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Tailoring the Porosity and Breathability of Nanofiber Webs with Mesh size of the Deposition Material

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Abstract

Nano and micro-pores of the electrospun webs present good moisture vapor transmission rate, while it maintains resistance to pressured air and resistance to liquid for some type of clothing. Laminating a nanofiber web to any textile structure could improve the desired resistance to air permeability with providing excellent breathability. In the present study, hydrophobic thermoplastic polyurethane (TPU) and hydrophilic poly (vinyl alcohol) (PVA) nanofiber webs were produced onto three different chromium sieve wires and then laminated to an interlining fabric and compared in means of pore size, breathability, and air permeability. Mesh count of the wires affected the pore size and smallest pore size are belong to 90 mesh wire. The water vapor permeability of the samples varied between 80% and 90% as well as providing relatively low air permeability values. With increasing nanofiber amount, air permeability decreased dramatically.

Keywords: Nanofibers, mesh count, porosity, water vapor permeability, air permeability

1. INTRODUCTION

Nanofibers are the fibers with diameters in the nanometer range and could be produced from different polymer with various additives. Thus, they have different physical and chemical properties, along with diverse application potentials [1-3]. Electrospinning is the mainly used method to generate nanofibers because of the easy and plain setup, the ability to produce continuous nanofibers from polymers, and the capability to generate nanofibers with controllable diameters, compositions, and orientations [4]. In an electrospinning setup, a static or a moving collector is made of conductive material which is electrically grounded are used for fiber deposition [5]. Thus, a stable potential difference between the source and the deposition area (collector) is achieved. With different collector designs various fiber patterns could be achieved [6]. The porosity and the character of the collector have an effect on the deposited fibers. Nanofiber membrane that are collected onto porous collector such as paper and metal mesh had a lower packing density than smooth surfaces such as aluminum foil. There is faster evaporation of residual fibers at a porous

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target, due to higher surface area while smooth surfaces may cause an accumulation of solvents around the fibers because of slow evaporation rate [7]. Liu et al selected copper mesh, aluminum foil and water, and paper as target materials. Fibers collected on paper showed smooth surfaces and few defects, fibers on water are more densely packed. On a nonconductive collector, the presence of electrostatic charges caused fibers to repel each other and gave a more loosely packed fibrous network. The packing density of fibers determines the overall porosity of the fibrous membranes. They observed that fiber packing was much less dense when collected on porous targets, such as paper and copper mesh, than on water and aluminum foil due to the differential diffusion and evaporation of solvents from nanofibers [8]. Sattary et al. used a flat plate and a novel rotating disc collector. Both a rotating disc and disc rotation speed affected fiber morphology and pore size. Due to the special geometry of the disc collector, which exposed the charged fibers in sediment, high-density nanofibers were collected on the copper wires, while low-density nanofibers were collected between them [9]. Wang et al. used a stainless-steel mesh with a wire diameter of 0.254 mm, and a wire spacing of 0.381 mm as a template collector for electrospun nanofibers. Produced Polycaprolactone (PCL) nanofiber meshes showed similar topological structures to the mesh collector. When compared with the randomly arranged electrospun nanofiber mats, this PCL nanofiber meshes with tailored architectures and patterns exhibited improved tensile strength with tensile modulus [10].

Electrospun nanofiber webs show controllable high porous character with high interconnectivity [11]. These nano and micro-pores of the electrospun webs provide good moisture vapor transmission rate, while it maintains resistance to pressured air and resistance to liquid for some type of clothing [12]. On the other hand, several conventional microporous membranes are already used for this purpose. Nevertheless, nanofiber webs show the advantage of better breathability, controllable air permeability, possibility to functionalization.

