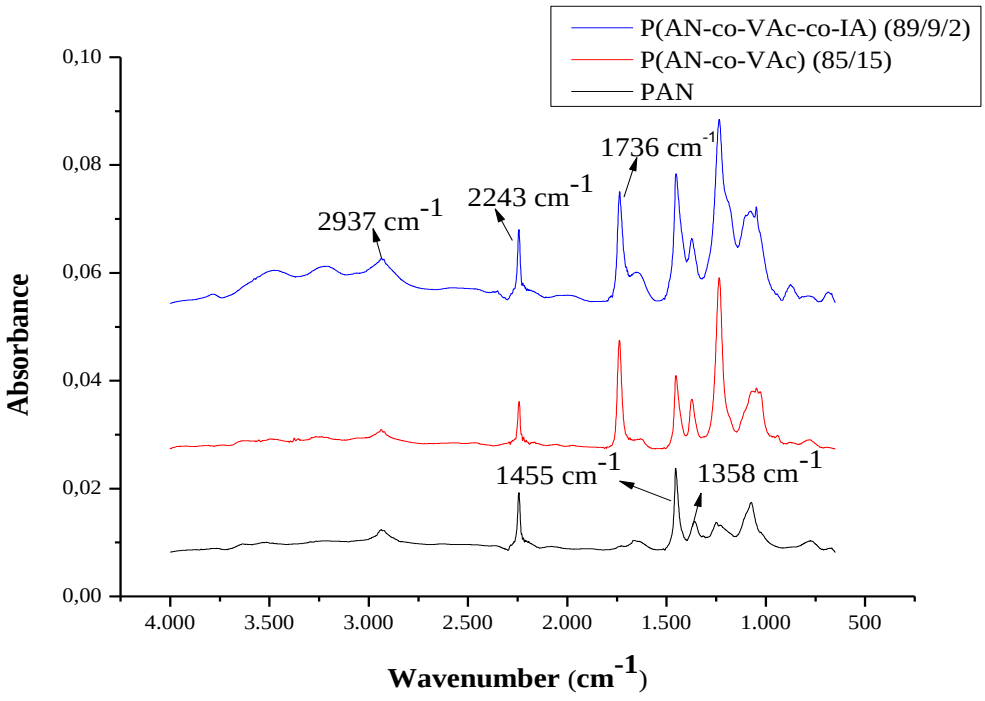


Figure 4. 3: FTIR-ATR spectrums of P(AN-co-VAc-co-IA) (I2), P(AN-co-VAc) (C2) and PAN (A2).

The absorption band at 1736 cm^{-1} is related to C=O groups of itaconic acid [52] and vinyl acetate [35]. The position of the band due to C=O streching vibration changes in the copolymer and shifts to 1665 cm^{-1} oft itaconic acid comonomer unit [52].

Terpolymers having different IA composition with IA monomer feed ratio varying from 1% to 5% caharacterized. The spectrums for five terpolymers are shown in the **Figure 4.4.**

The relation between acrylonitrile and itaconic acid units in the terpolymer was determined by comparing the peak absorptions of AN -C≡N streching vibration peaks at 2243 cm^{-1} and absorptions of C=O streching vibrations attributed to vinyl acetate and itaconic acid at 1736 (A_{1736}) cm^{-1} and 1665 cm^{-1} (A_{1665}) were determined. The ratio of the absorptions of the carbonyl groups to the absorption of the C≡N peak (A_{2243}) is plotted in the **Figure 4.5.** As seen from the Figure the absorbance ratios are increasing with the increment of the fed IA monomer. The initial vinyl acetate feed ratio same for all terpolymer monomer composition. The increase at the absorption of the C=O peaks at 1736 cm^{-1} and 1665 cm^{-1} attributed to the increment of the IA monomer feed ratio.

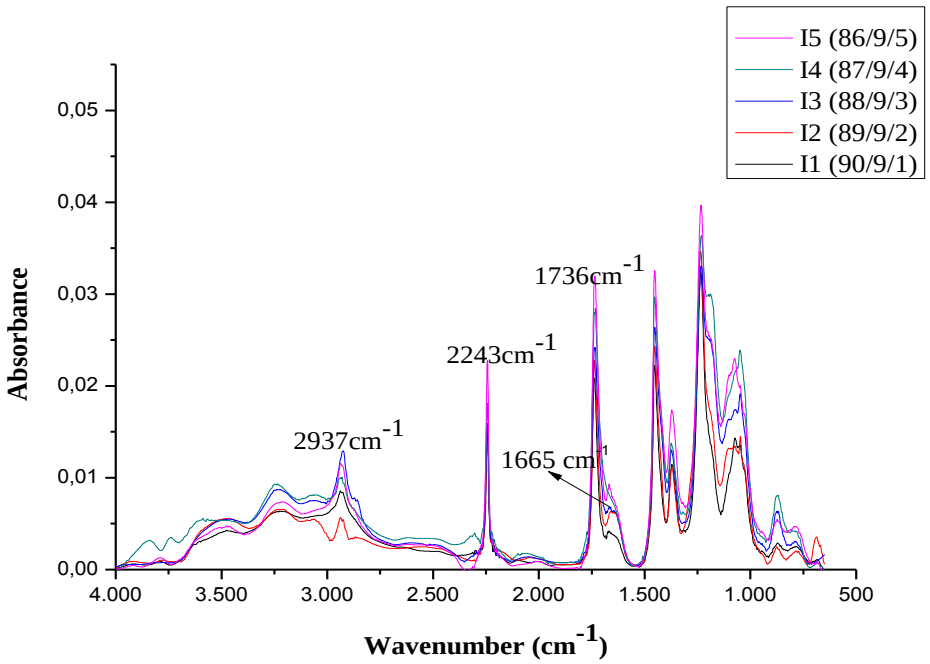


Figure 4. 4: FTIR-ATR spectrums of I1, I2, I3, I4 and I5 terpolymers.

It is procured from the graph at **Figure 4.5**. the absorbance ratios of the peaks is incerasing with increasing initial monomer feed ratio of itaconic acid.

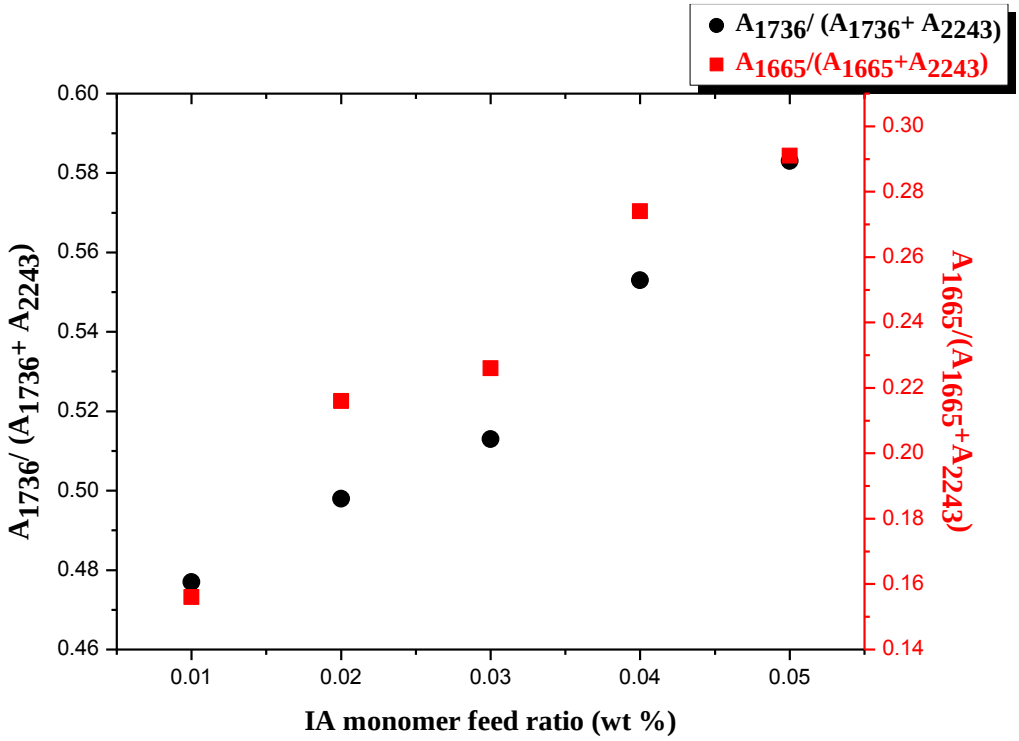


Figure 4. 5: The peak absorbance ratios of A_{1736} , A_{1666} , (A_{2243}) related to initial monomer feed ratios of itaconic acid monomer.

4.1.4. Nuclear magnetic resonance (NMR) spectroscopy

The synthesized terpolymers are characterized by the method of nuclear magnetic resonance spectrally. ^{1}H NMR method is used to indicate the composition of P(AN-co-VAc-co-IA) terpolymers. The ^{1}H NMR spectrum of terpolymer named as I4 is shown in **Figure 4.7.** The signal at 2.2 – 1.9 ppm is related to -CH_2 protons of both AN, VAc and IA [28]. The signals of -CH proton of AN (b) were observed at 3.25 – 3.09 ppm [54]. Observing other peak at 5.13 ppm due to –CH proton of VAc [53]. These peaks are in agreement with literature . The carboxylic proton signals of IA are shown around 6.3-7.8 ppm [28].

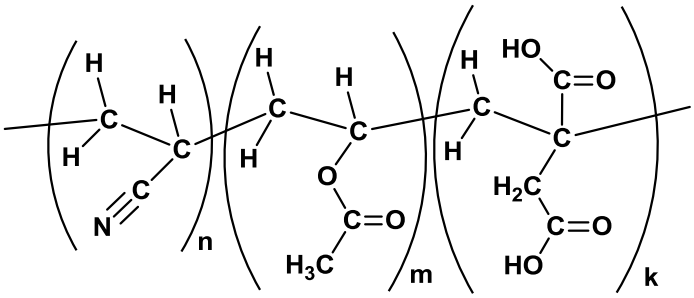


Figure 4. 6: Chemical structure of AN-co-VAC-co-IA terpolymer.

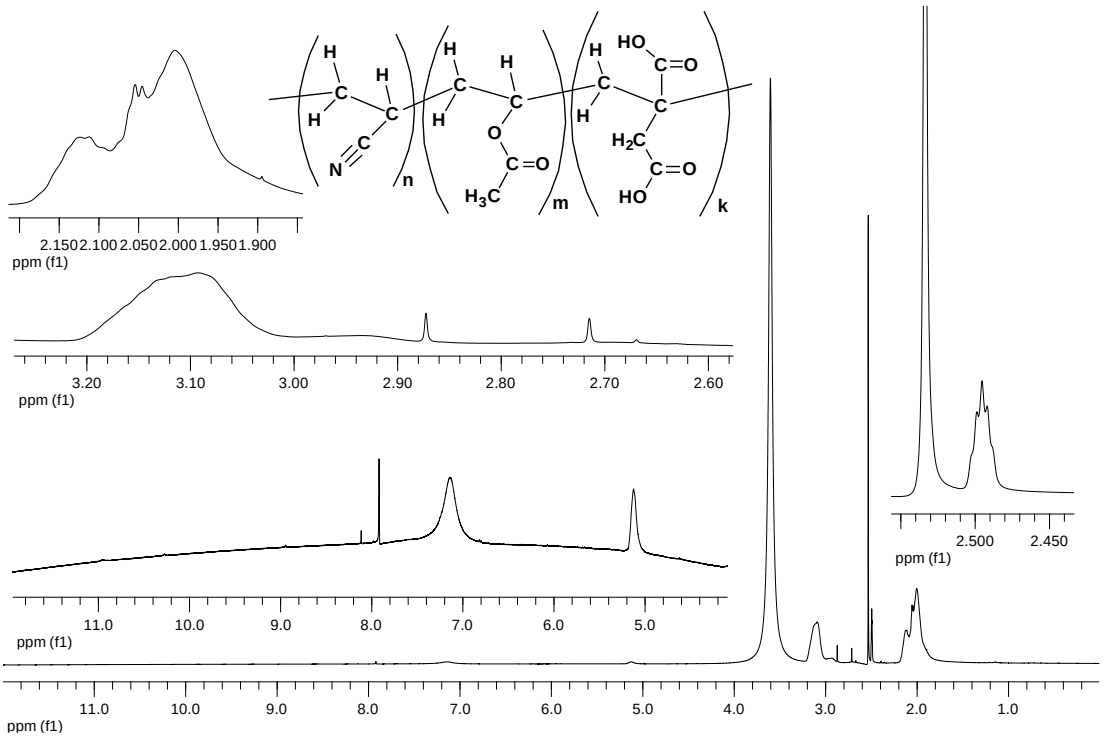


Figure 4. 7: NMR spectra of I4 (87/9/4) terpolymer.

