Investigation of the Effect of Phosphorous on the Flame Retardant Polyacrylonitrile Nanofiber

Mustafa Yılmaz, Ahmet Akar, Nesrin Köken, Nilgün Kızılcan

Abstract—Commercially available poly(acrylonitrile-co-vinyl acetate) P(AN-VA) or poly(acrylonitrile-co-methyl acrylate) P(AN-MA) are not satisfactory to meet the demand in flame and fire-resistance. In this work, vinylphosphonic acid is used during polymerization of acrylonitrile, vinyl acetate, methacrylic acid to produce fire-retardant polymers. These phosphorus containing polymers are successfully spun in the form of nanofibers. Properties such as water absorption of polymers are also determined and compared with commercial polymers.

Keywords—Flame retardant, nanofiber, polyacrylonitrile, phosphorous compound, membrane.

I. INTRODUCTION

POLYACRYLONITRILE (PAN) is a well-known polymeric material for manufacturing of textile fibers and membranes [1]. PAN has very polar and the nitrile groups in side chain offer hydrogen bonding sites for strong interaction with water. The highly polar nature of PAN led to high water sorption, whereas PAN membrane showed low permeability value of only about 8.5 $g/m^2/h$ [2].

PAN is a very common material for nanofiber production in very different areas with different properties [2]. The properties of PAN can be improved with comonomers. Generally vinyl acetate, methyl acrylate, methyl methacrylate or itaconic acid are used as a comonomer [3].

The phosphonic acid containing monomer such as vinyl phosphonic acid was copolymerized with acrylonitrile to dehydrate the water-pyridine mixture using a pervaporation process [2]. The phosphonic acid group has intended to form an in situ complex with pyridine in the feed. The effect of vinylphosphonic acid (VPA) in membrane to improve the separation capacity was evaluated [4].

Nanofibers can be produced with using PAN and its derivatives. Electrospinning method is a better method to produce nanofiber compared to mechanical drawing and phase separation [5], [6]. Electrospinning is very versatile process to create nanofibers from polymers with very different morphology. Furthermore, nanofibers produced with electrospinning process have high ratio surface area to volume, high porosity and good mechanical properties [7]-[9]. Electrospinning process is affected by process type and properties of the solution and polymer. These parameters are flow rate, electric field, collector type, viscosity, surface tension, distance and ambient parameters.

Flame retardancy is demanded in PAN based textile fabrics of work clothing, fire fighter apparel, institutional draperies, institutional upholstery, carpet, transportation, garments, and bedding. The flame retarded products provide thermal protection against hazards such as flash fire, electric arc and molten materials. These products could offer protection through resistance to ignition, reduction of burning rate and heat output, formation of protective char barrier and termination of fire at gas phase [10], [11]. Generally organic polymers are easily burned and emit fume and toxic gases. To avoid fire conditions, flame retardant materials can be used as an additive during production of polymer products. Flame retardant additives containing halogen produces toxic gases and hazardous fume during fire. For this reason, halogen free flame retardants should be preferred to avoid toxic gases release to the environment.

In this study, VP acid was used as additive monomer during polymerization and copolymerization of acrylonitrile to prepare fire-retardant polymers. Then, nanofibers of produced copolymers and terpolymers were prepared by electrospray method. FTIR, TGA and SEM are used for the characterization of polymers. Fire retardant properties were tested by burning method. Water absorption of polymers was compared with commercial polymers.

II. MATERIALS AND METHODS

The used equipment are analytical balance of Mettler Toledo PB303-S, mechanical stirrer of Heidolph RZR 2020, high voltage power supply of Gamma High Voltage ES50, syringe pump of New Era Pump Systems, Inc. NE-500 and heater of Heidolph MR 3001 K and water bath of Julabo.

Fourier transform infrared (FTIR) spectra were obtained with a recording model Perkin Elmer Spectrum One FTIR spectrophotometer with an attenuated total reflectance (ATR) sampling accessory.

TGA (Mettler Toledo, TGA1 Star System) was carried out in nitrogen atmosphere at a heating rate of 10 °C/min up to 600 °C temperature. Weight loss (%) of sample was calculated at temperature range of 20-600 °C.

Morphologies of products were examined by scanning electron microscope, ESEM XL30 ESEM-FEG Philips.

