

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**FLAME RETARDANT NANOFIBERS FROM ACRYLONITRILE,
METHYLACRYLATE AND VINYLPHOSPHONIC ACID TERPOLYMERS
WITH USING ELECTROSPINNING TECHNIQUE**



M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

JUNE 2018

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**AKRİLONİTRİL, METİLAKRİLAT VE VİNİLFOSFONİK ASİT
TERPOLİMERİ İLE ELEKTROSPİNNİNG YÖNTEMİ KULLANILARAK
ALEV GECİKTİRİCİ ÖZELLİKLİ NANOFİBER ELDESİ**

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Date of Defense : 5 June 2018





To my precious husband,



FOREWORD

I would firstly like to thank Assoc.Prof.Dr. Nesrin KOKEN, Prof. Dr. Nilgün KIZILCAN and Prof. Dr. Ahmet AKAR for their support, humanity, encouragement throughout the whole study and for providing me a peaceful environment to work at Istanbul Technical University.

I am also thankful to Mustafa YILMAZ for his great support, friendship and helps during the study.

During master education, for their support and friendship I would like to thank to my dear colleagues Gülçin Almina FIDANLIK and Serap ALACA.

I would like to thank to Hande ACIKALIN, Feyza Nur BUYUKNALCACI and Selin GUMRUKCU for their support and friendships.

Finally, I would like to thank my family and my husband Ercan ILMAN for their emotional assists and motivation for all the good and the bad days in my life for years.

May 2018

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ABBREVIATIONS

AHP	: Aluminium Hypophosphite
AMPS	: Ammonium Peroxodisulphate
AN	: Acrylonitrile
APP	: Ammonium Polyphosphate
DMAc	: Dimethylacetamide
DMF	: Dimethylformamide
DSC	: Differential Scanning Calorimetry
FTIR	: Fourier Transform Infrared Spectrometer
HVDC	: High Voltage Direct/Current Power Supply
MA	: Methyl Acrylate
NFs	: Nanofibers
P(AN-MA)	: Copolymer of AN and MA
P(AN-MA-VPA)	: Terpolymer of AN, MA and VPA
P(AN)	: Polyacrylonitrile
PE	: Polyethylene
POE	: Poly(ethylene oxide)
PP	: Polypropylene
PTFE	: Polytetrafluoroethylene
SEM	: Scanning Electron Microscopy
TGA	: Thermal Gravimetric Analysis
VPA	: Vinyl Phosphonic Acid



SYMBOLS

I	: Initiator
R*	: Initiator radical
M	: Monomer
k_d	: Thermal Decomposition Rate Constant
k_i	: Initiation Rate Constant For The Primary Radical
k_p	: Propagation Rate Constant
k_t	: Termination Rate Constant
k_{tc}	: Combination Termination Rate Constant
k_{td}	: Disproportionation Termination Rate Constant
P_n*	: Free Radical with “n” Monomeric Units
P_n	: Dead Polymer Chain with “n” Monomeric Units
T_g	: Glass Transition Temperature
η_{sp}	: Specific Viscosity



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FLAME RETARDANT NANOFIBERS FROM ACRYLONITRILE, METHYLACRYLATE AND VINYLPHOSPHONIC ACID TERPOLYMERS WITH USING ELECTROSPINNING TECHNIQUE

SUMMARY

Polymers have been used many areas in our lives with manufacturing different production methods. Due to the polymers have some advantages such as low cost and light weight so these advantages make them preferable material in many areas. Nanotechnology also effected our lives and polymers can be used as a raw material for nanofiber production via different production methods. Electrospinning is one of the suitable nanofiber production method which is very proper and simple way to create versatile properties of nanofibers.

Besides this developments, some disadvantages of polymers must be considered such as flammability. Due to the organic based structures of polymers that can be easily burn and cause very big bad results. To avoid fire conditions, flame retardant materials can be used as an additive during production of polymer products. Flame retardant additives can be halogen, halogen free or inorganic. Halogen flame retardants have a toxic gases during combustion and hazardous effects. For this reason, halogen free flame retardants should be used to avoid toxic gases release to the environment.

This study can be seprable into two main parts. The first part purpose is to synthesize and characterized acrylonitrile (AN), methyl acrylate (MA) and vinyl phosphonic acid (VPA) homopolymer, copolymers and terpolymers. And the second part is to produce nanofibers via electrospinning method with using synthesized polymers and add a flame retardant property to the produced nanofibers.

For first part, initially homopolymer of PAN was synthesized. Then with different percentage of initiator to chain transfer agent ratio was used to synthesize copolymers and terpolymers under same reaction conditions.

Synthesized P(AN) homopolymer, P(AN-MA) copolymers and P(AN-MA-VPA) terpolymers were characterized using Fourier Transform Infrared spectrometer (FTIR), differential scanning calorimeter (DSC), and thermal gravimetric analysis (TGA). The effect of MA and VPA content on the spectroscopic and thermal properties of AN-MA copolymers and AN-MA-VPA terpolymers were investigated.

In the second part of study, electrospinning process of the homo PAN, AN-MA copolymer and AN-MA-VPA terpolymers solutions in dimethyl formamide (DMF) was prepared successfully. Morphology of nanofibers was determined with using Scanning Electron Microscopy (SEM).



AKRİLONİTRİL, METİLAKRİLAT VE VİNİLFOSFONİK ASİT TERPOLİMERİ İLE ELEKTROSPİNNİNG YÖNTEMİ KULLANILARAK ALEV GECİKTİRİCİ ÖZELLİKLİ NANOFİBER ELDESİ

ÖZET

Günlük yaşantımızda birçok farklı malzemeden imal edilen ürünleri çok farklı ve önemli alanlarda kullanmaktayız. Bu ürünlerin birçoğunu polimer yapıda olan malzemeler oluşturmaktadır. Bu ürünler, kullanılacak alan ve yerine göre oldukça farklı üretim yöntemleri ile üretilmektedir. Çeşitli ve birçok farklı alanda kullanım imkanı bulan ve hayatlarımızı kolaylaştıran bu polimer yapıdaki malzemeler farklı yapıda hammaddeler kullanılarak üretilen, örneğin metal ya da seramik alternatiflerine göre birçok avantaja sahiptir. Bunlara en genel örnek olarak düşük maliyet ile üretim ve hafif yapıda olmaları verilebilir.

Polimerlerin hayatımızda bu kadar fazla yer alması farklı üretim yöntemlerini ve kullanım alanlarını da geliştirmektedir. Bunlara örnek olarak nanoteknoloji son yıllarda hayatımıza girerek çok farklı özellikleri ile çok iyi yönde gelişim göstermektedir. Çünkü nanoteknoloji malzemelerin makro boyutta sahip olduğu özelliklerden çok daha farklı özelliklere sahip olabileceğini göstermiştir. Son yıllarda nanoteknoloji üzerine yapılan ve giderek artan çalışmalar sayesinde oldukça farklı özelliklerde ürünler elde edilmekte ve çok farklı alanlarda kullanılabilmektedir.

Nanoteknoloji kullanılarak üretilen malzemelerden biri de nanoelyaflardır. Nanoelyaflar çok farklı üretim yöntemleri ile üretilmektedir. Bunlar arasında nanoelyaf üretiminde de uygun ve basit tekniği olması sayesinde elektrospinning yöntemi en fazla tercih edilen yöntemlerden biridir.

Elektrospinning yöntemi kolay kurulumu ve kolay üretim yapılabilme özellikleri sayesinde nanoelyaf üretiminde en çok tercih edilen üretim tekniklerindendir. Proses şemasında yüksek voltaj kaynağı, polimer çözeltisi, şırınga ve elyafların toplandığı yüzey, prosesin temel gereksinimlerini oluşturmaktadır. Bu ekipmanlar yatay ve dikey olarak kullanılabilmeye imkanı da sağlamaktadır. Ayrıca elektrospinning tekniği çok az ekipman ihtiyacına gerek duymasına rağmen proses ve polimer çözeltisi parametreleri değiştirilerek çok farklı özelliklere sahip olabilmektedir. Örneğin proses parametreleri olarak voltaj, akış hızı, toplayıcı yüzey farklılığı ya da şırınga çapında yapılan değişiklikler son ürünün özelliklerine etki edebilmektedir. Proses parametrelerine ek olarak polimer çözeltisi parametreleri de örneğin derişim, viskozite, solvent tipi gibi özellikler de son ürün yapısında değişikliklere sebep olabilmektedir. Bu gibi özellikler değiştirilerek üretimde en uygun çalışma koşulları ve en uygun nanoelyaf üretimi sağlanabilmektedir.

Polimerler kullanılarak üretilen birçok ürün günlük hayatımızda çok fazla alanda hayatımızı kolaylaştırmaktadır. Ancak polimer yapılı ürünlerin çok fazla hayatımızı kolaylaştıran özelliğinin olması yanında, organik yapıda bir malzeme olmasından dolayı aleve maruz kaldığında bazı kötü sonuçlara yol açabilmektedir. Bu nedenle evlerde, iş yerlerinde ya da toplu yaşam alanlarında herhangi bir yangın durumu ile karşılaşıldığında bu ürünlerin kolayca yanması, ortama zararlı gazları ortaya çıkarması ya da ortama verdikleri siyah is şeklindeki dumanlar dolayısı ile tahliye işlemini zorlaştırması sebebi ile yanma davranışlarını iyileştirmeye yönelik çalışmalara ihtiyaç duyulmaktadır. Bu gibi durumların yaşanmaması için polimerlerin sentezinde ya da üretimde bazı ek yardımcı katkı malzemeleri kullanılmaktadır. Bu malzemeler alev geciktirici malzeme olarak bilinmektedir ve polimerlere sentez sırasında ya da sentez işleminden sonra kullanım esnasında katkı malzemesi olarak katılabilmektedir.

Polimerler ile birlikte kullanılabilen çok farklı yapıda alev geciktirici hammaddeler bulunmaktadır. Alev geciktirici yapıda olan bu katkı malzemeleri halojenli, halojensiz ya da inorganik yapıda olabilir. Bu malzemeler tek başına kullanılabildiği gibi birden fazla yanma geciktirici katkı malzemesi aynı anda kullanılabilir. Aynı anda birden fazla alev geciktirici malzemenin birlikte kullanılması sinerjistik bir etki yaratarak yanma durumunun gecikmesini sağlamaktadır. Geçmiş yıllarda yanma geciktirici malzeme olarak halojen içeren katkı maddeleri çok fazla kullanılmaktaydı. Ancak halojen yapıda olan yanma geciktirici malzemeler yanma esnasında çevreye çok fazla miktarda toksik gazların çıkmasına neden olmaktadır bu nedenle yanma geciktirici malzeme kullanılırken son yıllarda halojen içermeyen katkıların kullanımı teşvik edilmektedir.

Yapılan bu çalışma iki ana kategoriye ayrılabilir. İlk kısımda amaçlanan çalışma, homopolimer, kopolimerler ve terpolimerlerin sentezlenmesi ve karakterize edilmesidir. Bu sentezlerde akrilonitril (AN), metil akrilat (MA) ve vinil fosfonik asit (VPA) monomerleri kullanılmıştır.

İkinci kısımdaki amaç ise, sentezlenen polimerleri uygun çözücü içersinde çözerek daha sonrasında elektrospinning prosesinde kullanarak nanoelyaf üretmek ve terpolimer elyafa yanmazlık özelliğinin kazandırılmasıdır.

İlk kısım için öncelikle homo poliakrilonitril polimeri sentezlenmiştir. Sonrasında farklı başlatıcı/zincir transfer ajanı oranlarında kopolimerler ve terpolimerler aynı reaksiyon koşullarında sentezlenmiştir.

Sentezlenen P(AN) homopolimeri, P(AN-MA) kopolimerleri ve P(AN-MA-VPA) terpolimerleri Fourier Transform Infrared spectrometre (FTIR), diferansiyel taramalı kalorimetre (DSC) ve termal gravimetrik analiz (TGA) yöntemleri ile karakterize edilmiştir. MA ve VPA içeriklerinin etkileri bu analiz yöntemleri ile incelenmiştir. Detaylı sonuçlar grafikler ile birlikte sonuçlar kısmında yer almaktadır. Ayrıca Fosfor içeriği yatini de ICP/OES yöntemi ile ölçülerek tespit edilmiştir.

İkinci kısımda ise, öncelikle sentezlenen P(AN) homopolimer, P(AN-MA) kopolimerleri ve P(AN-MA-VPA) terpolimerleri dimetilformamid (DMF) çözeltisi kullanılarak hazırlanmıştır. Hazırlanan bu çözeltiler elektrospinning prosesinde denenerek elde edilen nanoelyafın morfolojik çalışmaları taramalı elektron mikroskopu (SEM) ile yapılmıştır.

Yapılan polimer sentezi ve nanoelyaf çalışmaları sonrası gerekli miktarda hazırlanan polimer çözeltileri ile film çalışmaları yapılarak ürünlerin su emme kapasiteleri değerlendirilmiştir. Ayrıca filmler aleve maruz bırakılarak yanma davranışları incelenmiştir.

Yukarıda bahsedilmiş olan çalışmanın temel iki basamağı başarılı bir şekilde gerçekleştirilmiştir. Ayrıca bu çalışmalara istinaden yapılan karakterizasyon, morfoloji ve diğer deney çalışmaları da gerçekleştirilen deney ve istenilen gelişimin sonucu hakkında önemli bilgiler vermektedir.

İlk etapta sentezlenen polimerlerin deney sonuçları incelendiğinde, tüm polimerlerin (homopolimer, kopolimerler ve terpolimerler) başarı ile sentezlendiği görülmektedir ve yapılan Fourier Transform Infrared spectrometre (FTIR) ölçümü ile sentezlenen polimerlerin sentez sonuçları desteklenmektedir. Ayrıca vinil fosfonik asit (VPA) monomerinin Fourier Transform Infrared spectrometre (FTIR) ölçüm sonucuna göre başarılı bir şekilde yapıya katıldığı gözlemlenmiştir. Özellikle bu katılım literatür açısından da önemli bir yerde bulunmaktadır.

Diğer karakterizasyon testlerinden olan termal gravimetrik analiz (TGA) ile elde edilen bulgulara göre; sentezlenen P(AN-MA-VPA) terpolimerinin, yapıya katılan vinil fosfonik asit (VPA) monomeri sayesinde kül miktarında olumlu yönde artışa sebep olduğu tespit edilmiştir. Kül miktarındaki artış yanma davranışı incelendiğinde, toplam kül miktarının artması test sonucunda beklenen bir davranış olmaktadır.

Sentezleri gerçekleştirilen polimerler elektrospinning işlemi için kullanıma hazır hale gelmeden önce uygun solventte çözülmesi gerekmektedir. Ayrıca elektrospinning işleminin gerçekleşmesi için hazırlanan solventin konsantrasyon ve viskozite değerlerinin uygulama için en uygun değerde olması gerekmektedir. Bu nedenle çalışmaların yapılmadan önce optimum çalışma koşulları belirlenerek ilgili çözeltiler hazırlanmıştır. Bu değerlendirmeler sonrasında gerçekleştirilen elektrospinning prosesi sayesinde başarılı bir şekilde nano elyaf eldeleri gerçekleştirilmiştir. Elde edilen nano elyafların morfaolojik özellikleri incelenerek nano elyafların yapıları hakkında detaylı bilgiler elde edilmiştir.

Temelde iki ana basamağa ayrılan çalışmalar başarılı bir şekilde gerçekleştirildikten sonra kazandırılmak istenen özellik bakımından da polimerlerin yanma davranışları incelenmiştir. Bu amaca istinaden sentezlenen polimerler ile hazırlanan filmler optimum mesafeden aleve maruz bırakılarak yanma davranışları incelenmiş ve birbirleri ile kıyaslanmışlardır. Filmlerin birbiri ile kıyas edilme işlemlerinde ayrıca koku, duman gibi çevreye etki edebilecek kötü durumların da incelemesi yapılmış ve elde edilen sonuçlar detaylı bir şekilde verilmiştir.



1. INTRODUCTION

Nanotechnology has many good properties in the global economy as well as being a type of technology with many unique benefits in the industry. With increasing knowledge and technology about nanomaterials, many researchers in many sectors are working on new developments [1]. The reasons for the nanotechnology is an attractive area for researches that the properties of materials are different when they produce from macroscale to nano scale [2,3].

Nanofibers are the kind of nanotechnology product. They are superior than traditional microfibers [4,5]. Due to unique properties such as large surface area per unit volume, ultraviolet resistance, chemical resistance, low density and large porous structure nanofibers have big opportunity for industry. Additionally nanofibers can be used very different manufacturing area such as, drug delivery, fuel cells, tissue engineering, filtration systems, nanocomposites etc [4-7].

Poliacrylonitrile (PAN) is a very common used material for nanofiber production in very different usage area with different properties [8]. Generally polyacrylonitrile is used as a comonomer addition. With using comonomer for polyacrylonitrile, the properties of PAN can be developed better. Generally vinyl acetate, methyl acrylate, methyl methacrylate or itaconic acid can be used as a comonomer [9,10].