Although, conventional waterproof and breathable fabric structures include high-density woven fabrics, coated and laminated fabrics [13], the potential of using electrospun nanofibrous webs for waterproof, breathable, wind resistant textile application has been widely investigated. Yoon and Lee developed layered fabric structures by laminating mass produced electrospun polyurethane nanofiber webs that have a web density of 5.2 g/ m^2, to different substrates and produced layered structure, then investigated the breathability and waterproof characteristics [14] Sumin et al measured the water transfer properties of waterproofness and vapor permeability as well as the thermal transfer properties of warm/cool feeling and thermal conductivity of laminated nanofibers before and after laundering [15].

Gibson et al. pioneered using nanofibers in application of protective clothing. They produced polyurethane electrospun nanofibers for protective clothing and compared them with a wind-proof breathable membrane, ie, Goretex™ [16]. Gorji et al. produced polyurethane and poly (2-acryloylamido-2-methylpropanesulfonic acid)-graphene oxide nanofibers for protective clothing. They evaluated the nanofibrous membrane performance with their tensile strength, water vapor permeability, and contact angle and developed a dual-mode behavior on two opposite faces [17]. Sadighzadeh et al. studied waterproof-breathable fabric development by applying electrospun polyurethane, polyacrylonitrile, and polyethersulfone directly onto the substrate fabric. They compared the air permeability, water vapor transport rate, and resistance to water penetration for produced membranes with Goretex [18]. Oglakcioglu et al. used nanofibers to overcome the low air resistance of conventional weft knitted fabrics to develop windoproof textile surfaces even

open structures are in case. Thermoplastic nanofibers laminated between two single jersey fabrics and the effect of the nanofiber amount on the air resistance performance and breathability of the multilayered structure were investigated [12].

Air permeability is defined as the rate of airflow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of a material. Since a pressurized air is used in measurement, small pores of nanofibers can block the air but still allow water vapour to diffuse for breathability. So, body can still transfer the sweat from skin to environment while protecting from wind and prevent heat loss. Producing nanofibers directly onto a textile material or a deposition material are the options for combining nanofibers with textiles. When electrospinning is directly carried out onto textiles, a glue or a binder should be applicated prior to electrospinning process, then an additional layer may be laminated over nanofiber coated material. In case of using a deposition material such as mass production of standard membrane production, a silicone applied paper, or a similar material could be used as a carrier since nanofiber membranes are more fragile than conventional membranes. Then these membranes could be transferred and laminated to a textile material. Since deposition material has a significant effect on the porosity character of the nanofiber membrane, present study investigates the mesh size effect of the deposition material for mass production methods and aims to tailor the breathability.

Polyurethanes have been widely used to produce smart membranes because of several desirable properties, such as prominent elasticity, good abrasive resistance, and excellent hydrolytic stability [13]. Poly (vinyl alcohol) (PVA) nanofibers have diverse application areas when they are crosslinked [18-22].

In present study, hydrophobic thermoplastic polyurethane (TPU) and hydrophilic PVA nanofiber webs were produced onto three different chromium sieve wires with 90, 40 and 20 mesh and then, nanofiber webs were transferred to a knitted interlining in order to analyze the effect of mesh count on the pore sizes. Besides, for comparing the effect of nanofiber amount, nanofibers were produced with different deposition times ranging from 1 hour to 10 hours onto 90 mesh wire sieves. Nanofiber transferred interlinings' water vapor and air permeability were determined for both a hydrophobic and a hydrophilic structure.

2. MATERIAL AND METHOD

In this study commercial Pellethane 2103-80AE (Velox (Lubrizol Advanced Materials) was used as TPU Polymer. It was based on 4,4-methylene bisphenylene isocyanate, polytetramethyleneoxide and 1,4 butanediol. For hydrobhobic polymer PVA was supplied with average molecular weight of ~125,000 g/mol. A polycarboxylic acid 1,2,3,4 butanetetracarboxylic acid (BTCA), and it cataysyst sodium hypophosphite monohydrate ($NaPO_2H_2.H_2O$) were used for crosslinking. Dimethylformamide (DMF) was used as solvent for TPU and was supplied from Sigma Aldrich Chemical Company. Chromium wire sieves were used as deposition material. 90, 40 and 20 mesh sieves were purchased from Akyol Sanayi Malzemeleri. Vilene AP08 (Freudenberg), 100% polyester (PES) interlining was received from Gamateks.