Acrylonitrile (AN) (Merck ≥ 98%), methyl acrylate (MA) (Merck ≥ 98%), vinylphosphonic acid (VPA) (BASF), dimethyl formamide (DMF), sodium metabisulfite (($Na_2S_2O_5$) (≥ 97% Riedel-de Haen), ammonium peroxy disulphate

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(APS) (Lachema) were purchased with analytical grade and used without any purification.

III. EXPERIMENTAL PART

A. Synthesis of Polymers

For first synthesis trials, usual redox polymerization system was tried at 50 °C. Fe^{2+} was used as the redox agent. The polymerization was not started probably due to complex formation of Fe^{2+} ions with VPA. Therefore the polymerization system was modified by excluding Fe^{2+} ions and increasing the temperature. First, required start-up water was added into the three necked flask and started to heat up until the water was reached to 70-90 °C. The residual distilled water was used to dissolve the other ingredients. Water solution of ammonium persulfate $[(NH_4)_2S_2O_8]$ and $Na_2S_2O_5$ was added to the flask dropwise while stirring. $(NH_4)_2S_2O_8$ was used as initiator and $Na_2S_2O_5$ was used as chain transfer agent. The polymerization was carried out for 3 hours in a temperature controlled oil bath. Then the reaction was stopped by cooling and the precipitated polymer was washed with distilled water several times and dried at 50 °C in vacuum drying-oven. The detailed information of synthesized polymers is given in Table I.

B. Electrospinning of Polymers

Dried homo P(AN), P(AN-MA)2, P(AN-MA)3, P(AN-MA)4, P(AN-MA-VPA)2, P(AN-MA-VPA)3 and P(AN-MA-VPA)4 polymers were dissolved in DMF solvent. Each solution was stirred at room temperature for about 6 hours with closed bottle. Copolymer solution was prepared 10% by weight, homopolymer and terpolymers were prepared 5% by weight.

TABLE I
DETAILED INFORMATION OF SYNTHESIZED POLYMERS

Sample Name	Monomers			Initiator	Chain Tr. Agent	Specific Viscosity
	AN (gr)	MA (gr)	VPA (gr)	APS (gr)	$Na_2S_2O_5$ (gr)	η_{sp}
P(AN)	10	-	-	0.065	0.12	-
P(AN-MA) 2	12.25	0.25	-	0.075	0.15	0.37
P(AN-MA) 3	12.25	0.25	-	0.112	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	0.075	0.15	0.46
P(AN-MA-VPA) 3	12	0.25	0.25	0.112	0.15	0.45
P(AN-MA-VPA) 4	12	0.25	0.25	0.15	0.15	0.34

The electrospinning device has a syringe pump and DC power supplier. The solutions were loaded into a 5 ml syringe and pumped with 1 ml/h speed. Applied voltage was 20 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 aluminum foil surface. In Table II, electrospinning process parameters are listed.

TABLE II
ELECTROSPINNING PROCESS PARAMETERS

Solution concentration	10 %
Applied voltage	20 kV
Tip-to-collector distance	15 cm
Feed rate	1 mL/h

IV. RESULTS AND DISCUSSION

In this study, homo PAN, poly(acrylonitrile-ran-methylacrylate) and poly(acrylonitrile-ran-methyl acrylate-ran-vinylphosphonic acid)) polymers were synthesized. The ratio of ammonium persulfate (APS) to $Na_2S_2O_5$ was changed to produce polymers with different molecular weight. The formation reaction of poly(acrylonitrile-ran-methylacrylate-ran-vinylphosphonic acid) terpolymer is shown in Fig. 1.

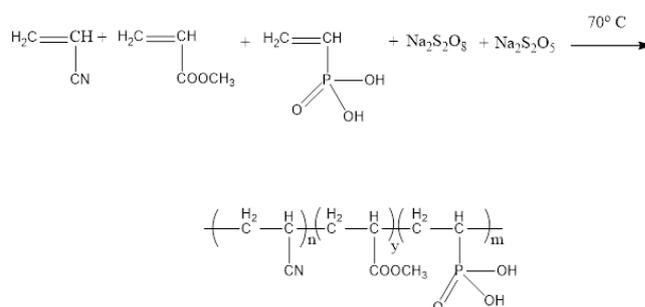
Fig. 1 Formation of poly(acrylonitrile-ran-methylacrylate-ran-vinylphosphonic acid) terpolymer

The polymerization yield was obtained between 75% and 90%. The properties of synthesized polymers are given in Table I.

