

Acrylonitrile/Vinyl Acetate Copolymer Nanofibers With Different Vinylacetate Content

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ABSTRACT: In this study, free radical copolymerization of acrylonitrile (AN)–vinyl acetate (VAc) was performed for five different feed ratio of VAc (wt %) by using ammonium persulfate (APS) in the aqueous medium. The effect of VAc content on the spectrophotometric and thermal properties of AN–VAc copolymers was investigated by Fourier Transform Infrared–Attenuated Total Reflectance spectrophotometer (FTIR–ATR), differential scanning calorimeter (DSC), and thermal gravimetric analyzer (TGA). Thermal stability of homopolymer of AN is improved after being copolymerized. The electrospun P(AN-*co*-VAc) nanofibers were fabricated and the effect of VAc content on the morphologic properties of nanofibers was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The viscosity of the solution had a significant effect on P(AN-*co*-VAc) electrospinning and the nanofiber morphology. The average diameters of P(AN-*co*-VAc) nanofibers decreased 3.4 times with increasing feed ratio of VAc wt %. The P(AN-*co*-VAc) electrospun nanofiber mats, with the feed ratio of 30 wt % VAc, can be used as a nanofiber membrane in filtration and as a carbon nanofiber precursor for energy storage applications due to high surface to volume ratio, high thermal stability, homogeneous, and thinner nanofiber distribution. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Polyacrylonitrile (PAN) is an interesting starting polymer for a whole range of engineering applications and is mainly used to produce synthetic fibers. It is highly polar with strong interchain interactions through nitrile groups and it decomposes before melting.^{1,2} During the heat treatments of homo and copolymers of acrylonitrile, instead of melting, some exothermic reactions, such as cyclization of nitrile groups takes place, which lead to formation of ladder like structure. PAN has a large magnitude of the dipole moments of the CN lead to strong intrachain and interchain interactions through secondary bonding. Therefore, incorporating a number of flexible comonomers weakens the dipolar interactions among CN and thereby decreases melting point or increases decomposition temperatures of the PAN based copolymers.³ Hence, it is important to consider the effect of comonomer on the thermal behavior of PAN-based copolymers.⁴ AN–VAc copolymers have the significant importance in the commercially available acrylic fibers due

to their thermal behavior and are also of interest as precursors in the production of high strength carbon fibers.^{5,6} Acrylonitrile (AN) based polymers have been widely used as plastics, rubbers, fibers, and in composites. AN is copolymerized with one or two comonomers, such as acrylates, methacrylates, styrene, and particularly vinyl acetate (VAc). The copolymer of AN and VAc can be used either as a plastic (VAc > 15 wt %) or as microfibers (VAc < 15 wt %).⁷ AN provides the copolymer with good processability, electrochemical and thermal stability; VAc provides the excellent mechanical stability.⁸

Electrospinning is a desirable technique to produce micro and/or nanofiber webs of copolymers by applying high voltage to a polymeric solution to create an electrically charged jet. It is fundamentally different from other mechanically driven spinning techniques in that the extrusion force is generated by the interaction between the charged polymer fluid and an external applied electric field. During electrospinning, a conical fluid structure called the Taylor cone is formed at the tip of the

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syringe. When a critical value of the electric field is attained, the electrostatic force overcomes the surface tension and a charged jet is ejected from the tip of the Taylor cone. The polymeric jet is then subjected to instability phenomena that stretch and reduce fiber diameter, before being randomly deposited onto a grounded target.^{9,10}

P(AN-*co*-VAc) electrospun nanofibers can be used especially as membranes for filtration and as carbon nanofiber precursors for energy storage applications. Electrospun nanofiber membranes provide a valuable increase in filtration efficiency. The diameter of nanofibers is decreased due to incorporation of VAc groups into the PAN structure corresponding the high surface area.¹¹ PAN is the most widely used polymer for the production of carbon nanofibers by electrospinning technique. However, the mechanical properties of these carbon nanofibers are not sufficient since PAN homo-polymer contains highly polar nitrile groups, hindering the alignment of macromolecular chains during fiber formation. To overcome this problem; P(AN-*co*-VAc) copolymers might be used as a precursor for electrospun nanofibers.

In our previous studies, we reported the free radical polymerization of AN-VAc copolymer containing only ~ 10 wt % VAc initiated by Ce(IV) in the aqueous medium in the presence of conjugated polymers.^{11–13} In this study, since water-phase precipitation polymerization has been a preferable technique for AN based copolymer synthesis, the AN-VAc copolymers having different VAc contents were synthesized by free radical polymerization initiated by APS in the aqueous medium. The effect of VAc content on the spectroscopic, morphologic, and thermal properties of nanofibers was studied in detail and the effect of VAc content on the nanofiber diameters was investigated.

EXPERIMENTAL

Materials

Acrylonitrile (Dow, 99.5>%) vinyl acetate (Innovence, 99.5>%) and ammonium persulfate (APS) were provided by the Aksa Acrylic Factory of Turkey. Dimethylformamide (DMF), nitric acid (HNO₃) and ethanol were all Merck reagents. All these reagents were used as received.

