Preparation Of Chemically Modified Poly(Acrylonitrile-Co-Itaconic Acid) Non-Woven Fibers

Nur Nida Syamimi Subri[1], Nur Aziera Hood[1] Nur Hana Faujan[2] and Siti Nurul Ain Md. Jamil[1,2*]
[1]Department of Chemistry, Faculty of Science,
Universiti Putra Malaysia 43400 UPM Serdang,
Selangor, Malaysia

[2]Centre of Foundation Studies for Agricultural Science,
Universiti Putra Malaysia 43400 UPM Serdang,
Selangor, Malaysia
corresponding author: ctnurulain@upm.edu.my

Abstract— **This paper describes the preparation of poly(AN-*co*-IA) non-woven fibers that was further chemically modified to contain thioamide chelating group on their surface *via* heterogeneous chemical reaction. Poly(AN-*co*-IA) and thiourea-modified poly (AN-*co*-IA) non-woven fibers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM). The conversion of poly(AN-co-AA) and thioamide-modified poly(AN-*co*-IA) into non-woven fibers were up to 58% and 51%, respectively. The SEM analysis showed that the average diameter of thiourea-modified poly(AN-*co*-IA) non-woven fiber was larger (139 nm) compared to the average diameter of poly (AN-*co*-IA) non-woven fiber (105 nm). The results indicate the potential of thiourea-modified poly(AN-*co*-IA) non-woven fiber for various applications, e.g: as polymeric sorbent.**

Keywords—polyacrylonitrile; copolymer; active surface area; microfiber

I. INTRODUCTION

Polyacrylonitrile (poly(AN)) is synthesized by free radical polymerisation of acrylonitrile (AN). PAN consists of a reactive pendant group (cyano group) that can be chemically modified by different types of reagents such as hydrazine and thiosemicarbazide through cycloaddition reaction and nucleophilic addition reaction [1]. Poly(AN) has hydrophobic character due to the presence of cyano group along the polymers chains. Thus, poly(AN) is copolymerized with acidic monomers such as itaconic acid (IA), acrylic acid, and methyl acrylic acid to reduce its hydrophobicity [2]. Poly(AN) is widely used in various fields especially in the textile industry and carbon fiber production. Poly(AN) is known for its excellent properties such as hardness and rigidity, chemical resistance, low gas permeability, and compatibility with a certain polar substance [3]. Poly(AN) can be prepared into nanoscopic fibrous materials by a facile fiber spinning, known as electrospinning. Poly(AN) microfibers have been modified extensively to contain a chelating group for multiple purpose, e.g: for ions removal [4]. Poly(AN) fibers are known as a remarkable materials due to their high surface area to volume ratio, nanometer range of pore size and can be chemically modified to tailor the chemical and physical properties of the fibers. Moreover, the nitrile group of poly(AN) chain contribute to the presence of π-bond along poly(AN) chains which are able to form the π-interaction with a complex compound including the aromatics compound [5]. Itaconic acid (IA) is monomer that soluble in water, ethanol and acetone, and slightly soluble in organic solvents [6]. IA has unsaturated solid bond that makes a conjugated system with two carbonyl group. The presence of IA comonomer in poly(AN) system helps to reduce the dipole-dipole interactions that present along the poly(AN) chains [7]. IA also reduces the cyclisation temperature and increase the hydrophilicity of poly(AN) [8].

There are many methods to produce micro and nano-fiber such as electrospinning, phase separation, template synthesis and self-assembly [5]. The electrospun nano-fiber has unique advantages, such as high surface area to volume ratio and high porosity with small interconnected pore structure with submicron pore sizes. Thus, more active sites are available to interact with targeted analytes. Thus, electrospun fiber is known as an excellent material to capture analytes from various system [9]. The present paper describes preparation of thioamide-modified poly(AN-co-IA) non-woven fibers. The non-woven fiber is expected to contains thioamide moiety that is beneficial to provide active functional groups on high surface area non-woven fibers. To date, surface chemical modification of poly(AN-co-IA) non-woven fibers with thiourea has not been reported elsewhere.