The FTIR spectra of PAN and P(AN-ran-MA) copolymers are shown in Fig. 2. The characteristic strong absorption peak of nitrile groups (C≡N) is observed at 2243 cm^{-1} in PAN homopolymer, copolymers and terpolymers. The characteristic C=O stretching peak of MA appeared at 1725 cm^{-1} in copolymers. Peaks at 1453 cm^{-1} 1364 cm^{-1} and 1228 cm^{-1} are due to the C-H bending. 2937 cm^{-1} is assigned to C-H stretching.

The FTIR spectra of P(AN-MA-VPA) terpolymers are shown in Fig. 3 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 P-OH bending and O-P-O asymmetric stretching are observed at 2347-2355 cm^{-1}. The peaks observed at 1026 cm^{-1} as small shoulder correspond to the symmetric and asymmetric P-O(H) bands of phosphonic acid units. The peak observed at 1069 cm^{-1} corresponds to a P-O bonding.

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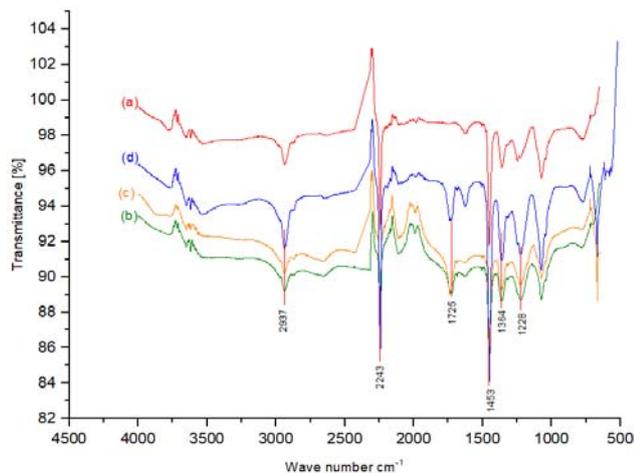International Journal of Chemical and Materials Engineering
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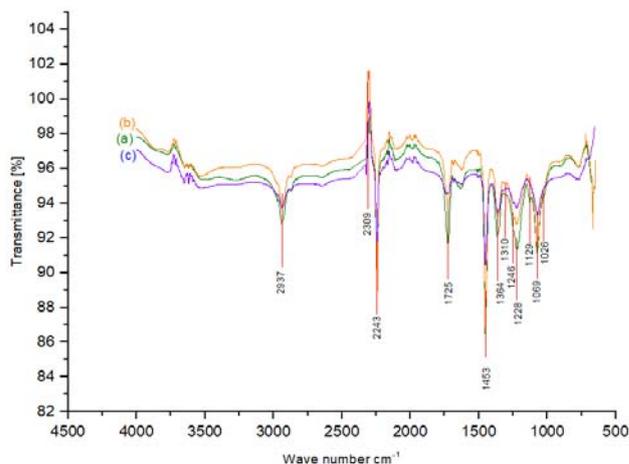Fig. 2 FTIR spectrum of P(AN) (a), P(AN-MA)2 (b), P(AN- MA)3 (c), P(AN-MA)4 (d)