Copolymerization

Copolymer of AN-VAc was synthesized by free radical polymerization using APS as an oxidant in the aqueous medium. Copolymerization was carried out in a flat-bottomed flask equipped with a stirrer and a condenser by the addition APS dissolved in distilled water to an aqueous solution of monomers. The calculated amounts of AN and VAc were stirred in distilled water and after 20 min, the dissolved APS was added to the aqueous solution. The copolymerization temperature was adjusted to 70°C and continued for 3 h under stirring. After the copolymerization, the precipitated polymer was washed and filtered with dilute nitric acid, distilled water, and ethanol. The filtered polymer was dried at room temperature.

Nanofiber Formation

The polymer solutions were prepared with 3 wt % concentration in DMF at room temperature and were used to prepare nanofiber mats. The electrospinning apparatus consists of a sy-

ringe pump (NE-500 model, New Era Pump Systems) 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) and a grounded 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. The feeding rate of the polymer solution was controlled by syringe pump and solutions were electrospun horizontally onto the collector. All the conditions were kept constant for different nanofiber formations.

Figure 1 shows the schematic representation of P(AN-*co*-VAc) electrospinning process. The electrospinning conditions are as following, Solution concentration: 3%; Applied voltage: 14 kV, Tip-to-Collector Distance: 16 cm, Feed Rate: 0.04 mL/h.

Characterization

FTIR-ATR spectrophotometric analysis of polymers was performed by FTIR reflectance spectrophotometer (Perkin-Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal). ¹H-NMR spectrums were obtained by using a 250 MHz Bruker.

AC Aspect 3000 NMR spectrometer. Deuterated dimethyl sulphoxide (DMSO) was used for ¹H-NMR analysis. The glass transition temperatures of polymers was determined by differential scanning calorimetry (TA Q1000 DSC instrument) under N₂ atmosphere from -30°C to 250°C at a heating rate of 20°C/min. The thermal stability of copolymers was investigated by thermo-gravimetric analysis (Perkin Elmer Pyris 1 TGA instrument) under N₂ atmosphere from 25°C to 600°C at a heating rate of 10°C/min. The intrinsic viscosity of the polymer solutions in DMF was determined by Ubbelodhe viscometer at 25°C for PAN and 30°C for P(AN-*co*-VAc) and PVAc. The molecular weights were calculated for PAN (a) and P(AN-*co*-VAc) (b) by the Mark-Houwink equations $[\eta] = K \times M_v^\alpha$

$$\text{a. } K = 3.92 \times 10^{-4}, \quad \alpha = 0.75,^{14}$$

$$\text{b. } K = 2.78 \times 10^{-4}, \quad \alpha = 0.75.^{15}$$

Morphological studies of nanofibers were performed by a Gemini Leo Supra 35 VP scanning electron microscope (SEM) and Nanosurf EasyScan2 atomic force microscope (AFM). In all AFM analysis, the non-contact mode was employed by using Al coated high resonance frequency silicon tips (190 kHz) with 7 μm thickness, 38 μm mean width, 225 μm length, and 48 N/m force constant. Nanofibers were coated by gold before SEM observations. Thickness of gold coating was 30 nm.

RESULTS AND DISCUSSION

The results of the copolymerization of AN-VAc and feed ratio of monomers are given in Table I. The conversion of AN-VAc copolymers is lower than polymerization of AN without VAc.

The intrinsic viscosity of the copolymers decreases as the VAc content increases. This might be due to the copolymer radicals with AN units at the chain ends are considerably more active than the PVAc growing radicals. Molecular weight of PAN and P(AN-*co*-VAc) copolymer of 20 wt % VAc feed ratio were calculated as 142,800 and 212,500 g/mol, respectively.^{14,15}