II. METHODS

Materials

The reagents used for polymer synthesis were acrylonitrile (AN) (≥99% grade, Merck, Netherlands), and itaconic acid (IA) (≥99% grade, Aldrich Chem.Co, Milwaukee, USA). Potassium persulphate (KPS) and sodium bisulphite (SBS) were used as initiators and supplied by Sigma Aldrich (Dorset, UK). Methanol (Sigma-Aldrich, UK) and thiourea (ChemPUR System, Poland) were used as reagents for chemical modification reactions. Dimethylformamide (DMF) was supplied by R&M Chemicals (UK). Commercial PAN was purchased from Sigma Aldrich (UK). AN was purified by passing them through a short column of neutral alumina. All other reagents were used as received.

Redox Polymerizations

The polymerization reaction was carried out inside a three neck round bottom flask at 40 ˚C under nitrogen atmosphere. The flask was fitted with the condenser and the third neck was used for nitrogen gas purging. The temperature was maintained at 40 ˚C±2 ˚C. Then, 97 mol% of AN and 3 mol% of IA were added into deionized water (as reaction medium) in the round bottom flask. 2.00 g of SBS initiator was added into the medium followed by 2.00 g of KPS initiator to initiate the polymerization reaction [10].

The polymerization was allowed to proceed for 4 h with the continuous nitrogen purging and stirred at 200 rpm. The polymerization was then terminated by pouring the polymer suspension into 50 mL of methanol and let to precipitate for 1 h. The mixture was then filtered using the Buchner funnel and washed thoroughly with 50 mL methanol and 100 mL of deionised water to remove traces of unreacted monomers and initiators. The poly(AN-*co*-IA) was dried in a vacuum oven at 50 ˚C till a constant weight was obtained.

Polyacrylonitrile homopolymer was prepared with similar procedure. The conversion monomers into polymers was calculated using Equation (1).

$$monomer\ conversion = \frac{weight\ of\ polymers\ (g)}{monomer\ feed\ (g)} \ x \ 100$$
(1)

Preparation of the poly(AN-*co*-IA) non-woven fibers

Poly(AN-*co*-IA) solution was prepared at 10 wt % in DMF. The prepared solution was then electrospun (under fixed electric field of 16 kV/20 cm, using a Gamma High Voltage Research (North U.S) D-ES30PNM692 DC power supply) onto an aluminium sheet wrapped around a rotating cylinder (width and OD of the cylinder ≈ 15 cm; rotational speed ≈ 50 rpm), which was used as the collector. Each of the electrospun fibers mat was collected continuously for 3 h.

The conversion of polymers into non-woven fibers was calculated using Equation (2).

$$Fiber\ conversion = \frac{weight\ of\ non-woven\ fibers\ (g)}{weight\ of\ polymer\ (g)} \ x \ 100$$
(2)

Chemical modification of poly(AN-*co*-IA) non-woven fibers

2.00 g of the non-woven fiber of poly(AN-*co*-IA) and 3.00 g of thiourea were added into 25.00 mL of methanol in a round bottomed flask that was fitted with reflux condenser. The mixture was stirred for 2 h on a heater plate. Then, 1.80 g of sodium hydroxide was added to neutralize the mixture solution. After 6 h of reactions at 70 ˚C, the product was filtered and rinsed with ethanol. The product was dried in an oven at 40 ˚C until a constant weight was obtained.

Characterizations

a) Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectra were recorded using a spectrum 100 BX Perkin Elmer (U.S.A) with UATR technique to identify the presence of the functional groups in the polymers. The infrared spectra of the samples were measured in the range between 280 cm^{-1} and 4000 cm^{-1} at 25 ˚C.

b) Scanning Electron Microscopy

Scanning electron microscope (SEM) (JEOL JSM 6360LA, Japan) was used to observe the morphology of the non-woven fibers. A steel stub was coated with conductive copper using double-sided adhesive tape. A thin layer of sample was then deposited onto the coated steel stub. Platinum coating of the immobilized sample was carried out for 8 minutes. A coated sample was placed inside the SEM chamber and a vacuum was applied. Micrographs were acquired at accelerating voltages of 10.0 kV or 25.0 kV.

III. RESULTS AND DISCUSSION

Yields of polymerization

As shown in Table 1, polyacrylonitrile (poly(AN)) achieved the highest conversion at 81%. This mainly due to minimal abnormality or defects present in the polymer chains since the polymerization was not incorporated with other monomers [10]. As predicted, the yield of poly(AN-*co*-IA) is lower than poly(AN) at 78%.