4.1.5. Thermal gravimetric analysis (TGA)

Thermal Gravimetric Analysis of I1, I2, I3, I4 and I5 terpolymers powder were realized in order to determine thermal characteristic of the synthesized samples. The thermogram for the terpolymers are seen in the **Figure 4.8.** The process is practiced in the presence of N_2 with feeding rate of 90 ml/min. The heating rate for this system was 20°C/dk.

As seen from the thermograms of the samples, in the presence of N_2 during the process at high temperatures up to ~ 800°C the remaining polymer in the system is approximately 35% of the total mass fed to the system.

The obtained curves can be evaluated in three parts according to the extent of weight loss. The first step is up to ~ 300°C, where weight loss is very small. This reaction theoretically does not cause any weight loss [55]. The second step is between 300 °C to about 500°C. The rate of weight loss becomes quite rapid, which is mainly due to the dehydrogenation. It implies that IA has promoted the dehydrogenation to some extent [56]. In the last step, fragmentation of polymer chains occurs producing volatile particles leading to weight loss, on the other hand the oxygen uptake reactions taking place cause a certain amount of weight gain through the generation of oxygen-containing groups such as –OH and C=O. Thus, the net weight loss is the total of weight loss and weight gain [2].

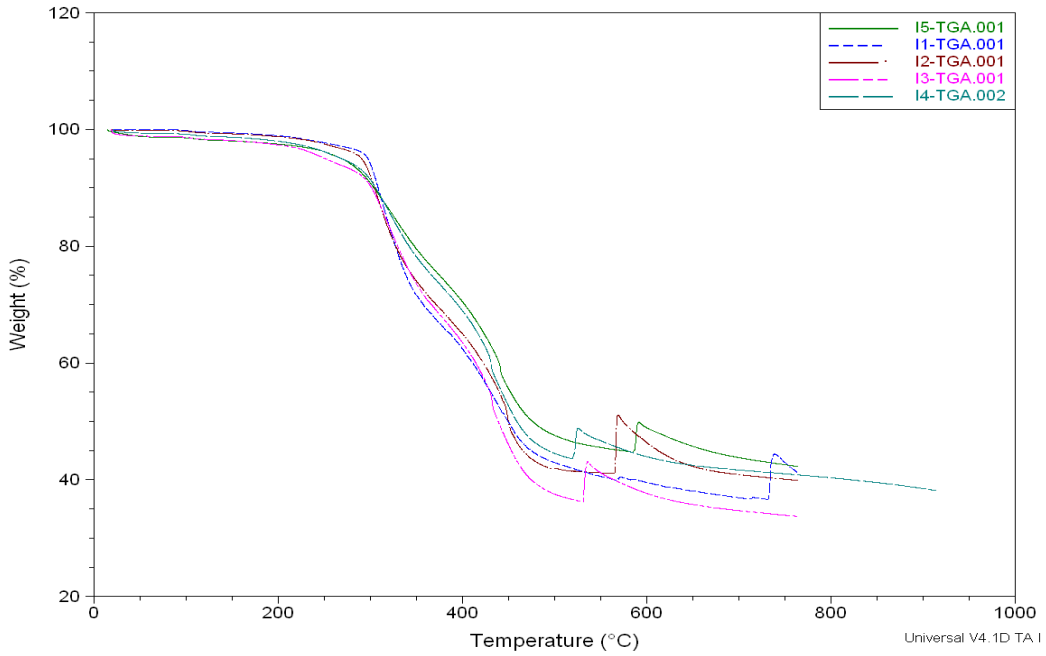


Figure 4. 8: Thermograms of the I1, I2, I3, I4 and I5 polymers.

4.1.6. Differantial scanning calorimetry (DSC)

The thermal caharacteristic of the synthesized terpolymers of I1, I2 and I5 is indicated by Differantial Scanning Calorimetry method. The heating rate of the system was 10 °C/dk. The samples were heated up to 250 °C.

The heated P(AN-co-VAc-co-IA) terpolymers all show a doublet exothermic peak between 85 – 240°C as seen from the **Figure 4.9.** This is because itaconic acid (IA) can initiate the cyclization reactions at a lower temperature through an ionic mechanism [55]. This new exothermic peak at the lower temperature is mainly corresponding to the ionic cyclization reactions. With increasing IA monomer feed ratio, the initial exothermic peak decreases to lower temperatures as shown in the **Table 4.2.**

The initial temperature $(T_{peak})_1$ decrease wtih the icrement of IA monomer feed ratio, that suggests IA is effective to control the exothermic behavior and improve then stabilization treatment. The first exothermic peak $(T_{peak})_1$ at the lower temperature side is assigned to both cyclization reactions and dehydrogenation, and the second peak $(T_{peak})_2$ is attributed to the oxidative reaction [56-57].

Table 4. 2: Exothermic behaviour and related peaks from DSC curves.

Code	$(T_{peak})_1$ (°C)	$(T_{peak})_2$ (°C)
I1	96.35	232.98
I2	91.22	230.10
I5	89.38	227.84

It is stated that in the literature that with the slow heating rate of polyacrylonitrile and polyacrylonitrile based copolymers degrade by underigoing exhothremic cyclization reactions before melting. PAN and its copolymers melts only ander very high heating rates. Under high hetaing rates as 80 °C/min. and above polymer ungergoes melting point before the ezhothermic cyclization reactions occur. When the PAN homopolymer is heated with a heating rate 80°C/min. polymer has a melting point at 340°C and at 160°C/min it melts at 165 °C in the presence of nitrogen. Acrylonitrile copolymer with acidic comonomer usch as acrylic acid doesnt Show a melting endotherm ut with acidic groups of the comonomer the acylization reactions initiate at lower temperatures [58].

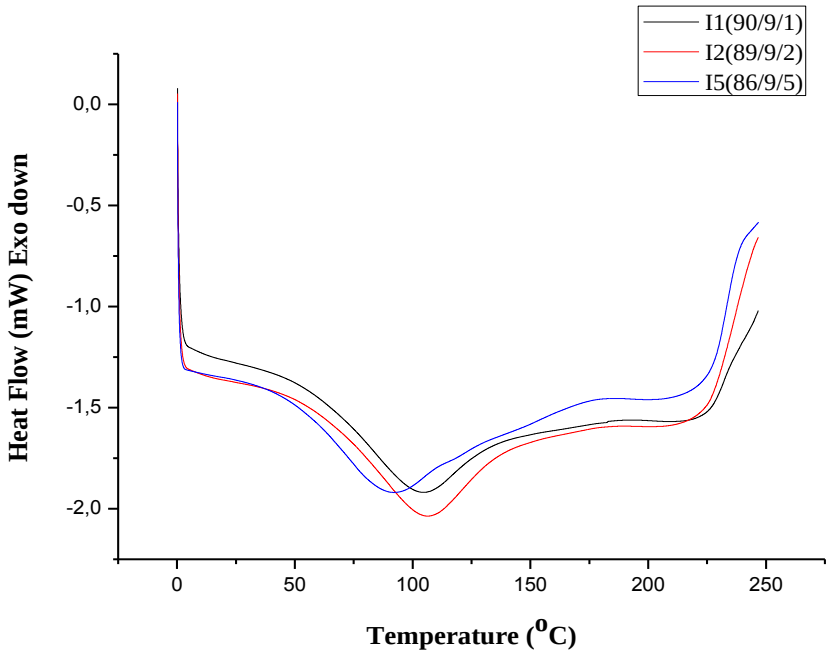


Figure 4. 9: DSC curves of the polymers coded I1, I2 and I5.

4.2. Electrospinning of P(AN-co-VAc-co-IA) Nanofibers

The synthesized terpolymers were dissolved in DMF. 4% (wt %) polymer solutions of the terpolymers which are seen in the **Figure 4.10** were used to electrospin.

The spinning parameters were reported according to the optimum condition to obtain nanofibers of the terpolymers. The electrospinning parameters were same for each polymer. The applied voltage was 17 kV, the distance between the top of the needle to the collector was 20 cm and the feeding rate of the system is 0,8 ml/h. The electrospinning setup is shown in the **Figure 4.11**.

Figure 4. 10: The terpolymer solutions for electrospinning.

The electrospinning apparatus includes a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) with feeding rate from 5.5 μL/h to 400 mL/h, high voltage DC power supplier generating positive DC voltage up to 50 kV DC power supply (ES50 model, Gamma High Voltage Inc., USA) and a grounded alumium collector which is covered with aluminum foil. Solution was loaded into a syringe having 12 mm diameter and positive electrode was clipped onto the dispensing needle having 0.8 mm outer diameter.

Figure 4. 11: Electrospinning equipment.

4.3. Morhology of Elecrospun Nanofibers

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) methods are used to analyze the morphological properties of the polymers nanofiber mat**.** The avarage fiber diameters were measured on the SEM images of the nanofiber mats. 100 number of samples were measured. The Image J program is used to determine the fiber diameters.

4.3.1. Scanning electron microscope (SEM) analysis

Electrospun nanofibers of I1, I2, I3, I4 and I5 terpolymers are morphologically characterized by SEM. The SEM images of the polymers are shown in **Figure 4.12.** All images are obtained from electrospun nanofiber mats of the terpolymers.

The synthesized terpolymers compositions are explained in detail in **Table 4.3** according to their monomer fed ratios to the polymerization system. The terpolymers were electrospun with parameters 17 kV, 20 cm and 0.8 ml/h. Tehe electrospun fibers avaragae fiber diameters are obtained from İmage j program. It is

determined in **Figure 4.13** that with the incerasing itaconic acid monomer feed ratio to the polymerizaton media, avarage fiber diameters are decreasing.

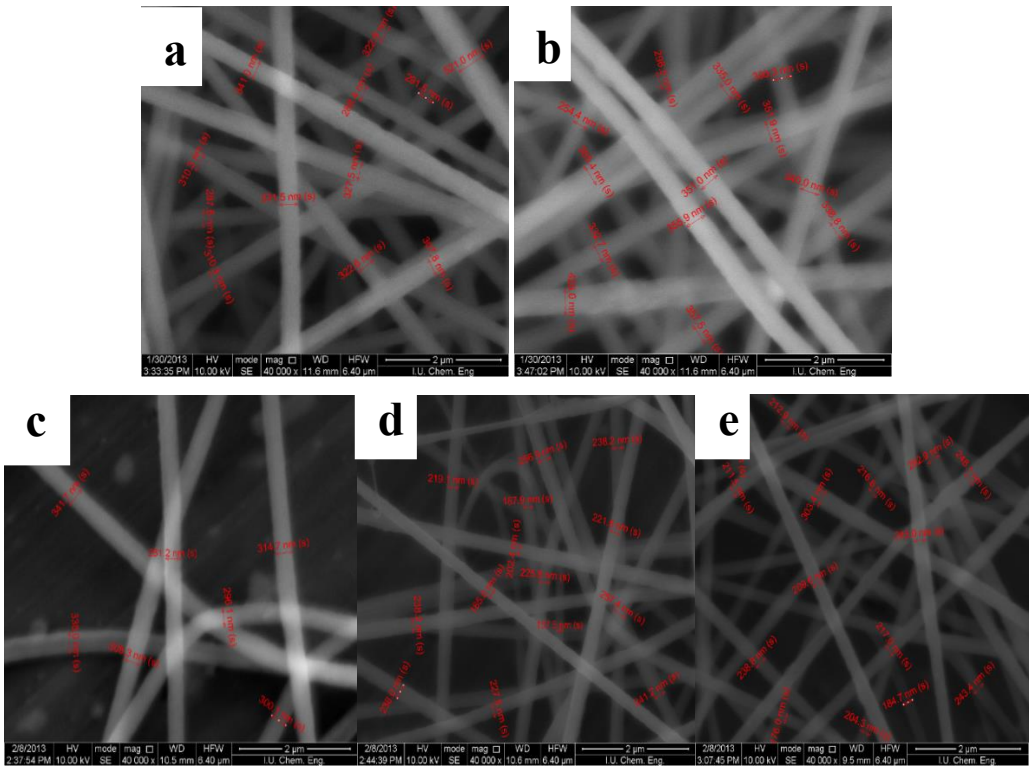


Figure 4. 12: The SEM images of electropun nanofibers of a) I1, b) I2, c) I3, d) I4 and e) I5 terpolymers.

Table 4. 3: The percentage of the monomer feed ratios and average fiber diameter values for electrospun nanofibers of I1, I2, I3, I4 and I5 terpolymers.

Code	AN (%)	VAc (%)	IA (%)	Avarage Fiber Diameter (nm)
I1	90	9	1	362±63
I2	89	9	2	342±65
I3	88	9	3	333±42
I4	87	9	4	235±41
I5	86	9	5	212±47

Avarage fiber diameters for the terpolymers are decreasing from approximately 360 nm to 200 nm. This shows as that with the increasing itaconic acid monomer fed to the terpolymer, fibers with smaller fiber diameters can be obtained. The relationship between the itaconic acid monomer feed raito and avarage fiber diameter and specific viscosity of the polymers are shown in the Figure **4.14**. It is observed from te results that with the increasing itaconic acid monomer feed ratio the

avarage fiber diameter and the specific viscosity values for each terpolymer are decreasing at the same time.

