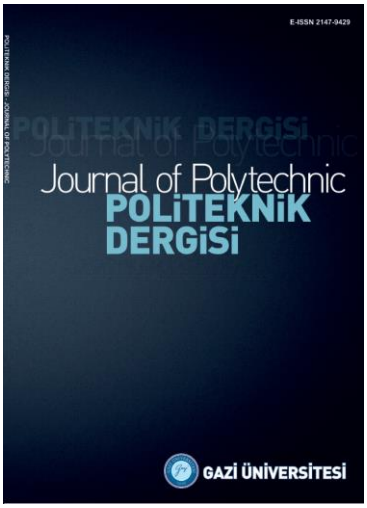

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Enabling the electrospinnability of PS/PVC/Bi_2O_3 nanocomposite fibers via wet electrospinning

Islak elektroeğirme ile PS/PVC/Bi_2O_3 nanokompozit liflerin elektriksel eğirilebilirliğinin sağlanması

***Yazar (Author)**: Hayriye Hale AYGÜN*

ORCID[1]: 0000-0002-2812-8079

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Enabling the Electrospinnability of PS/PVC/Bi_2O_3 Nanocomposite Fibers via Wet Electrospinning

Highlights

- *Bi_2O_3 loading to binary polymer solution*
- *Nano-sized fiber manufacturing from wet and dry electrospinning*
- *Bead dominant structure and inadequate fiber formation occurence with dry electrospinning*
- *A few bead formation occurence, better nanofiber continuity, high thickness with wet electrospinning*
- *Similar crystalline characteristics and no novel bond occurence in fabricated nanocomposite fibers*

Graphical Abstract

PS/PVC/Bi_2O_3 nanocomposite mats were succesfully fabricated by addition of distilled water into collector despite all other electrospinning parameters were kept constant.

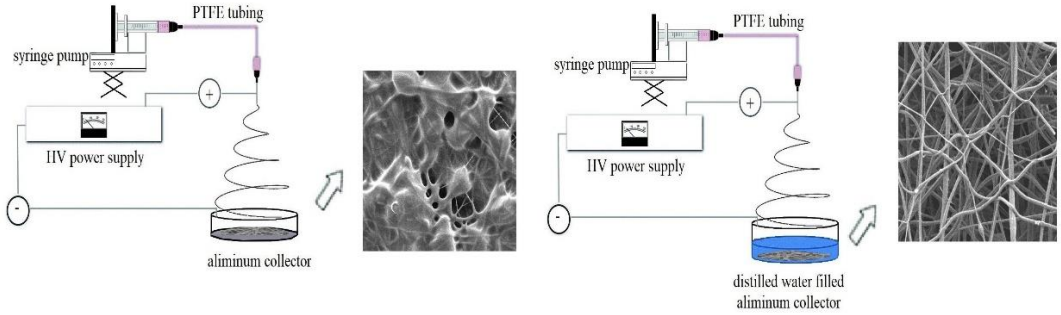

Figure. Dissimilar surface morphology of wet and dry electrospun PS/PVC/Bi_2O_3 nanocomposite mats

Aim

Investigation of electrospinnability of Bi_2O_3 powder in binary polymer solution

Design & Methodology

Ultrasonicated Bi_2O_3/DMF solution was incorporated into b*inary polymer solution containing PS/THF and PVC/DMF polymer solutions. Bi_2O_3 loaded polymer solution was electrospun with dry and wet electrospinning techniques with identical electrospinning parameters. Morphological properties of electrospun mats were examined with FESEM, XRD and FTIR analysis. Average mat thickness and average fiber diameters of mats were determined. Porosity of electrospun mats were inspected with ImageJ software based on FESEM images.*

Originality

Bi_2O_3 was incorporated into nanocomposite fiber structure without any further synthesis or application. Manufacturing of nanosized composite fibers was succesfully carried out and nanocomposite fiber continuity was obtained by the help of wet electrospinning.