In our lives, we use lots of polymeric material in different areas such as houses or public areas. In this case fire prevention gains importance due to bad effect on the people and environment [11]. For this reason, flame retardant additives such as halogen or halogen free materials can be added into the polymers [12,13]. Due to the halogenated flame retardants have toxic gases during combustion, halogen free flame retardants are preferred [14].

Nanofibers can be produced with using polyacrylonitrile and its derivatives. Phase separation, mechanical drawing or electrospinning can be used to produce nanofiber and electrospinning method is the important and good method among these [15,16]. Electrospinning is very useful process to create nanofibers from polymers with very

different morphology. And also, nanofibers have large surface area to volume ratio, high porosity and good mechanical properties with using electrospinning process [5,17,18]. Electrospinning process can be effected process and solution parameters. These are flow rate, electric field, collector type, viscosity, surface tension, distance, ambient parameters etc [1].

The main objective of this study is to produce electrospun nanofiber structures by using polyacrylonitrile, methyl acrylate and vinyl phosphonic acid derivatives with using electrospinning process and create the flame retardant properties in the terpolymer structure.



2. THEORETICAL PART

2.1 Radical Polymerization

Free radical polymerization is a method used in the production of many different plastic materials, which can be used in rubber or fiber production [12,13]. Additionally free radical polymerization method is used for the polymerization processes of vinyl monomers that containing carbon-carbon double bonds are used widely in the industry. Low density poly ethylene, polystyrene, acrylic polymers can be produced with this polymerization technic. According to reaction enviroment, free radical polymerization progress in bulk, suspension, solution or emulsion process [19].

Basically, this reaction occurs in three parts which are initiation, propagation, and termination steps. These polymerization reactions can be started by anions, cations or free radicals [12,19,20]. Also heat, visible light, electricity, ionizing light can start the free radical initiation [13]. Reactions known as chain transfer during free radical polymerization can occur [19]. In addition, free radical polymerization occurs rapidly [13]. Reaction mechanisms characterize free radical polymerization. It has been found that the molecular weight of the polymer rapidly increases while the monomer consumption is relatively slow [19].

The terms of free radical polymerization are given in Table 2.1.

Initiation;



Propagation;





Termination;

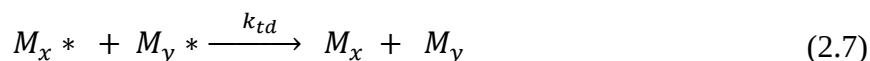
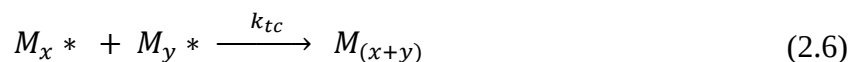


Table 2.1 : Terms of free radical polymerization

I	Initiator	k_d	thermal decomposition rate constant
R^*	Initiator radical	k_i	The initiation rate constant for the primary radical
M	Monomer	k_p	the propagation rate constant
P_n^*	free radical with “n” monomeric units	k_{tc}	the combination termination rate constant
P_n	dead polymer chain with “n” monomeric units	k_{td}	the disproportionation termination rate constant

The rate of free radical reaction steps are given below:

$$\text{Rate of decomposition } R_d = 2k_d[I] \quad (2.8)$$

$$\text{Rate of initiation } R_i = k_i[R^*][M] \quad (2.9)$$

$$\text{Rate of propogation } R_p = k_p [M^*][M] \quad (2.10)$$

$$\text{Rate of termination } R_t = k_t [M^*][M^*] \quad (2.11)$$

$$k_t = k_{tc} + k_{td} \quad (2.12)$$

2.2 Initiators of Free Radical Polymerization

One of the most widely used methods is the free radical polymerization technique for the synthesis of macromolecules. When the free radical reaction starts, the first obtained materials are called radicals. These radicals can be obtained by various

methods and generally the use of initiators is preferred [21]. The initiator types used in the radical polymerization are divided into three groups such as thermal (peroxides and azo), redox and photoinitiators. Additionally, electrons can be used as an initiator [22]. These initiator types depends on the ffect of the alkyl groups [23]. Additionally, a good initiator should be stable under room conditions but should be easily separable at polymerization process [22].

The most commonly used materials in this method are azo and peroxy compounds. These initiators have an ability to form suitable radicals at a narrow temperature range. These initiators are evaluated according to the half-life and dissociation constant k_d . But these initiators can lead to gaseous side products if they are used in non-mixed environments. Azo compounds are separated into a pair of radical species with nitrogen in the reaction and peroxides lead to the formation of peroxy radicals and carbon dioxide. They may not be directly used in practical applications due to they can cause bubbles to form in the material [21,22,24].

The molecular structure of azobisisobutyronitrile is given in Figure 2.1.

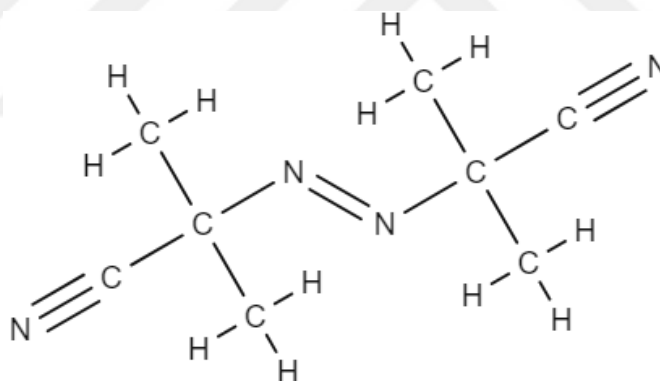


Figure 2.1 : Molecular structure of azobisisobutyronitrile

Oxidation and reduction mechanisms are also used to initiate free radical polymerization. These initiators also contain a metallic ion which provides electron transfer. To occur redox reaction, hydroperoxides, peroxides, persulfates and other peroxides can be used with using reducing agents such as Co^{2+} , Fe^{2+} , Ce^{4+} or Cr^{2+} . Generally redox initiators are soluble in water and are generally preferred in emulsion polymerization. The redox initiators progress rapidly and are more suitable at low temperatures [22,24].

Photoinitiation can be used as an initiator also and this type of reaction is independent from temperature. Additionally the reaction can be easily stopped by removing light source [22].

Ammonium persulphate structured initiators can be used in emulsion and other polymerization types that occur in aqueous media. The major causes of which are high solubility in water. It can be decomposed by thermally or photochemically [25]. Ammonium persulfate (AMPS) (Figure 2.2) has generally been used in many studies in the reaction of many vinyl monomers with a wide variety of synthetic or natural monomers [26].

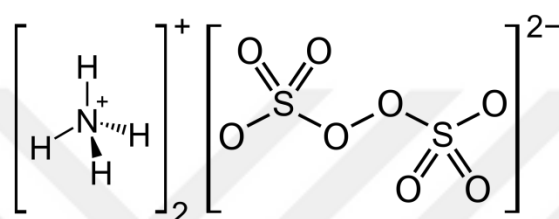


Figure 2.2 : Molecular structure of ammonium persulphate (AMPS)

2.3 Acrylonitrile and Polymerization of Acrylonitrile

The first synthesis of acrylonitrile and polyacrylonitrile was made by French chemist Moreau at 1893 [27,28]. He performed the acrylonitrile synthesis (Figure 2.3) first then the polyacrylonitrile (PAN) synthesis [28].

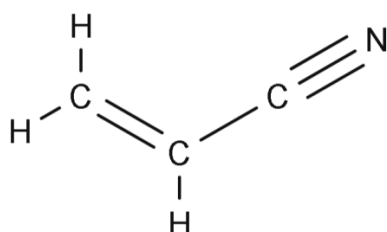


Figure 2.3 : Molecular structure of acrylonitrile

Generally Sohio process (Figure 2.4) are used to produce acrylonitrile from propylene and ammonia. Applied catalyst and the reaction arrays determine the differences between the production methods [29]. Vinyl chloride, vinyl acetate, styrene, acrylic acid methylester, methacrylic acid ethylester, vinylidene chloride, itaconic acid are the commonly used comonomers with acrylonitrile [29].

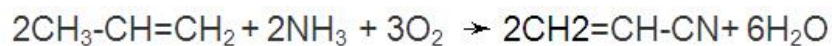


Figure 2.4 : Sohio process

Polyacrylonitrile is a very important polymer for the industry due to its important properties, for example hardness, rigidity, low gas permeability, high strength, moisture resistant, good weatherability, tough, resistant to fungi and chemicals [13,27]. Polyacrylonitrile is the most popular material used in carbon fiber production. Information about the behavior of the degradation of polyacrylonitrile can be obtained by thermal analysis methods. Thermal analysis methods are very important to understand the properties of polymer materials such as DSC and TGA. These methods can be used to determine the moisture and volatile substances contained in the material. So, the substances causing the effect on the physical and chemical properties of the polymer can be determined by these method. In addition, thermal characterization of polyacrylonitrile and duration of degradation time can be determined by these methods [30].

Polymerization of acrylonitrile is theoretically simple, including the use of comonomers or not. Studies on this situation are included in the literature [29]. Due to polyacrylonitrile is not a melting property, it degrades before its melting point because of the its high secondary bonding originating from the nitrile groups in the polyacrylonitrile [29,30]. For this reason a solvent or emulsion system should be used for the polymerization process. After the polymerisation process, the polymer is washed, dried and a very fine powdery polymer is obtained [29]. Acrylonitrile is a highly flammable, hazardous, toxic and carcinogenic liquid. Therefore, caution should be exercised during its use [28].

Polyacrylonitrile is the basis for many fibers and copolymers. The terms acrylic or acrylic fiber are used in fiber production. The first development of acrylic fibers began in Germany in the early 1930's. Commercial development took place in the 1950s by DuPont (Orlon) and Monsanto (Acrilan) in the USA [13]. High polarity solvents can be used such as N, N-dimethylformamide (DMF), dimethylacetamide (DMAc), or dimethyl sulfoxide to prepared mixture of process [30].

The fibers are divided into groups according to the acrylonitrile ratio. If there is more than 85 percent acrylic in the fiber content, this fiber is called acrylic fiber. If this ratio is in the range of 35-85%, this fiber is called modacrylic fiber. Modacrylic

fibers are complemented by other materials to improve flame retardant properties [13,28,39].

Acrylic fibers can be used instead of wool used in textile products. It is also possible to imitate fur with PAN. Also products such as nitrile rubber, gas filtration systems, fiber-reinforced concrete, outdoor applications, isolations, flame retardant fibers blouses, rugs, curtains, shirts can be produced with P(AN) [13].

2.4 Copolymers of Acrylonitrile

Copolymers of acrylonitrile are generally used in the production of acrylic fibers, automotive coatings, antioxidants, emulsifying agents, crosslinking agents, adhesives, biomedical industry etc [9,10]. Free radical polymerisation is used in the synthesis of these copolymers [8]. When using polyacrylonitrile alone, the obtained fibers have some disadvantages such as high glass transition temperature, low dyeability and low segmental movements. Therefore, suitable comonomers are used together with acrylonitrile to overcome these disadvantages [31,32].

When acrylonitrile is used as a copolymer by using a suitable monomer, the newly obtained copolymer shows a decrease in melting point and an increase in the decomposition temperature due to the deterioration of the bipolar relation between nitrile (-CN) groups [33,34]. Because polyacrylonitrile has a very high crystalline melting point and is dissolved in a very limited solvent resulting from intermolecular forces in the polymer chains [35]. Finally the copolymerization of acrylonitrile gives the new copolymer good properties such as good crystallinity or molecular relaxation by disturbing bipolar forces between nitrile (-CN) groups [34,36].

The comonomers used with acrylonitrile may be ionic or neutral. Monomers such as methyl acrylate, vinyl acetate, methyl methacrylate for neutral comonomers. Ionic copolymers may be ketones, ethers or alcohols [33,37-41].

Methyl acrylates are colorless and volatile liquids. they can be dissolved well in alcohol, ether and many organic solvents, while their solubility in water is low [42].

Phosphonates are used in many applications for their good properties. Vinyl phosphonic acids (VPA) are also commonly used in fields such as flame retardant, membrane, drug, catalyst production [43,44]. Additionally, due to the vinyl

phosphonic acid has a terminal vinyl group, it can be easily addapt in the radical polymerization to the present radical [45].

2.5 Flame Retardancy

In our daily lives, the use of polymers is very common and fire prevention are the main reasons due to their hazard during combustion behaviour [11].

Polymers such as polyethylene (PE) and polypropylene (PP) can easily burn which are generally used in daily life products [12]. They are expected to be non-flammable when used in daily life, for example in places like living areas. At the same time some polymers such as polytetrafluoroethylene (PTFE) has a high burning resistance from these polymers. But they can show burning behavior when appropriate combustion conditions are provided [12,13].

Combustion reaction occurs in the form of chain formation. The free radicals may initiate and promote the combustion. Many flame retardant materials are produced with using halogen or halogen free content. The reason is that halogens or halogen free compounds react with the free radicals then the combustion is terminated by this blends [13].

Halogen or halogen free containing polymers may be used to provide flame retardant properties. These materials can also be added into polymers which are already a flame retardant structure. The flame retardants can be used as a blend and they more successful than the flame retardants are used alone. This type flame reterdants are named synergistic [12,13].

Halogen containing flame retardant compounds in many different types and configurations are used in the industry in a great many ways. The main reasons for their excessive use in the market are high flame efficiency ratios and low cost. But halogenated flame retardants also have bad results in addition to their benefits such as toxicity [14]. For this reason the European Community has put restrictions on the halogenated flame retardants due to their toxic smokes and environmental pollution. Nowadays halogen-free flame retardant additives are being emphasized to remove these bad effects of halogeneted flame retardants. For this reason, materials containing phosphorus or nitrogen halogen free flame reterdants are developed such as ammonium polyphosphate (APP), aluminium hypophosphite (AHP) or vinyl

phosphonic acid (VPA) [46,47]. In addition to phosphoric acid, phosphorus acids and phosphorus salts, phosphonates also play an important role in flame retardant systems [11].

2.6 Nanofibers

Nanotechnology is an emerging technology that has been characterized as an important scientific and commercial enterprise with global economic benefits [1]. It divides into many areas to research and nanofibers are a different kind of nanotechnology branch whose main purpose is to produce nanostructured fibers to create superior functions [7]. Because, when the polymer fiber materials are downscaling micrometers to nanometers there occurs various different properties such as large surface area to volume ratio, flexibility, stiffness and good tensile strength [2,3,48].

Nanofiber makes reference to fibers have a diameter less than 1 μm , but National Science Foundation specifies the nanofibers should have 100 nm or less [49].

Polymeric nanofibers have important advantages than traditional microfibers [4,5]. Because of its unique properties, extensive research and wide range of commercial applications makes nanofibers exciting materials. They can form highly porous network nets with outstanding consistency among resources making it an attractive option for many advanced applications [50]. Also, they have large surface area per unit volume, comfort of use, functionalization, ultraviolet resistance, biodegradability, low density, tight pore size and excellent mechanical properties in compare with bulk properties of materials. These superior properties makes them preferable materials for many applications such as filtration, drug delivery, gas sensors, nanocomposites, tissue scaffolds, electronics, fuel cells, nanowires, nanorods, membranes and aerospace structures [4-7].

Additionally, the important effect of the nanofiber technology can be seen from wide range of current materials such as, natural polymers, synthetic polymers, carbon based materials and composite materials can be used to create nanofibers [50].

Due to the high surface to volume ratio, nanofibers can be used when much porosity is wanted. Nanofibers which have porous structure is a dynamic system, the pore

dimension and shape can be modified in contrast to rigid structures. At the same time, if it is wanted, nanofibers can be formed rigid structure [51].

In recent years, there have been many great quantity of reports about nanofibres were published [4]. There are different production techniques can be used to create nanofiber which are solvent dispersion, melt blowing, flash spinning, centrifugal spinning, hydrothermal, drawing, electrospinning, phase separation, self assembly, template synthesis etc [2,3].

Among these techniques, electrospun nanofibres easy to control for surface modifications, simple and cost effective process. In recent years, lots of researchers changed their attention from nanoparticles to nanofibers because of their possible applications. Also, in this thesis study; electrospinning was used for fabrication of nonwoven fibers. Therefore, electrospinning process was given in the next section in detail [1,4].

2.7 Evolution of Electrospinning

Electrospinning method first happened in the literature more than a century ago [49,51,52]. Then electrospinning has been first informed by Lord Rayleigh in 1882. He mentioned that, highly charged droplets are unsteady and easily decompose into smaller droplets when these charged droplets run through a syringe at applied potential gradient [3,15].

In 1902, Cooley and Morton patented devices and techniques separately [49,51,52]. In 1934, A. Formhals registered the first patent on electrospinning method. He used a cellulose acetate for his patent study. After this patent, lots of publications and patents about electrospinning have been published by different researches [2,15,49,51,53]. Until 1990s, the electrospinning was not a popular subject to research [49,51,52].