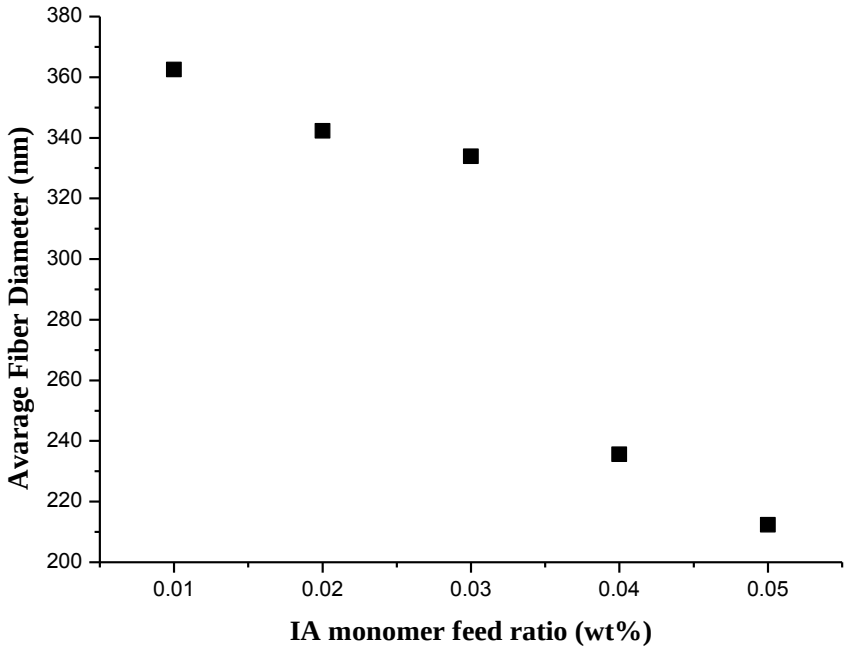


Figure 4. 13: The change at the avarage fiber diameters of the nanofibers with the change of the initial IA monomer feed ratio.

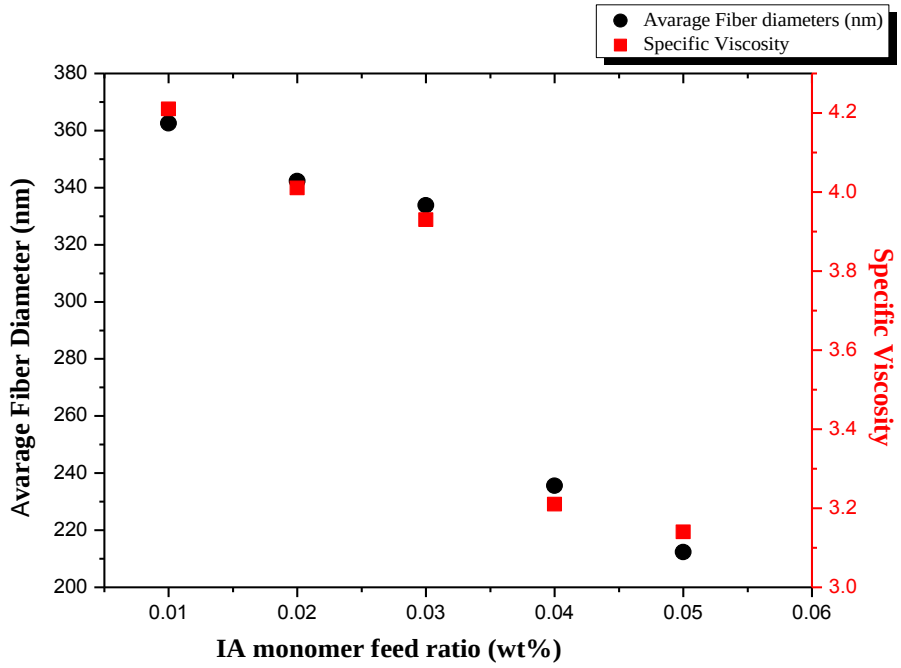


Figure 4. 14: The change of the average fiber diameter of nanofibers and the specific viscosity of terpolymers with the change of the initial IA monomer feed ratio.

4.3.2. Atomic force microscopy (AFM)

The 4% (wt%) solutions of I1, I2, I3, I4 and I5 terpolymers are electrospun. The electrospun fibers are characterized by AFM to attain the surface characteristic of the nanofiber mats. The AFM images of the electrospun nanofibers are seen in **Figure 4.15.**

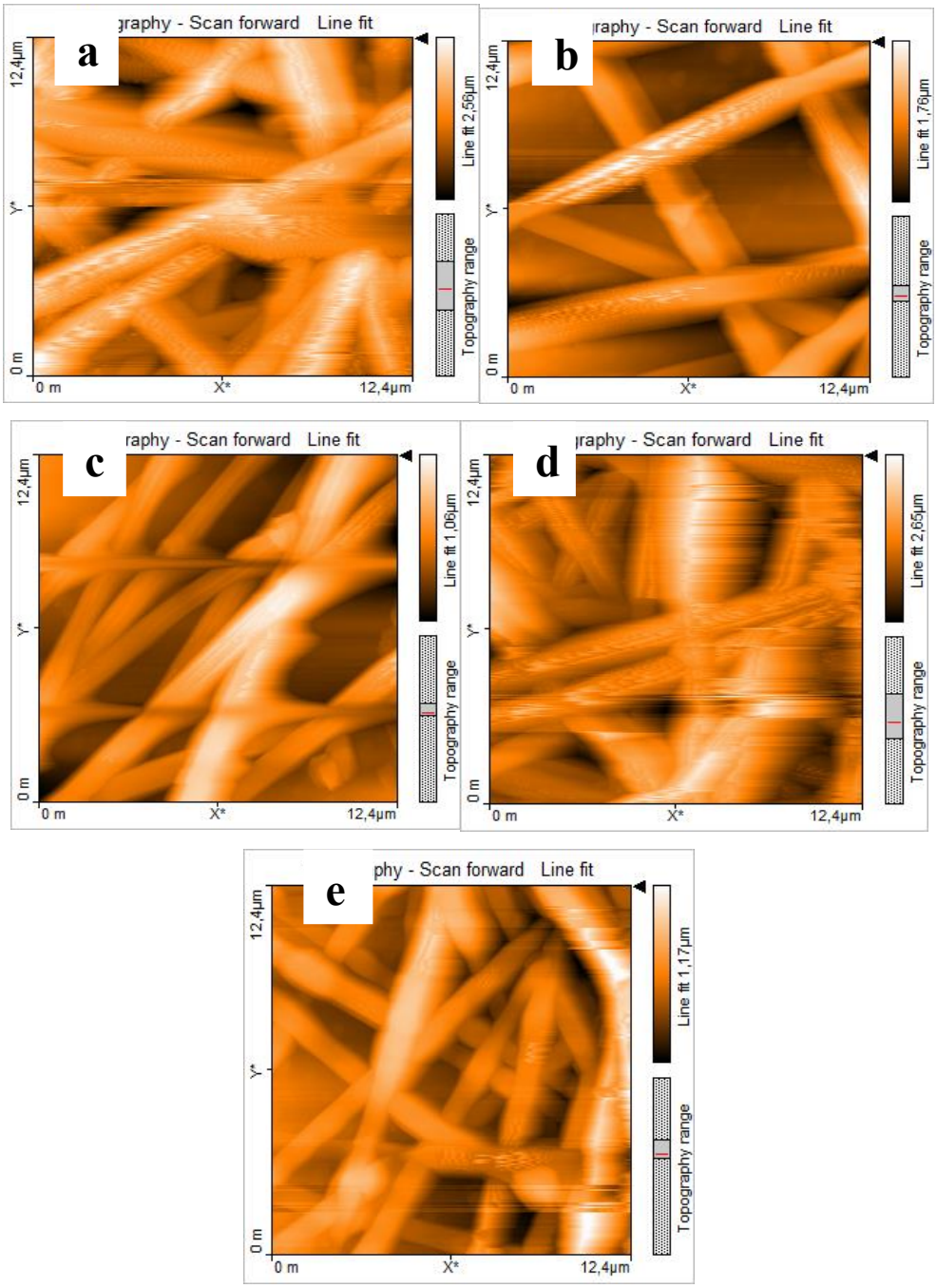


Figure 4. 15: The AFM images of electrospun nanofibers of a) I1, b) I2, c) I3, d) I4 and e) I5 terpolymers.

Table 4. 4: The percentage of the monomer feed ratios and surface roughness values for electrospun nanofibers of I1, I2, I3, I4 and I5 terpolymers.

Code	AN (% wt)	VAc (% wt)	IA (% wt)	Surface Rougness (nm)
I1	90	9	1	337
I2	89	9	2	210
I3	88	9	3	146
I4	87	9	4	234
I5	86	9	5	155

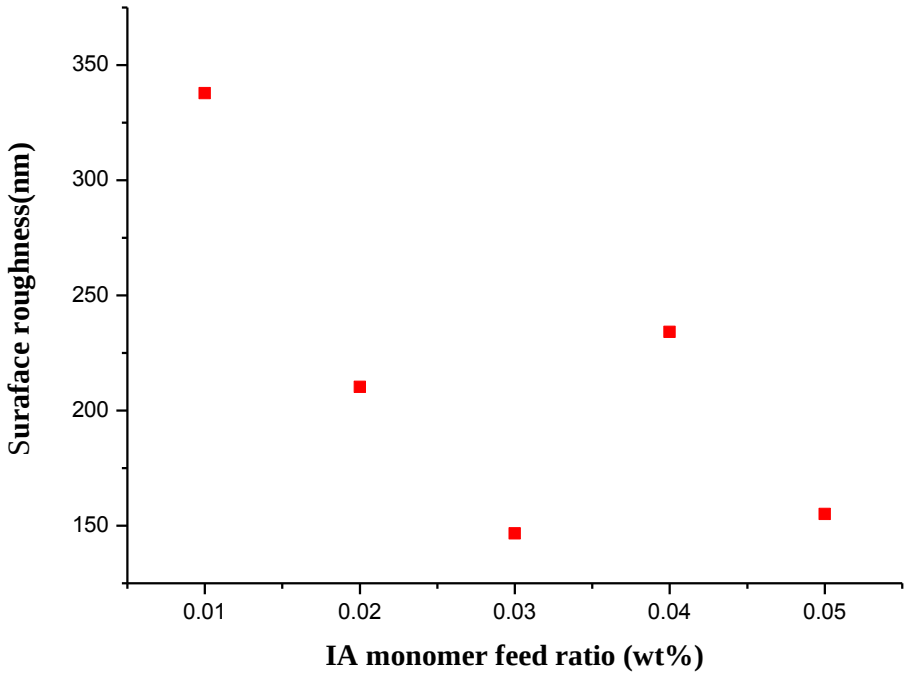


Figure 4. 16: Surface roughness values for I1, I2, I3 ,I4 and I5 terpolymers related to itaconic acid monomer feed ratios.

4.4. Characterization of Oxidized Nanofibers

The 4% (wt %) terpolymer solutions were prepared in DMF and electrospun with the parameters of 17 kV, 20 cm and 0.8 ml/h. The nonafibera were collected on the alumina folio covered collector. The electrospining is proceed for 2 hours at room temperature. The electrospun nanofibers are oxidized at different temperatures varying from 200°C to 325°C in the presence of air for 5 hours. The colour trend of the oxidized nanofibers are shown in the **Figure 4.17**.

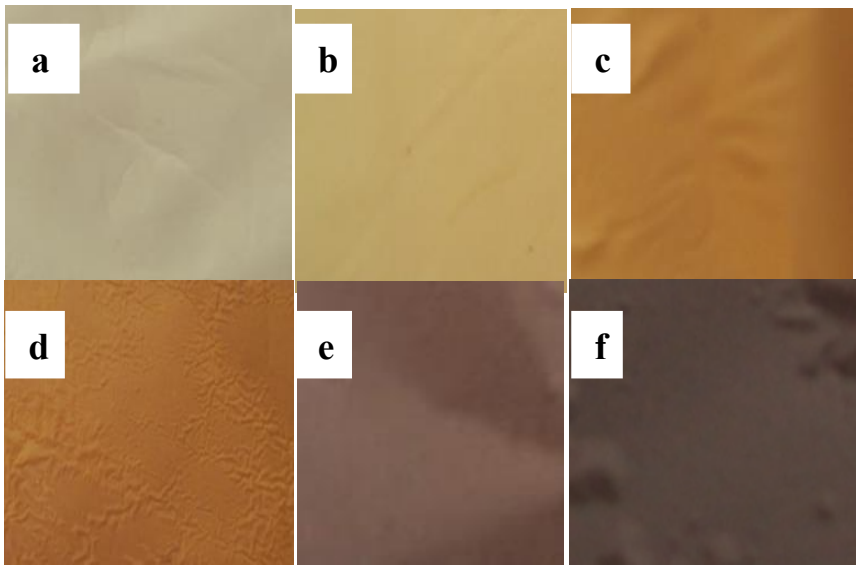


Figure 4. 17: The images of the oxidized nanofibers of I5 (86/9/5) at a) 200°C, b) 225°C, c) 250°C, d) 275°C, e) 300°C and f) 325 °C.