Fig. 3 FTIR spectrum of P(AN-MA-VPA)2 (a), P(AN-MA-VPA)3 (b) and P(AN-MA-VPA)4 (c)
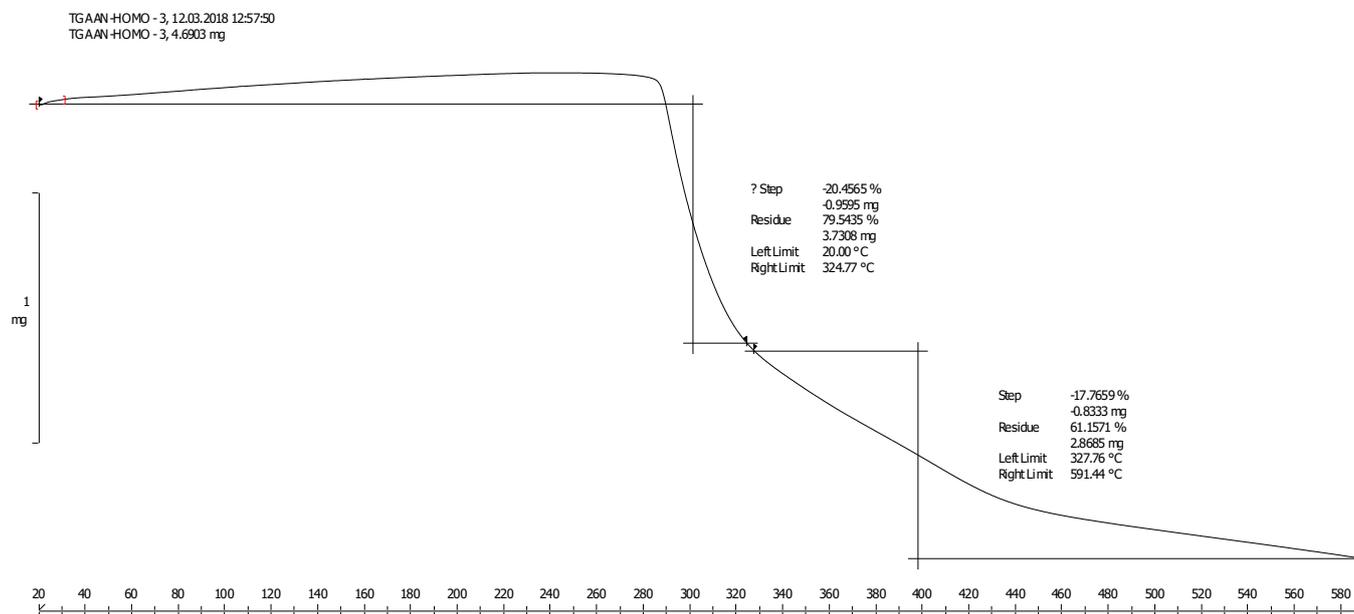

Fig. 4 TGA curves of P(AN) homopolymer

P(AN) homopolymer, P(AN-*ran*-MA) copolymers and P(AN-*ran*-MA-*ran*-VPA) terpolymers were analyzed by thermal gravimetric analysis (TGA) to find out thermal stability and char yield. According to Fig. 4 true char yield of P(AN) homopolymer was about 61%.

As seen in Figs. 5 and 6, true char yield of P(AN-*ran*-MA) copolymers was around 46%. This is due to the MA units that act as defects in the PAN chains. The first weight loss step of P(AN-*ran*-MA) resulted from loss of volatiles. The indicated weight loss in the second step was caused by the thermal degradation of the P(AN-*ran*-MA).

According to Figs. 7 and 8 and Table III, there is a significant increase at true char yield of terpolymers. On the contrary of P(AN-*ran*-MA) copolymers, adding VPA as a flame-retardant monomer enhanced true char yield of P(AN-MA-VPA) to about 48-71%. This increase in the char yield indicates that, adding VPA as a monomer gives positive flame retardant effect to the synthesized terpolymer.

Morphology of Electrospun Nanofibers

Morphological examinations of nanofibers 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 Figs. 9 and 10. The morphology of nanofibers changed with varying of synthesis composition. The most suitable value for diameter was obtained from P(AN-MA-VPA)4 terpolymer.

In Fig. 9, the SEM pictures of P(AN-MA-VPA)3, some uncompleted and distorted fibers can be seen. The average diameters of samples are given in Table IV.

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TGA AN-MA2 - 1,1, 23.02.2018 08:46:49
TGA AN-MA2 - 1,1, 8.9688 mg

Step	-22.7473 %
	-2.0401 mg
Residue	76.1753 %
	6.8320 mg
Left Limit	33.02 °C
Right Limit	326.66 °C

Step	-27.7618 %
	-2.4899 mg
Residue	48.0955 %
	4.3136 mg
Left Limit	328.10 °C
Right Limit	597.15 °C