Findings

XRD and FTIR results showed that crystallinity and molecular structure of dry and wet electrospun fibers were identical. 65 times thicker nanocomposite mats were fabricated with wet electrospinning. Numerous beading formation and irregular pore distribution were observed in dry electrospun mats. Despite the number of pores were close to each other, % porosity and porous area of wet electrospun mats were higher than those of dry electrospun mats.

Conclusion

Addition of distilled water into collector improved fiber continuity and porosity characteristics of electrospun mats because fibers were trapped on liquid due to high surface tension of water. This case inhibited direct immersing of fibers and fibers gained time for contacting with adjacent fibers before complete solidification.

Declaration of Ethical Standards

The author of this article declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Enabling the Electrospinnability of PS/PVC/Bi_2O_3 Nanocomposite Fibers via Wet Electrospinning

Research Article

***Hayriye Hale AYGÜN*[1,2]**

[1]Department of Design, Vocational School of Technical Sciences, Kahramanmaras Sutcu Imam University, Turkey
[2]Department of Material Science and Engineering, Institute of Science, Kahramanmaras Sutcu Imam University, Turkey

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ABSTRACT

It has been well-known that process, solution and environmental parameters have significant effects on characteristics of electrospun mats. Electrospinning is a promising technique for manufacturing of functional, lightweight and novel surfaces due to producibility of fibrous mats from polymer solutions loaded with various additives. In this study, Bi_2O_3 was incorporated into binary polymer solutions prepared with polymers having high and moderate shielding efficiency (PS and PVC, respectively) and their appropriate solvents. The characterization of electrospun mats showed that prepared solution was able to electrospun with wet electrospinning at identical process, solution and environmental conditions. It was noticed that the average fiber diameter was 979.18 nm, thicker nanofibrous mats were fabricated and a few bead formation was observed in wet electrospun mats. But bead-dominant structure was obtained in dry electrospun mats despite of finer average fiber diameter (271.22 nm). Similar crystalline structure and no distinct bond occurence was observed in wet and dry electrospun nanocomposite mats. The average mat thickness of wet electrospun mats was approximately 65 times higher than dry electrospun mat. In wet electrospinning, use of liquid in collector promoted surface unevenness, decreased beading formation, facilitated fiber-to-fiber interaction and influenced pore distribution positively due to high surface tension of distilled water.

Keywords: Bismuth oxide, polstyrene, polyvinyl chloride, wet electrospinning technique

Islak elektroeğirme ile PS/PVC/Bi_2O_3 nanokompozit liflerin elektriksel eğirilebilirliğinin sağlanması

ÖZ

İşlem, çözelti ve çevresel parametrelerin elektrospun yüzeylerin karakteristik özellikleri üzerinde önemli etkilerinin olduğu bilinmektedir. Elektrospinning yöntemi, çeşitli katkı maddeleri ile takviyelendirilmiş polimer çözeltilerden lifsi yüzey üretimine olanak tanıdığından dolayı, fonksiyonel, hafif ve yenilikçi yüzeylerin üretimi açısından gelecek vaad eden bir tekniktir. Bu çalışmada yüksek ve orta düzeyde radyasyon kalkanlama etkinliklerine sahip olan PS ve PVC polimeri ve bu polimerlerin çözücüleri ile hazırlanan ikili polimer çözeltisine Bi_2O_3 tozu ilave edilmiştir. Elektrospun yüzeylerin karakterizasyonu sonucunda, hazırlanan polimer çözeltisinin işlem, çözelti ve çevresel parametreler sabit tutularak ıslak elektroeğirme tekniği ile eğirilebilirliğinin mümkün olduğu gözlenmiştir. Islak elektroeğirme yöntemi ile üretilen yüzeylerde ortalama lif çapının 979.18 nm olduğu, daha kalın yüzey eldesinin sağlandığı ve sadece bir kaç boncuk oluşumunun var olduğu görülmüştür. Ancak kuru elektroeğirme tekniği ile üretilen yüzeylerde ortalama nanolif çapı daha ince (271.22 nm) olmasına karşın yoğun boncuk oluşumu tespit edilmiştir. Islak ve kuru elektroeğirme yöntemleri ile üretilen yüzeylerin benzer kristalin özellikler sergiledikleri tespit edilmiş ve moleküller arası yeni bağ oluşumuna rastlanmamıştır. Islak elektroeğirme tekniği ile üretilen yüzeylerin, kuru elektroeğirme ile üretilen yüzeylerden yaklaşık 65 kat daha kalın olduğu görülmüştür. Islak elektroeğirmede, kollektör içerisinde distile su gibi yüksek yüzey gerilimine sahip akışkan kullanımın üretilen yüzey düzgünsüzlüğünü geliştirdiği, boncuk oluşumunu azalttığı, lif-lif arası etkileşimi kolaylaştırdığı ve gözenek dağılımını olumlu yönde etkilediği tespit edilmiştir.