TABLE 1. POLYMERIZATION YIELDS OF POLY(AN) AND POLY(AN-*CO*-IA)

Sample	Ratio AN/IA, mol%	Yield, %
P1	100/0	81
P2	97/3	78

Conversion of poly(AN-co-IA) non-woven fiber

The parameter for blend solution to be electrospun was at flow rate of 2 mL/h with applied voltage of 18 kV [4].

Table 2 shows that commercial poly(AN) achieved the highest non-woven fiber conversion (70%) followed by P1 poly(AN) at 58% Meanwhile, P2 copolymer showed slightly lower non-woven fiber conversion at 51%.

As expected, polyacrylonitrile has better conversion into non-woven fibers due to the minimal abnormality or defects present in the polymer chains since the polymerisation was not incorporated with other monomers [10]. The conversion of P1 into non-woven fiber was lower compared to the commercial poly(AN), and that might be due to the presence of impurities from the initiators.

TABLE 2. CONVERSION OF POLY(AN) AND POLY(AN-CO-IA) INTO NON-WOVEN FIBERS

Sample	Ratio AN/IA, mol%	Conversion into non-woven fibers,%
Commercial poly(AN)	100/0	70
P1	100/0	58
P2	97/3	51

FT-IR Analysis

Fig. 1 shows the FT-IR spectra of commercial poly(AN) and P1 poly(AN). In both cases, the absorption band at 2932 cm^{-1} are corresponded to the alkyl C-H stretching vibrations. The IR spectra showed the characteristics bands of nitrile groups at 2244 cm^{-1}. The major absorption band at 2282 cm^{-1} is corresponded to the C≡N stretching. Some C≡N bonds are converted into C-N stretching vibrations, and this is proved by the presence of absorption band at 1242 cm^{-1} [11].
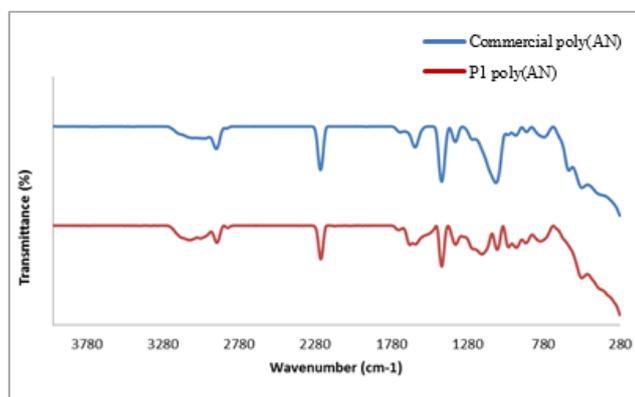

Fig. 1. *FT-IR spectra of commercial poly(AN) and P1 poly(AN)*

The FT-IR spectra of the P2 poly(AN-*co*-IA) and thioamide-modified poly(AN-*co*-IA) are shown in Fig. 2. The absorption band in the range of 1780 cm^{-1} until 1710 cm^{-1} indicated the presence of C-O stretching vibrations that was contributed by IA group. The absorption bands at 1726 cm^{-1} was appeared due to the C-O-C stretching vibrations. The 1680 cm^{-1} absorption band appeared due to the overlapping of -C=C and C=N functional groups. The absorption band at 2278cm^{-1} corresponded to the −C≡N stretching vibration [12].

An absorption band at 1120 cm^{-1} that was observed in the FT-IR spectrum of the thioamide-modified poly(AN-*co*-IA) proved the presence of C=S functional group [13]. The intensity of absorption band at ~1780 cm^{-1} was decreased due to the conversion of carboxylic acid into thioamide groups. The FT-IR spectra confirm that the surface chemical modification was successful.
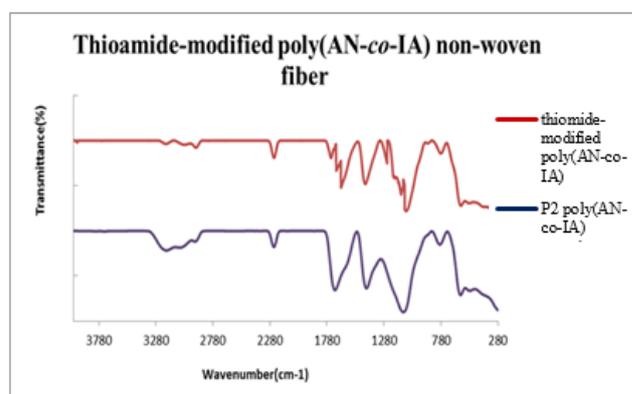

Fig. 2. *FT-IR spectra of P2 poly(AN-co-IA) and thioamide-modified poly(AN-co-IA)*

SEM Analysis

Fig. 3(a) showed that the surface morphology of commercial poly(AN) appeared as smooth surface with uniform diameter size. Similar observation on the morphologies of poly(AN) was reported by [14]. Meanwhile, P1 poly(AN) has rougher surface (Fig. 3(b)).