5 mg
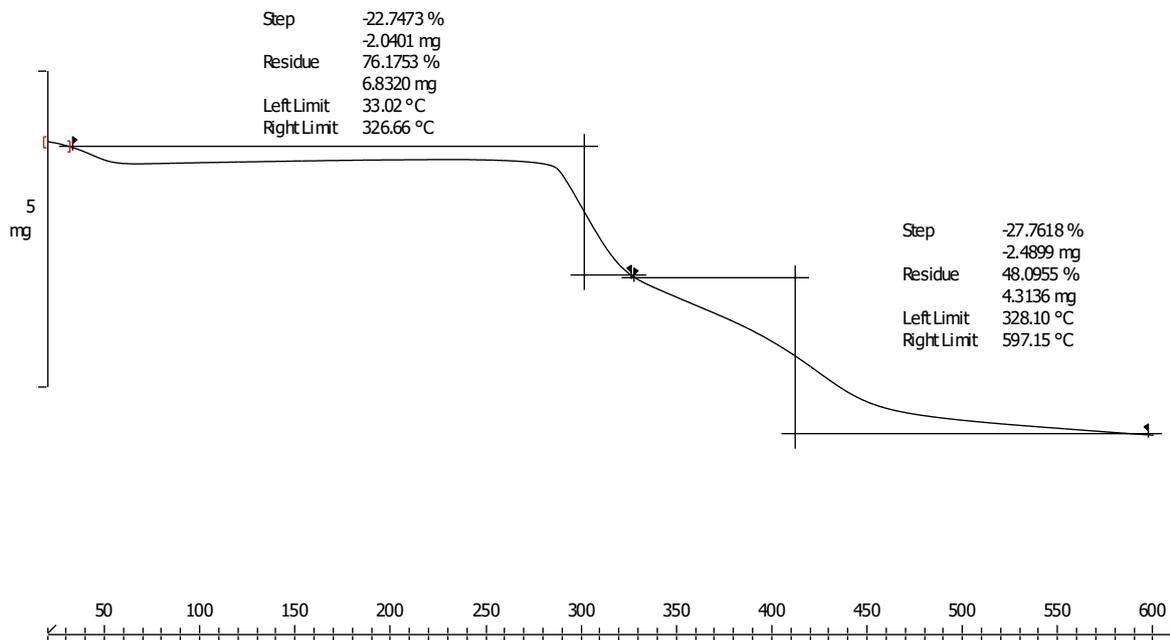
Fig. 5 TGA curves of P(AN-MA)2 copolymer

TGA AN-MA3 - 1,2, 23.02.2018 10:17:20
TGA AN-MA3 - 1,2, 29.8420 mg

Step	-72.9424 %
	-21.7675 mg
Residue	25.8448 %
	7.7126 mg
Left Limit	35.19 °C
Right Limit	150.91 °C

Step	-13.9493 %
	-4.1628 mg
Residue	11.8975 %
	3.5505 mg
Left Limit	153.08 °C
Right Limit	594.98 °C

20 mg
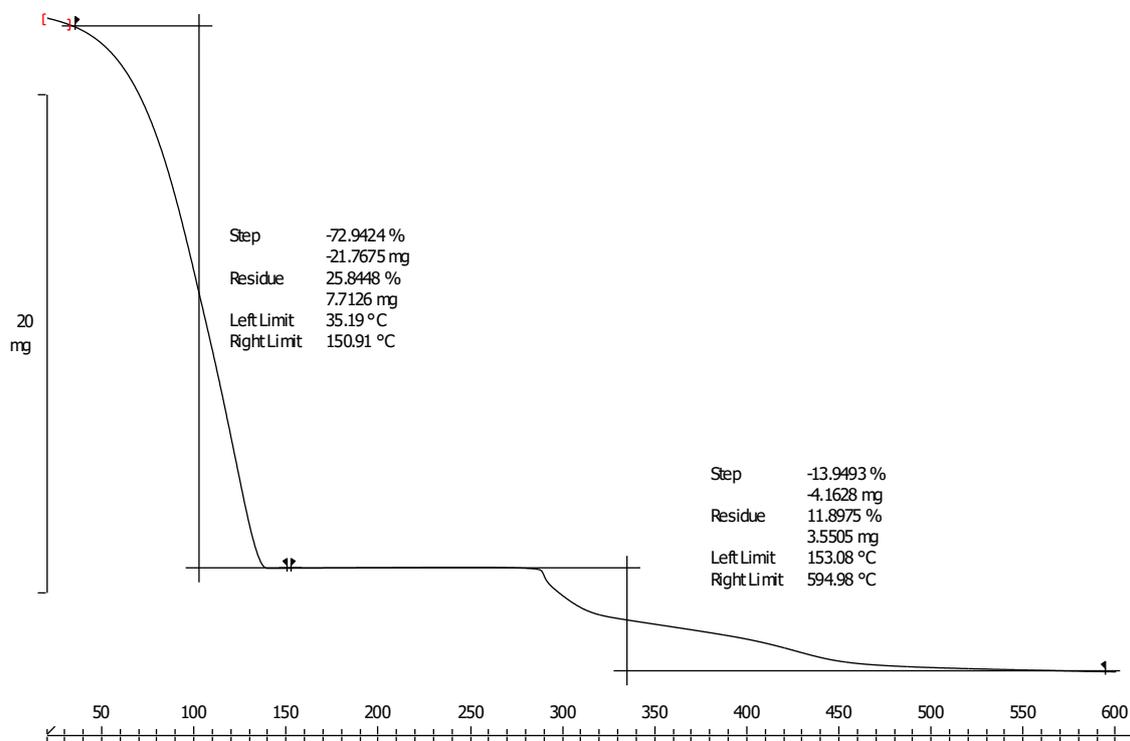
Fig. 6 TGA curves of P(AN-MA)3 copolymer