It is obviously seen from the images that the colour of the nanfiber mat is going to get darker with the increasing oxidation temperature. This trend shows that the initial step of the carbonization proceeds expectedly.

4.4.1. Fourier transform infrared –attanuated total reflectance (FTIR-ATR) spectroscopy of oxidized nanofibers

The oxidized nanofiber mats of I5 terpolymer is characterized by FTIR-ATR spectroscopy. %4 (%wt) solution of I5 terpolymer is prepared in DMF. The polymer solution is electrospun for 2 hours at the parameters of 17 kV, 20 cm and 0.8 ml/h. The electrospun nanofiber mat is stabilized at different temperatures varying from 200°C to 325°C for six different temperature values.

The FTIR spectrum for I5 polymer is given in Figure 4.18 for original polymer and the oxidized I5 nanofiber mat. At the Figure 4.18 a) the peak at 2243 cm-1 is attributed to C≡N peak of AN monomer unit. The peaks at 1736 cm-1 attributed to the C=O group of IA and VAc monomer units. The peak at 3100-3600 cm-1 is related to OH streching vibration of IA monomer unit. Peaks at 2937 cm-1and 2870 cm-1 is respectively related to symmetric and asymmetric streching vibration peak of –CH2 group. 1450 cm-1is attributed to bending vibration peak of –CH2 [2,52,53,56].

The peak at 1235 cm^{-1} is due to the twisting mode of the methylene group CH_2 coupled with methine group [52].

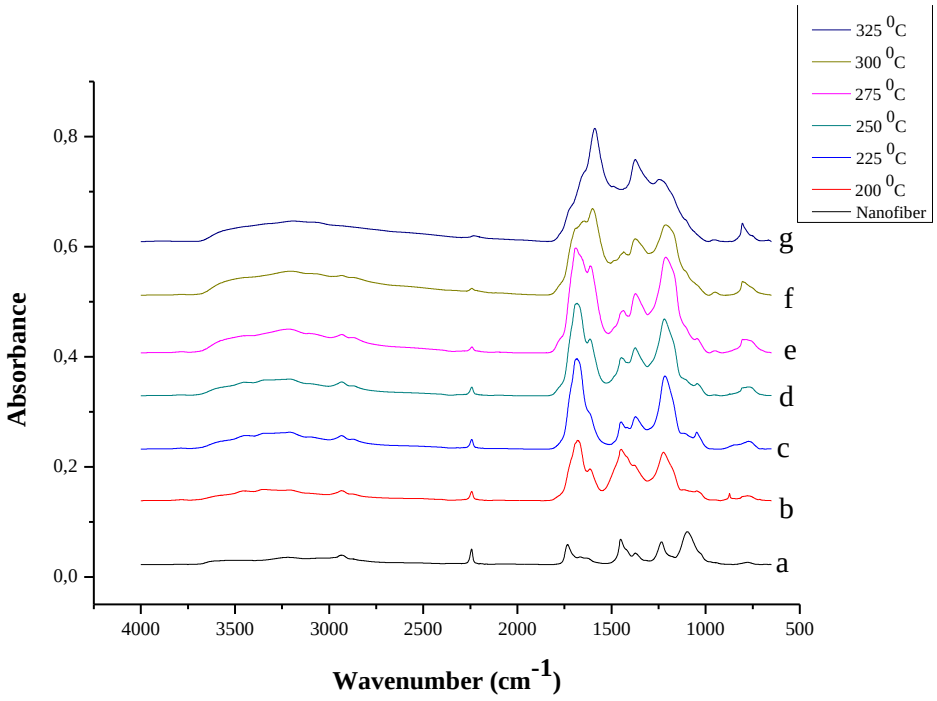


Figure 4. 18: FTIR-ATR spectrums for I5 terpolymer at different oxidation temperatures a) original P(AN-co-VAc-co-IA), b)at 200°C, c) 225°C, d) 250°C, e) 275 °C, f) 300°C, g) 325°C.

The obtained spectrums for I5 polymer at different oxidation temperatures are compared with each other to observe the changes of the specific peak intensities and the possible new peaks were examined at **Figure 4.19.**

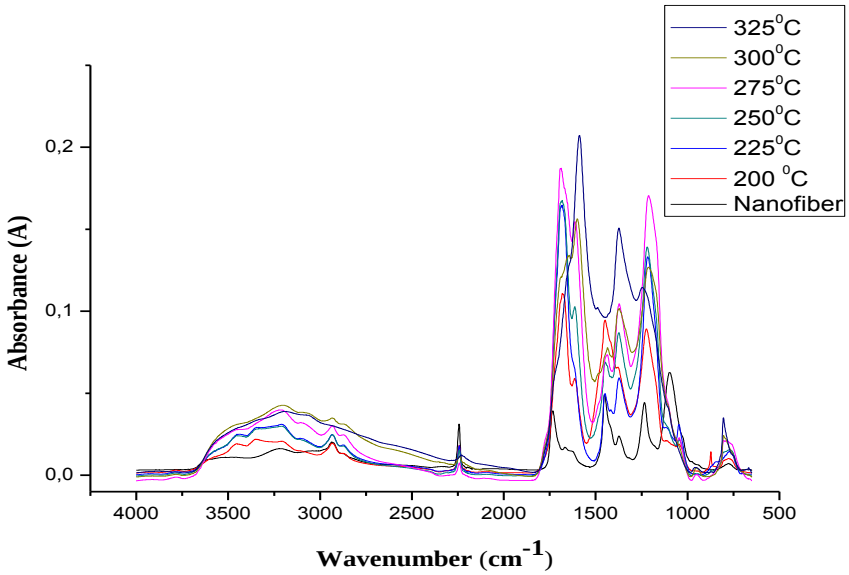


Figure 4. 19: The FTIR spectrums of the terpolymer coded as I5(86/9/5) at different oxidation temperature.

At the region between 1700 cm^{-1} and 1000 cm^{-1} huge changes are observed from the **Figure 4.20**. Some new peaks were appeared and change at peak intensities of some specific vibration bands were observed at this region which can be attributed to the overlapping of frequencies of different vibration modes resulting from C= C, C=N, C-O, and N−H [52].

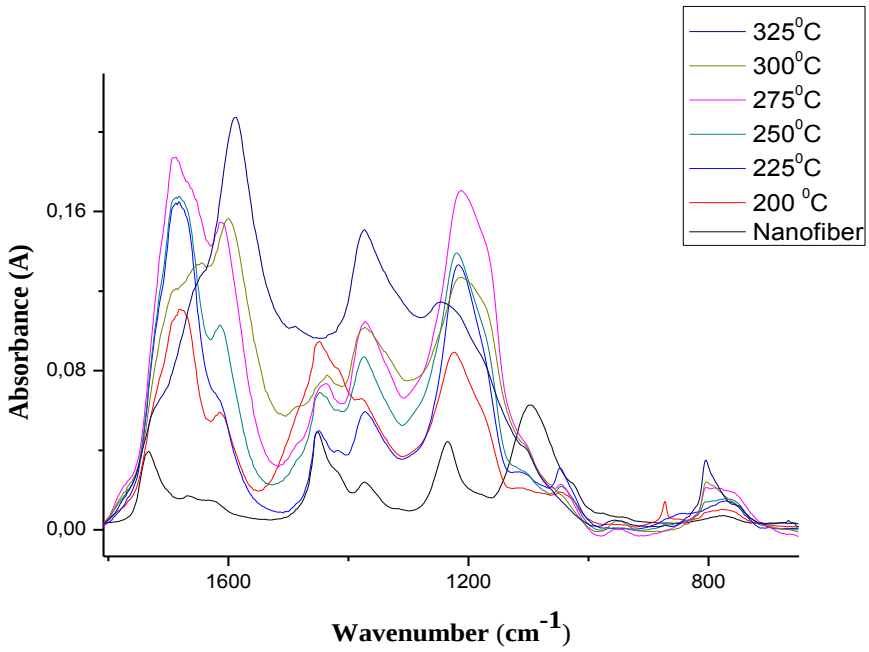


Figure 4. 20: The spectrum region of 1700 cm^{-1} – 1000 cm^{-1}.

The decrease and finally the dissapperance of the the -C≡N peak at 2243 cm^{-1} shows the cyclization of -C≡N group to -C=N- . As seen from the **Figure 4.21**, **Figure 4.22** and **Figure 4.23** broad peaks at 1580− 1620 cm^{-1} is formed which represents the formation of cyclic –C=N− group and indicated successful cyclization. This broad peaks at 1580−1620 cm^{-1} is attributed to vibrations of –C=N− groups with C=C and N−H groups, where the C=C and N−H groups originated from dehydrogenation reaction as part of the oxidation and tautomerization reactions [59].

The broad band between 1620 and 1580 cm^{-1} can be found. With temperature increasing, this broad band continues to grow and finally overtakes the 2243 cm^{-1} band. This means cyclization and dehydrogenation have been promoted by the comonomer IA. It is widely accepted that in PAN the cyclization of nitrile groups only can be initiated at a higher temperature through a free radical mechanism [2].

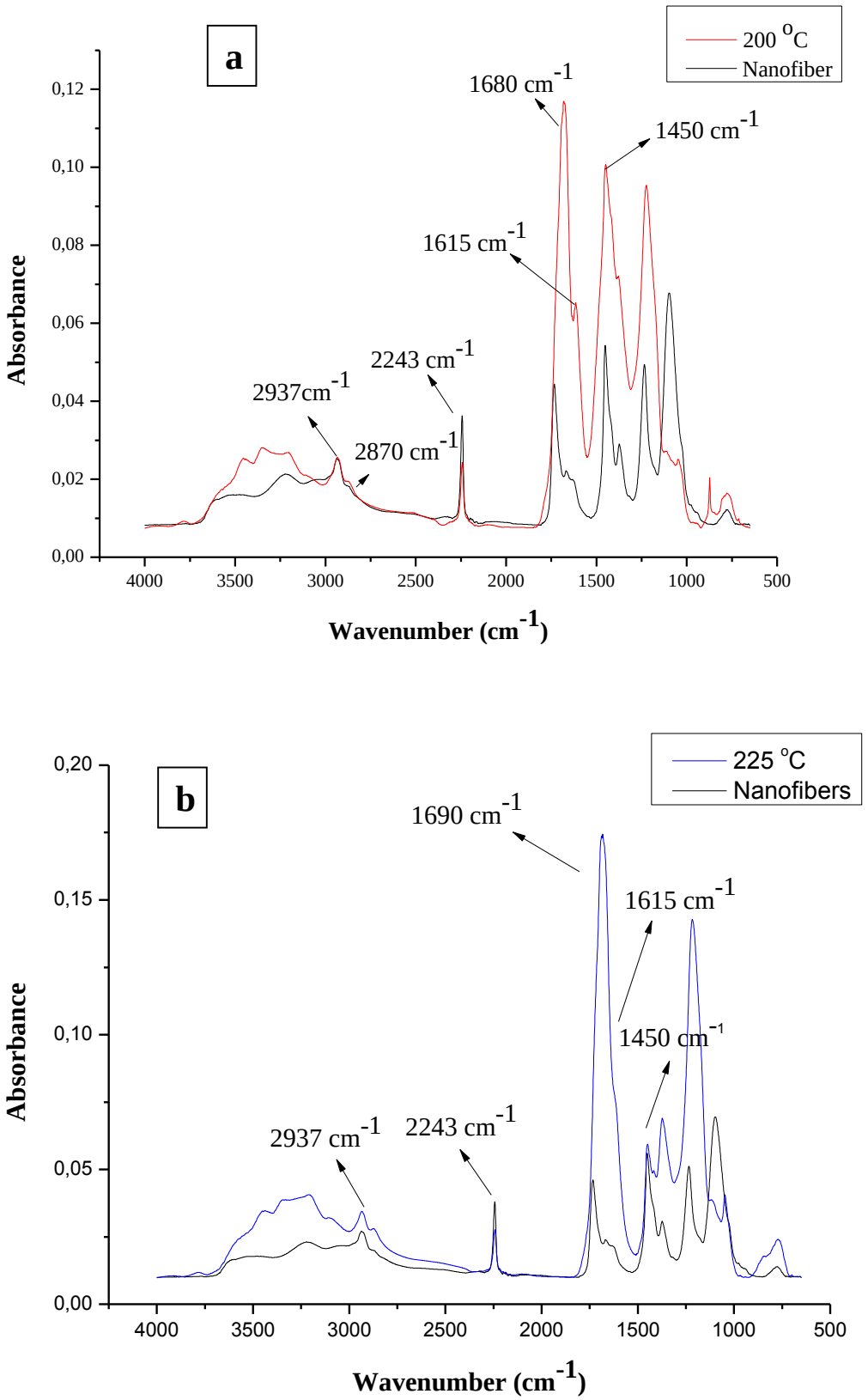


Figure 4. 21: The comparison of oxidized nanofibers spectrums individually with original one a) oxidized at 200°C b) oxidized at 225°C.