In the 1990s, Reneker's group carried out pioneer studies about electrospinning and they drew attention on electrospinning. Recent two decades, electrospinning method has been largely adopted to create polymer, composite, carbon fibers with several measures. Currently, electrospinning method and the resulting nanofibres not only interest for academia, many companies have started industrial studies for several applications [49,54]. Now, an increasing number of scientists are interested

to this highly impressive technique for obtaining various nanostructures that can find applications in virtually every field [1,55].

Electrospinning process has been getting more attention in scientific area and industry since 20th century due to the its important properties such as, versality, potential to use in a many applications and commercial economic benefits. Several production methods for nanofiber fabrication can be found in literature [1,53,55]. These are, phase separation, mechanical drawing, electrospinning etc. Among these techniques, electrospinning technique is easy and suitable for the production of ultrafine nanofibers. In this technique, also orientation of fibers can be easily controlled [15,16].

Electrospinning is an elementary, multiple and favourable process to create nanofibers from polymers due to the particular fiber configuration. Because of large scale of productions can be produce with this simple process. And the excellent properties of electrospun nanofibers, for instance large surface to volume ratio, high density pores in very small area, mechanical strength makes the electrospun nanofibers superior material for several applications. For example, filtration, noise absorbing materials, wound healing, drug delivery, gas chemical or biosensors, wound healing, environmental materials, catalysis, electronic devices etc [1,5,17,18,48,56].

According to their large surface area per unit mass and small pore size, the nanofibers are ultrasmall solid fibers characterized by very small diameters less than 100 nm [16,48].

Surfaces that are nanostructured, can lead to magnificent effects, for instance, the lotus effect (self cleaning). Nano-scale is also especially related to biological systems, since the size of proteins, viruses and bacteria fall within this range of sizes. A comparison with the diameters of these materials indicates that the diameters of the electrospun fibers can be in a relatively wide range (Figure 2.5) [55].

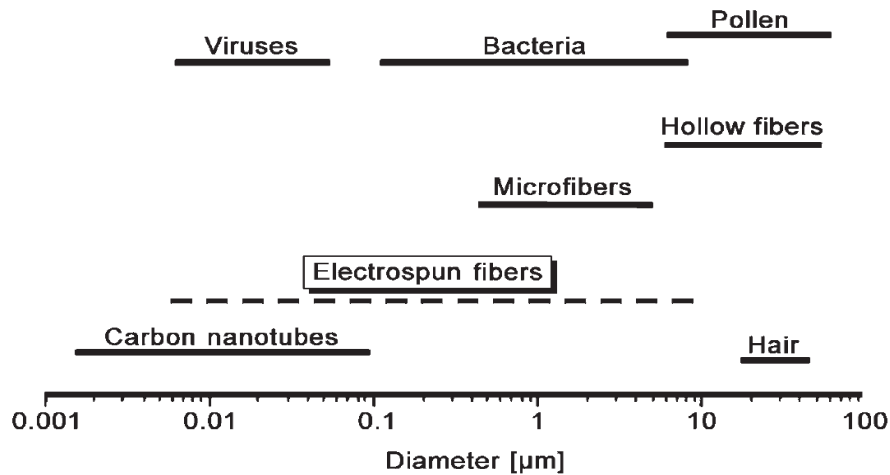


Figure 2.5 : Comparison of the electrospun fibers diameters to those of technological and biological objects [55].

Electrospinning process can be assumed as a kind of electrospraying process [49]. It consists of “electrospray” and “spinning” terms. A high electric field is performed to the droplet which can be melt or solution coming out from a syringe which behaves as one of the electrodes. The droplet deformation occurs and finally ejection of a charged jet from the syringe accelerating the counter electrode leading to the creation of continuous fibers [18].

Electrospinning technique is a easy technique to synthesize nanofibers from versatile materials such as synthetic or biodegradable polymers, metals, ceramics, composites, polymer alloys etc. Additionally, these nanofibers can be modified by modifying the surface or by mixing with functional additives, like bio-active materials, drugs, semiconductors, catalyst nano materials or sensitive substances [1,49,55]. This technique is also able to scale up for production of large quantities of materials and is simple [52]. Additionally, electrospinning technique has some advantages such as low cost and high production rate comparing to other nanofiber production methods [51].

Different surface morphologies can be seen from Figure 2.6. Beaded, ribbon, porous and core shell fibers can be obtained during spinning and it determines the usage area limitations [51].

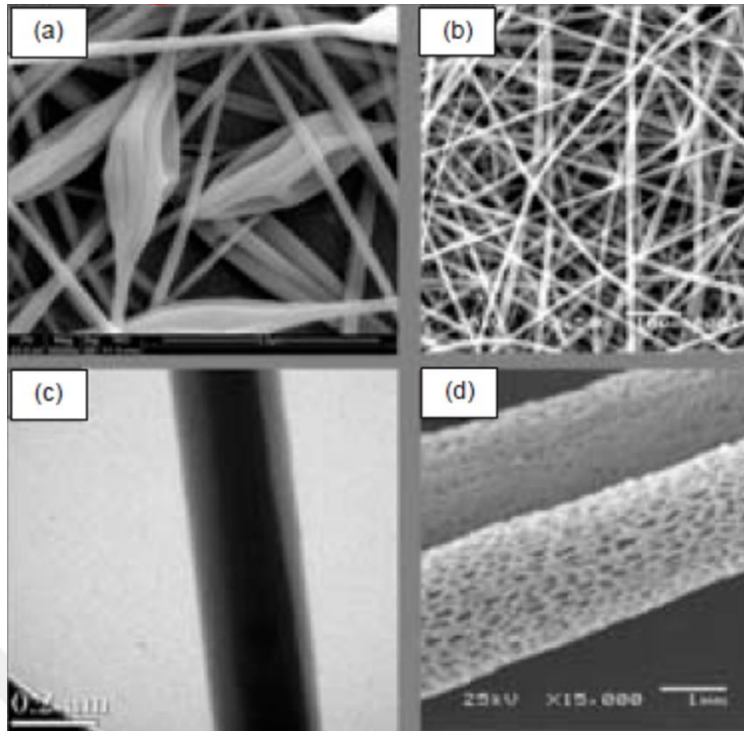


Figure 2.6 : Different fiber morphologies: (a) beaded, (b) smooth, (c) core-shell and (d) porous fibers [51].

The processing parameters, for example, applied voltage, rate of flow and the distance between electrodes, influence the formation of fiber or diameter. In some cases, environmental conditions, like temperature or humidity, also influence the morphology of the fibers. In addition, the properties of the polymer solution, like viscosity, conductivity or surface tension, besides influence the morphology of the fibers. In general, the size of nanofibers decreases with decreasing polymer solution concentration, increasing the applied voltage and increasing the distance between the electrodes [53,56].

When prepared a nonwoven mat, the composed fabrics are highly porous. For instance they have a huge interconnected void volume in the range of 50% to 90% and these percentages highest surface to volume ratio in all porous materials. They can be produced as a woven or nonwoven structure (Figure 2.7) [57].

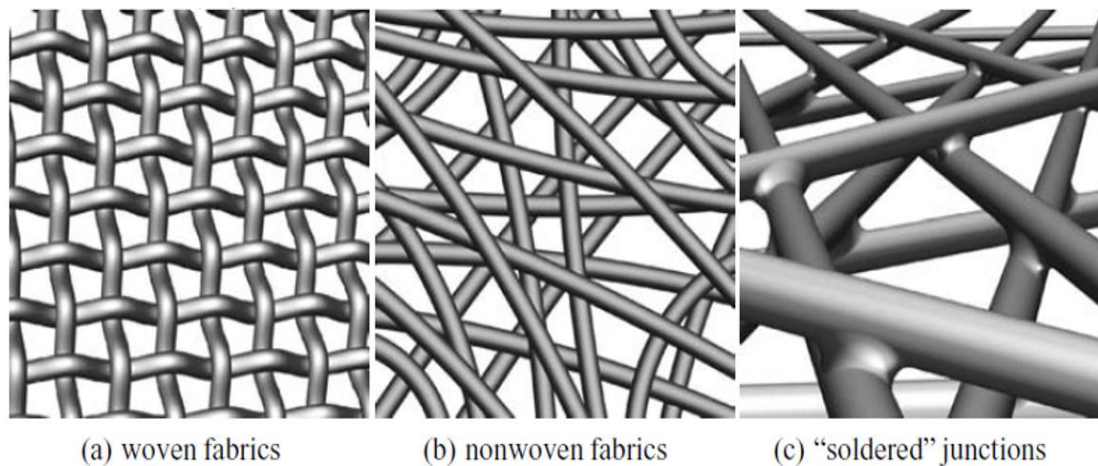


Figure 2.7 : Different fibers representations. [57].

2.8 Electrospinning Process

Nanofibers, which diameters less than 100 nm and up to a kilometer in length can be manufactured using an electrostatic forced jet of polymer solution (or melt form of polymer) [5]. Polymers can be tranformed into nanofibers with using elektrospun method. Lots of research has been done one electrospinning technique [1]. During this method, there are some targets to become ideal, fibers diameters be steady or controlable, surface of fiber without defect or controllable defects, single nanofibers be collectable and continious [2]. At first view, due to the simplicity and easy controlled method, electrospinning technique gives the impression to produce of fibers with wide range dimensions [55].

Electrospinning is a process which creating a one dimessional nanofiber with using solution or molten liquid by applying high voltage. This method also simple, versatile and inexpensive to produce wide range of nanofibers from nanometers to micrometers with using lots of different raw materials [58].

Electrospinning methos has some parameters such as process and solution. According to changes of these parameters, size of nanofibers can be controlled. Viscosity, feed rate, voltage, conductivity, surface tension, distance, needle type and collector is the parameters of the electrospinning system [58].

The technology of fiber formation is depending on the basis of "electrostatic attraction" of charges [4]. To create good functional fibers, electrospinning method is the best approach with using electrostatic forces [48,49]. Electrospinning process (Figure 2.8) contains there main parts to perform the process. These are, high voltage

power source, capillary tube with spinneret and collector [2,4,58]. Conventional electro-spinning process works with high voltage power supply and create an electrical field to produce nanostructured fibers [49]. The needle contains a liquid solution and the high voltage is linked to the end of it. An electric field is generated by high voltage supplier. When the electric supplier works, electric fields occurs and increase, then Taylor Cone shape droplet is formed. The high voltage is continued between needle tip and conductive collector then electric field exceed the surface tension of droplet [1,2,5,30,48,49,55,58]. First the charged jet undergoes a stable stretching. After, bending and whipping behaviours occurs and it causes to the further stretching due to the solvent evaporation and charge repulsion [49]. The electrically charged solution is ejected to the collector. During the process, the solvent evaporates then charged fibers is collected on the collector. Variable cross sectional shapes and dimensions of fibers can be create with using different polymer [1,2,5,30,48,49,55,58]. Electrospun fibers can be produced with small pore size and high surface area [48].

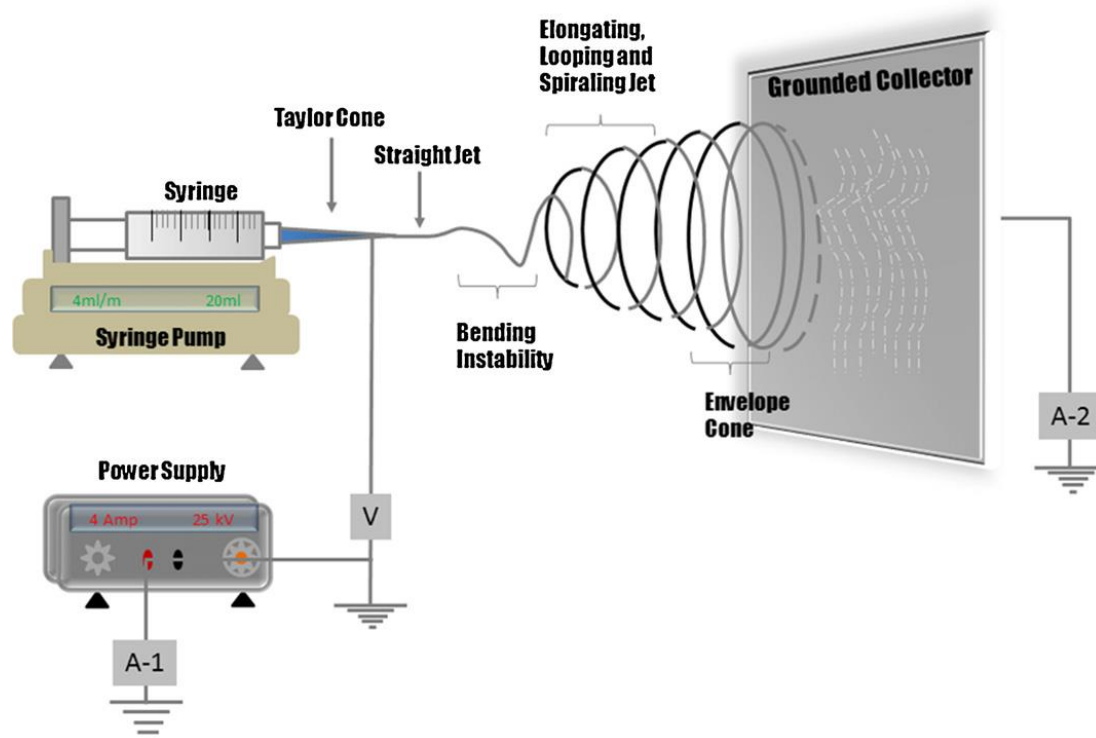


Figure 2.8 : The electrospinning process schematic illustration [35].

Many kinds of electrospinning tools are available on the market nowadays. Spinneret and collector types are differ from the process. Some devices use the electrode material as a spinneret, while some others use a needleless spinneret [4]. But most

tools have the latest type. In practice, there are two main classes of instruments, such as horizontal and vertical (Figure 2.9). In the horizontal type, applied voltage produce an effective charged force and and opposite charged collector with attractive forces that pulls the fibers. In the vertical type, fibers are driven by two different forces which are collector charges and gravitonal forces [4,58].

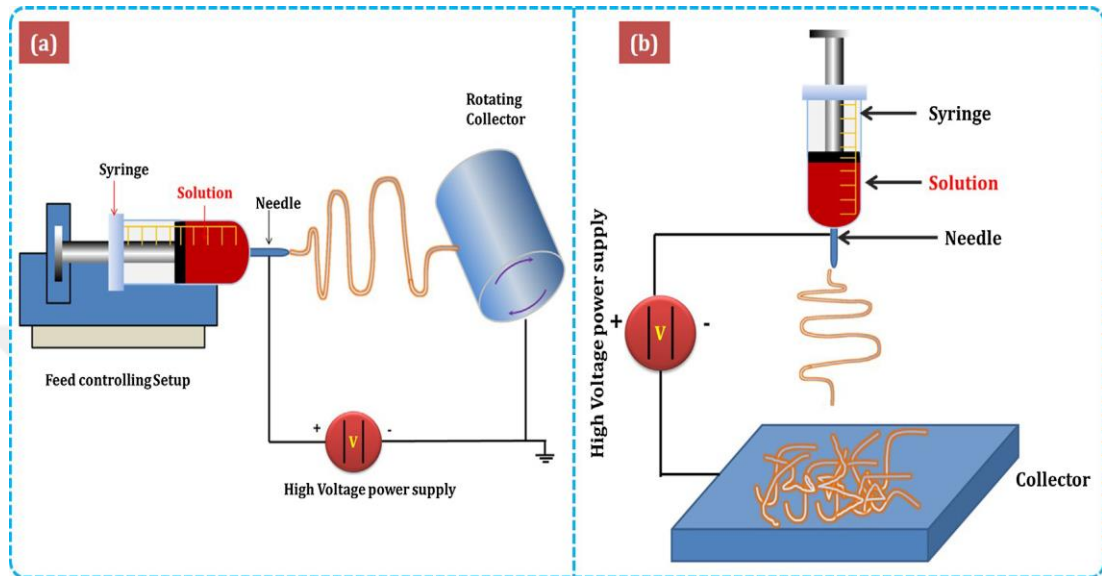


Figure 2.9 : (a) Horizontal Electrospinning (b) Vertical Electrospinning [58].

It is well known that single-jet electro spinning results in very low productivity. For instance an electrospun nanofiber mat with 1 g of weight may take many hours to create using a single spinneret. the practical way of solving this problem is the use of multi-jet electrospinning process with many spinnerets [49]. Additionally, in traditional electrospinning technique, the functionalization of nanofibers in some fields such as sensors, tissue engineering, drug delivery etc. leads to some obstacles. Generally the problem is the keeping stable of the functionalization agents during processing. The other problem can be difference of molecular weight of materials that can be effect the fiber morphology. Therefore, electrospinning method can be modified as coaxial electrospinning (Figure 2.10). To produce electrospun tissues with using different fiber materials can be manufactured with several syringes in multijet electrospinning (Figure 2.11) [55].