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AN-MA-VPA2 1,1, 02.03.2018 09:12:20
AN-MA-VPA2 1,1, 6.3756 mg

? Step   -14.4756 %
              -0.9229 mg
Residue   85.5244 %
              5.4527 mg
Left Limit   25.00 °C
Right Limit   331.38 °C

Step   -29.6624 %
              -1.8912 mg
Residue   55.7832 %
              3.5565 mg
Left Limit   331.81 °C
Right Limit   599.58 °C

2 mg
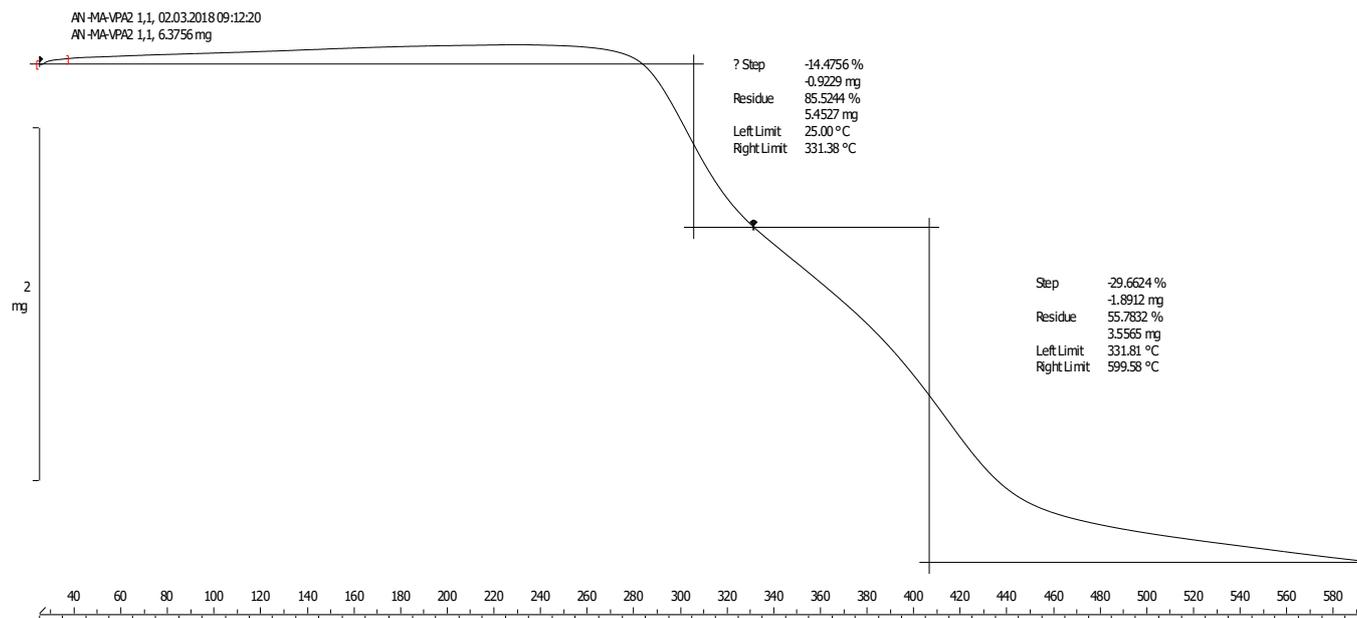
Fig. 7 TGA curves of P(AN-MA-VPA)2 terpolymer