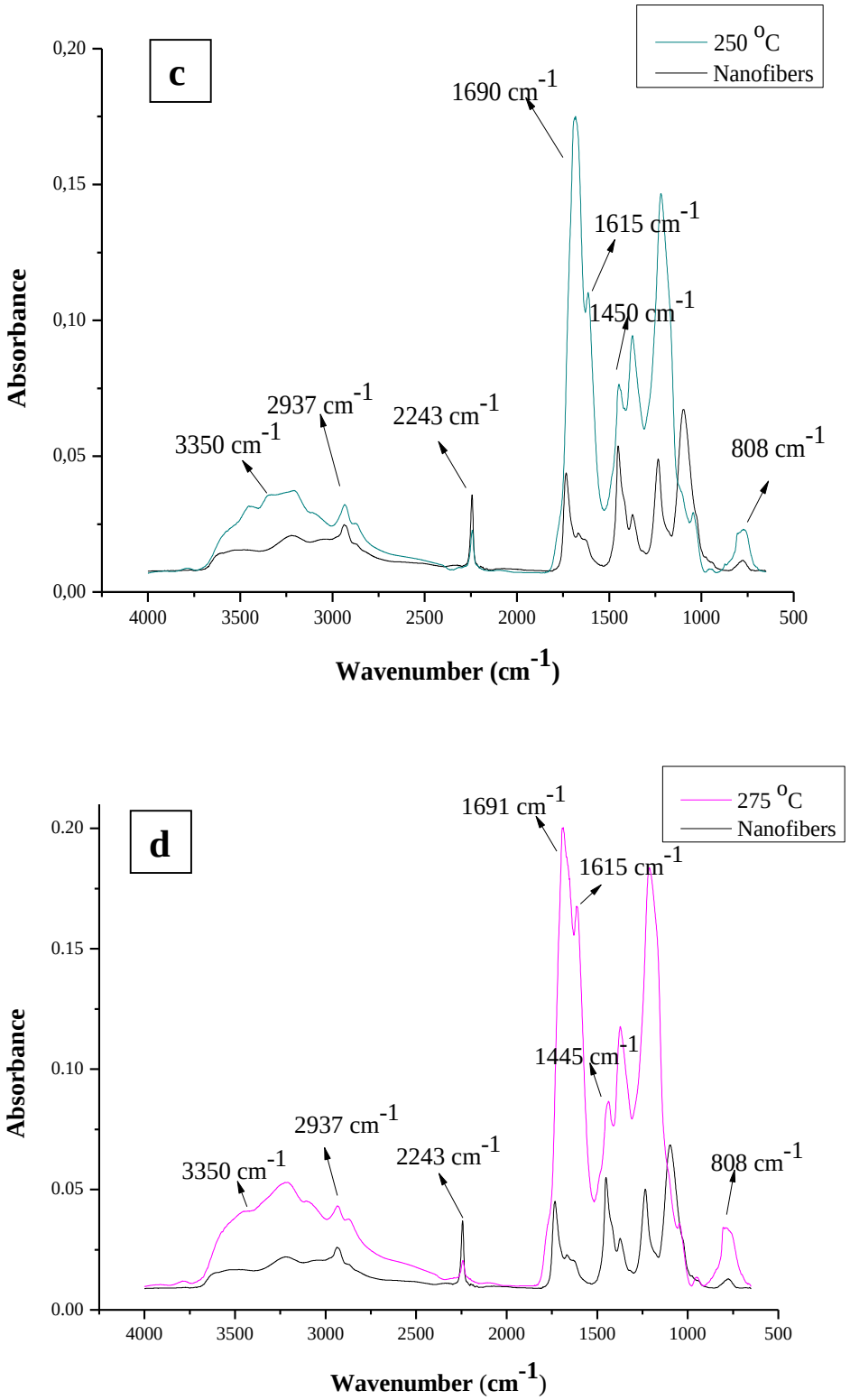


Figure 4. 22: The comparison of oxidized nanofibers spectrums individually with original one c) oxidized at 250°C d) oxidized at 275°C.

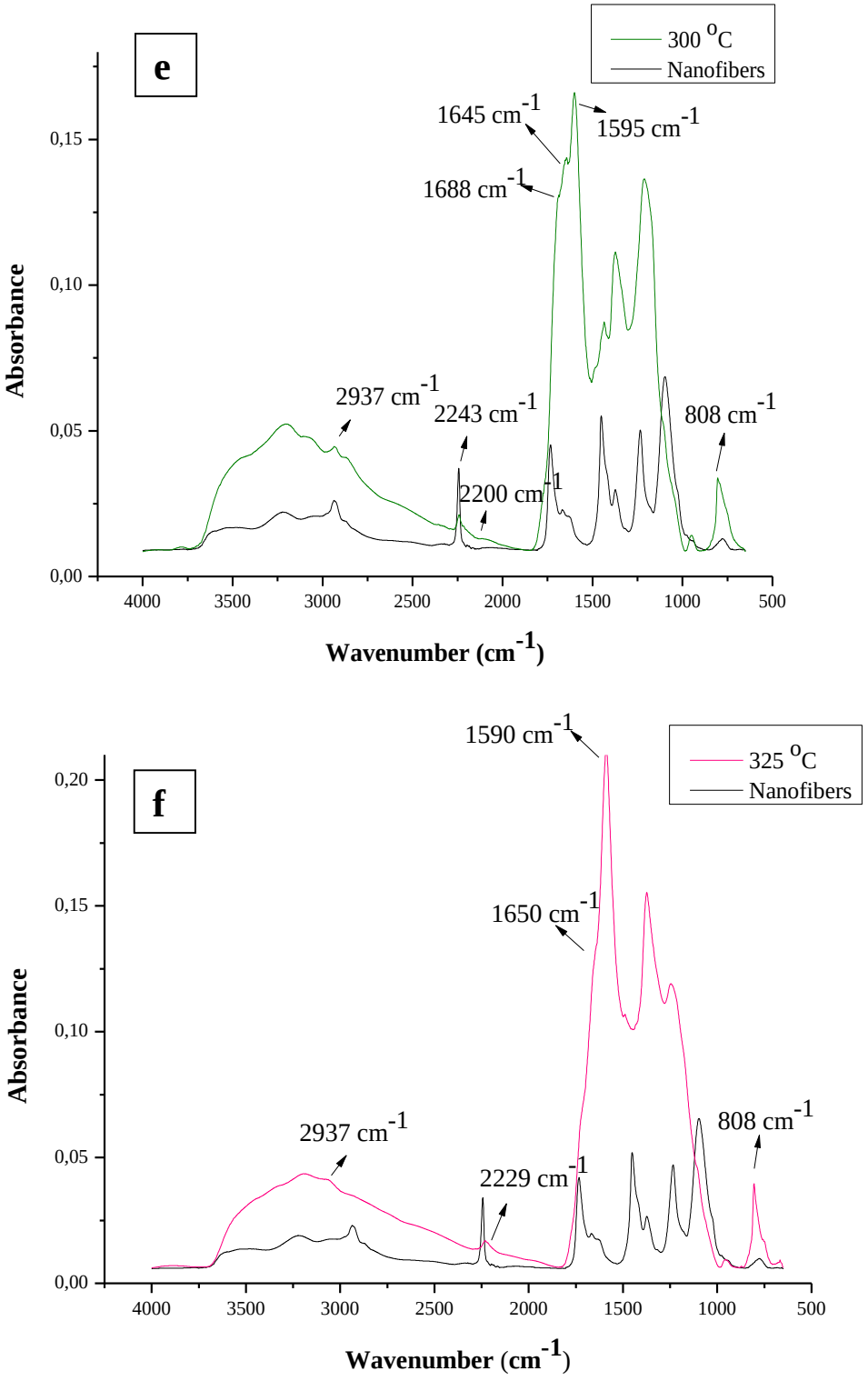


Figure 4. 23: The comparison of oxidized nanofibers spectrums individually with original one e) oxidized at 300°C f) oxidized at 325°C.

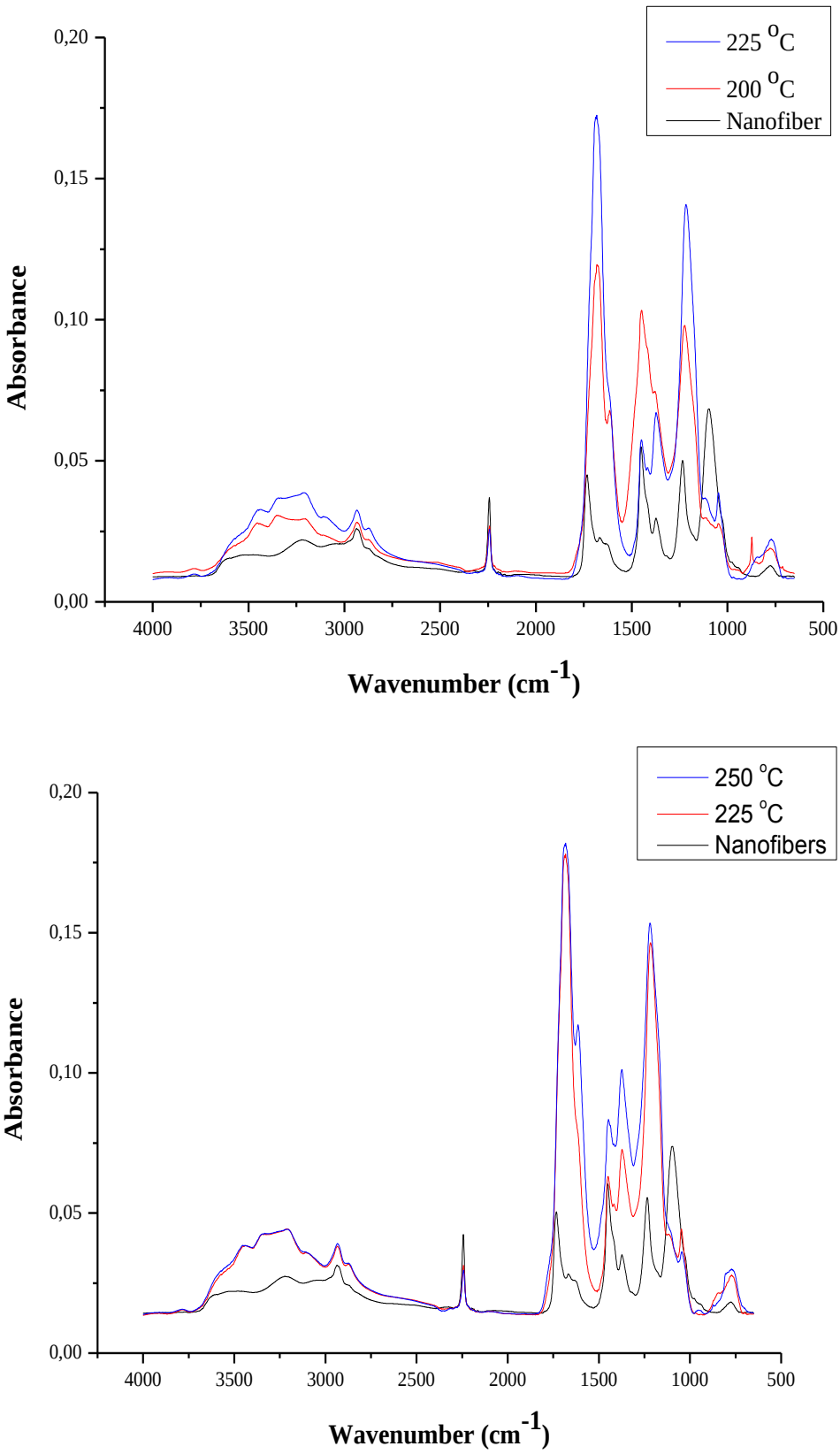


Figure 4. 24: The spectrums at different thermal oxidation temperatures for determination of change of the specific peak absorbance changes.