Anahtar Kelimeler: Bizmut oksit, polistiren, polivinil klorid, ıslak elektroeğirme tekniği.

1. INTRODUCTION

Electrospinning is a functional and cost-efficient technique which is based on stretching of polymer jet and harvesting of solidified or semi-solidified nano or microsized fibers on collector. Nowadays, the popularity of this technique has increasingly grow due to distinct properties of electrospun fibrous mats such as presence of interconnected and size-adjustable pores among fibers, incorporation of non-polymer based materials into fibers by effective encapsulation, variety of morphological structure and high specific surface area [1-5]. Some researchers studied on modifying of traditional electrospinning set-up to improve nanofiber properties, increase mass production, fabricate multi-functional

**Corresponding Author*
e-mail : hsolak@ksu.edu.tr

surfaces from electrospun fibers and enable the processability of different input materials [2, 6-10]. Wet electrospinning is arised from wet spinning which is a traditional spinning technique used for mono- or multi-filament manufacturing from synthetic polymers in a coagulation bath [11]. Wet electrospinning differentiates from traditional electrospinning by means of deposition of electrospun fibers on a non-solvent containing collector instead of solid collector. The transformation of polymer solution to fiber depends on polymer type, flow rate and needle gauge and the type of non-solvent available in collector influences mat thickness, distribution of fibers and porosity [10,12]. The effect of non-solvent on morphological properties of electrospun mats has been examined by some studies [13-16].

Metal oxide particles are one of the mostly used reinforcements in manufacturing of electrospun composite fibers. Bismuth oxide (Bi_2O_3) is the most commonly used derivative of bismuth which is known as environmentally-friendly and non-carcinogenic heavy metal [17]. Although Abudayyak et.al. (2017) claim that Bi_2O_3 particles decrease cell viability by disrupting on mitochondrial and lysosomal functions in HepG2, NRK-52E,Caco-2, and A549cells in a dose-dependent manner [18], bismuth and its derivatives are accepted as non-toxic with respect to high-toxic lead. Because human body has high tolerance to bismuth and it is reported that toxic intake level for a 70 kg human is 1 mg for lead but $15x10^3$ mg for bismuth and its compounds [19]. Previous researches report that Bi_2O_3 has less adverse effects [20] and exhibits optical and electrical properties [21], photocatalytic activation [22], antimicrobial activity [23] and protective shielding characteristics [24,25]. By means of protective shielding applications, Bi_2O_3 has been extensively subject of many studies due to its low density (8.9 g cm^{-3}) and high attenuation constant of Bi (90.5 keV) [26] but electrospinning of Bi_2O_3 particles has been studied only a few studies in which Bi_2O_3 has been loaded into a unique polymer matrix [27-29] In this study, it is aimed to electrospin Bi_2O_3 microparticles in a binary matrix of polystyrene and polyvinyl chloride polymers, at once. The reason of selection of these polymers is high resistance of polystyrene and moderate resistance of polyvinyl chloride to gamma radiation [30].