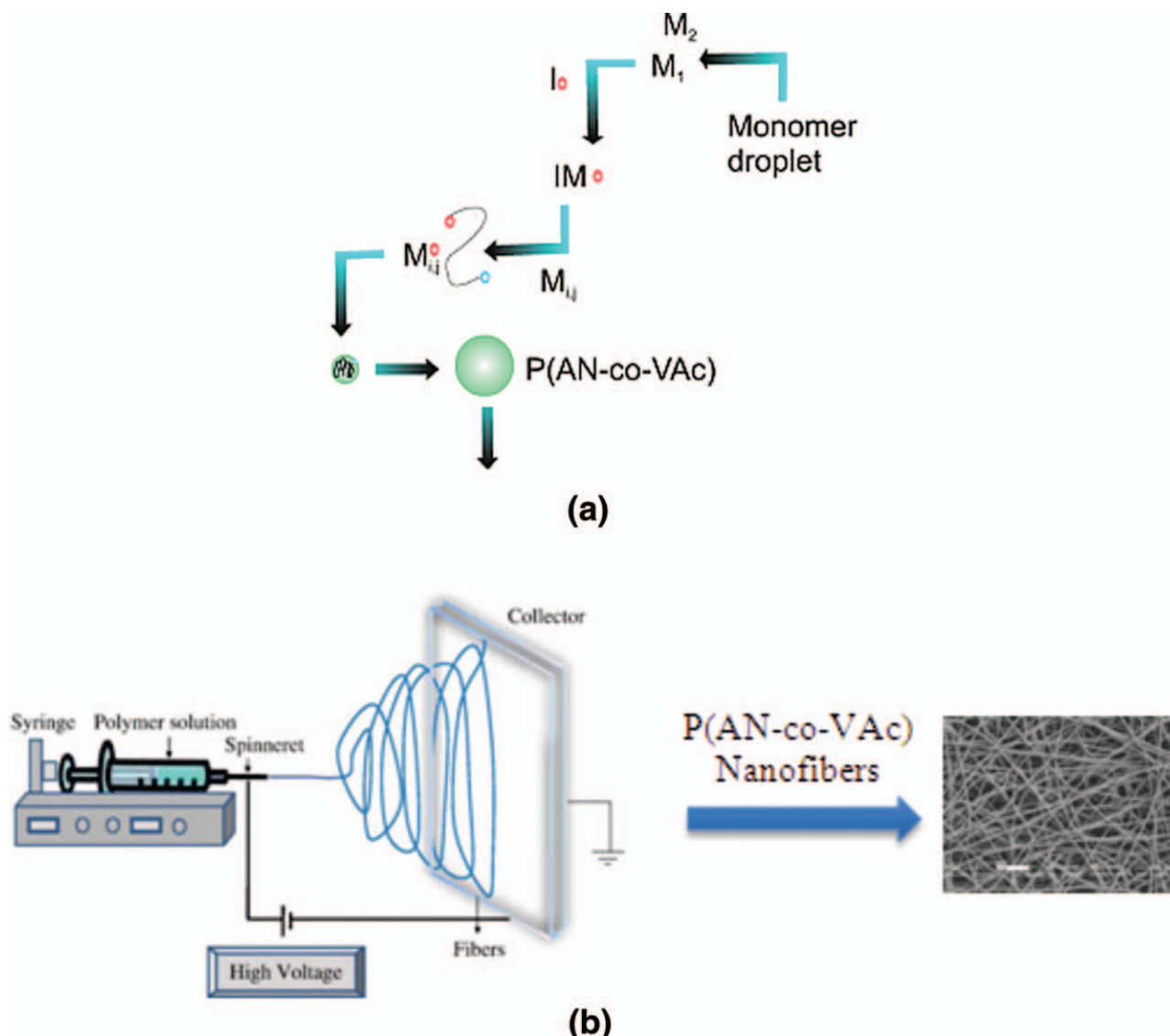


Figure 1. (a) Scheme of free radical polymerization of P(AN-co-VAc) copolymer, (b) Schematic diagram of P(AN-co-VAc) electrospinning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The synthesis of PAN and its related copolymers are typically carried out via free-radical polymerization.¹⁶ Redox systems are widely used as initiators in radical polymerization. Compared to other methods, they have the prime advantage of operating at very moderate temperatures. This means that the probability of side chain reactions can be minimized.¹⁷ Water-phase precipitation polymerization has been a preferable technique for AN based polymer synthesis to achieve high molecular weight, which is important for mechanical properties of polymer. Acrylonitrile, which is a partially water-soluble monomer, is added to the medium, a small fraction of acrylonitrile dissolved in the continuous aqueous phase where initiator is present. The initiation step of polymerization occurs in aqueous phase. Then, chain growth starts and continues in water until polymer precipitate (Figure 1). After the precipitation, the polymerization

Table I. Compositions for AN-VAc Copolymers for Different Feed Ratio of VAc wt %

| AN/VAc feed ratio (w/w) | Conversion % | Intrinsic viscosity $[\eta]$ (dL/g) | AN/VAc composition (mol/mol) |
|-------------------------|--------------|-------------------------------------|------------------------------|
| 100/0 | 95 | 2.88 | 100/0 |
| 90/10 | 83 | 3.15 | 92.3/8.7 |
| 80/20 | 84 | 3.11 | 85.3/14.7 |
| 70/30 | 72 | 2.98 | 75.1/24.9 |
| 60/40 | 80 | 2.61 | 64.3/35.7 |
| 50/50 | 79 | 2.52 | 54.5/44.5 |

[APS] = $5 \times 10^{-2} M$, $t = 3$ h at $70^\circ C$.

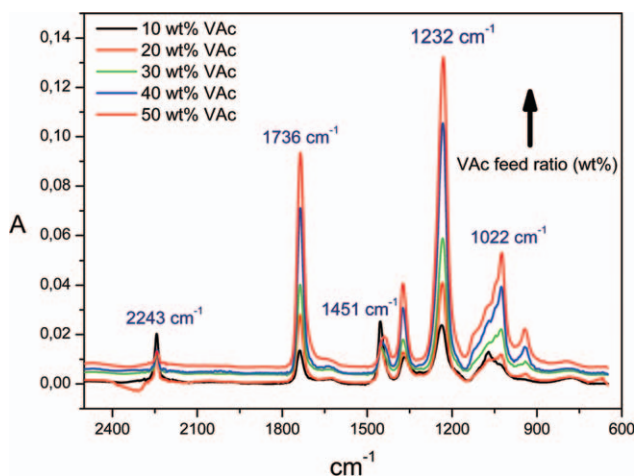


Figure 2. FTIR-ATR spectra of P(AN-*co*-VAc) copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transfers from homogeneous phase to heterogeneous phase. The polymerization is carried out both in water and at the surface of the micro-particles precipitated from the water. In this process, the possibility of chain termination and chain transfer are low, therefore, the molecular weight and the yield of the polymer increase.^{18,19} The copolymers of AN-VAc were characterized by FTIR-ATR spectrophotometer and the change of VAc was investigated depending on the changes in the absorbance values of VAc characteristic peaks. FTIR-ATR spectrums of P(AN-*co*-VAc) copolymers are shown in Figure 2.