AN-MA-VPA3 - 1,2, 02.03.2018 11:04:18
AN-MA-VPA3 - 1,2, 7.1934 mg

Step   -15.8261 %
              -1.1384 mg
Residue   84.2249 %
              6.0587 mg
Left Limit   32.84 °C
Right Limit   315.78 °C

Step   -35.8882 %
              -2.5816 mg
Residue   48.0817 %
              3.4587 mg
Left Limit   316.63 °C
Right Limit   595.29 °C
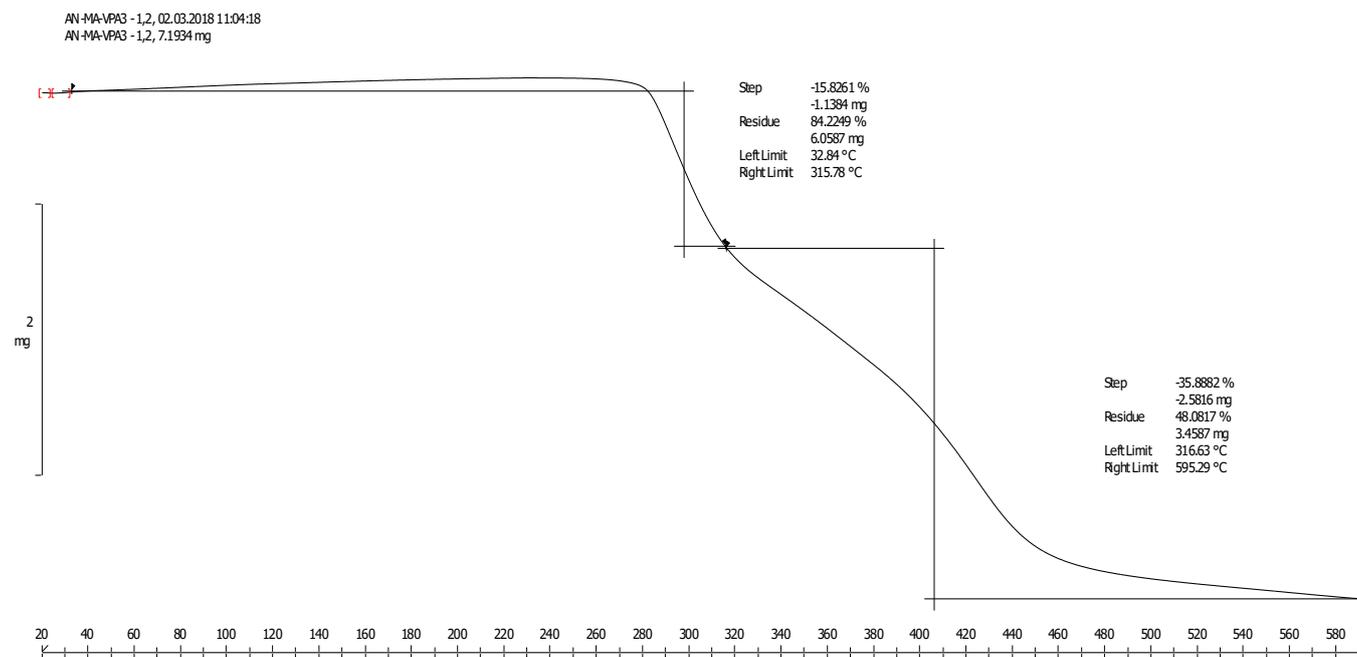
2 mg

Fig. 8 TGA curves of P(AN-MA-VPA)3 terpolymer

TABLE III
TGA VALUES OF SAMPLES

Sample Name	Onset (ºC)	First Residue (%)	Last Residue (%)	True char
P(AN)	289	79	61	61
P(AN-MA) 2	285	76	48	48
P(AN-MA) 3	5	26	12	46
P(AN-MA) 4	20	32	15	47
P(AN-MA-VPA) 2	270	85	56	56
P(AN-MA-VPA) 3	280	84	48	48
P(AN-MA-VPA) 4	282	91	71	71
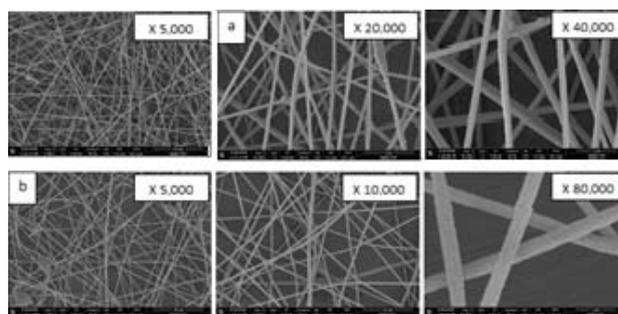
Fig. 9 SEM images of nanofibers (a) P(AN) (b) P(AN-MA)3