2. MATERIAL and METHOD

2.1. Materials

Polystyrene (PS) (CAS: 9003-53-6; Mw: 35.000 g mol^{-1}), polyvinyl chloride (PVC) (CAS: 9002-86-2; Mw: 80.000 g mol^{-1}), tetrahydrofuran (THF) (C_4H_8O, purity 99.9%, CAS: 109-99-9) and dimethyl formamide (DMF) (C_3H_7NO, 99.8% purity, CAS: 68-12-2) were purchased from Sigma Aldrich. Bismuth oxide powder (Bi_2O_3, 99.9% purity, 8.9 gr cm^{-3}, CAS: 1304-76-3) was obtained from Acros Organics. All agents were used as received without further purification.

2.2. Method

The 7 g of PS granules and 3 g of PVC powder were added into 13 g THF and 17 DMF, respectively and were dissolved for 2 h at 80 °C with hot-plate magnetic stirrer [31]. Meanwhile, 10 g Bi_2O_3/DMF mixture with 25 wt% powder concentration was sonicated in an ultrasonic bath for 2 h at 80 °C. PS/THF and PVC/DMF polymer solutions were gathered in a flask and stirred for 45 min at 80 °C in order to increase solubility of polymers in cross solvents and improve the total homogenity of mixture while ultrasonicated Bi_2O_3/DMF mixture was being mechanically stirred via hot-plate magnetic stirrer at the same condition. Then 10 g Bi_2O_3/DMF was incorporated into polymer solution and mixed for 17 h at room temperature. 25 g of Bi_2O_3 loaded polymer solution was transferred to a syringe with 21 gauge. Electrospinning was performed with applied voltage of ~16.5 kV, flow rate of 1.25 mLh^{-1}, needle tip-to-collector distance of 13 cm via top-to-bottom vertical electrospinning set-up. Aluminium plate with 12 cm inner diameter and 2 cm height was used as collector and 20 ml distilled water was added into negavely-charged collector for wet electrospinning. Relative humidity, environmental temperature and spinning duration were 45%, 23±2 °C and 45 min. Electrospun samples were conditioned at ambient temperature for 48 h before sample characterization. Figure 1 illustrates the steps followed for solution preparation.

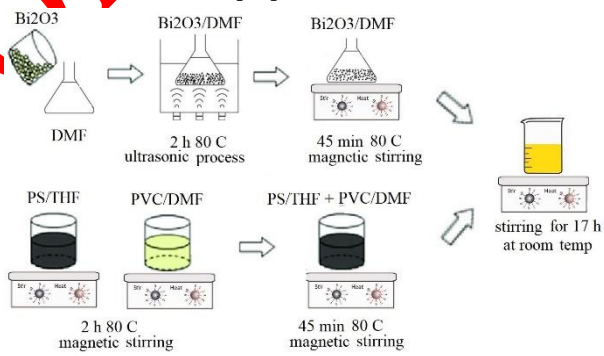

Figure 1. Schematic illustration of solution preparation conditions

2.3. Sample Characterization

Surface characteristics of electrospun mats were examined by field emission scanning electron microscopy (FESEM, Zeiss GeminiSEM 300) after Au/Pd(20/80) amalgam coating with sample preparation device (Emitech SC7620). Average fiber diameter and bead size were obtained after 10 measurements from FESEM images. X-ray diffraction (XRD, PANanalytical Xpert Pro MPD) was used to characterize the crystalline structure of electrospun mats. The measurements were carried out at a 2θ scanning rate of 3°/min in the range of 10°–90°. Molecular structure and chemical composition were observed with fourier transform infrared (FTIR, Spectrum 400 Perkin Elmer) and the spectra data were detected in the range of 400-4000 cm^{-1}. Digital thickness gage (Mitutoyo Absolute, Japan) with a high sensitivity

of 0.001 mm was used to determine average thickness of mats after 5 different measurements. Pore count and pore area of electrospun mats were obtained by ImageJ software.