PAN shows its characteristic absorption peaks at 2243 cm^{-1} and 1451 cm^{-1} , corresponding to CN stretching and CH bending, respectively. The C=O stretching, C-O-C stretching and C-O stretching vibration peaks can be observed at 1736, 1232,

and 1022 cm^{-1} , respectively, for PVAc. The strong absorption bands for P(AN-*co*-VAc) are C=O stretching (1736 cm^{-1}) and CN stretching (2243 cm^{-1}).^{11,20} These results are in agreement with literature.

An increase in the absorbance values at 1736 cm^{-1} was observed corresponding to VAc wt % feed ratio. The copolymer composition of the p(AN-*co*-VAc) copolymers was determined from $^1\text{H-NMR}$ spectrum. The signal at 2.05 ppm is related to $-\text{CH}_2$ protons of both AN and VAc. The signals of $-\text{CH}$ proton of AN and VAc monomers occur at 3.14 ppm and 5.13 ppm, respectively.^{4,5} $^1\text{H-NMR}$ spectra of copolymer with 30% VAc feed ratio is seen in Figure 3

Figure 4 presents the relation between absorbance ratio of characteristic VAc peaks to AN and VAc peaks in FTIR ATR spectrums and VAc content calculated from $^1\text{H-NMR}$ spectrums corresponding to VAc feed ratio (wt %). The ratio of the absorbance of C=O stretching band at 1736 cm^{-1} to the total absorbance of CN stretching band at 2243 cm^{-1} and C=O stretching band at 1736 cm^{-1} was obtained from FTIR-ATR. VAc content of copolymers was calculated from the intensity of NMR signals. The correlation between the absorbance ratios of FTIR ATR results and VAc content from NMR were observed

Thermal properties of electrospun P(AN-*co*-VAc) nanofibers are investigated using TGA and DSC characterizations. Figure 5 depicts the TGA results of P(AN-*co*-VAc) for different VAc contents. The free radically produced PAN displays a glass transition temperature of 105°C and a melting point around 317°C. PAN tends to decompose before its melting point reaches. It is well known that the melting and glass transition points of semi-crystalline polymers can be reduced through incorporating comonomer units.¹⁵

The TGA results of the different P(AN-*co*-VAc) and PAN are shown comparatively in Figure 4. According to a previous

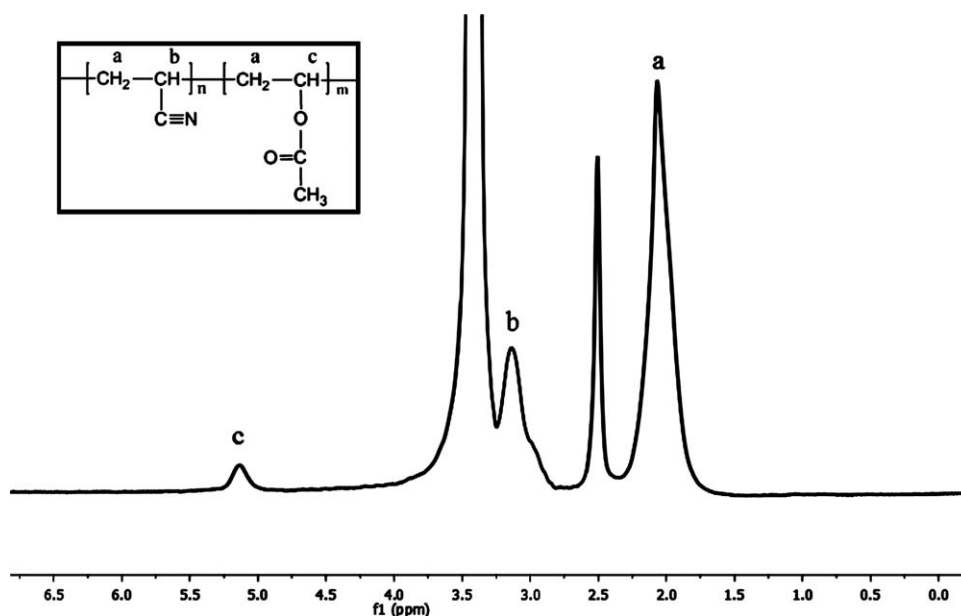


Figure 3. $^1\text{H-NMR}$ spectra of copolymer with 30% VAc feed ratio.

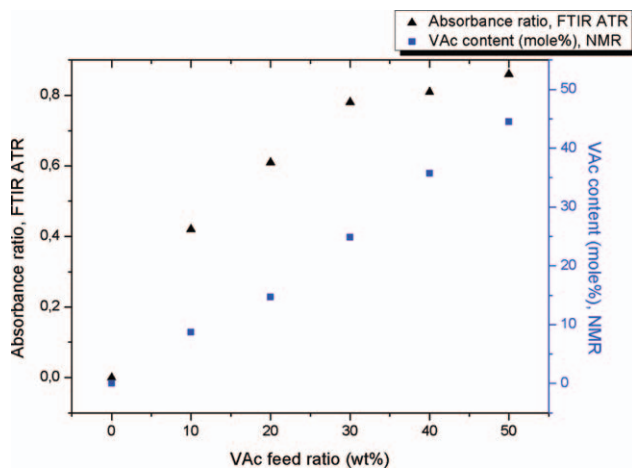


Figure 4. The relation between the FTIR-ATR absorbance ratio $[(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1})/(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1} + \text{CN}$ str. at $2243\text{ cm}^{-1})]$, VAc feed ratio (wt %), and VAc content (mole%) calculated from ^1H -NMR results of copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