TPU solutions were prepared by dissolving 10% (w/w) of TPU granulates in DMF. PVA solutions were prepared by dissolving again 10% (w/w) PVA powder in distilled water at 100°C. BTCA as crosslinking agent, was added to the PVA solutions in the ratio of 10% ($w/w_{polymer}$) with sodium hypophosphite monohydrate as catalyst in ratio of 2:1 (w/w) PVA solutions were further stirred for 10-15 min.

TPU and PVA solutions were electrospun at a voltage of 13 kV and 18 kV respectively and a tip-to-collector distance of 18 cm with a feeding rate of 0.5 ml/h were used. Rotating metal drum collector covered by chromium wire sieve and was grounded to achieve negative potential in order to travel nanofibers to the depostion area. Produced TPU and PVA nanofibers were coded with their collection sieve and period and given in Table 1. For PVA nanofibers different fixation methods can be used [23]. In this study a polycarboxylic acid, BTCA was used, thus after electrospinning, PVA nanofibers were heat set at 130ºC for 20 min in an oven to enhance the crosslinking reaction. Each nanofiber web was transferred onto PES interlining by a heat transfer machine to simulate combining these layers with textiles.

Table 1 Collection parameters and coding of TPU and PVA nanofibers

Parameters	***TPU Coding***	***PVA Coding***
1h collection onto 90 mesh	TPU1	PVA1
3h collection onto 90 mesh	TPU2	PVA2
5h collection onto 90 mesh	TPU3	PVA3
10h collection onto 90 mesh	TPU4	PVA4
5h collection onto 40 mesh	TPU5	PVA5
5h collection onto 20 mesh	TPU6	PVA6

In order to characterize the surface morphology of TPU and PVA nanofibers scanning electron microscopy (SEM, FEI Quanta 250FEG) images were taken. A thin film of gold was coated onto the nanıfibers. EMITECH K550X ion sputtering device was used for coating.

Air permeability measurement was carried out according to EN ISO 9237 with FX3300 (Textest, Switzerland). 5 cm^2 measurement area and 200 Pa pressure drop were used for the measurement. It is the rate of air flow passing through a known area under a prescribed air pressure differential between the two surfaces [24]. The air is drawn through the specimen into a closed chamber and out through an orifice that measures the flow.

Water vapor permeability measurements were carried out of Permetest (Sensora Company, Liberec, Czech Republic) in accordance with ISO 11092. The instrument works according to the principle of heat flux sensing. The temperature of the measuring head is kept at room temperature for isothermal conditions. Some heat is lost after the water flows into the measuring head. This instrument measures the heat loss from the measuring head due to the evaporation of water in bare state (without a sample) and covered with sample [25, 26].

Relative water vapour permeability of the textile sample P_{wv} determined from the equation (1):

$$P_{wv}\ [\%] = 100\ U_s / U_o \quad (1)$$

Here, U_s means the instrument reading without a sample (heat loses of the free wet surface), and U_s presents the heat loses of the wet measuring head (skin model) with a sample [27].

3. RESULTS AND DISCUSSION

In Figure 1 and Figure 2, the representative SEM images with two magnifications were given. Bead free smooth TPU and PVA nanofibers were electrospinned. Fiber diameter of TPU and PVA nanofibers were measured as 966 nm and 320 nm, respectively. Mesh structure of the wire sieve could be better seen at TPU nanofibers. Since PVA nanofibers were thinner, mesh structure disappeared at longer collections.