3. RESULTS and DISCUSSION

3.1. FESEM Analysis

FESEM micrographs are shown in Figure 2. In both electrospinning methods, encapsulation of Bi_2O_3 particules was achieved but surface homogenity was improved by only wet electrospinning. Average fiber diameter of wet and dry electrospun fibers were 979.18 nm and 271.22 nm, respectively. In dry electrospinning, a few thin nanofibers were available among numeruous beads. However, a few bead was observed and fiber continuity was improved in wet electrospinning. The morphological variation between wet and dry electrospinning was result of surface tension of liquid. In dry electrospinning, fibers strike to aluminum surface directly but in wet electrospinning, higher surface tension of distilled water available in aluminium collector prevents direct immersing of fibers and fibers are trapped on liquid. Besides, fibers are in contact with adjacent fibers and mats with small pores are fabricated before complete solidification [15]. The presence of distilled water in collector facilitated the occurence of nanofiber formation. As considering that particle size of Bi_2O_3 powder is in range of 650.4 nm-1.754 µm and average particle size is 1.246 µm [32], it is necessary to focus on bead size available in wet electrospun mats. The average bead size obtained from 10 different measurements was found as 3.583 µm (s.d.:0.345). Bead dominant morphology available in dry electrospun mats was based on formation of polymer skin in the early stage of polymer jet disintegration [33]. In dry electrospun mats, unevenness beads are observed by means of size and shape and this unevenness lead to significant differences in overall performance of surface [34]. For eliminating a few bead occurence in wet electrospun mats, it is concluded that more homogeneous surface continuity could be handled by increasing ultrasonification time or decreasing Bi_2O_3 concentration before wet electrospinning [35-37].

3.2. Porosity of Samples

Porosity of PS/PVC/Bi_2O_3 nanocomposite mats were inspected by ImageJ software. Surface porosity of electrospun mats are given in Figure 3. The % porosity, porous area and pore counts were 4.879%, 854.801 µm^2 and 1265 units for wet-electrospun mats and 1.358%, 40.706 µm^2 and 1148 units for dry-electrospun mats. Zhang et. al. (2023) state that pore size and distribution in an electrospun fibrous mat can be regulated by altering spinning parameters, environmental humidity and solvent composition [38]. Considering that preparation conditions of polymer solution, process parameters and environmental conditions were kept constant for wet and dry electrospinning of PS/PVC/Bi_2O_3 composite mats, it was concluded that porosity characteristics of wet-electrospun mats should be improved by the help of high surface tension of water (70-72.58 mN/m) in collector as fibers were being oriented with the interaction among themselves before complete solidification [15].