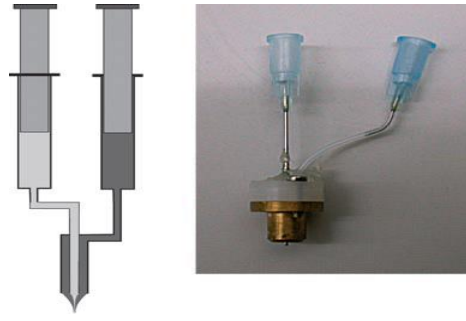


Figure 2.10 : A setup for coaxial electrospinning (left side). And the experimental setup for coaxial electrospinning (right side) [55].

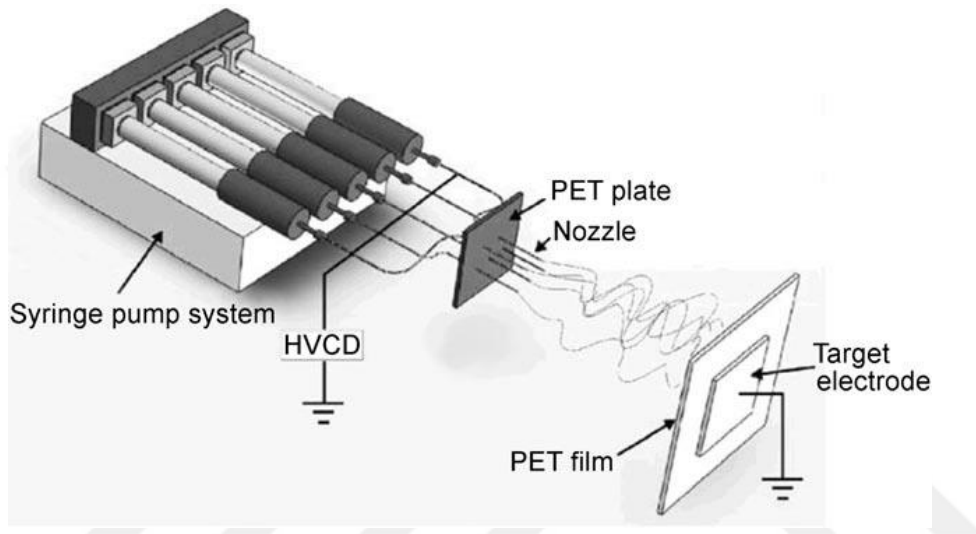


Figure 2.11 : An experimental setup of multijet electrospinning [55].

2.8.1.Process parameters

Many parameters can affect the modification and morphology of nanofibers during electrospinning. These parameters contain, like electric field, velocity, conductivity, viscosity, surface tension, needle, distance, collector type and ambient parameters as solution temperature, humidity and air velocity in the electrophasing chamber [1-3] to produce smooth and without bead nanofibers, the effect of parameters should think during process [1].

2.8.1.1 Tip to collector distance

The morphology and structure of electrospun fibers are mainly influenced from the distance between the collector and tip of needle because of the dependence on deposition time and instability interval or whipping. If the distance between collector and tip of needle will be closer, flight-time will be shorter but applied voltage will be higher. The shorter flight-time may cause bead formation. Because there may not be

enough time for evaporation of the solvent. On the other hand, higher voltage may cause jet acceleration. For this reason, the collector and tip of needle distance must be defined optimum for the preparation of uniform and smooth electrospun nanofibers. Any of changes for both side of distance may affect the nanofibers morphology. Optimum distance should be defined to obtain enough time for evaporation of the solvent [1,48,53,58].

2.8.1.2 Types and effects of collectors

Many researchers have been used different type of collectors such as aluminium foil, rotating drums, wire mesh, cloth, conductive paper or grided bar. However, aluminium bar is the common one due to its low price, availability, easy of changing during the analysis of different samples. Rotating drums are preferred also to create uniform thickness NFs and to get reproducible test results. SEM results of electrospun nanofibers which collected from different type of collectors were shown on Figure 2.12 [53,58].

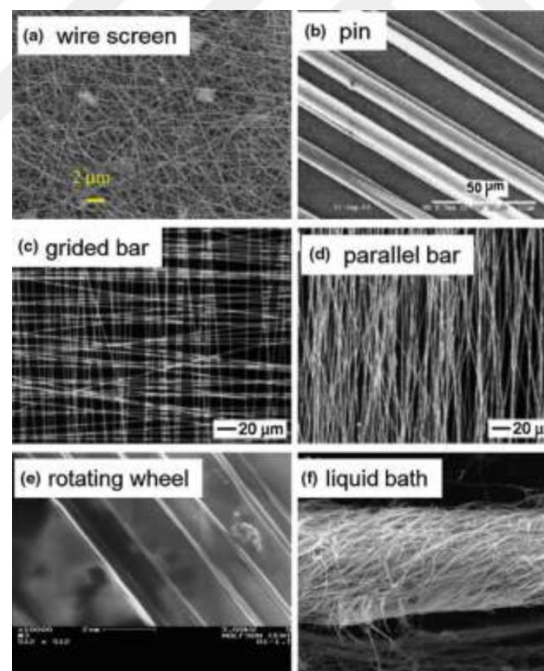


Figure 2.12 : The different electropun products SEM images with different type of collectors [53].

2.8.1.3 Feed rate/flow Rate

Solution flow with pressure applied is called as feed rate or flow rate. Flow rate is a significant proses parameter that the material jet velocity and transfer rate are effected directly. The feed rate should be slow to obtain enough time for evaporation

of the solvent. Otherwise higher flow rate may cause bead formations. In general, the low flow rate of the solution supports the polymer solution polymerization. With an higher flow rate, the diameter of pore and the diameter of fibers are increased in parallelly. The fibers varied in bead morphology and average pore size from 90-150 nm with the higher flow rate (Figure 2.13) [1,4,48,53,58].

Electrospun nanofibers with an uniform beaded can be prepared with an optimum flow rate of polymeric solution. The optimum flow rate value is changed with the polymer system. So optimum flow rate should be defined for each polymer system [1].

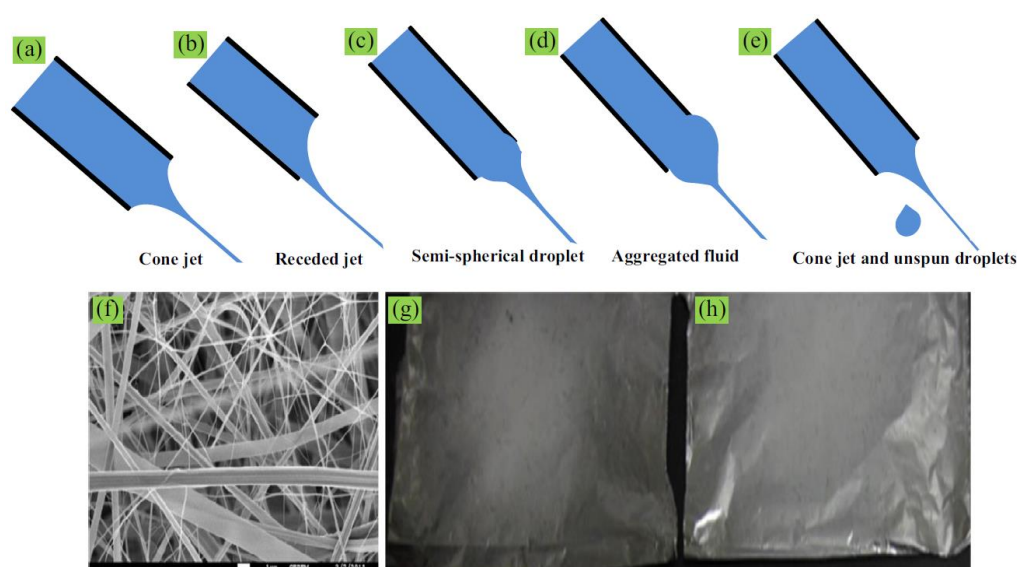


Figure 2.13 : Formation of various jets by increasing flow rate of nylon 6. The SEM image shows large diameter of nanofiber (f), and the digital images show the solution drop (g) and electrospun fiber of chitosan deposited on the aluminum foil (h) [1].

2.8.1.4 Applied voltage

The applied voltage is another process parameters that affect the diameter of fibers. Generally, the high voltage application (7 – 32 kV) through the electrospinning process cause the globular droplet to deformation into the Taylor cone formation and the solution gets charged. The high voltage reduces the fiber diameter and the flight time between the collector and the needle pin. High voltage application causes the change in the shape of jet starting point, which changes the structure and morphology of the fibers [1,2,58].

2.8.1.5 Ambient parameters

Humidity and temperature are related environmental parameters related to the fiber formation technique. The water concentrates on the fibers that will affect fiber morphology at high humidity. Moisture-increasing pores on the surface will form. The temperature increase will reduce the moisture content and evaporate the solvent faster [1,4,53,58].

2.8.2. Solution parameters

2.8.2.1 Concentration

After electrospinning process, beads and pores can be seen with SEM analysis (Figure 2.14). Beads formation can be effected by polymer concentration. It has been found that, if polymer concentration increases the bead formation decreases. When a polymer concentration changed from few to high quantity, shape of beads change from spherical to rodlike shape [2].

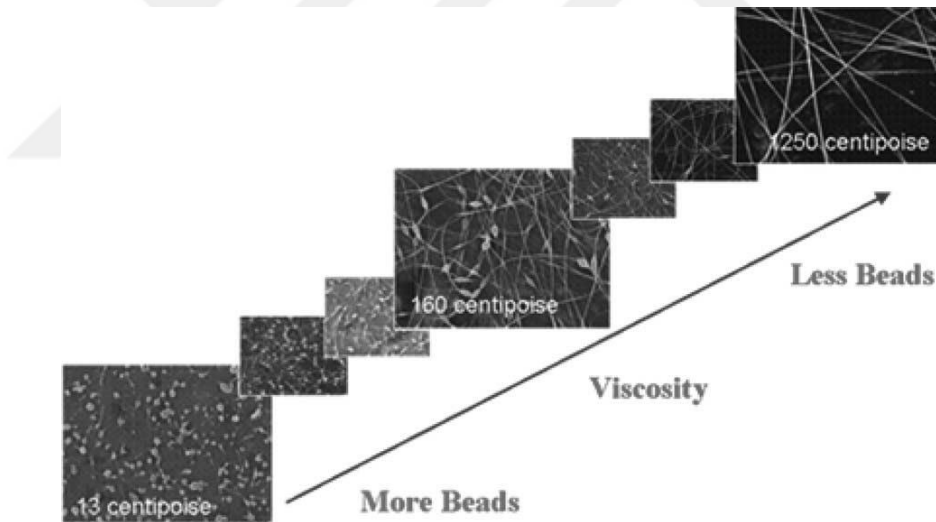


Figure 2.14 : Electrospun nanofibers SEM photographs from the different polymers concentration solutions [2].

Viscosity of solution will increase with enhances the concentration of polymer. Then chain entanglement will go up thorough polymer chains. Surface tension can be defeated with chain entanglements therefore without bead and uniform nanofibers occur. Additionally, if critical concentration value exceed, the polymer solution will be dried at the end of the needle then faulty or beaded nanofibers occur. Due to the changing of viscosity, the shape of beads will change to different types [1].

The polymer concentration and the viscosity are directly proportional to the amount of polymer dissolved in the solvent. Nanofiber diameters are increased with high polymer concentration and high viscosity value. There is a minimum concentration required for fiber production by electrospinning, otherwise electrospray is happened instead of electrospinning when the concentration is too low. The shape of the resulting beaded structures can be improved by increasing the concentration of the solution so that regular and high diameter fibers can be obtained. Due to the bead formation at low concentration and bad influences at high concentration, the optimum concentration should be determined [53].

2.8.2.2 Molecular weight

Molecular weight is one of the most important factors in determining the properties of nanofibers. Although the polymer material is the same, it is seen that the fiber diameters also vary when the molecular weight is changed. The most suitable molecular weight polymers should be used for the production of uniform and unique nanofibers [4].

The molecular weight of the polymer also affects the morphology of the nanofiber. At the same time the viscosity and surface tension properties will change if the molecular weight changes. For example, when the solution concentration is kept constant, the bead structure of the solution, prepared with the very low molecular weight polymer is formed, whereas when the solution is prepared with the high molecular weight, more uniform and higher diameter nano fibers are obtained (Figure 2.15) [53].

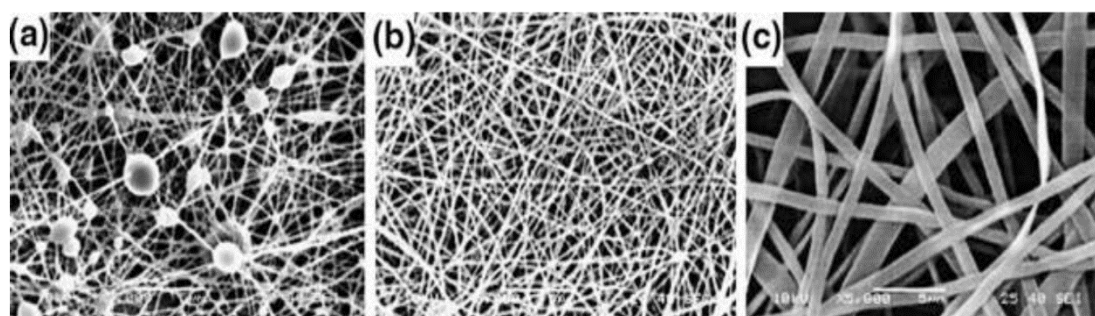


Figure 2.15 : SEM pictures showing typical structures in the electrospun polymer with various molecular weights; 9.000-10.999 g/mol (a), 13.000-23.000 g/mol (b), 31.000-50.000 g/mol (c) (solution concentration 25wt.%) [53].

2.8.2.3 Viscosity

The polymer solution must have appropriate molecular weight and viscosity values to produce uniform and unique nanofibers. Solution viscosity and surface tension play an important role in determining the required concentration range in the electrospinning process. If a polymer with a very low molecular weight is used during the process, the electrospray process happens and particles are occurred instead of nanofibers [53,58]. High diameter and less beaded nanofibers are obtained when a high viscosity solution is used during the process (Figure 2.16) [2,16].

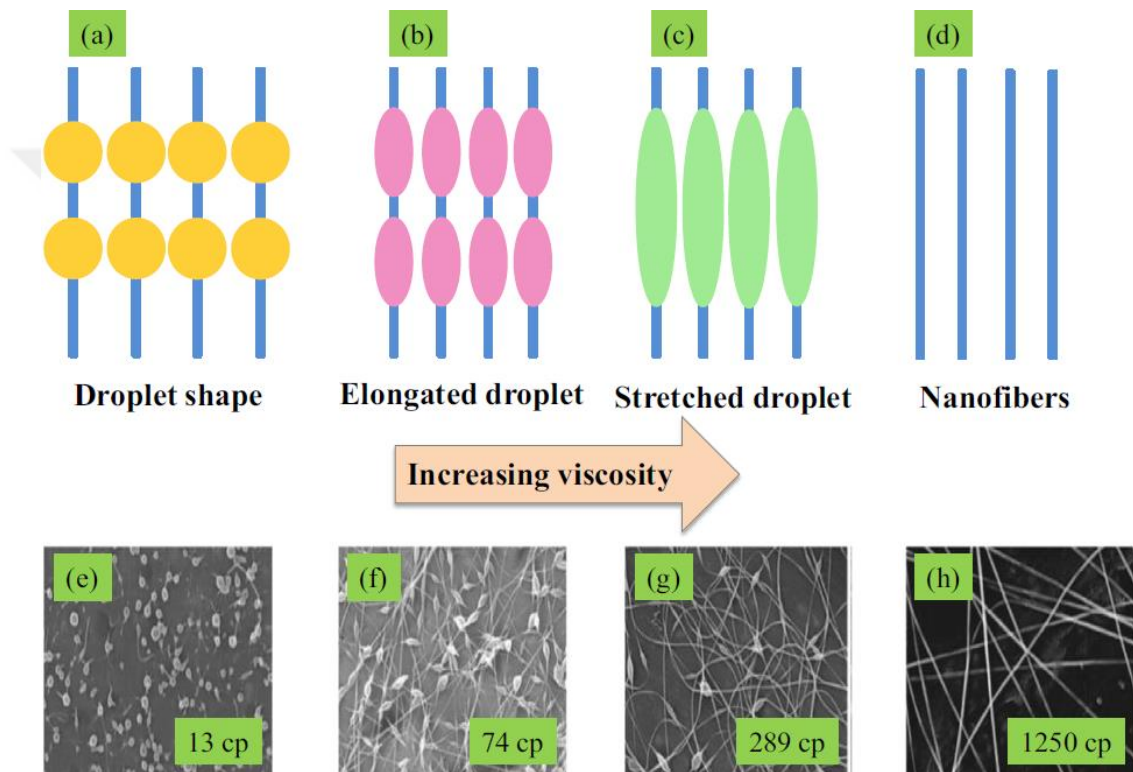


Figure 2.16 : POE's change in viscosity and morphology of electrospun nanofibers: (a–d) schematic and (e–h) SEM micrographs [1].