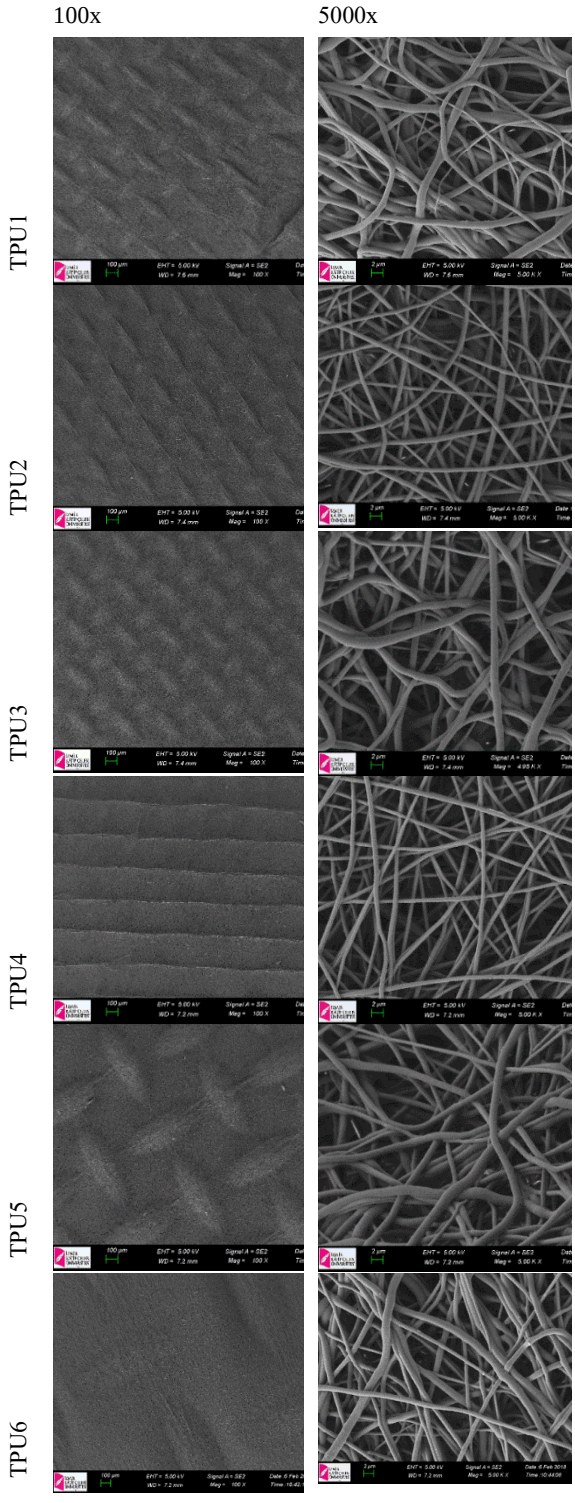

Figure 1 SEM images TPU nanofibers with 100x and 5000x magnification

The pores of the nanofiber membranes are caused by the entanglement of the nanofibers. When nanofiber diameter is constant, more nanofiber covering a specific area would result in narrower pore size distribution along with smaller pores [28]. Thus, with increasing collection period mean flow pore size (MFP) of TPU nanofiber decreased to 2.28 from 3.45µm (Table 2). Sparse mesh resulted in 3.09 µm of MFP for 20 mesh, 2.78 for 40 mesh and 2.69 for 90 mesh for same amount of nanofiber. For PVA nanofibers, due to thinner nanofiber diameter, all PVA webs had smaller pore sizes. Similar to TPU nanofibers, with increasing collection period MFP of PVA nanofiber webs decreased to 1.06 from 1.85 µm. MFP of PVA nanofibers was 1.73 for 20 mesh, 1.56 for 40 mesh and 1.44 µm for 90 mesh. That showed pore size of the nanofibers could be controlled with mesh count of deposition material.

Table 2 Pore size of TPU and PVA nanofiber webs

Nanofibers	***Biggest Bubble Point (µm)***	***Mean Flow Pore Size (µm)***	***Smallest Pore Size (µm)***
TPU1	6.67	3.45	2.43
TPU2	6.32	2.89	1.65
TPU3	4.82	2.69	1.87
TPU4	4.82	2.28	1.71
TPU5	6.03	2.78	1.69
TPU6	6.51	3.09	1.74
PVA1	2.72	1.85	1.51
PVA2	2.05	1.60	1.30
PVA3	2.22	1.44	1.44
PVA4	1.90	1.06	0.64
PVA5	2.08	1.56	1.40
PVA6	2.35	1.73	1.16

Understanding of the relation between mesh structure of the deposition material and transport properties of electrospun nanofibrous membrane will help to design tailored comfortable nanofiber laminated fabrics. Figure 3 and 4. present the water vapor and air permeability of nanofiber samples.