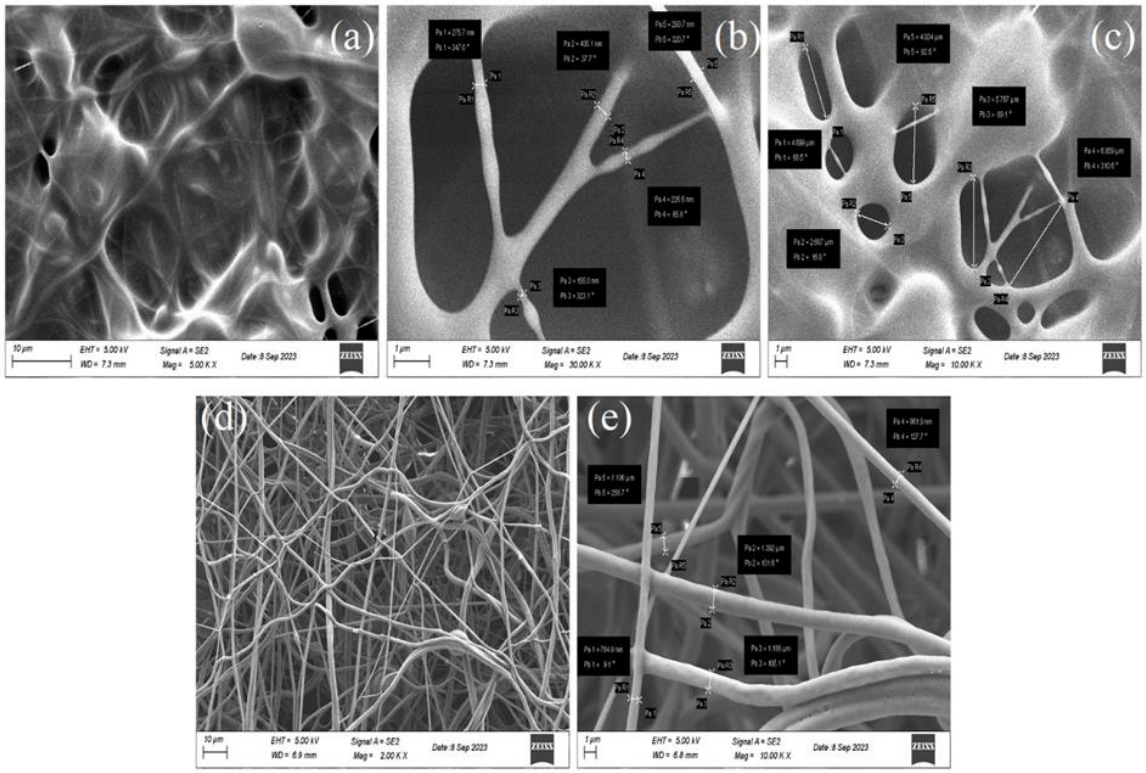

Figure 2. FE-SEM micrographs of dry (a, b, c) and wet (d,e) electrospun nanocomposite mats

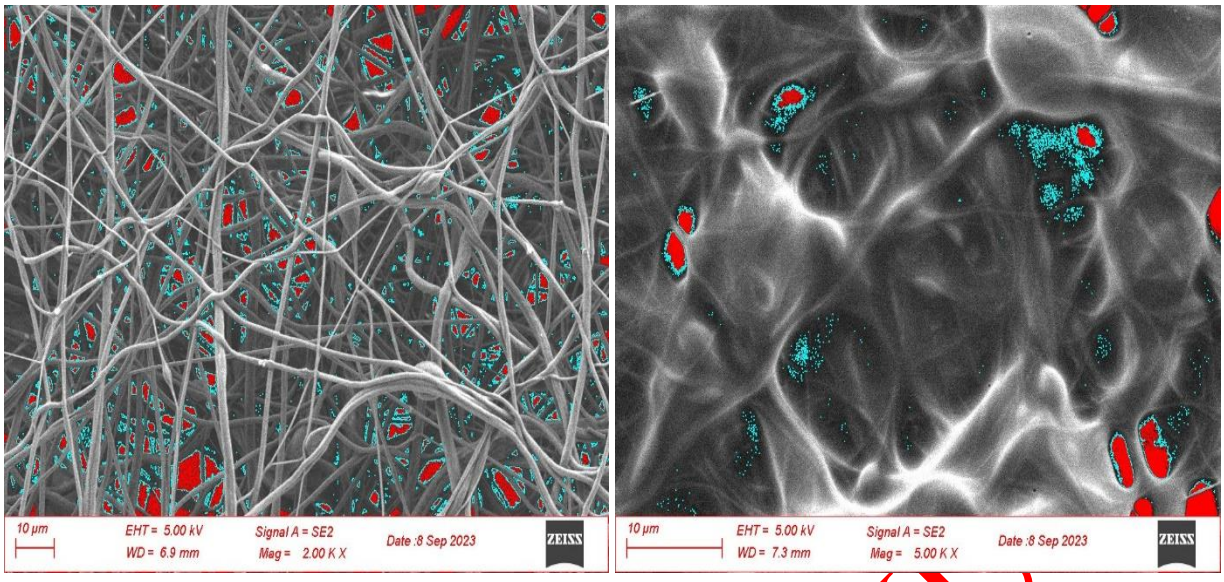

Figure 3. Comparison of surface porosity; wet electrospun mat (on left) and dry electrospun mat (on right) views obtained by ImageJ software