2.8.2.4 Surface tension

The ratio of the force applied to the surface plane to the unit length is called surface tension. A voltage is applied to the polymer solution in the electrospinning process to be converted into nanofibers and it must be large enough to exceed the surface tension of this voltage [4].

In electrospinning process there are several solvents can be used and as a result several surface tensions can be occurred. It may be necessary to reduce the surface tension to produce nanofibers in the bead-free structure. But this parameter is not

always the most appropriate variable. If the other parameters are constant, the process effect of surface tension can be seen more clearly. If the concentration is kept constant, less beaded structures can be obtained when surface tension is reduced [53].

2.8.2.5 Volatility of solvent

It is very important to choose the solvent to produce nanofiber without beads and smooth surface. There are two effective factors in solvent selection. These are, the used polymer must be completely soluble in preferred solvent, additionally the boiling point of the solvent should be medium value. The boiling point gives information about volatility of the solution. For example, volatile solvents evaporate rapidly during processing and move away from the nanofibers more quickly. However, when the boiling point decrease, drying at the tip of the syringe may occur due to the high evaporation rate, which may cause the process to stop. Furthermore, when the boiling point rises, the drying process of the jet takes a long time and the solvent can not be removed during the formation of the nanofiber and accumulates on the collector, which leads to the formation of beaded structures [1].

2.9 Applications of Nanofibers

Elektrospinning technology was used for manufacture and mount the nanofibers to the membranes. In recent years, intercalarily to composite reinforcement, different application areas based on electrospin nanofibers (Figure 2.17) have been constantly expanded. Electrospin nanofibers are used for optical, electronic, nanosensor, protective clothing, battery, filters, sensors, membranes, scaffolds, catalyst and wound dressing. The early stages, applications in the field of tissue engineering and biomedical have elucidated research on nanofibers. After the years, applications have spread across many areas, depending on the surface and chemical properties of the nanofibres [1,2,4].

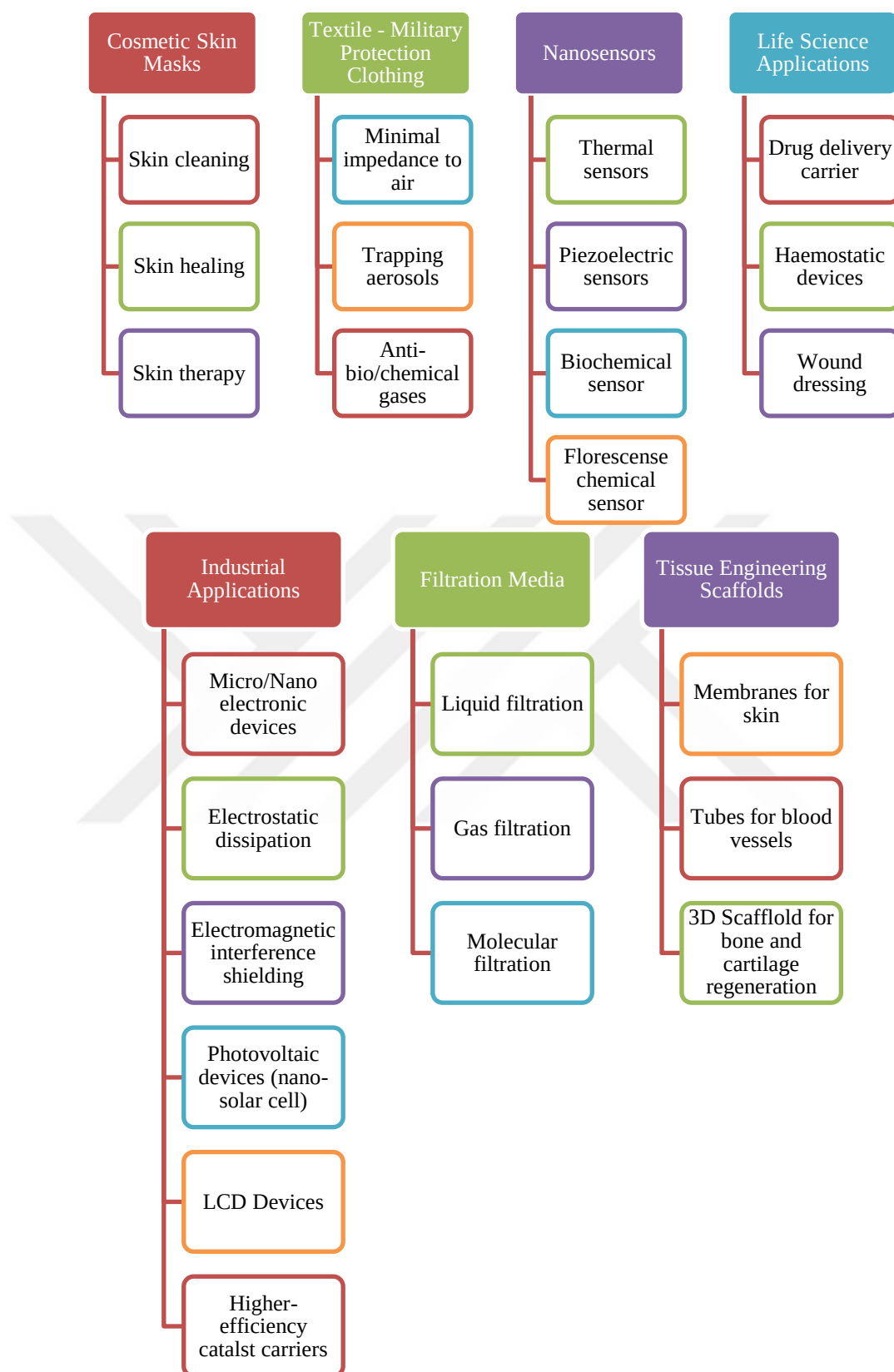


Figure 2.17 : Potential applications of nanofibers



3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile (AN) (99≥%) and Methyl Acrylate (MA) (99≥%) were supplied from Merck. Vinylphosphonic acid (VPA) (90≥%) was supplied from Aldrich. Ammonium peroxodisulphate (AMPS) (98≥%) was purchased from Lachema. Its color is white and it is in the form of pellets. Sodium metabisulfite (NMBS) (97≥%) was supplied by Riedel-de Haen. Its color is white. Dimethylformamide (DMF) was supplied from Akkim.

All of these chemicals were analytical and used as received.

3.2 Equipments

Heater (Heidolph, MR 3001 K), Analytical balance (Mettler Toledo, PB303-S) and mechanical stirrer (Heidolph, RZR 2020) were used to prepare the polymerization process and polymer solutions. Water bath (Julabo) was used to keep temperature constant during specific viscosity measurements. Fourier transform infrared spectroscopy (FTIR) was used to determine the absorption peaks of the polymers that recorded using a Perkin Elmer, Spectrum One. The morphology of the products was determined by scanning electron microscopy (SEM; FEI, QUANTA FEG 250) and the samples for the SEM measurement were prepared by platinum coating. Differential scanning calorimetry (Seiko Exstar, DSC 7020) was performed under a nitrogen atmosphere with a heating rate 10 °C/min. Thermo gravimetric analysis (Mettler Toledo, TGA1 Star System) was used to determine polymers char yields. The electrospinning device consist of high voltage power supply (Gamma High Voltage Inc., ES50) and syringe pump (New Era Pump Systems, Inc., NE-500) with collector at the end of the system. The produced electrospun films were collected on grounded aluminum foil. The electrospinning conditions were kept at room temperature, 25 °C.

3.3 Synthesis of Polymers

All reactions (homo polyacrylonitrile, poly(acrylonitrile-*ran*-methylacrylate) and poly(acrylonitrile-*ran*-methylacrylate-*ran*-vinylphosphonic acid)) (Figure 3.1) were synthesized by same steps. The synthesis steps were determined in this section and details of reactions are listed below. The percentages of ammonium persulfate (AMPS) to sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) were changed to create differences between polymers.

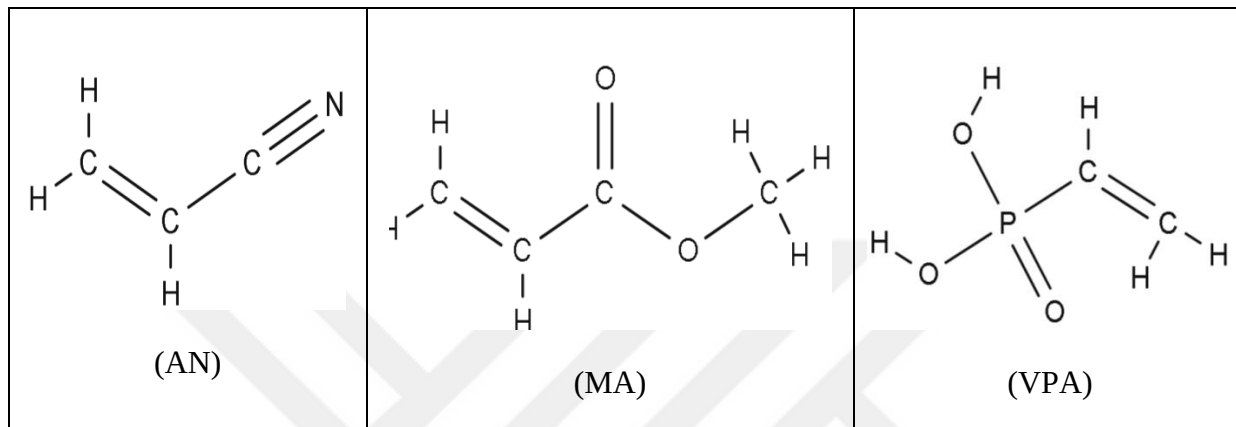


Figure 3.1 : Chemical structure of AN, MA and VPA monomers

For first synthesis trials, redox polymerization system was tried. Fe^{2+} was used as a redox agent. After reaction started, it was determined that the materials were not reacted each other. In this situation some synthesis was tried and same conditions occurred. Therefore, in this synthesis it was determined that, VPA and Fe^{2+} were interacted each other then the reaction not occurred.

Reaction mechanisms were made following steps; firstly, distilled water was prepared and required start-up water was added into the three necked flask and started to heat until the water was reached to the $70\text{ }^{\circ}\text{C}$. The residual distilled water was used to mix the other ingredients. Ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ and sodium metabisulfite $[\text{Na}_2\text{S}_2\text{O}_5]$ (Figure 3.2) were weighed and dropped into the residual water and mixed. Ammonium persulfate was used as initiator and sodium metabisulfite was used as chain transfer agent during the reaction.

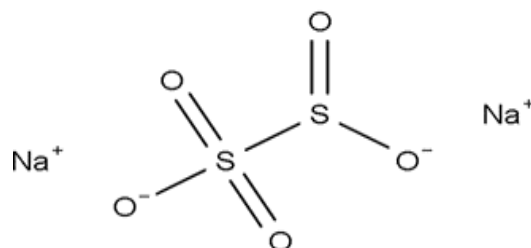


Figure 3.2 : Chemical structure of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$)

The monomers were prepared for required quantity for each different polymer synthesis which are listed detailly below and added into the reactor respectively. They were mixed for 3 hours in an oil bath. Then the reaction was finished by stopping heater and then cold water from outside was applied on the reactor surface. The precipitated polymer was washed with distilled water several times and polymers were dried at 50°C in vacuum drying-oven. Experimental setup of the polymerization was demonstrated in Figure 3.3.

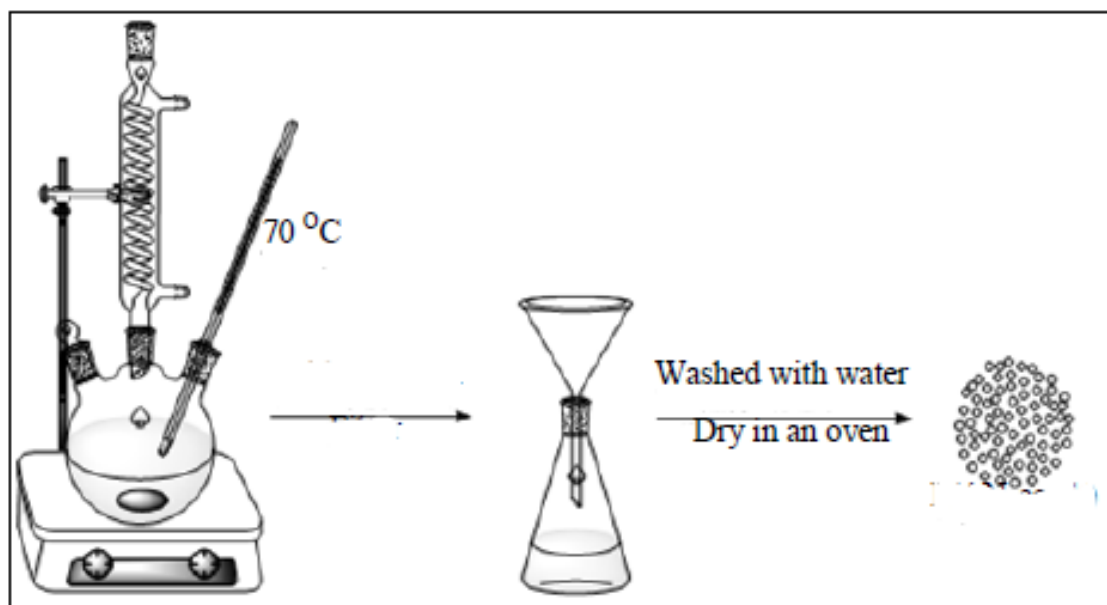


Figure 3.3 : Experiment scheme

The detailed information of synthesized polymers are given in Table 3.1.

Table 3.1 : Detailed informations of synthesized polymers

Sample Name	AN (g)	MA (g)	VPA (g)	Total Water (g)	Start-up Water (g)	AMPS (g)	Na ₂ S ₂ O ₅ (g)
P(AN)	10	-	-	56	40	0.065	0.12
P(AN-MA) 2	12.25	0.25	-	70	56	0.0755	0.15
P(AN-MA) 3	12.25	0.25	-	70	56	0.1125	0.15
P(AN-MA) 4	12.25	0.25	-	70	56	0.15	0.15
P(AN-MA-VPA) 2	12	0.25	0.25	70	56	0.0755	0.15
P(AN-MA-VPA) 3	12	0.25	0.25	70	56	0.1125	0.15
P(AN-MA-VPA) 4	12	0.25	0.25	70	56	0.15	0.15

3.4 Electrospinning of Polymers

Dried homo polyacrylonitrile, poly(acrylonitrile-*ran*-methylacrylate) 2, poly(acrylonitrile-*ran*-methylacrylate) 3, poly(acrylonitrile-*ran*-methylacrylate) 4, poly(acrylonitrile-*ran*-methylacrylate-*ran*-vinylphosphonic acid) 2, poly(acrylonitrile-*ran*-methylacrylate-*ran*-vinylphosphonic acid) 3 and poly(acrylonitrile-*ran*-methylacrylate-*ran*-vinylphosphonic acid) 4 polymers were dissolved in DMF solvent. Each solutions were stirred at room temperature for average 6 hours with closed bottle. Copolymers were prepared 10% by weight, homopolymer and terpolymers were prepared 5% by weight. The Table 3.2 and Figure 3.4 shows the composition of nanofiber solutions.

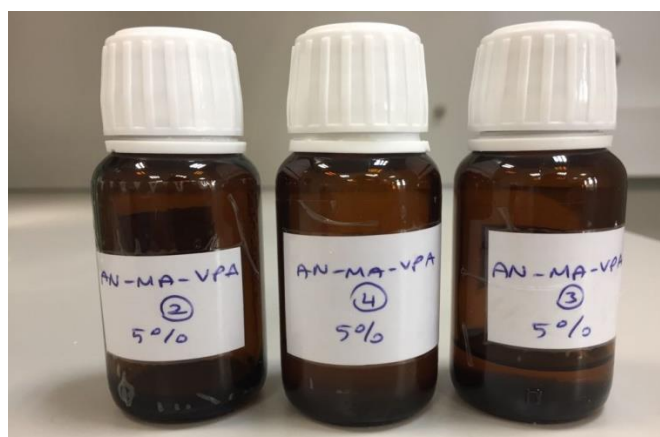
**Figure 3.4** : Mixing bottles

Table 3.2 : Prepared (polymer – solvent) electrospinning process solutions list

Polymer Name	Sample Name	Polymer concentration (wt%)	Solvent
Homo Polyacrylonitrile	P(AN)	5	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate) 2	P(AN-MA) 2	10	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate) 3	P(AN-MA) 3	10	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate) 4	P(AN-MA) 4	10	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate- <i>ran</i> -vinylphosphonic acid) 2	P(AN-MA-VPA) 2	5	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate- <i>ran</i> -vinylphosphonic acid) 3	P(AN-MA-VPA) 3	5	DMF
Poly(acrylonitrile- <i>ran</i> -methylacrylate- <i>ran</i> -vinylphosphonic acid) 4	P(AN-MA-VPA) 4	5	DMF

The electrospinning device contains a syringe pump and DC power supplier. The solutions were then loaded into a 5 ml syringe and pumped with 1 ml/h speed. Applied voltage was 15 kV. The metal collector was covered with an aluminum foil. All experiments were carried out under atmospheric pressure and at room temperature. The positive electrode wire was hooked at the metal part of the needle and negative part of the electrode was attached to the metal collector. A horizontal setup was chosen for electrospinning process. Nanofibers were accumulated on to the aluminium foil surface. In Table 3.3, electrospinning process parameters are listed. Obtained fibers were characterized by FTIR, TGA, DSC devices.