study,²¹ PAN fiber decomposes at 295°C after cyclization reaction and interchain polymerization of nitrile groups are completed. The homopolymer of AN showed the main thermal decomposition at 276°C . However, with introducing and increasing the feed ratio of VAc from 10 to 50 wt %, the thermal decomposition temperatures were increased from 306 to 343°C (Figure 4). These values are all higher than that of homopolymer of AN, indicating that thermal stability of PAN is improved after being copolymerized with VAc, and thus confirming the effect of VAc functional groups existed in P(AN-co-VAc) in addition to nitrile groups of PAN.

Figure 6 presents the relation between the C=O stretching band absorbance ratios of VAc obtained from FTIR-ATR and thermal decomposition values obtained from TGA of AN/VAc copolymers as a function of feed ratio of VAc wt %. The TGA results are correlated with FTIR-ATR results in Figure 4. A systematic

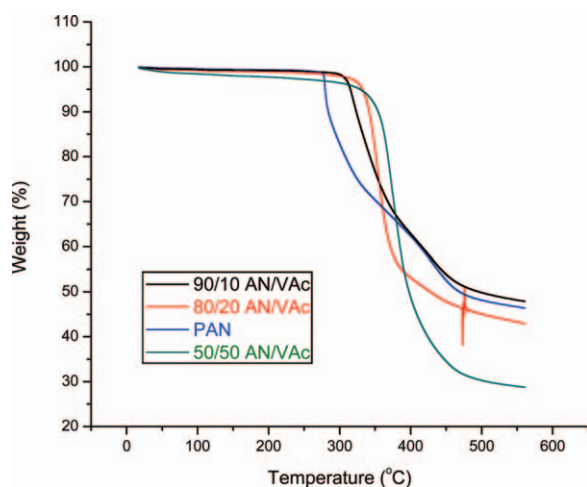


Figure 5. TGA thermograms of AN homopolymer and AN-VAc copolymers.

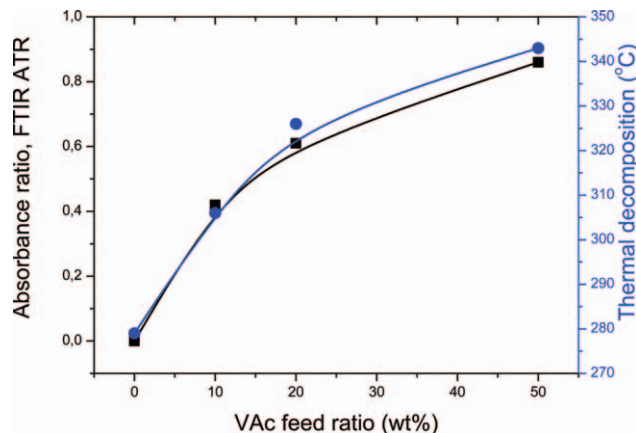


Figure 6. The correlation between the FTIR-ATR absorbance ratio $[(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1})/(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1} + \text{CN}$ str. at $2243\text{ cm}^{-1})]$, VAc feed ratio (wt %), and thermal decomposition temperature (TGA) in AN-VAc copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase of the thermal decomposition temperatures of copolymers is observed with the increase of VAc content.

The correlation between the T_g values obtained from DSC and viscosity values of P(AN-co-VAc) solutions obtained from Ubbelohde viscometer as a function of C=O stretching band absorbance ratio of VAc (taken from FTIR-ATR spectrophotometer) are shown in Figure 7. It is observed that the T_g decreases from 100 to 85°C when the content of VAc is increased. The viscosity of the P(AN-co-VAc) solutions decreases from 3.15 to 2.65 as the VAc content is increased up to 40 wt %. This result is associated with the incorporation of VAc molecule units, which disorders the symmetry of AN chains and increases the amorphous region of copolymers, therefore reduces the glass transition temperatures and copolymers solution viscosity.

Figure 8 illustrates the SEM images of P(AN-co-VAc) electro-spun nanofibers with increasing VAc wt % feed ratio under the other process parameters are constant. At VAc feed ratio 10 wt

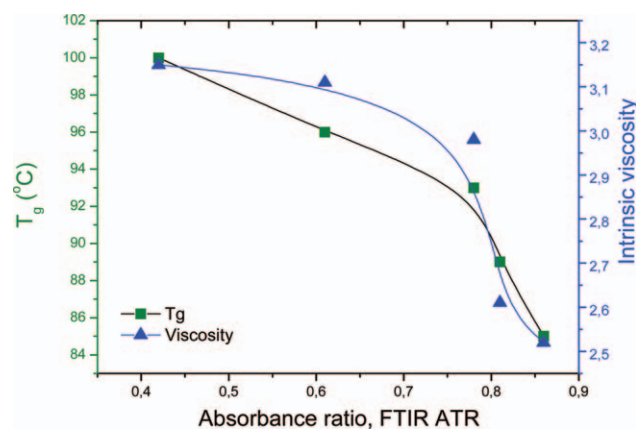


Figure 7. The relation between the FTIR-ATR absorbance ratio $[(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1})/(\text{C}=\text{O}$ str. at $1736\text{ cm}^{-1} + \text{CN}$ str. at $2243\text{ cm}^{-1})]$, intrinsic viscosity, and T_g ($^\circ\text{C}$) values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