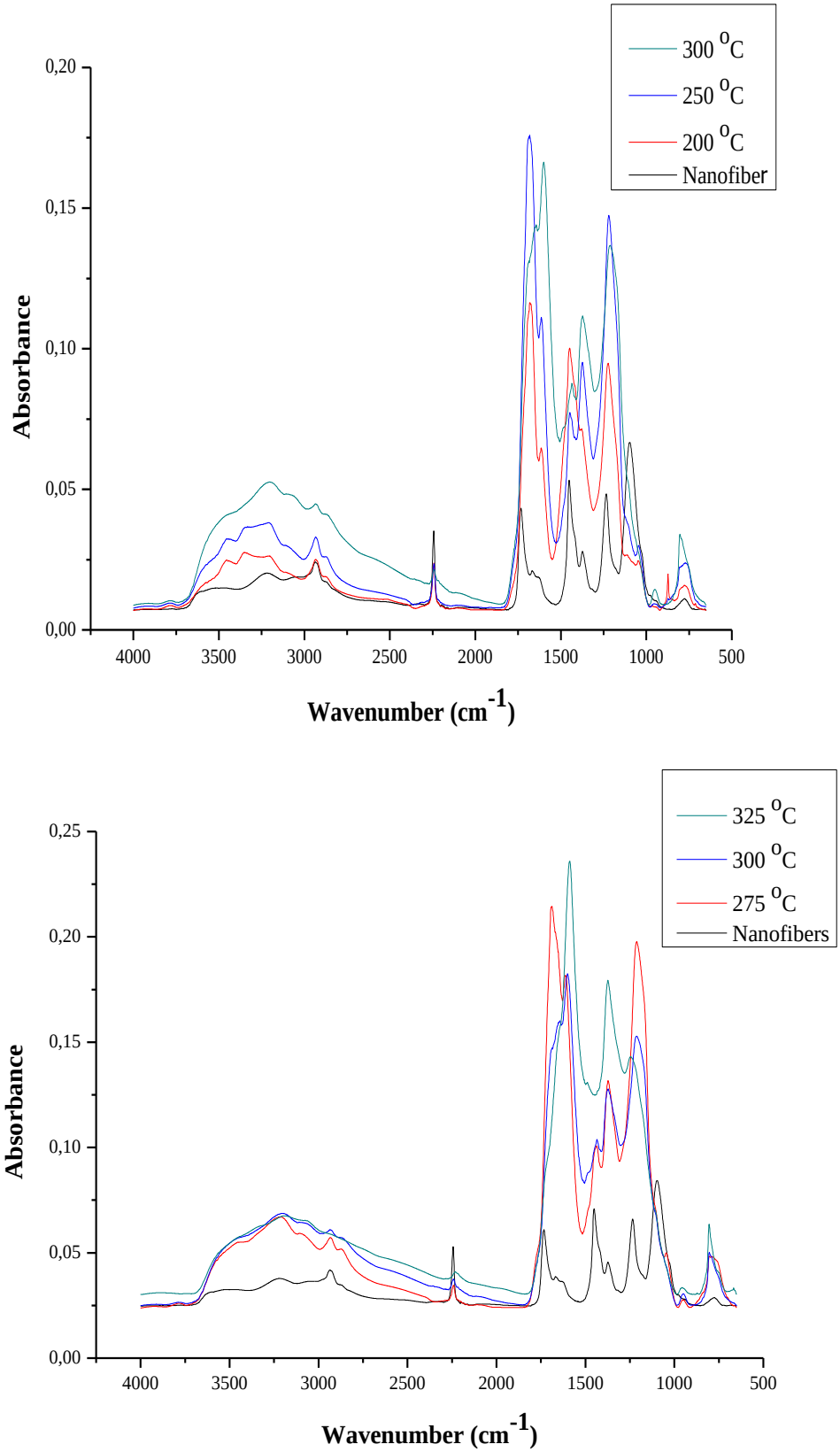


Figure 4. 25: The spectrums at different thermal oxidation temperatures for determination of absorbance changes.

It is observed from the **Figure 4.24** and **Figure 4.25.,** there was a decrease in the intensities of the peaks at 2937 cm^{-1} that is related to symmetric streching vibration of $–CH_2$ group and 2870 cm^{-1} asymmetric streching of $–CH_2$ due to the dehydrogenation reactions occured.

The peaks at 3350 cm^{-1} and 808 cm^{-1} were appeared with the increasing oxidation temperature. These peaks were attributed to representing N−H stretching vibration, and the out-of-plane bending of =C−H in saturated rings, respectively [59].

A new band at about 2200 cm^{-1} was observed with the increasing oxidation temperature for the polymers. Also, this band was suggested to be assigned to the α,β -unsaturated nitrile groups arose from dehydrogenation, or from tautomerization and isomerisation of the ladder polymer [2,59].

The change of the absorbances of specific peaks of -C≡N A_{2243} , =C−H in saturated rings (A_{808}) are determined from **Figures 4.26** according to the varying oxidation temperature.

The absorbance of each peak at the current temperature was divided to the sum of peak absorbance of n the originan non-oxidized and the absorbance at the current temperature.

$(A_{2243})_T$ represents the absorbance of C≡N peak at the current temperature where $(A_{2243})_I$ represents the absorbance of C≡N peak at the original fiber.

$(A_{808})_T$ represents the absorbance of =C−H peak at the current temperature and $(A_{808})_I$ states the absorbance of =C−H peak at the original fiber.

It is observed from the **Figure 4.26** that the absorbance of the C≡N peak decreasing with the increment of the oxidation temperature. On the other hand, it is clearly indicated that absorbance of =C−H peak is increasing with the increasing oxidation temperature.

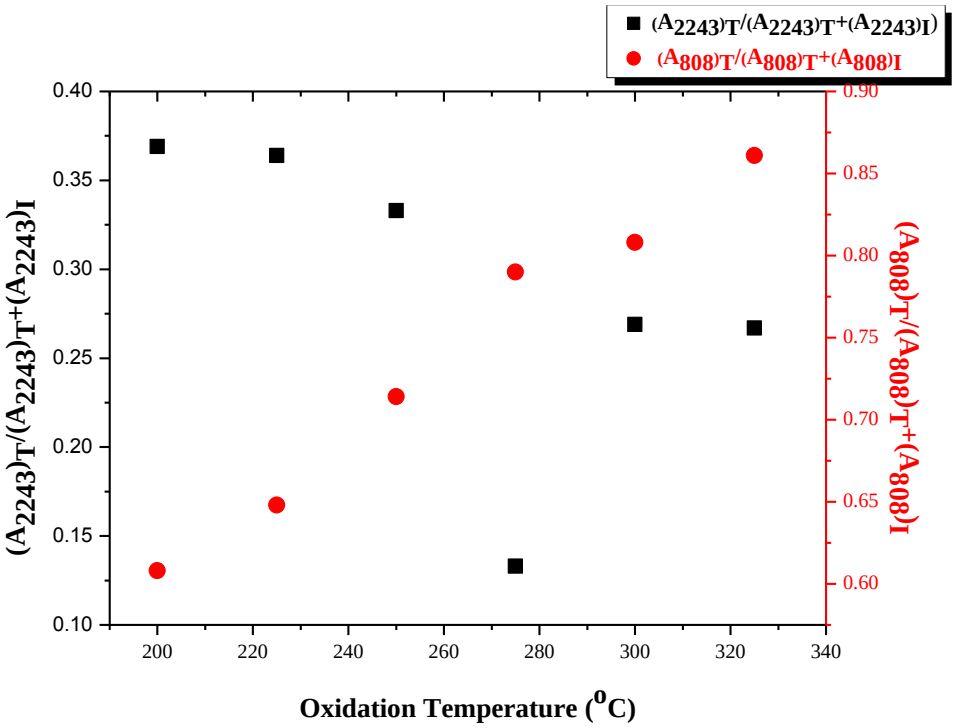


Figure 4. 26: The change of the peak ratios with increasing oxidation temperature.

4.4.2. Scanning electron microscopy of oxidized nanofibers

Morphologic characterization of the oxidized nanofibers of the terpolymer samples are performed by SEM and AFM methods. At least 50 measurements were done to calculate the avarage fiber diameters.

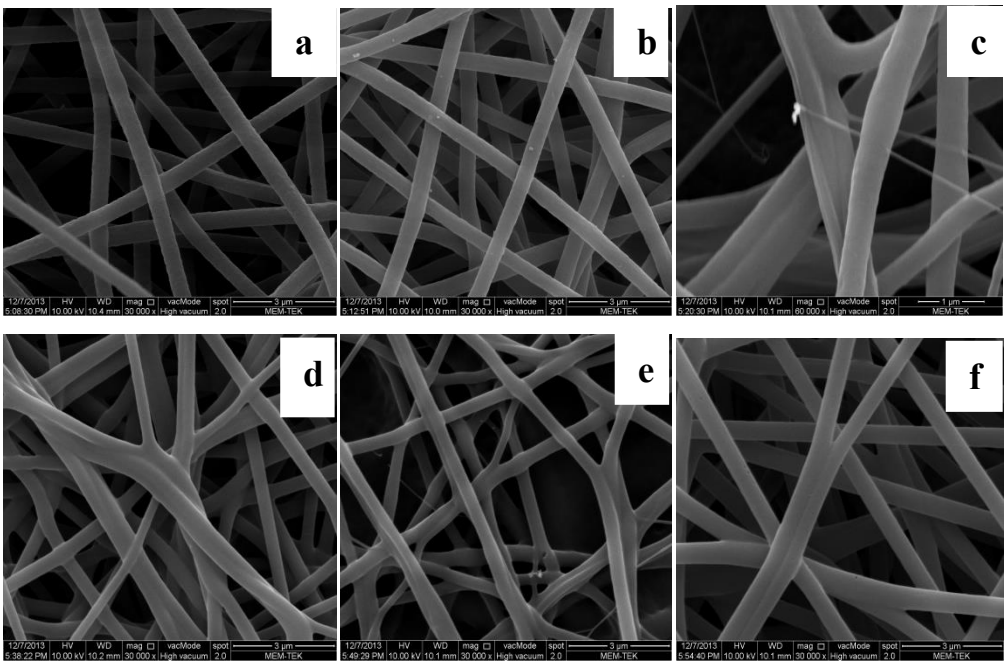


Figure 4. 27: SEM images of I2 coded polymer at different oxidation temperatures a) 200°C, b) 225°C, c) 250°C, d) 275°C, e) 300°C and f) 325 °C.

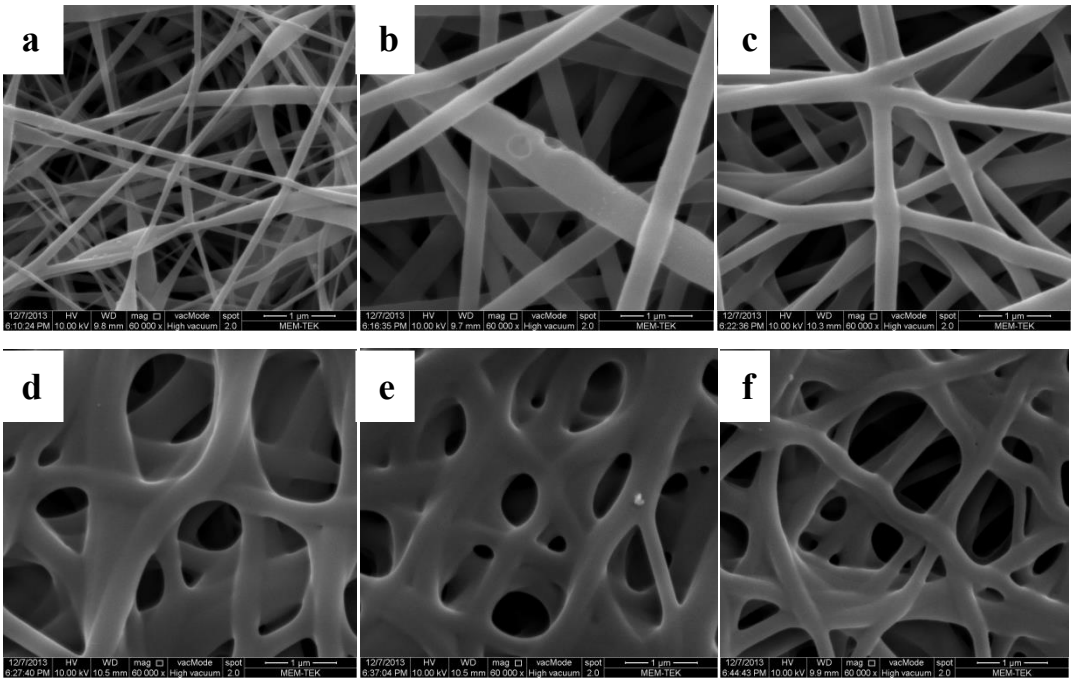


Figure 4. 28: SEM images of I5 coded polymer at different oxidation temperatures a) 200°C, b) 225°C, c) 250°C, d) 275°C, e) 300°C and f) 325 °C.