3.3. Measurement of Mat Thickness

Average thickness of wet and dry electrospun mats were calculated as 202.2 µm and 3.2 µm, respectively. The relationship between average fiber diameter and mat thickness is given in Figure 4. In literature, mat thickness is generally associated with spinning duration [39,40] and contradictory results are reported in terms of the relation between fiber diameter and mat thickness [41,42] for conventional electrospinning systems. Despite the identical spinning duration (45 min) and electrospinning parameters, average thickness of wet electrospun mat was found as approximately 65 times higher than dry electrospun mat. Similar results were outlined in following studies. Yokoyama et al. (2009) studied on PGA nonwoven fabrication with conventional and wet electrospinning systems by using different liquids in collector. They showed that the mats electrospun with conventional electrospinning were tight in the direction

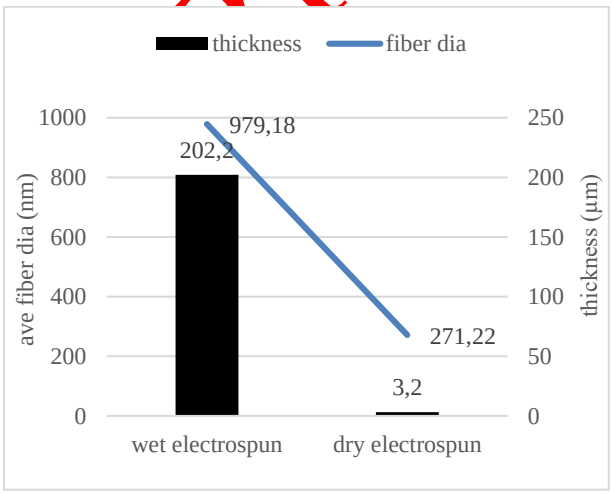

Figure 4. Comparison of mat thickness with respect to average fiber dia

electrospun mats had lower than wet electrospun mats because conventional electrospinning yielded dense 2D mats [44]. The use of distilled water did not allow the of thickness but spongiform 3D structures were obtained by wet electrospinning [43]. In addition, Sonseca et. al. (2020) claimed that the thickness of conventional electrospun fibers to sink and contributed to fiber distribution [10,45] therefore thick mats with high porosity but with well-aligned fiber formation were observed by wet electrospinning (Figure 2 and 3).

3.4. XRD Analysis

XRD patterns of dry and wet electrospun mats are shown in Figure 5. X-ray diffractographs of mats were found similar to each other. Crystallinity of electrospun mats is affected from how polymer jet is stretched. When collector distance is too long, electrical field intensity is low. In contrast to this, high electrical field intensity lead to instant acceleration of polymer jet. In both cases, stretching of polymer jet will be poor [14]. Considering

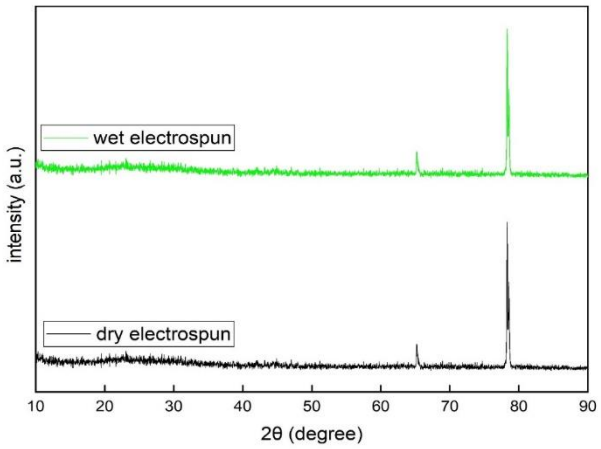

Figure 5. XRD diffractographs of samples

that electrospinning conditions were identical for wet and dry electrospinning, it was concluded that presence of distilled water in collector had no significant effect on crystallinity of electrospun mat. In previous studies, characteristic peaks of electrospun PS and PVC mats were reported as ~21° and 12°-35°, respectively and researchers claimed that these electrospun mats exhibited amorphous characteristics [46,47]. In this study, two different peaks with intensities of 260 a.u. (2θ=78.31) and 46 a.u. (2θ=65.58) were observed. These peaks existed due to the presence of Bi_2O_3 in structure [48,49]. Incorporation of Bi_2O_3 improved crystallinity of electrospun mat.