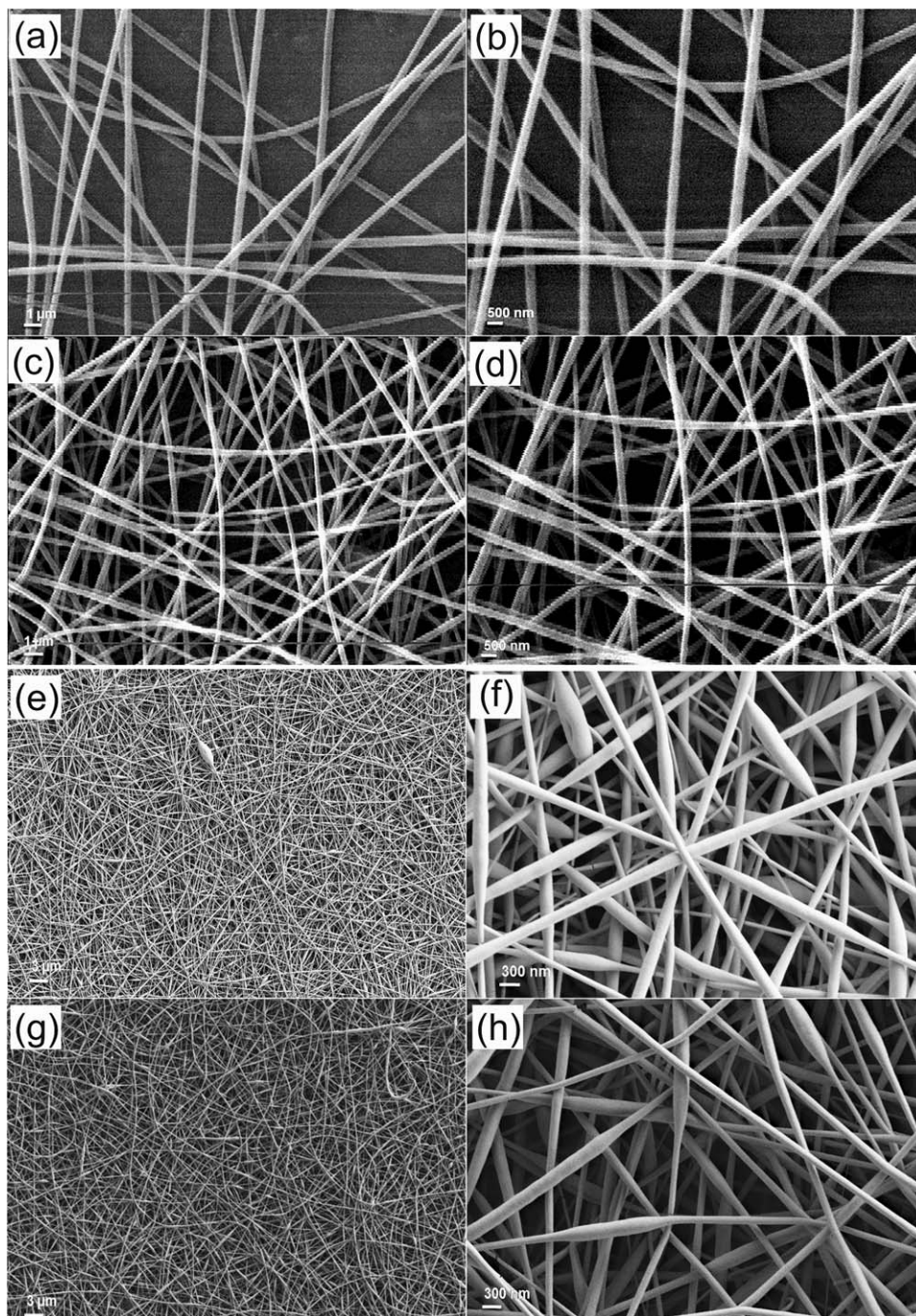


Figure 8. SEM micrograph of P(AN-co-VAc) nanofibers down from different VAc wt % feed ratio: (a and b) 10 wt %, (c and d) 20 wt %, (e and f) 30 wt %, (g and h) 40 wt %.

%, the average diameters of nanofibers are 445 nm. With increasing VAc feed ratio from 10 to 40 wt %, average nanofiber diameters decrease correspondingly with the viscosity of the solutions.