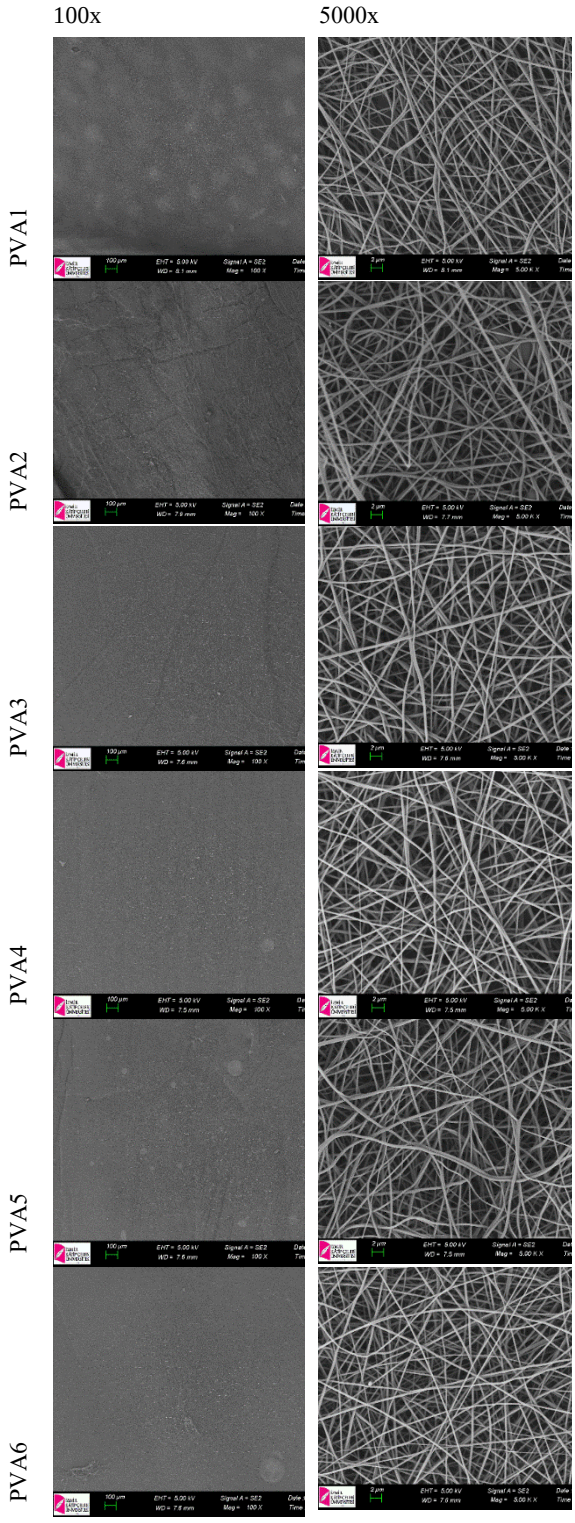

Figure 2 SEM images PVA nanofibers with 100x and 5000x magnification

Similar to the study of Gibson et al., this interconnected nanofiber webs present minimum resistance to moisture vapor diffusion [29]. The water vapor permeability of the TPU and PVA nanofiber webs varied between 80% and 90% as well as providing relatively high air resistance values. It was observed that the mesh count and different nanofiber amount caused by different deposition time significantly changed the permeability properties and it is possible to achieve good breathable structures with different air permeability characteristics. Water vapor permeability values were not much affected from the hydrophilic or hydrophobic character of the polymer, because both 1 h collected nanofibers water vapor permeability values are about 90%. Even the densest coatings of 10 h collections showed 81.1 and 82.9% for TPU and PVA nanofibers, respectively. Highly porous structure allowed water vapor passing through the nanofiber membranes. These results indicate that not only the nanofiber diameter, but deposition material mesh structure/design may also contribute to the porosity of the final composite material, and hence, the water vapor transport performance of the material.