Table 3.3 : Electrospinning process parameters

Electrospinning Parameters	
Applied voltage	15 kV
Tip-to-collector distance	15 cm
Feed rate	1 mL/h

3.5 Film Preperation of Polymers

Each synthesized polymers were dissolved in DMF with same percentage as electrospinning solutions and they were stirred at magnetic stirrer. Then they were poured into a glass surface with determined area. They were dried in closed vacuum oven 24 hours at 40 °C and then they were waited under closed vacuum oven to evaporate all of solvent from the film until water absorbance test. Through, water absorbtion from air was avoided until water absorbance test.

3.6 Viscosity Test

Specific viscosity measurement of synthesized polymers were performed by Oswald viscosimeter (Figure 3.5) device at 25 °C and 0.1% solutions were prepared with using DMF solvent.

The viscosity values are calculated according to below specific viscosity formulation;

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (4.1)$$

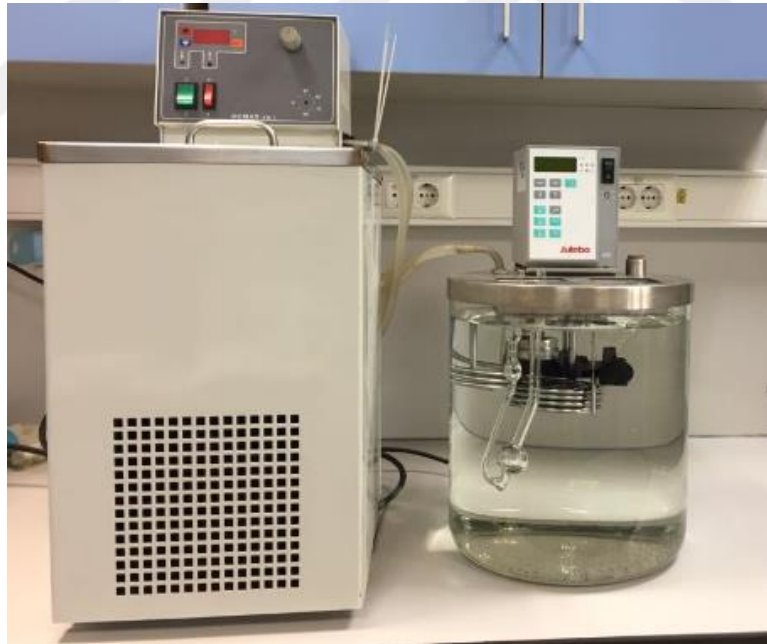


Figure 3.5 : Viscosity measurement device

3.7 Water Absorbance Test

Dried films were peeled off the glass surface. They were weighed before adding into the distilled water. They were added into the water separately and closed then waited for one day. After one day they were weighed and all results were listed in result section. Water absorbance test cups are prepared as shown in Figure 3.6.



Figure 3.6 : Water absorbance test cups

3.8 Burning Test

The obtained film samples were exposed to the flame and flame resistant behaviours of all films were investigated. Firstly the film sample distance kept 15 cm from flame. At this point any burning behaviour was not determine. Then 10 cm distance was tried and same behaviour was obtained. After that 5 cm distance was kept constant and burning behaviours of films were investigated easily. Burning behaviours and ignition times of samples were recorded by camera.



4. RESULTS AND DISCUSSION

In this study, homo polyacrylonitrile, poly(acrylonitrile-ran-methylacrylate) and poly(acrylonitrile-ran-methylacrylate-ran-vinylphosphonic acid)) polymers were synthesized by same steps. The synthesis steps and details were determined in previous section. The percentages of ammonium persulfate (AMPS) to sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) were changed to create differences between polymers. The polymerization yield were obtained between 75%-90%. The properties of synthesized polymers are given in Table 4.1.

Table 4.1 : Properties of synthesized polymers

Sample Name	Monomers			Initiator	Chain Tr. Agent	Specific Viscosity
	AN (g)	MA (g)	VPA (g)	AMPS (g)	$\text{Na}_2\text{S}_2\text{O}_5$ (g)	η_{sp}
P(AN)	10	-	-	0.065	0.12	-
P(AN-MA) 2	12.25	0.25	-	0.0755	0.15	0.37
P(AN-MA) 3	12.25	0.25	-	0.1125	0.15	0.30
P(AN-MA) 4	12.25	0.25	-	0.15	0.15	0.21
P(AN-MA-VPA) 2	12	0.25	0.25	0.0755	0.15	0.46
P(AN-MA-VPA) 3	12	0.25	0.25	0.1125	0.15	0.45
P(AN-MA-VPA) 4	12	0.25	0.25	0.15	0.15	0.34

4.1 FTIR Analysis

The FTIR spectra of acrylonitrile homopolymer and p(AN-ran-MA) copolymers are shown in Figure 4.1 and it was recorded in the transmittance mode. The characteristic absorption peaks at 2243 cm^{-1} shows the nitrile groups stretching ($\text{C}\equiv\text{N}$) are observed as a strong absorption peak both homo polyacrylonitrile and all copolymers. The characteristic peak of a Methyl Acrylate (MA) is at 1725 cm^{-1} and it shows the $\text{C}=\text{O}$ stretching in copolymers. 1453 cm^{-1} , 1364 cm^{-1} and 1228 cm^{-1} corresponds to the C-H bending. 2937 cm^{-1} are assigned to C-H stretching.

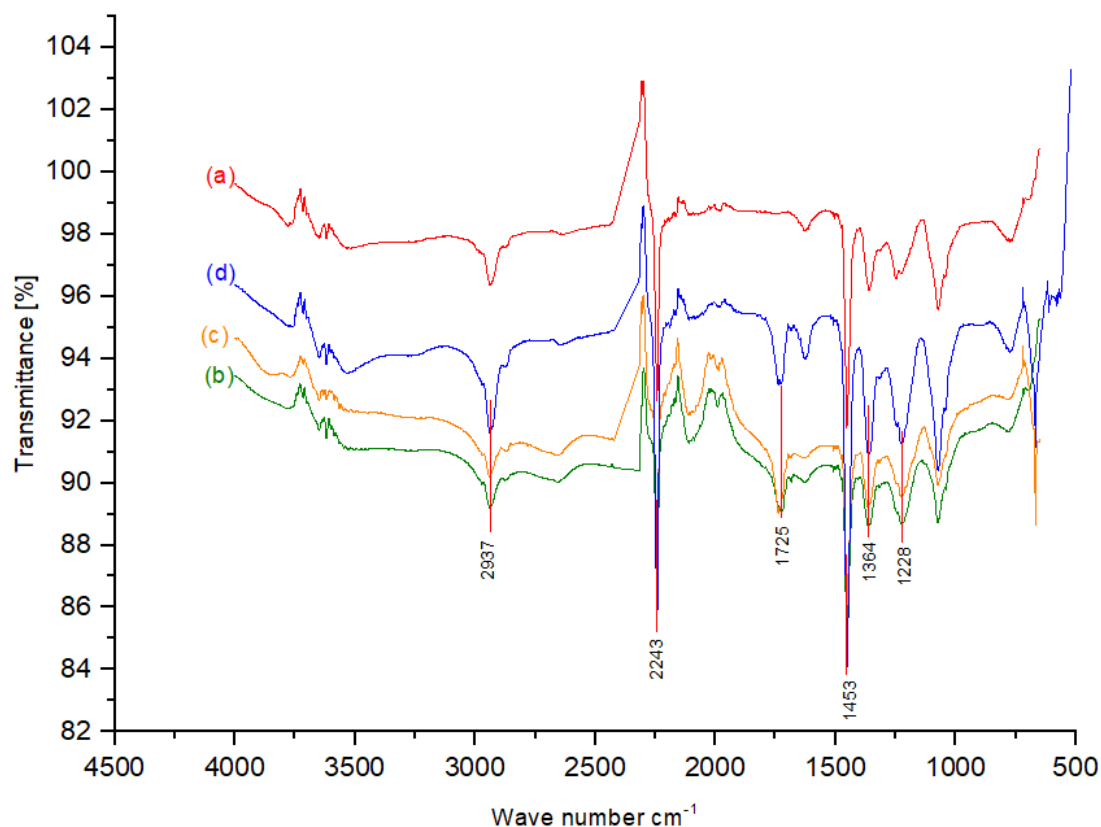


Figure 4.1 : FTIR spectrum of P(AN) (a), AN-MA-2 (b), AN-MA-3 (c), AN-MA-4 (d)

The FTIR spectra of P(AN-MA-VPA) terpolymers are shown in Figure 4.2 and it was recorded in the transmittance mode. Characteristic peaks of phosphonic acid units appears at 1246 cm^{-1} and 1129 cm^{-1} and corresponds to a P=O stretching for all terpolymers. The peaks corresponding to the POH bending and O-P-O asymmetric stretching are observed at 2347-2355 cm^{-1} . The peaks were observed at 1026 cm^{-1} correspond to the symmetric and asymmetric P-O(H) bands of phosphonic acid units. The peak was observed at 1069 cm^{-1} correspond to a P-O bonding. The peak was observed at 2300 cm^{-1} correspond to a P-OH stretching band.

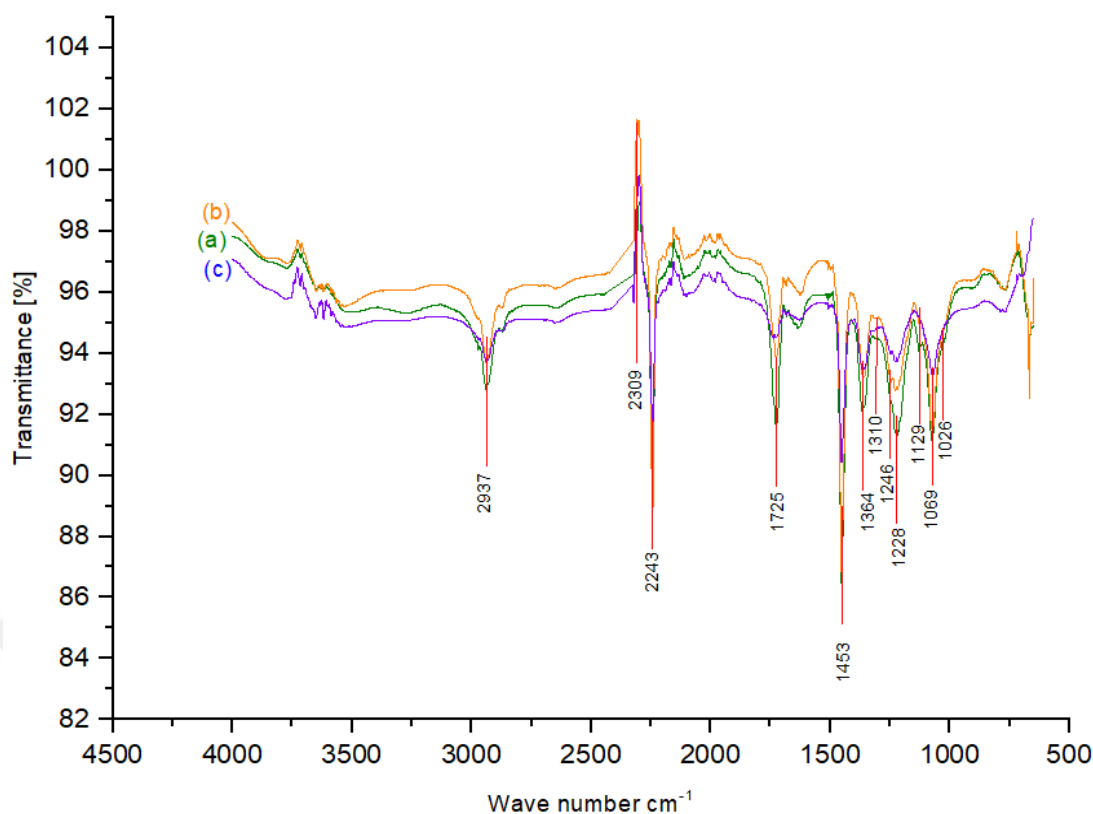


Figure 4.2 : FTIR spectrum of P(AN-MA-VPA)2 (a), P(AN-MA-VPA)3 (b) and P(AN-MA-VPA)4 (c)

4.2 Differential Scanning Calorimetry (DSC)

Synthesized polymers differential scanning calorimetry analysis were scanned at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. Acrylonitrile homopolymer glass transition temperature (T_g) was obtained at $97.9\text{ }^{\circ}\text{C}$ from the differential scanning calorimetry (DSC) measurement and it is showed at Figure 4.3. Generally melting temperature and glass transition temperature of polymers decreases with effect of the comonomer addition. Because the comonomers effect the regularity sequence along the P(AN) chains.

Contrary of P(AN) glass transition temperature , the T_g values of the P(AN-*ran*-MA) samples were determined as $140\text{ }^{\circ}\text{C}$, $217.5\text{ }^{\circ}\text{C}$, $173.9\text{ }^{\circ}\text{C}$, respectively, and the T_g values of the P(AN-*ran*-MA-*ran*-VPA) samples were determined as $100.1\text{ }^{\circ}\text{C}$, $97.5\text{ }^{\circ}\text{C}$, $120.9\text{ }^{\circ}\text{C}$, respectively at Figure 4.4,

According to this result, the high T_g values can be determined as the formation of the hydrogen bond formed by the electronegative atoms in the methyl acrylate monomer and the vinylphosphonic acid monomer.