3.5. FT-IR Analysis

FTIR spectra of electrospun mats are given in Figure 6. As seen in figure, position and shape of peaks were not influenced from different electrospinning methods. The transmission peaks at about 1491.18 cm^{-1} and 1452.3 cm^{-1}, 749.05 cm^{-1} and 696.89 cm^{-1} reflect the stretching vibrations of C-C bonds available in benzen ring of PS polymer, CH bending and aromatic ring deformation, respectively [47, 50-53]. Low intensity but wide impulsive peaks at 2908,85 cm-1, 1427 cm^{-1}, 964 cm^{-1} and 613 cm^{-1} are originated from PVC polymer chain and refer to C-H stretching, CH_2 deformation, CH oscillation and C-Cl stretching, respectively [54-57]. The peak at about 549 cm^{-1} and 980 cm^{-1} is probably resulted from metal-oxygen bending vibrations (Bi-O-Bi) and Bi-O bonds stretching vibrations [58]. It was revealed that any distinct peak occurence was not observed depending on electrospinning method and molecular structures of components were preserved. The characteristic peaks in FTIR spectra confirmed the presence of components in nanocomposite fibers.

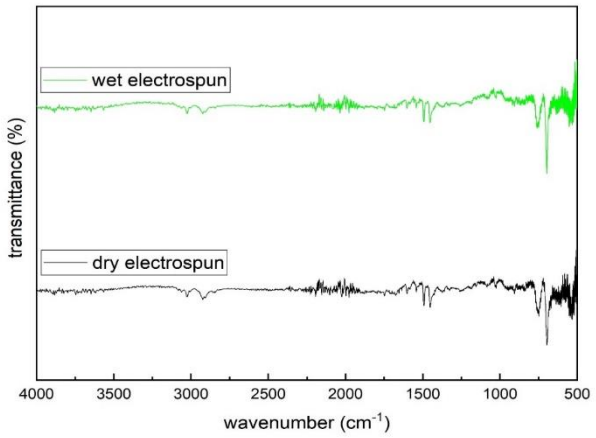

Figure 6. FTIR spectrums of samples

5. CONCLUSION

This study focused on producibility of PS/PVC/Bi_2O_3 composite surfaces with electrospinning technique. Without changing electrospinning parameters, electrospinnability of composite surface was achieved by only addition of distilled water into collector. Addition of liquid in collector caused to easily extraction of deposited electrospun fibers from collector. FESEM results showed that Bi_2O_3 powder was encapsulated with binary polymer matrix and as-spun fibers were nanoscale in size both with dry and wet electrospinning techniques. However, the continuity seen in wet-electrospun nanofibers was not observed in dry-electrospun mats. With dry-electrospinning, thinner mats with imperfect surface characteristics and improper pore distribution were fabricated due to unsufficient fiber-to-fiber interaction. From XRD and FTIR analysis, similar patterns were obtained in both dry and wet electrospun nanofibers. The high surface tension of distilled water within collector promoted surface unevenness, decreased beading formation, facilitated fiber-to-fiber interaction and influenced pore distribution positively. Electrospinnability of PS/PVC/Bi_2O_3 nanocomposite mats with wet electrospinning proved that environmental conditions and solution properties were not responsible from pore distribution and beading formation occurence was not only related with process and solution parameters. In addition, slightly-potential toxicity of bismuth oxide is eliminated by encapsulation of particles with electrospinning technique. Functionality and characteristics of this kind of electrospun surface can be improved by incorporating bismuth oxide nanoparticles which will improve surface homogenity and lead to finer nanofiber manufacturing. This study will enlighten the further studies to be performed on novel polymer-based radiation shieldings because electrospinning enables encapsulation of loaded particle and flexible surface fabrication due to nanofiber entaglement.

DECLARATION of ETHICAL STANDARDS

The author of this article declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

CONFLICT of INTEREST

There is no conflict of interest in this study.

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