The viscosity of the solution has a significant effect on P(AN-co-VAc) electrospinning and the nanofiber morphology. Generally, the solution viscosity is related to the extent of polymer molecule chains entanglement within the solution.²² At lower viscosity, where generally the polymer chain entanglements are

Table II. The Correlation Between the Average Nanofiber Diameter and VAc Feed Ratio (wt %)

| VAc feed ratio (wt %) | Average nanofiber diameter (nm) | Standard deviation (nm) |
|-----------------------|---------------------------------|-------------------------|
| 10 | 445 | 71.17 |
| 20 | 280 | 59.12 |
| 30 | 170 | 47.26 |
| 40 | 130 | 45.47 |

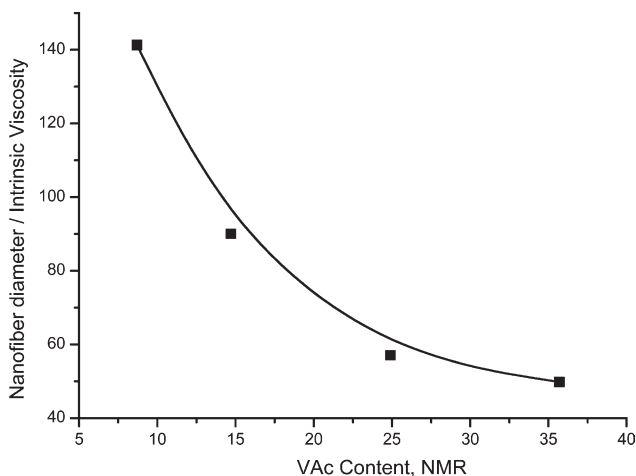


Figure 9. Relation between nanofiber diameter/intrinsic viscosity and VAc content determined by ¹H-NMR.

lower, the beaded nanofibers are obtained instead of smooth fibers.²³

In our study, when the intrinsic viscosity of copolymers decrease from 3.15 to 2.65, some beaded nanofibers are observed. The P(AN-co-VAc) solution with a feed ratio of 10 wt % VAc has exhibited the highest average nanofiber diameter (445 nm), which is related to the increased intrinsic viscosity of the electrospinning solution. Conversely, in P(AN-co-VAc) solution with highest VAc content, the lowest average nanofiber diameter (130 nm) was determined which is due to the decreased viscosity. (Table II). Nanofiber diameters (obtained from SEM)

were divided by intrinsic viscosity of copolymers decreased with VAc content of copolymer (obtained from NMR) (Figure 9). The influence of viscosity was eliminated by this way.

In a previous study, the viscosity and surface tension of the solution and the net charge density carried by the electrospinning jet are claimed the main factors that affect the nanofiber formation with or without beads.²⁴ For the polymer solution with lower viscosity the formation of the beads are caused by the capillary breakup of the jet during the electrospinning by surface tension. In this case the filaments formed between the beads are stabilized and the beads form on a string like structure as that observed in Figure 7(f–h).

The nanofibers transport charge across the distance between the charged needle and the grounded collector in electrospinning process. During the electrospinning process the electric current due to ionic conduction of charge in the polymer solution is so small that is considered negligible,²⁵ so the only mechanism of charge transport is the flow of polymer from the syringe to the grounded target when all other variables are held constant. At 14 kV, the repulsive force of the charged polymer overcomes easily the surface tension of the P(AN-co-VAc) solution as a function of increased electric current and decreased solution viscosity. So the diameters of nanofibers become thinner and beaded nanofibers are observed.

Figure 10 shows the surface morphologies by SEM and AFM image of nanofibers resulting from a solution with 3 wt %

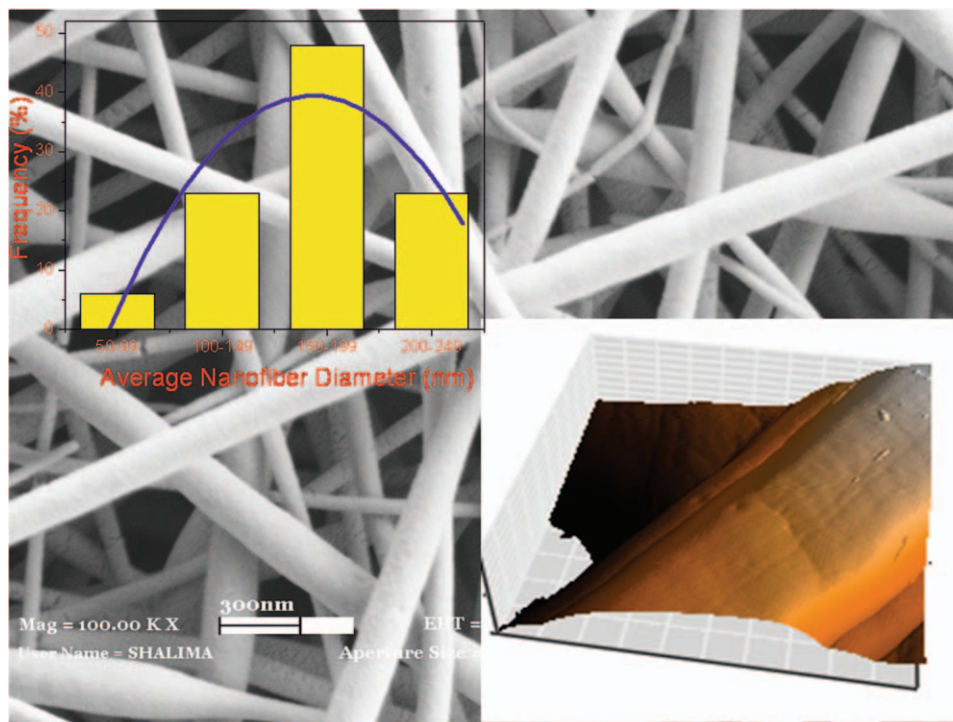


Figure 10. SEM image of P(AN-co-VAc) nanofiber containing 30 wt % VAc at 100,000 K \times magnification [Inset figure: AFM image of a single P(AN-co-VAc) nanofiber]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