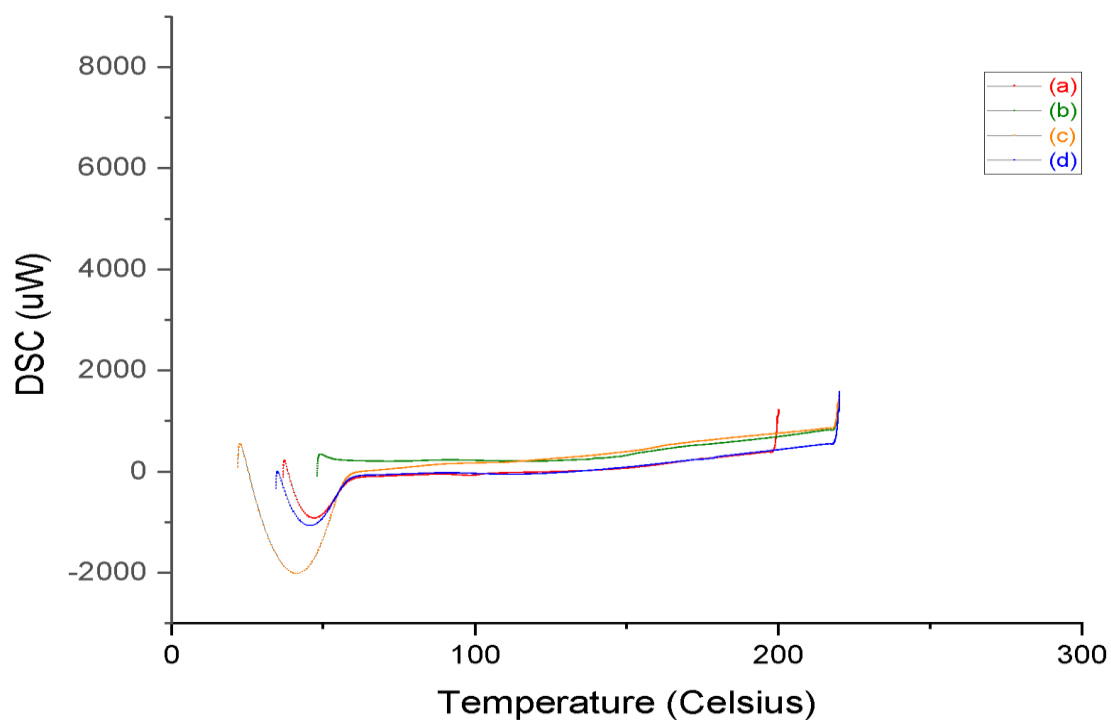


Figure 4.3 : DSC curve of AN-homopolymer (a), P(AN-MA)2 (b), P(AN-MA)3 (c), P(AN-MA)4 (d)

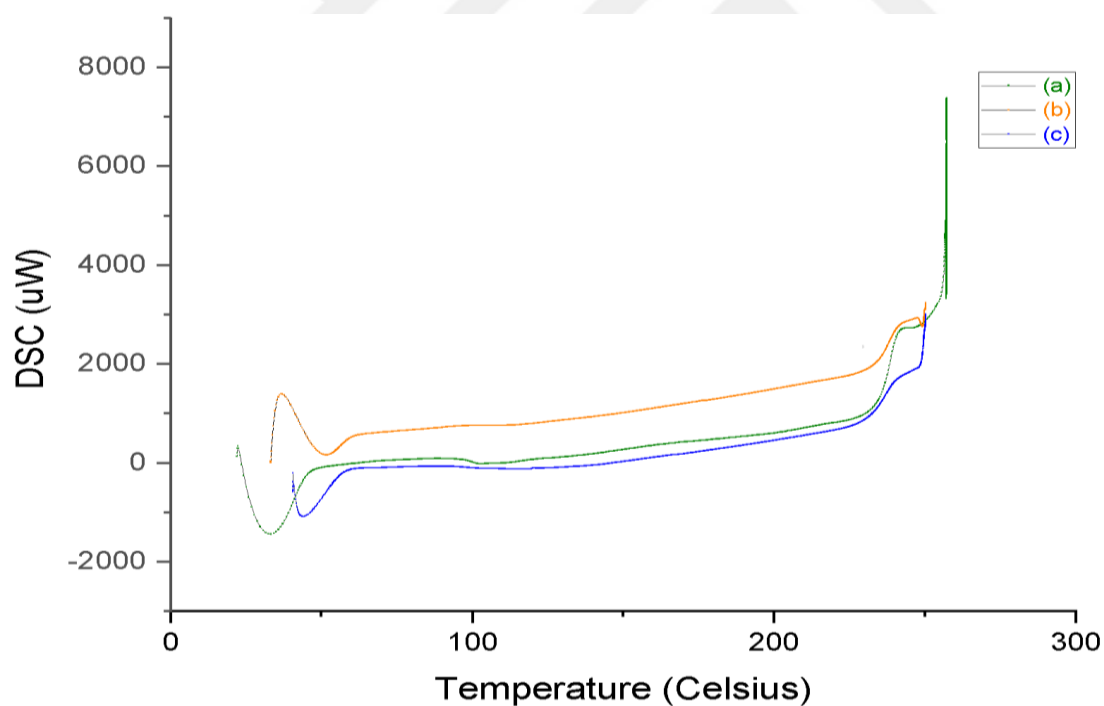


Figure 4.4 : DSC curve of P(AN-MA-VPA)2 (a), P(AN-MA-VPA)3 (b) and P(AN-MA-VPA)4 (c)

4.3 Thermal Gravimetric Analysis (TGA)

P(AN) homopolymer, P(AN-*ran*-MA) copolymers and P(AN-*ran*-MA-*ran*-VPA) terpolymers were analyzed by thermal gravimetric analysis (TGA) device to determine thermal stability and char yield. According to Figure 4.5 the char yield of P(AN) homopolymer was found at 61.15 %.

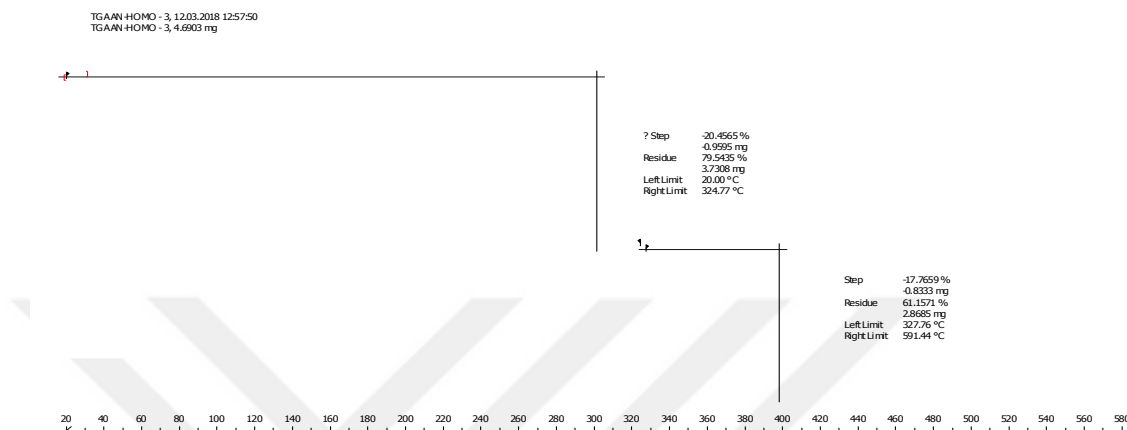


Figure 4.5 : TGA curves of P(AN) homopolymer

According to Figure 4.6, Figure 4.7 and Figure 4.8, there is an decrease at the char yield when MA added into the polymer. The char yield of P(AN-*ran*-MA) copolymers were determined at mean 24.3%. This is due to the MA units that act as defects in the PAN chains and it reduces the char yield. The first weight loss step of P(AN-*ran*-MA) resulted from elimination of residuals and the loss of absorption water. The indicated weight loss in the second step was caused by the thermal degradation of the P(AN-*ran*-MA) polymers.

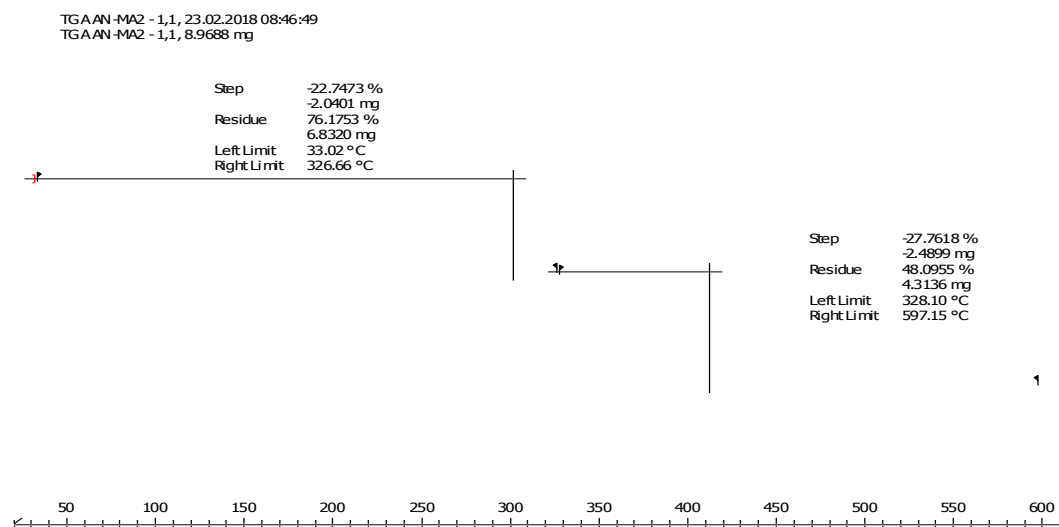


Figure 4.6 : TGA curves of P(AN-MA) 2 copolymer

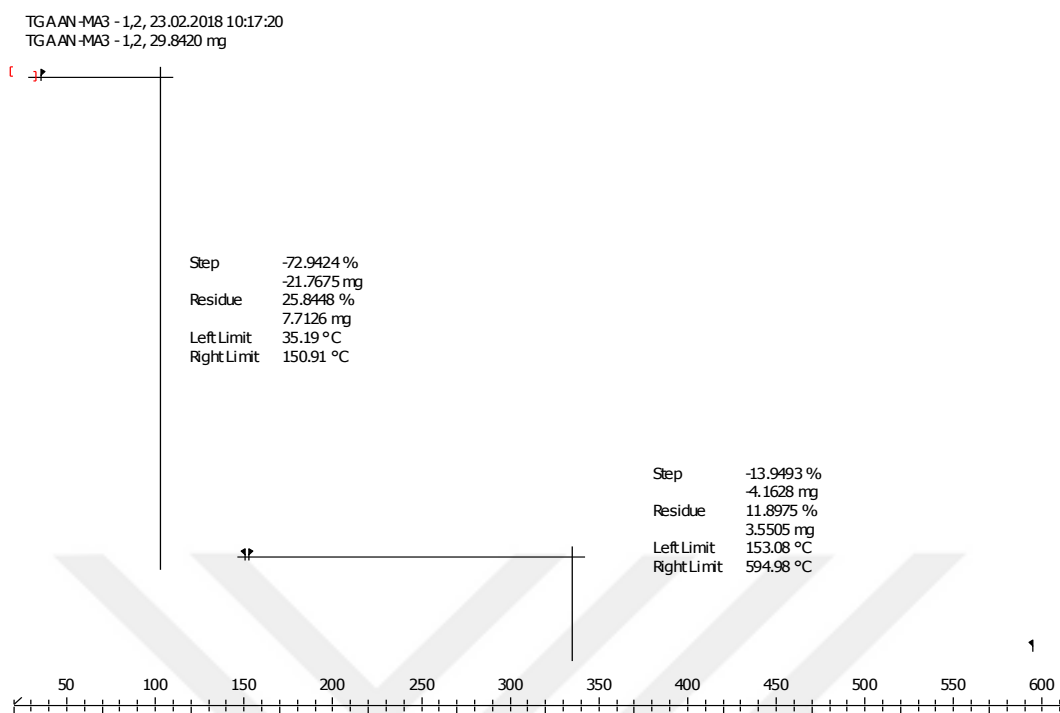


Figure 4.7 : TGA curves of P(AN-MA) 3 copolymer

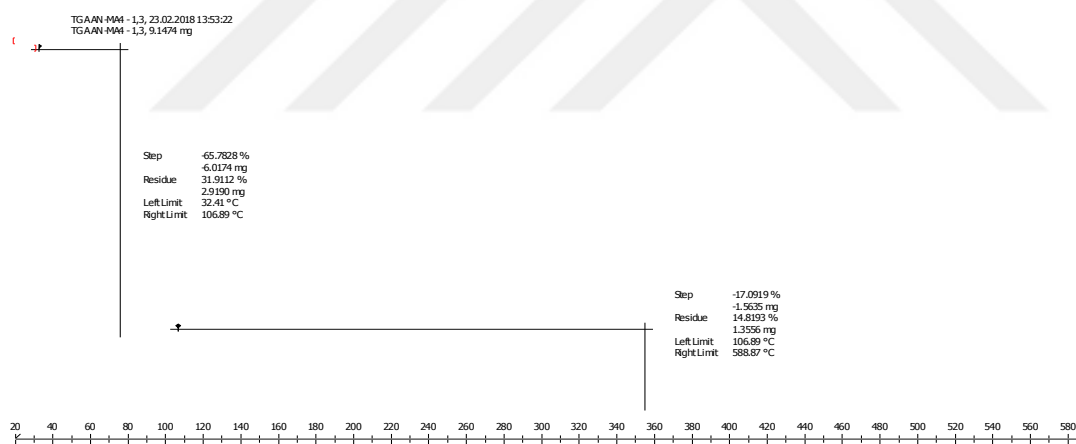


Figure 4.8 : TGA curves of P(AN-MA) 4 copolymer

According to Figure 4.9, Figure 4.10 and Figure 4.11 there is an significantly increases at the char yield of terpolymers. On the contrary of P(AN-*ran*-MA) copolymers, adding of the VPA as a flame retardant monomer enhanced the char yield to the mean 52%. This high increase about char yield shows that, adding of a vinyl phosphonic acid as an flame retardant material gives positive effect to the synthesized polymer.

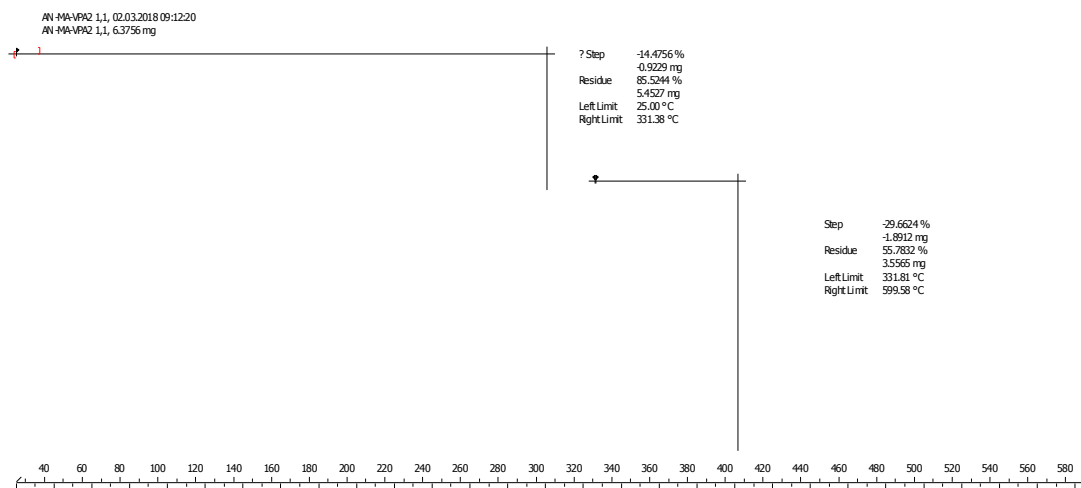


Figure 4.9 : TGA curves of P(AN-MA-VPA) 2 terpolymer

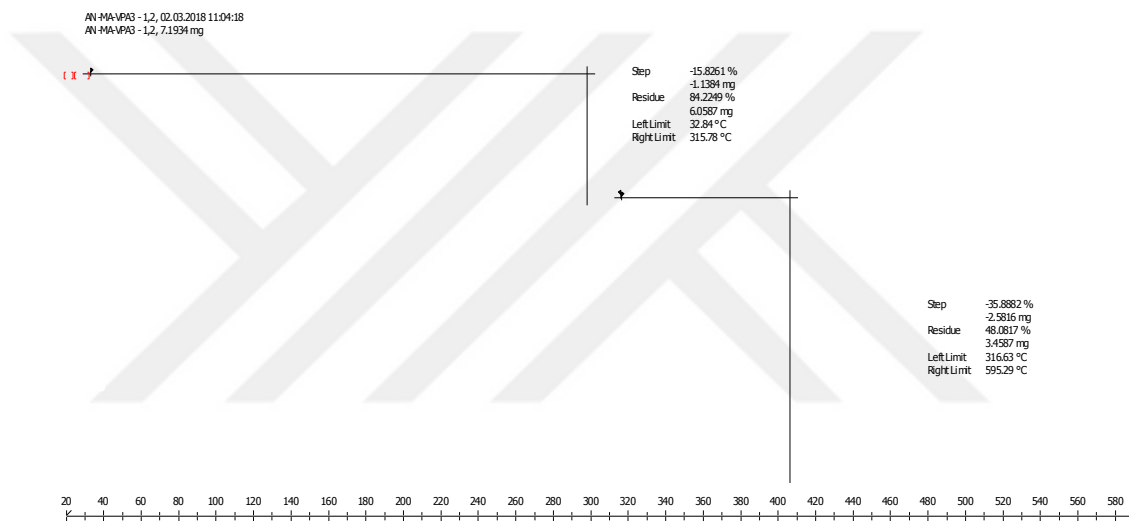


Figure 4.10 : TGA curves of P(AN-MA-VPA) 3 terpolymer

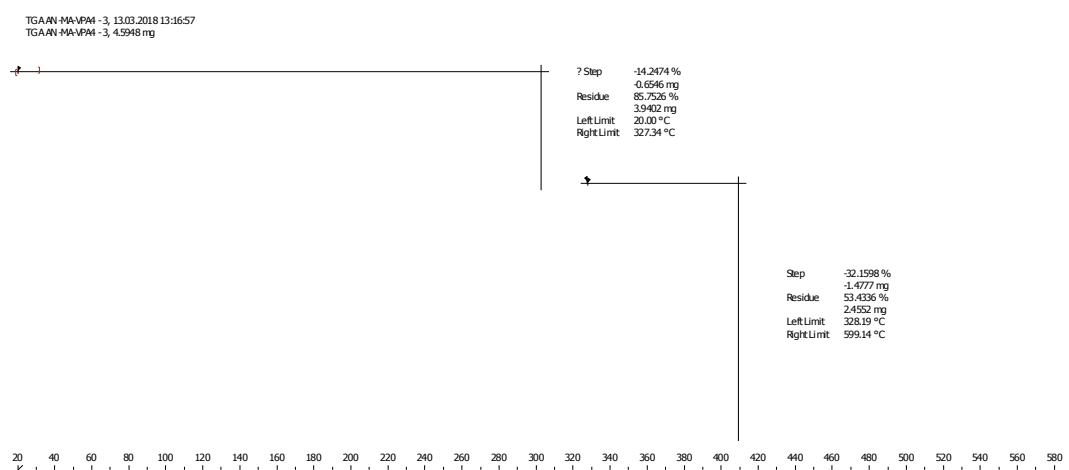


Figure 4.11 : TGA curves of P(AN-MA-VPA) 4 terpolymer

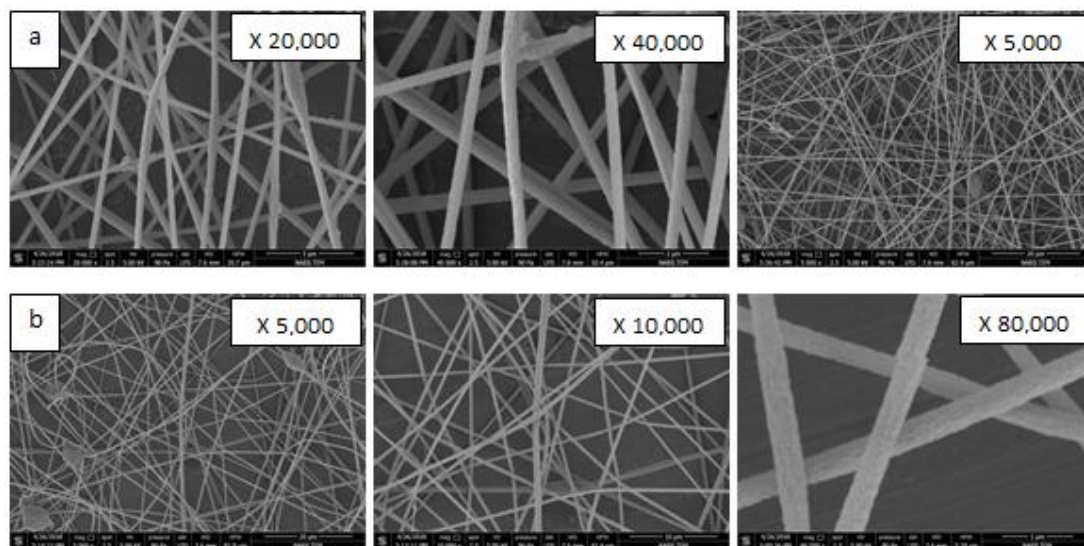
TGA values of samples are given in Table 4.2.