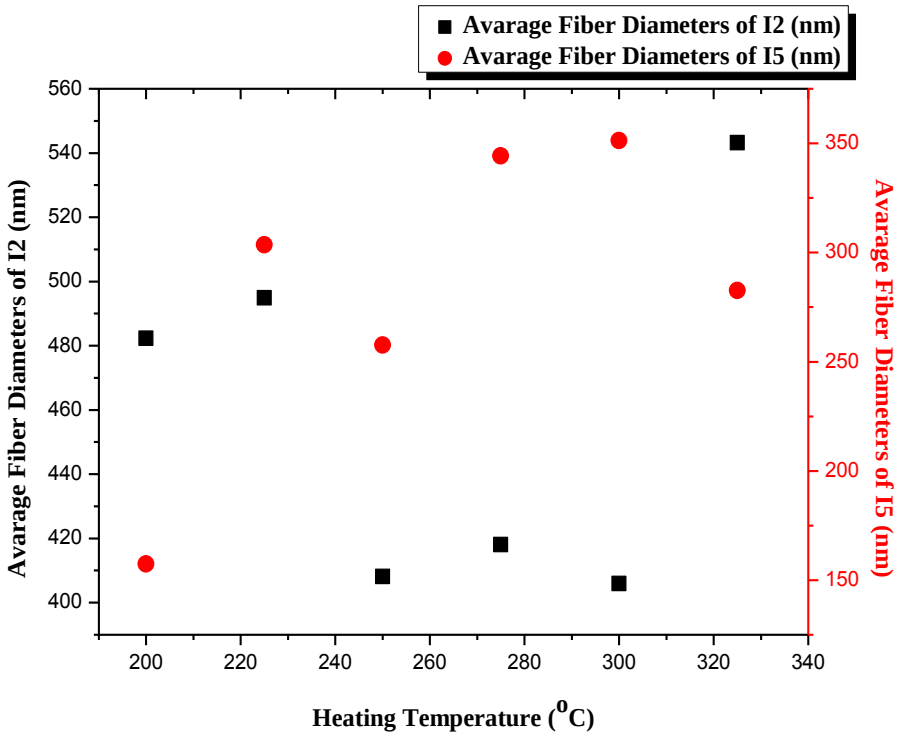


Figure 4. 29: The change of the average fiber diameters with increasing oxidation temperature.

It is observed from the graph that distinct trend of increasing or decreasing for the avarage fiber diameters of nanofibers.

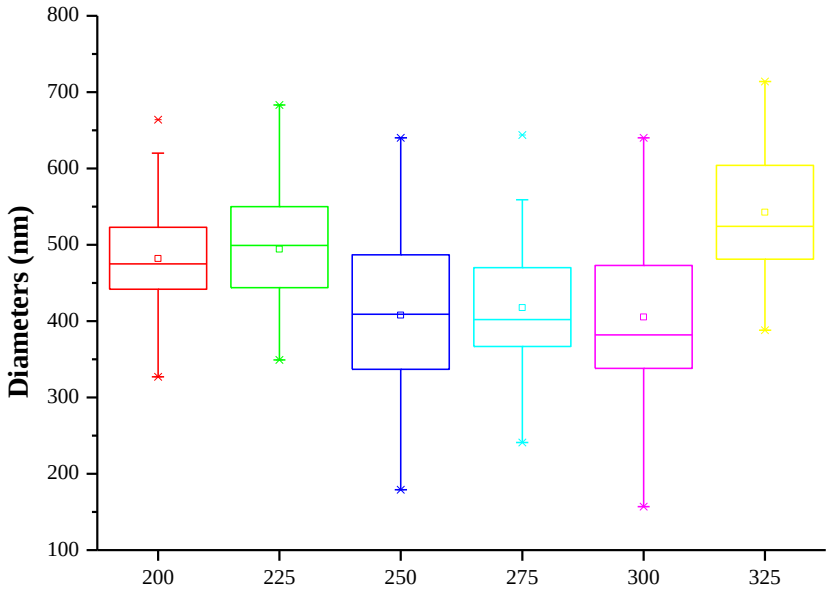


Figure 4. 30: Fiber diameters distribution of I2 terpolymer oxidized at different temperatures.

4.5. Characterization of Carbonized Nanofibers

The nanofibers of the terpolymer coded as I2 and I% are oxidized at 200°C ,carbonized in the presence of N_2 for 2.5 hours at 1100 °C. The heating rate of the furnace is 5°C/dk. The flow rate of N_2 is 0.1 L/min.

Carbolite 1 & 3 Zone Wire-Wound Tube Furnace model high temperature oven is used in carbonization operation. Maximum operating temperature of oven is 1200°C and designed to accept process tubes up to 6 cm. Furnace provides rapid heat-up operating temperature.

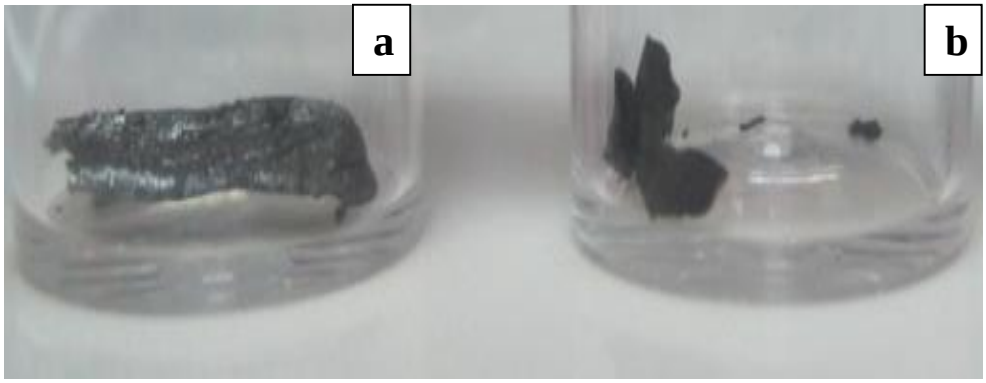


Figure 4. 31: Carbonized nanofibers of a) I2 and b) I5 samples.

As shown in **Figure 4.31** the nanofiber mats became completely black after the cabonization process.

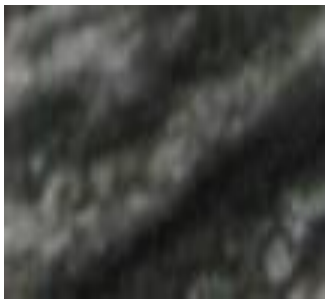


Figure 4. 32: Color of the carbonized nanofiber of I2 terpolymer at 1100 °C.

4.5.1. Fourier transform infrared –attanuated total reflectance (FTIR-ATR) spectroscopy of oxidized nanofibers

The FTIR-ATR spectrums of the non-oxidized, oxidized and carbonized nanofibers of I2 terpolymer are shown in the **Figure 4.33.**

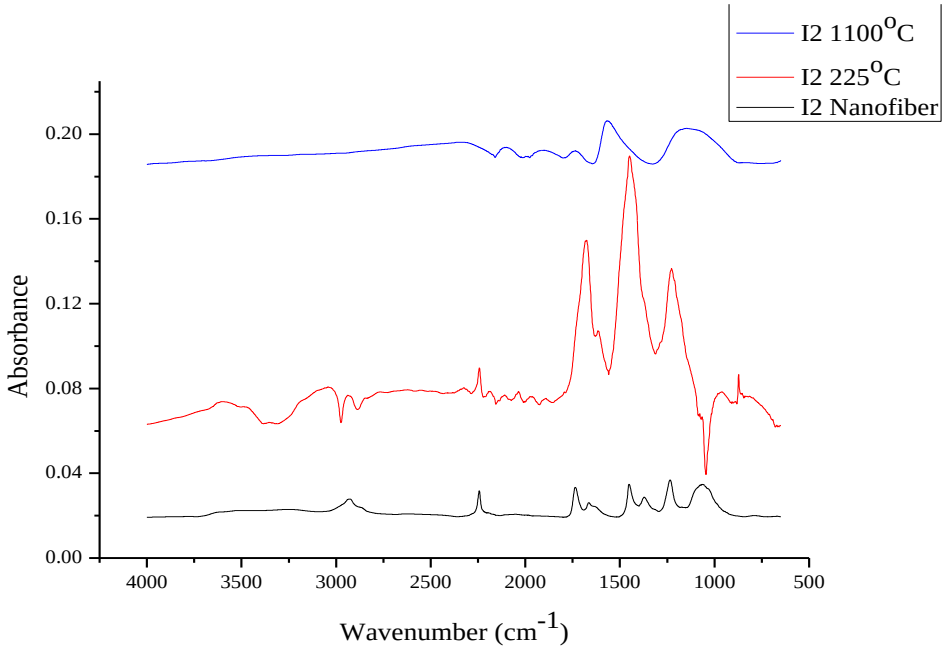


Figure 4. 33: FTIR-ATR spectrums of non-oxidized, oxidized and carbonized nanofibers of I2 terpolymer.

It has primarily been observed from the previous spectrum that the -C≡N peak related to acrylonitrile monomer units n the terpolymer chain decreasing with the incerasing oxidation temperature. It is finally observed that the -C≡N peak disappears with after the carbonization step.

4.5.2. Scanning electron microscopy of carbonized nanofibers

The carbonized nanofibers of I2 terpolymers at 1100 °C are morphologically characterized by SEM. SEM images at different magnification are shown at **Figure 4.34.** The fiber form of the polymers are conserved .

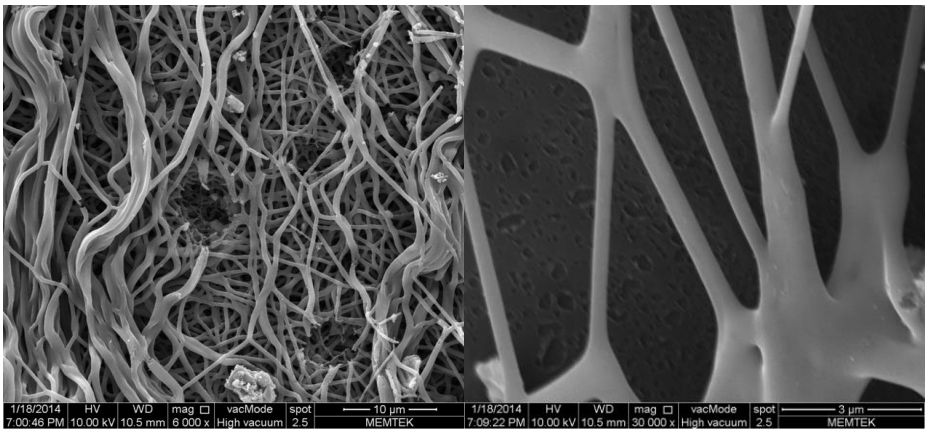


Figure 4. 34: SEM images for carbonized electrospun nanofibers of I2 terpolymers.

5. CONCLUSIONS

P(AN-VAc-IA) terpolymers were sythesized in different monomer feed composition in aqueous medium. The yield of the reaction is approximately 90% for all the polymerizations. The incerasing IA monomer feed ratio result in decrease at the specific viscosity vlalues. The IA content of the polymer is determined by the specific peaks related to IA comonomer using FTIR ATR. The specific peaks of 1665 cm^{-1} and 1735 cm^{-1} is attributed to C=O peaks of vinyl acetate and itaconic acid. These peaks absorbances are compared with C≡N peak of acrylonitrile unit of polymer chain. Tha absorbance ratio had an increment with the increasing itaconic acid monomer feed ratio. It is predicted from ^{1}H-NMR that the specific hydrogen bands of AN, VAc and IA units were existing.

Thermal gravimetric analysis of the synthesized polymers show that the polymer percentage of the remaining polymer at temperatures about 800°C is ~35%. This high percantage show the thermal stability of the polymers. The decrease trend of the polymers indicated the steps of the heat treatment of oxidation and dehydrogenation which are important parameters for carbon fiber production.

In the second part of study, the electrospun nanofibers of P(AN-VAc-IA) are obtained. The elecrospinning of the terpolymer solutions in dimethyl foramide (DMF) was performed succesfully. The electrospininndg parameters were 17 kV, 20 cm and 0,8 ml/h. Morphologic characteristic of the nanfibers are determined by SEM and AFM. It is calculated from SEM that the avarage fiber diameters ot the obtained fibers decrasing from about 350nm to 200 nm with increasing itaconic acid monomer feed ratio.

The obtained nanofibers were oxidized at different oxidation temperatures varying from 200°C to 325°C under air atmosphere. The thermally stabilized nanofiber mats were characterized spectroscopically by FTIR-ATR. In obtained spectrums, it is observed that there was decrease at the absorbance of C≡N is related to the conversion of C≡N peaks to -C=N peaks. The absorbance change of the specific

C≡N of acylonitrile unit and =C−H of the bending peak in saturated ring is proportionated. The color of the nanofiber mat converted from white to the yellow, orange and finally tan-brown with incerasing oxidation temperature. to about 300°C

The oxidized nanofibers were carbonized at 1100 °C for 2.5 hours in the presence of N_2 . The color of the nanofiber mat is totally became black.