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TABLE IV
THE AVERAGE DIAMETER OF SAMPLES

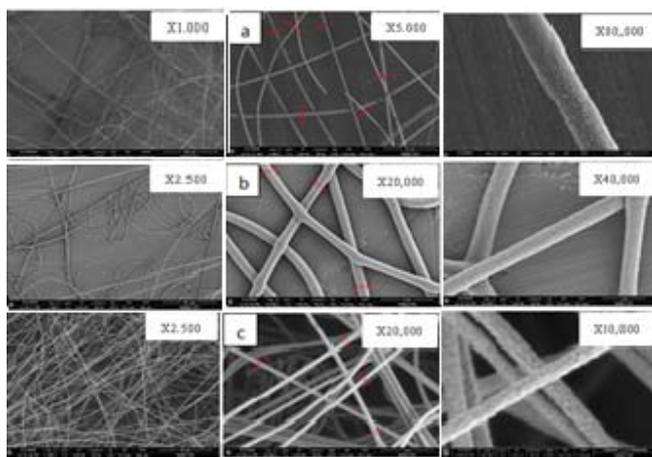| Sample Name	Avg. Diameter of NFBs (nm)
AN-MA-VPA 2	751
AN-MA-VPA 3	945
AN-MA-VPA 4	451

Fig. 10 SEM image of nanofibers (a) P(AN-MA-VPA)2 (b) P(AN-MA-VPA)3 (c) P(AN-MA-VPA)4

P(AN-*ran*-MA) copolymers and P(AN-*ran*-MA-*ran*-VPA) terpolymers were synthesized by changing initiator to monomer ratio. The effect of this ratio on the viscosity was listed at Table V. As a result, increasing the ratio of initiator to monomer caused a decrease the specific viscosity polymer.

TABLE V
SPECIFIC VISCOSITY OF POLYMERS

Polymer	Specific Viscosity (η_{sp})
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

TABLE VI
WATER ABSORBANCE OF POLYMERS

Sample Name	Water absorbance (%)
PAN	3.7
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

Thin film of synthesized polymers was put into the distilled water for 24 h and then the absorbed water was determined and listed at Table VI. Water absorption value of copolymers were higher than terpolymers.

The obtained film samples were exposed to the flame from 5 cm distance and flame-resistant behaviors of all films were investigated. All results and observations are listed in Table

VII.

TABLE VII
BURNING BEHAVIOR OF THE POLYMERS

Name	Ignition (sec)	Burning type	Fire spreading	Smoke Intensity
PAN	3	blaze	+	++++
AN-MA2	5	smoky	+	++++
AN-MA3	10	blaze	+	++++
AN-MA4	2	blaze	+	++++
AN-MA-VPA2	10	smoulder	-	++
AN-MA-VPA3	50	smoulder	-	+
AN-MA-VPA4	40	smoulder	-	+

Burning tests suggest addition of VPA into the polymerization system, the flame retardancy properties of terpolymers were getting better.

V. CONCLUSION

PAN, P(AN-MA) and P(AN-MA-VPA) were synthesized by using different ratio of initiator to chain transfer agent. According to the FTIR results, it was observed that VPA can be copolymerized and terpolymerized with AN and methylacrylate. The intrinsic viscosity of polymers decreased with increasing the ratio of chain transfer agent to initiator.

According to TGA results, the average char yield of P(AN-MA-VPA) was higher than P(AN-MA). Also the addition of VPA to the polymer structure increased the water absorbance value much higher than PAN.

P(AN-MA-VPA) terpolymers solutions were prepared in DMF and nanofibers were produced by electrospinning. The morphology of terpolymers was investigated by SEM. The lowest average diameter value was obtained at P(AN-MA-VPA)4. Terpolymers produced from AN, methacrylate and VPA can be produced as nanofiber with flame retardant properties.

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