Table 4.2 : TGA values of samples

Sample Name	2nd Degradation T ($^{\circ}$ C)	First Residue (%)	Last Residue (%) At 590 $^{\circ}$ C
P(AN)	324.77	79.54	61.15
P(AN-MA) 2	326.66	76.17	48.09
P(AN-MA) 3	150.91	25.84	11.89
P(AN-MA) 4	106.89	31.91	14.81
P(AN-MA-VPA) 2	331.38	85.52	55.78
P(AN-MA-VPA) 3	315.78	84.22	48.08
P(AN-MA-VPA) 4	327.34	91.22	71.33

4.4 Morphology of Electrospun Nanofibers

Morphological structures of polymers were performed by scanning electron microscopy (SEM). Before the measurement, the samples were coated with gold. The obtained results of SEM images are shown at Figure 4.12. and Figure 4.13. SEM images show that, the morphology of nanofibers changed with changing of synthesis composition. The most suitable value for diameter was obtained from AN-MA-VPA 4 terpolymer. This result can be observed from viscosity measurement. Because of the decrease of the viscosity the molecular weight is decrease and the smaller diameter fibers can be obtained.

**Figure 4.12 : SEM image of nanofibers P(AN) (a), P(AN-MA)3 (b)**

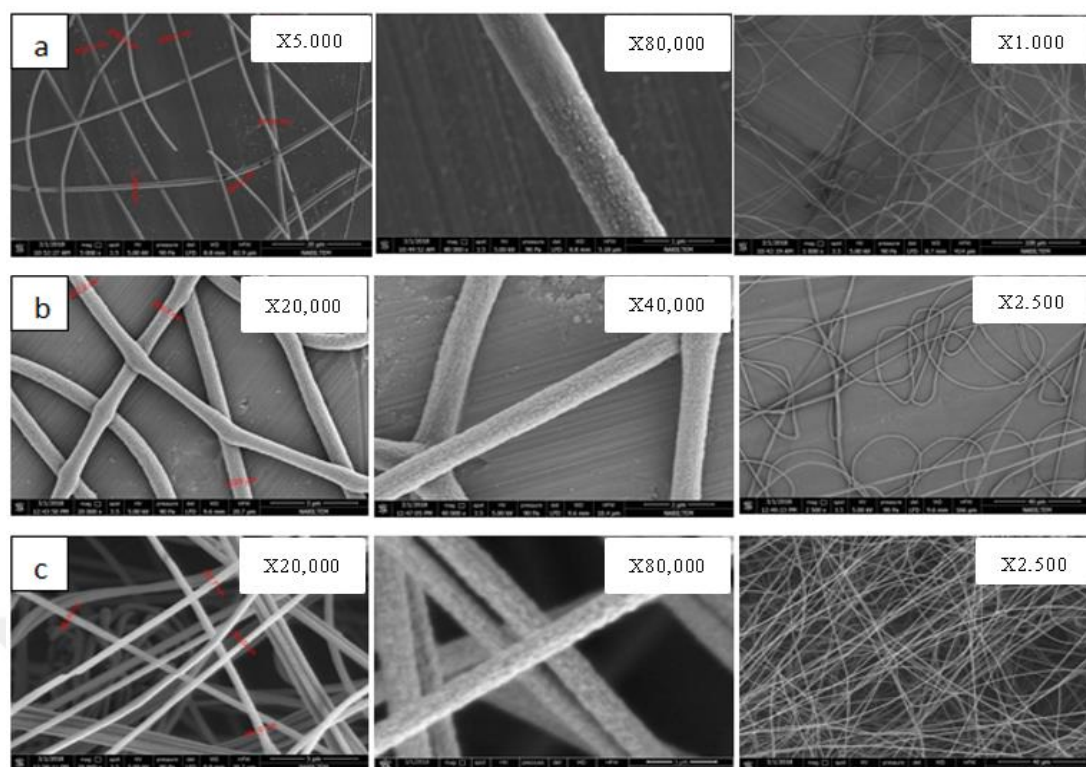


Figure 4.13 : SEM image of nanofibers P(AN-MA-VPA) 2 (a), P(AN-MA-VPA)3 (b), P(AN-MA-VPA) 4 (c)

The average diameter of samples are given in Table 4.3.

Table 4.3 : The average diameter of samples

Sample Name	Avg. Diameter of NFBs (nm)
P(AN)	364
P(AN-MA)3	340
AN-MA-VPA 2	751
AN-MA-VPA 3	945
AN-MA-VPA 4	451

According to the SEM pictures of P(AN-MA-VPA) 3 fiber, due to the incomplete fiber formation, some fibers diameters were distorted and solvent residual was dispersed on the collector surface. Due to the smooth structure of fiber, the solvent was not evaporate completely and when it touched the surface the fibers get ovalition at intersection points.

4.5 Viscosity Measurement of Polymers

P(AN-*ran*-MA) copolymers and P(AN-*ran*-MA-*ran*-VPA) terpolymers were synthesized by changing initiator to chain transfer agent ratio. The effect of changing ratio to the viscosity measurement were listed at Table 4.4. The changing was

increased through to the from P(AN-MA-VPA)2 to P(AN-MA-VPA)4. As a result, increasing of initiator to the chain transfer agent ratio was decreased the viscosity and as result the molecular weight of polymers were decreased.

Table 4.4 : Specific viscosity of polymers

Polymer	Specific Viscosity [η] (ml/mg)
P(AN-MA)2	0.37
P(AN-MA)3	0.30
P(AN-MA)4	0.21
P(AN-MA-VPA)2	0.46
P(AN-MA-VPA)3	0.45
P(AN-MA-VPA)4	0.34

4.6 Water Absorbance

Synthesized polymers were added into the distilled water and then the absorbance of water values are listed at Table 4.5. According to Table 4.5 copolymers water absorbance values are better then terpolymers. The reason for this may be due to the nature and effectiveness of the hydrogen bonding between phosphonic acid groups that makes them unavailable for hydrogen bonding with water. According to the results, water absorption values of terpolymers were obtained 100% higher than homo polyacrylonitrile. This property gives the terpolymers higher heat keeping to the vaporation of liquids. Also, during combustion conditions, gas phased vinyl phosphonic acid (VPA) keeps the free radicals and slows down the reaction.

Table 4.5 : Water absorbance of polymers

Sample Name	Water absorbance (%)
PAN	3.70
P(AN-MA)2	10.0
P(AN-MA)3	11.1
P(AN-MA)4	6.3
P(AN-MA-VPA)2	6.7
P(AN-MA-VPA)3	4.3
P(AN-MA-VPA)4	6.3

4.7 ICP/OES Analysis

P(AN-AM-VPA)3 sample ICP/OES analysis was performed and the result is listed below at Table 4.6 . The average phosphorus content of terpolymer is 5.70 ppm.

Table 4.6 : ICP/OES Analysis result

Sample Name	Phosphorus (P) (ppm)
P(AN-MA-VPA)3	5.70

4.8 Burning Test

Burning test of films were done 5 cm distance from flame. To chose suitable distance, 15 cm, 10 cm and 7 cm distances were tried but most proper results were obtained from 5 cm distance.

All results and observations are listed in Table 4.7.

Table 4.7 : Burning behaviour of film samples

Sample	Flame Exposure Time (sec)	Burning time (sec)	Burning Behaviour	Fire Furthering	Flaming Fire	Smoke Intensity	Smell Intensity	Droplet
P(AN)	3	1	blaze	+	+	++++	+++	-
AN-MA 2	5	1	smoky	+	-	++++	+++	+
AN-MA 3	10	2	blaze	+	+	++++	+++	-
AN-MA 4	2	1	blaze	+	+	++++	+++	+
AN-MA-VPA 2	10	-	smoulder	-	-	++	+	-
AN-MA-VPA 3	50	-	smoulder	-	-	+	+	-
AN-MA-VPA 4	40	-	smoulder	-	-	+	+	-

According to burning test results, it can be easily seen that, the samples of P(AN) homopolymer and P(AN-MA) copolymers were easily burned and showed blaze fire behaviour during fire exposing (Figure 4.14). And also they gived intensive smoke with bad smell to the enviroment. This burning behaviour also bad effect for during combustion. Additionally they were created droplets during fire exposure and this droplets may be further the combustion.

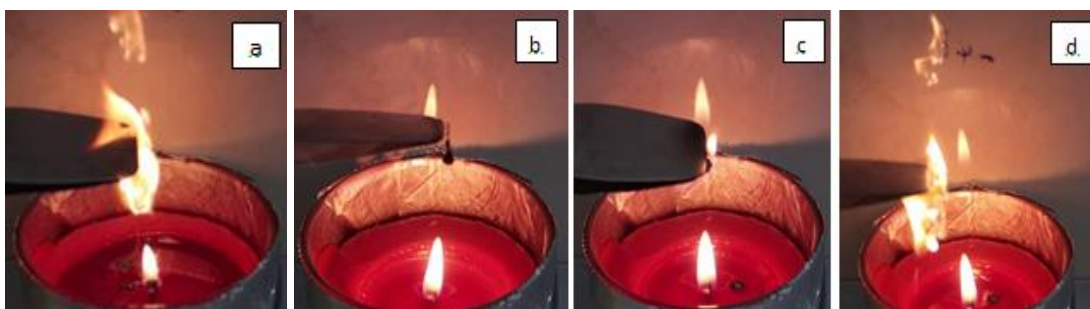


Figure 4.14 : Burning behaviour of film samples P(AN) (a), P(AN-MA 2) (b), P(AN-MA 3) (c), P(AN-MA 4) (d),

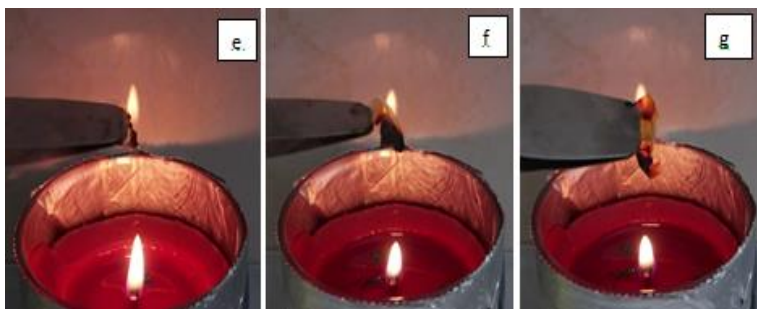


Figure 4.15 : Burning behaviour of film samples P(AN-MA-VPA 2) (e), P(AN-MA-VPA 3) (f), P(AN-MA-VPA 4) (g)

When the flame exposure process applied to the samples of P(AN-MA-VPA) terpolymers (Figure 4.16), the burning behaviour of films were getting better. The flames did not show any blaze and they did not create any flame or droplet during flame exposure. And also the terpolymers created char on the surface and they did not further the fire. Smoke and smell outputs are also better than P(AN) homopolymer and P(AN-MA) copolymers. And also it can be obtained from the table, the P(AN) homopolymer and P(AN-MA) copolymers were easily burned when the flame was applied to the films and the burning time of the samples were very short. But when the terpolymers of P(AN-MA-VPA) were exposed to the flame, the total exposing times were increased and additionally all of the films were not burned totally and a little unburned films were always get at the end of the burning test.

As a result of burning test, addition of VPA into the polymerization system, the flame retardancy properties of terpolymers were getting better. Additionally combustion behaviour of terpolymers get improvement according to results. This improvements are also important for decreasing fire furthering and gives prevention of hazards to the environment.

5. CONCLUSION

In this thesis, poly(acrylonitrile) homopolymer, poly(acrylonitrile-ran-methylacrylate) and poly(acrylonitrile-ran-methylacrylate-ran-vinylphosphonicacid) terpolymers were synthesized according to different initiator to chain transfer agent ratio and characterized by FTIR spectroscopy. According to the this FTIR results, it was observed that vinyl phosphonic acid derivatives had successively polymerized in the structure for the first time. It was obtained from viscosity measurement, increasing initiator to chain tr. Agent ratio, the intrinsic viscosity of polymers decreased and accordingly the molecular weight of polymers decreased. The synthesized polymers thermal characterization were performed by differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) device. Contrary to the decreasing molecular weight, the glass transition temperature (T_g) of polymers were obtained higher. According to this result, the high T_g values can be determined as the formation of the hydrogen bond formed by the electronegative atoms in the methyl acrylate monomer and the vinylphosphonic acid monomer.

According to TGA results, the mean char yield was obtained at 61.14%, 24.3% and 52% of P(AN), P(AN-MA) and P(AN-MA-VPA) polymers respectively. It can be obtained from this result, the homo polyacrylonitrile has higher char yield but it can be processed hardly. Methyl acrylate monomer is added to ease processability of homo polyacrylonitrile. But in this situation the char yield decreases due to the methyl acrylate acts as a defect behaviour. For this reason, vinyl phosphonic acid was added to the polymer chain as a flame retardant material and the char yield of polymers were increased positively. The positive flame retardant effect of P(AN-MA-VPA) terpolymers were supported by water absorbance test. The adding of VPA to the polymer structure was increased the water absorbance 100% higher than homo polyacrylonitrile.

Synthesized P(AN-MA-VPA) terpolymers were prepared with using DMF solvent for electrospinning solution and electrospun nanofibers of these terpolymers were obtained first time. The morphology study of terpolymers were investigated by

scanning electron microscopy (SEM). The best average diameter values were obtained at P(AN-MA-VPA) 4 terpolymer. It can be occurred due to the low molecular weight distrubution due to the high initiator ratio effect.

According to directly flame test, P(AN) homopolymer and P(AN-MA) copolymers were burned fastly with high amount of smoke and smell. And they showed blaze fire behavior during combustion. According to the P(AN-MA-VPA) terpolymers behoviours, it can be obtained from the results, the addition of VPA into the polymerization, it effects the flame retardancy positively. Because, with using VPA in the polymerization, the fire resistance time was increased and any blaze behavior was not obtained. And also terpolymers did not give much smoke or smell into the enviroment. Additionally fire furthering was not obtained by all terpolymers.

As a result of these informations, it can be said that the obtained terpolymers and nanofibers can be used as a flame retardant materials in nanofiber industry. For further studies, the decreasing average diameter of nanofiber and flame retardant properties can be developed.

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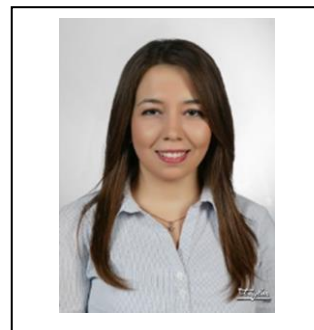
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