The average diameter of all non-woven fibers are tabulated in Table 3. The average diameter of commercial poly(AN) non-woven fiber is 248 nm. Meanwhile, the average diameter of P1 is larger (410 nm). The average diameter of P2 poly(AN-co-IA) is 105 nm. The average particle diameter of thioamide-modified poly(AN–*co*-IA) non-woven fiber is 139 nm which is larger than the P2 poly(AN–*co*-IA) non-woven fiber (105 nm). This might be due to chemical modification on the surface of fiber, in which the cyano group that was converted into thioamide group has larger molecular size than the cyano group [15].
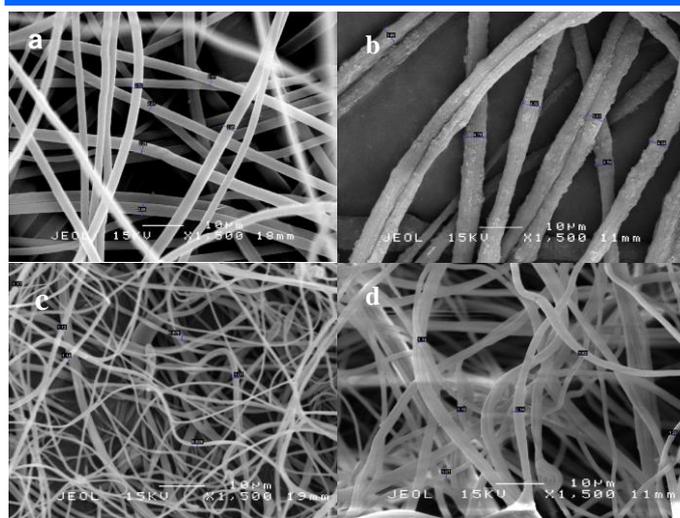
Fig. 3. *SEM micrographs of (a) commercial poly(AN), (b) P1 poly(AN), (c) P2 poly(AN-co-IA) and (d) thioamide-modified poly(AN-co-IA)*

TABLE 3. AVERAGE DIAMETER OF COMMERCIAL POLY(AN), P1 POLY(AN), P1 POLY(AN-*CO*-IA) AND THIOAMIDE-MODIFIED POLY(AN-*CO*-IA)

Sample	Ratio AN/IA, mol%	Average diameter, nm
Commercial poly(AN)	100/0	248
P1	100/0	410
P2	97/3	105
Thioamide-modified P2	-	139

SEM images proved that the P2 poly(AN–*co*-IA) and thioamide-modified poly(AN-*co*-IA) non-woven fibers are in micro-size range (indicator to large surface areas) which is an advantage for various applications, e.g: as sorbents to capture analytes and micro-pollutants.

IV. CONCLUSION

The FT-IR results proved that the synthesis of acrylonitrile-based non-woven fibers was successfully carried out. The SEM images showed that the poly(AN-*co*-IA) and thioamide-modified poly(AN-*co*-IA) fibers are in-micro-size range which reflect their high surface areas. Thus, thioamide-modified poly(AN-co-IA) might have potential in many applications such as for adsorption or extraction of analytes.

REFERENCES

[1] M.M. Rao, J.S. Liu, W.S. Li, Y.H. Liao, Y. Liang, L.Z. Zhao, Polyethylene-supported poly(acrylonitrile-co-methyl methacrylate)/nano- Al 2O 3 microporous composite polymer electrolyte for lithium ion battery, J. Solid State Electrochem. 14 (2010) 255–261. doi:10.1007/s10008-009-0784-7.

[2] R. Devasia, C.P. Reghunadhan Nair, P. Sivadasan, K.N. Ninan, High char-yielding poly[acrylonitrile-co-(itaconic acid)-co-(methyl acrylate)]: Synthesis and properties, Polym. Int. 54 (2005) 1110–1118. doi:10.1002/pi.1811.