Consequently, the obtained results show that the synthesized terpolymers can be suggested as carbon fiber precursors.

REFERENCES

[1] Sharifnejad, F., Bahrami, S., Noorpanah, P. (2005). Kinetics studies on copolymerization of acrylonitrile vinyl acids by solvent-water suspension polymerization**,** *Journal of Applied Polymer Science* **, 97, 1284-1291.**

[2] Ouyang, Q., Cheng, L., Wang, H., Kaiki, L. (2008). Mechanism and Kinetics of the stabilization reactions of itaconic acid-modified polyacrylonitrile, *Polymer Degradation and Stability*, **93, 1415-1421.**

[3] Farsani, E., Raissi, S., Shokuhfar, A., Sedghi, A. (2009). FT-IR study of stabilized PAN fibers for fabrication of carbon fibers, *World Academy of Science, Engineering and Technology*, **50, 430-433.**

[4] Ju, Q., Guang, S., Yao Xu, H. (2012). A novel poly[acrylonitrile-co-(3-ammoniumcarboxylate-butenoic acid-methylester)] copolymer for carbon fiber precursor, *Chinese Chemical Letters*, **23, 1307-1310.**

[5] Xiang, Y., Yulan, L., Limin, W., Yizhen, Y., Chengguo, W. (2010). Characterization of copolymerization of acrylonitrile with the functionalized comonomers in dimethyl sulfoxide solvent and copolymers suitable for carbon fibers, *e-Polymers*, **135.**

[6] Devasia, R., Nair, R., Sivadasan, P., Ninan, K. (2005). High char yielding poly [acrylonitrile-co-(itaconic acid)-co- (methyl acrylate)] : synthesis and properties, *Polymer International*, **54, 1110-1118.**

[7] Mukundan,T., Bhanu, V., Wiles, KB., Johnson, H., Bortner, M., Baird, D., Naskar, A., Ogale, A., Edie, D., McGrath, J. (2006). A photocrosslinkable melt processible acrylonitrile terpolymer as carbon fiber precursor, *Polymer*, **47, 4163-4171.**

[8] Zussmann, E., Chen, X., Ding, W., Calabri, L., Dikin, D., Quintana, J., Ruoff, R. (2005). Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers, *Carbon*, **43, 2175-2185.**

[9] Ge, H., Liu, H., Chen, J., Wang, C. (2008). The skin-core structure of poly(acrylonitrile-itaconic acid) precursor fibers in wet spinning, *Journal of Applied Polymer Science*, **108, 947-952.**

[10] Mahdavian, A., Abdollahi, M. (2007). Kinetic study of radical polymerization. VII. Investigation into solution copolymerization of acrylonitrile and itaconic acid by real-time H NMR spectroscopy, *Journal of Applied Polymer Science*, **103, 3253-3260.**

[11] Yu, H., Wu, Y., Gao, J., Wenxiang, W., Zhang, Z., Zhu, X. (2012). Copper(0) mediated radical copolymerization of vinyl acetate and acrylonitrile in DMSO at ambient temperature, *Journal of Polymer Science Part A: Polymer Chemistry*, **50, 4983-4989.**

[12] Frushour, B.,Knorr, R. (2006). Handbook of Fiber Cehemistry: Acrylic Fibers, *Tylor and Francis Group*, **812-816.**

[13] Rahaman, M., Ismail, A., Mustafa, A. (2007). A review of heat treatment on polyacrylonitrile fiber, *Polymer Degradation and Stability*, **92, 1412-1432.**

[14] Fang, J., Wang, H., Niu, H., Lin, T., Wang, X. (2010). Evolution of fiber morphologies during polyacrylonitrile electrospining, *Macromol. Symp*., **287,155-161.**

[15] McCann, J., Lim, B., Ostermann, R., Rycenga, M., Marguez, M., Xia, Y. (2007). Carbon nanotubes by electrospining with a polyelectrolyte and vapor deposition polymerization, *Nano Letters*, **7, 2470-2474.**

[16] Senthil, T., George, G., Anadhan, S. (2013). Chemical-resistant ultrafine poly(styrene-co-acrylonitrile) fibers by electrospining: process optimization by design of experiment, *Polymer Plastics Technology and Engineering*, **52, 407-421.**

[17] Dai, T., Ebert, K. (2012). Electrospinning of solvent-resistant nanofibers based on poly(acrylonitrile-co-glycidyl methacrylate), *Journal of Applied Polymer Science,* **126, 136-142.**

[18] Zhang, W., Wang, Y., Sun, C. (2007). Characterization on oxidative stabilization of polyacrylonitrile nanofibers prepared by electrospinning, *J Polym Res*, **14 ,467–474.**

[19] Duan, Q., Wang, B., Wang, H. (2012). Effects of Stabilization Temperature on Structures and Properties of Polyacrylonitrile (PAN)-Based Stabilized Electrospun Nanofiber Mats, *Journal of Macromolecular Science : Part B: Physics*, **51, 2428–2437.**

[20] Chung, D. (1994). Carbon Fiber Composites: Carbon Fibers, *Elsevier*, **3-5.**

[21] Xue, Y., Liu, J., Liang, J. (2013). Correlative study of critical reactions in polyacrylonitrile based carbon fiber precursors during thermal-oxidative stabilization, *Polymer Degradation and Stability* **, 98, 219-229**.

[22] P.J. Sanchez-Soto,P., Aviles, M., Rıo, J., Gines, J., Pascual,J., Perez-Rodrıguez , J.L. (2001). Thermal study of the effect of several solvents on polymerization of acrylonitrile and their subsequent pyrolysis, *Journal of Analytical and Applied Pyrolysis***, 58–59, 155–172.**

[23] Bashir, Z. (1991). A critical review of the stabilizaiton of polyacrylonitrile, *Carbon*, **29, 1081-1090.**

[24] Dalton, S., Heatley, F., Budd, P. (1999). Thermal stabilization of polyacrylonitrile fibres, *Polymer*, **40, 5531-5543.**

[25] Niu, S., Zhang, L., Zhu, J., Zhang, W., Cheng, Z., Zhu, X. (2012). Synthesis of high molecular weight and norrow molecular weight distribution polyacrylonitrile via RAFT polymerization, *Journal of Polymer Science*, **51, 1197-1204.**

[26] Fıtzer, E., Frohs, W., Heine, M., (1986). Optimization of stabilization and carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibres, *Carbon*, **24, 387-395.**

[27] Liu, J., Wang, P., Li, RY. (1994). Continuous carbonization of polyacrylonitrile based oxidized fibers: aspects on mechanical properties and morphological structure, *Appl Polym Sci*, **52, 945- 950.**

[28] Bajaj, P., Sreekumar, T., Sen, K., Kumar, R., Brar, A.S. (2003) Structural investigation of acrylonitrile-vinyl acid copolymers by NMR spectroscopy, *Journal of Applied Polymer Science,* **88, 1211-1217.**

[29] Vargün, E., Sankır, M., Usanmaz, A., Kanbur, Y., Abacı, U., Güney, Y. (2012). Preparation and chracaterization of acrylonitrile-ethyl methacrylate copolymers and the effect of $LiClO_4$ salt on electrical properties of copolymer films, *Journal of Applied Polymer Science,* **124, 840-846.**

[30] Devasia, R., Reghunadhan Nair, C., Ninan, K. (2003). Copolymerization of acrylonitrile with itaconic acid in dimethlyformamide : effect of triethylamine, *European Polymer Journal,* **39, 537-544.**

[31] Unsal, C., Kalaoglu, F., Karakas, H., Sarac, S. (2013). Polypyrrole/Poly(acrylonitrile-*co*-butyl acrylate) Composite, *Advances in Polymer Technology,* **32, 784-792.**

[32] Aviles, M., Gines, J., del Rio, J., Pascual, J., Perez-Rodriguez, J. L., Sanchez-Soto, P. J. (2002). Thermal analysis of acrylonitrile polymerization and cyclization in the presence of N,N-dimethylformamide, *Journal of Thermal Analysis and Calorimetry,* **67, 177-188.**

[**33**] **Houtz RC.** (1950). "Orlon" Acrylic Fiber: Chemistry and Properties, *Textile Research Journal,* **20, 786-801.**

[34] Grassie, N., Hay, J.N., McNeill, I. (1958). Coloration in acrylonitrile and methacrylonitrile polymers, *Journal of Polym Science*, **31, 205.**

[35] Burlant, W.J., Parsons, J.L. (1956). Pyrolysis of polyacrylonitrile, *Journal of Polym. Sci*., **22, 249-256.**

[36] LaCombe, E.M., (1957). Color formation in polyacrylonitrile**,** *J Polym Sci*, **24, 152-154.**

[37] Coleman, M., Petcavich, R., (1978). *J Polym Sci Polym Phys Edn,* **16, 821.**

[38] Fochler, H,S., Mooney, JR., Ball, LE., Boyer, RD., Grasselli, JG. (1985). *Spectrochim Acta,* **41, 271.**

[39] Xue, TJ., McKinney, MA., Wilkie, CA. (1997). *Polym Degrad Stab*., **58,193.**

[40] Grassie, N., Hay, JN. (1962). *J Polym Sci,* **56, 189.**

[41] Olive, GH., Olive, S. (1979-1983). *Adv Polym Sci*, **32, 12; 51,1.**

[42] Schurz, J. (1958). *J Polym Sci*, **28, 438.**

[43] Berlin, AA., Dubinskaya, AM., Moshkovski, Y. (1966). *Polym Sci,* **6, 2145.**

[44] Fester, W. (1965). *Textil rundshau,* 20**, 1.**

[45] Devasia, C. P. Nair, R. Sadhana, N. S. Babu, Ninan, K. N. (2006). Fourier Transform Infrared and Wide-Angle X-Ray Diffraction Studies of the Thermal Cyclization Reactions of High-Molar-Mass Poly(acrylonitrile-co-itaconic acid), *J. App Poly Sci.,* **100, 3055–3062.**

[46] DeRosa, R. (2008). Intrinsic Viscosity Characterization of PS and PMMA, Alfred Universty.

[47] Sandler, S., Karo,W., Bonesteel,J., Pearce,E. Polymer Synthesis and Characterization , **13, 83-97, 14, 98-107, 15, 108-119, 16, 120-130, 18, 140-151.**

[48] Abdollahi, M., Massoumi, B., Yousefi, M.R., Ziaee, F. (2012). Free-Radical Homo- and Copolymerization of Vinyl Acetate and n-Butyl Acrylate: Kinetic Studies by Online H NMR Kinetic Experiments, *Journal of Applied Polymer Science*, **123, 543–553.**

[49] Paramita,P, Instrumental Techniques used for Thermal analysis of Rubbers and Rubbery Materials, **5-64.**

[50] Caludy, PM. (2003). Measurement of the Thermodynamic Properties of Single Phases : Calorimetry, **7, 348-350.**

[51] Meyer, E. (1992). Atomic Force Microscopy, *Progress in Surface Science*, **41, 3-49.**

[52] Bajaj, P. Sen, K. Hajir Bahrami, S. (1996). Solution Polymerization of Acrylonitrile with Vinyl Acids in Dimethylformamide, *Journal of Applied Polymer Science,* **59, 1539-1550.**

[53] Cetiner, S., Sen, S., Arman, B., Sarac, A.S. (2012). Acrylonitrile/Vinyl acetate copolymer nanofibers with different vinylacetate content, *Journal of Applied Polymer Science.*, **127, 3830-3838.**

[54] Lee, J.M., Kang, S., Park, S. (2009). Synthesis of polyacrylonitrile based nanoparticles via aqueous dispersion polymerization, *Macromolecular Research,***17, 817-820**

[55] Bajaj, P., Sreekumar, T., Sen, K., (2001). Thermal Behaviour of acrylonitrile copolymers having methacylic and itaconic acid comonomers, *Polymer*, **42, 1707-1718.**

[56] Shimada, I., Takahagi, T. (1986). FT-IR study of the stabilization reactions of polyacrylonitrile in the production of carbon fibers, *Journal of Polymer Science Part A Polymer Chemistry*, **24,1989–1995.**

[57] Ouyang, Q., Cgeng, L., Wang, H., Li, KX. (2008). DSC study of stabilization reactions in poly (acrylonitrile-co-itaconic acid) with peak-resolving method, *Journal of Thermal Analysis and Calorimetry*, **94, 85-88.**

[58] Gupta, A., Palıwal, D., Bajaj, P. (1998). Melting behavior of acrylonitrile polymers, *Journal of Applied Polymer Science*, **70, 2703-2709.**

[59] Nguyen-Thai, N., Hong, S.C. (2013). Structural evolution of poly (acrylonitrile-co-itaconic acid) during thermal oxidative stabilization for carbon matierials, *Macromolecules*, **46, 5882-5889.**

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