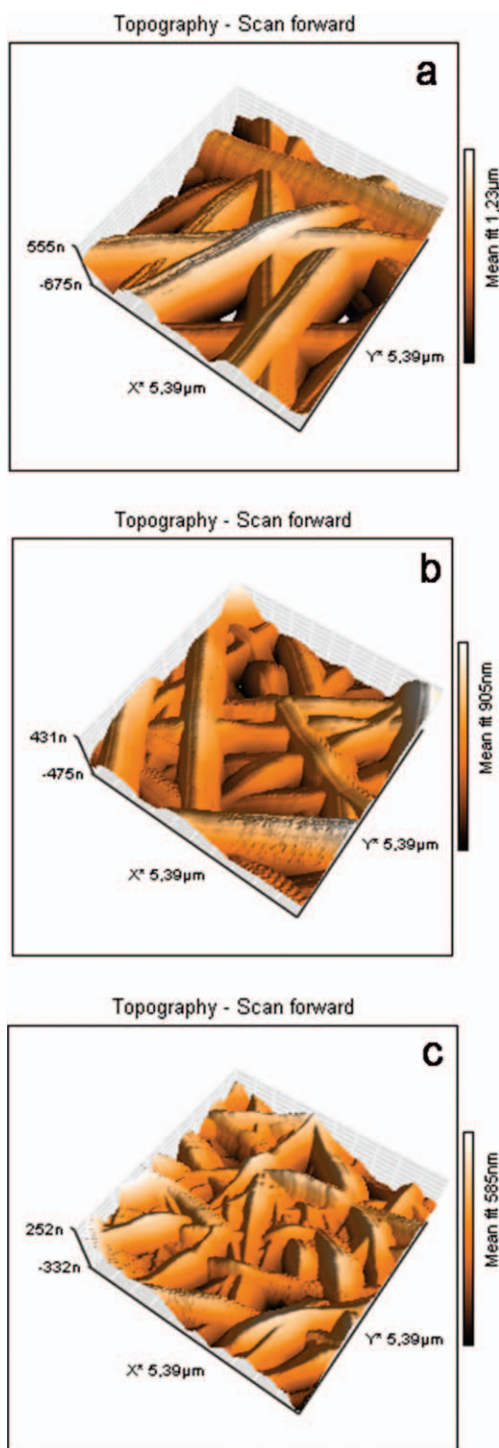


Figure 11. 3D AFM images of P(AN-*co*-VAc) nanofibers for different feed ratio of VAc: (a) 20 wt %, (b) 30 wt %, (c) 40 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

P(AN-*co*-VAc) having a feed ratio of 30 wt % VAc. The SEM and AFM images indicate that the P(AN-*co*-VAc) nanofiber containing 30 wt % VAc exhibited a smooth and regular surface. AFM image illustrates the 3D topographic image of a single nanofiber (Figure 11).

The surface roughness value (RMS) of electrospun nanofibers derived from 20 wt % feed ratio of VAc is 230 nm by AFM measurements. Additionally, RMS values of P(AN-*co*-VAc) nanofibers electrospun from solutions which have 30 and 40 wt % feed ratio of VAc decrease from 148 to 90 nm, respectively. The surface area of nanofiber mats is 29 μm^2 . The change in surface roughness is due to increase of VAc content and decrease of solution viscosity. The nanofibers having smaller diameters and less roughness values are obtained by decreasing viscosity of the solutions. However, surface of nanofiber mats show some irregularities and beaded nanofiber formations especially in 40 wt % feed ratio of VAc. The feed ratio of 30 wt % VAc was found a desirable content due to thinner and homogeneous diameter distribution for nanofiber formation.

CONCLUSIONS

Thermal stability of PAN is improved after being copolymerized with VAc, and thus confirming the effect of VAc functional groups existed in P(AN-*co*-VAc) in addition to nitrile groups of PAN. A systematic increase of the thermal decomposition temperatures of copolymers is observed with the increase of VAc content. The decreasing of T_g and viscosity with increasing VAc content is related to the incorporation of VAc units, which disorders the symmetry of AN chains and increases the amorphous region of copolymers. The viscosity of the solution has a significant effect on P(AN-*co*-VAc) electrospinning and the nanofiber diameter. At lower viscosity where generally the polymer chain entanglements are lower, the beaded nanofibers are obtained instead of smooth fibers. The average diameters of P(AN-*co*-VAc) nanofibers decrease from 445 to 130 nm with increasing feed ratio of VAc wt %. The P(AN-*co*-VAc) solution with a feeding of 10 wt % VAc has the highest average nanofiber diameter. Conversely, in P(AN-*co*-VAc) solution with the highest VAc content, the lowest average nanofiber diameters was determined which is due to the decreased viscosity of the solution. The P(AN-*co*-VAc) containing the feed ratio of 30 wt % VAc can be used for textile filtration nanofiber mats and for carbon nanofiber precursor in energy storage applications. The P(AN-*co*-VAc) electrospun nanofiber mats especially the copolymer which has the feed ratio of 30 wt % VAc can be used as a nanofiber membrane in filtration and as a carbon nanofiber precursor for energy storage applications due to high surface to volume ratio, high thermal stability, homogeneous, and thinner nanofiber distribution.

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