[3] R. Jalili, M. Morshed, S.A.H. Ravandi, Fundamental parameters affecting electrospinning of PAN nanofibers as uniaxially aligned fibers, J. Appl. Polym. Sci. 101 (2006) 4350–4357. doi:10.1002/app.24290.

[4] P. Kampalanonwat, P. Supaphol, The study of competitive adsorption of heavy metal ions from aqueous solution by aminated polyacrylonitrile nanofiber mats, Energy Procedia. 56 (2014) 142–151. doi:10.1016/j.egypro.2014.07.142.

[5] A.H. Jadhav, X.T. Mai, F.A. Ofori, H. Kim, Preparation, characterization, and kinetic study of end opened carbon nanotubes incorporated polyacrylonitrile electrospun nanofibers for the adsorption of pyrene from aqueous solution, Chem. Eng. J. 259 (2015) 348–356. doi:10.1016/j.cej.2014.07.127.

[6] S.G. Del Blanco, L. Donato, E. Drioli, Development of molecularly imprinted membranes for selective recognition of primary amines in organic medium, Sep. Purif. Technol. 87 (2012) 40–46. doi:10.1016/j.seppur.2011.11.018.

[7] G. Zong, H. Chen, C. Wang, D. Liu, Z. Hao, Reverse atom transfer radical polymerization of acrylonitrile catalyzed by FeCl3/lactic acid, J. Macromol. Sci. Part A Pure Appl. Chem. 47 (2010) 804–808. doi:10.1080/10601325.2010.492186.

[8] Y. Mei, C. Yao, K. Fan, X. Li, Surface modification of polyacrylonitrile nanofibrous membranes with superior antibacterial and easy-cleaning properties through hydrophilic flexible spacers, J. Memb. Sci. 417–418 (2012) 20–27. doi:10.1016/j.memsci.2012.06.021.

[9] S.A. Theron, E. Zussman, A.L. Yarin, Experimental investigation of the governing parameters in the electrospinning of polymer solutions, Polymer (Guildf). 45 (2004) 2017–2030. doi:10.1016/j.polymer.2004.01.024.

[10] S.N.A.M. Jamil, R. Daik, I. Ahmad, Redox copolymerization of acrylonitrile with fumaronitrile as a precursor for carbon fibre, J. Polym. Res. 14 (2007) 379–385. doi:10.1007/s10965-007-9120-z.

[11] A. Ju, S. Guang, H. Xu, Effect of comonomer structure on the stabilization and spinnability of polyacrylonitrile copolymers, Carbon N. Y. 54 (2013) 323–335. doi:10.1016/j.carbon.2012.11.044.

[12] D.S. Can, H. Baskan, S. Gumrukcu, A.S. Sarac, A Novel Carbon Nanofiber Precursor: Poly(acrylonitrile-co-vinylacetate-co-itaconic acid) Terpolymer, J. Nanosci. Nanotechnol. 19 (2019) 3844–3853. doi:10.1166/jnn.2019.16309.

[13] N. Amirah, M. Zahri, S. Nurul, A. Jamil, L.C. Abdullah, T. Choong, S. Yaw, M.N. Mobarekeh, S.J. Huey, N. Salimah, M. Rapeia, Improved Method for Preparation of Amidoxime Modified Poly(acrylonitrile-co-acrylic acid): Characterizations and Adsorption Case Study, (2015) 1205–1220. doi:10.3390/polym7071205.

[14] N.N.S. Subri, P.A.G. Cormack, S.N.A. Md. Jamil, L.C. Abdullah, R. Daik, Synthesis of poly(acrylonitrile-co-divinylbenzene-co-vinylbenzyl chloride)-derived hypercrosslinked polymer microspheres and a preliminary evaluation of their potential for the solid-phase capture of pharmaceuticals, J. Appl. Polym. Sci. 135 (2018). doi:10.1002/app.45677.

[15] D. Liu, H. Chen, P. Yin, N. Ji, G. Zong, R. Qu, Synthesis of polyacrylonitrile by single-electron transfer-living radical polymerization using Fe(0) as catalyst and its adsorption properties after modification, J. Polym. Sci. Part A Polym. Chem. 49 (2011) 2916–2923. doi:10.1002/pola.24727.