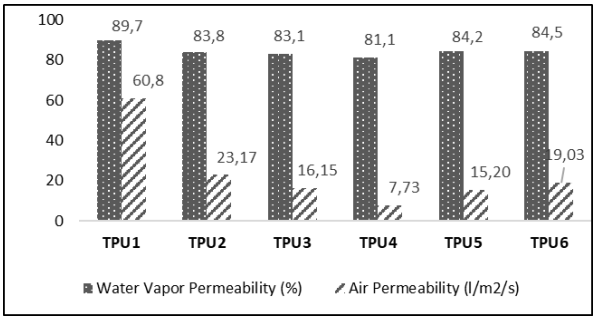

Figure 3 Water vapor and air permeability results of TPU nanofibers

In case of air permeability, significant difference could be seen at minimum amount of nanofiber (1h collection), thinner TPU nanofiber web had the highest air permeability value. Since the pore size of the TPU nanofiber membrane had the biggest (3.45 μm) MFP, it allowed higher pressured air penetration. On the other hand, with finer PVA nanofibers 1h collection onto 90 mesh, air permeability was about half of the TPU nanofiber web as 29.07 l/m2/s and it was close to the 5 h collection onto 20 mesh. Since the difference of the pore size was more significant at TPU nanofibers because of the thicker nanofiber diameter, the air

permeability results showed significant differences. It was seen that the air permeability properties of the nanofiber webs could be controlled by the character of the deposition material and finer nanofibers were much affected from the character of deposition material. Air permeability of the PVA nanofibers which were collected for 5 hours onto 90 mesh was 10.11 and 25.6 l/m2/s for 20 mesh, while they were 16.15 and 19.03 l/m2/s for TPU nanofibers. Besides, finer PVA nanofibers of 1h collection onto 90 mesh was similar to the 5 h collection onto 20 mesh.

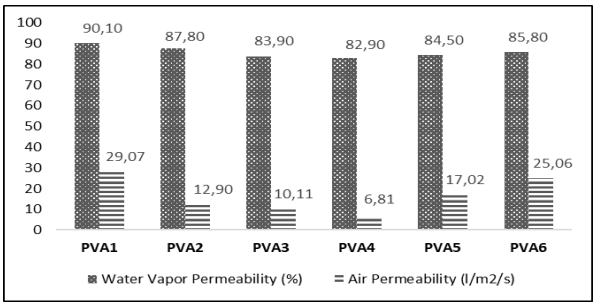

Figure 4 Water vapor and air permeability results of PVA nanofibers

4. CONCLUSIONS

Electrospun nanofiber webs have high porous character with nano and micro-pores. These nano and micro-pores of the electrospun webs provide good moisture vapor transmission rate, while it maintains resistance to pressured air and resistance to liquid for some type of clothing and may be controlled with the feature of the collector.

When stainless steel wire meshes were used as a deposition material, by changing the mesh count, it is possible to modify the porosity of the produced nanofiber membrane.

After the production of nanofibers onto a deposition material, common mass production practice is transferring it onto a textile material for waterproof and breathable fabrics. In this study, TPU nanofiber webs are investigated because of its several commercial applications as hydrophobic and breathable textile membrane and compared with hydrophilic PVA nanofiber webs. Nanofibers were densely deposited on the wires and sediment to the gaps; thus, mesh structure of wire could be easily seen. However, because of the thinner nanofiber diameter of PVA nanofibers (320 nm), at longer collection periods, mesh structures disappeared. When collection period is increased at same mesh count, pore size of TPU membranes decreased to 2.28 μm. 20 mesh count resulted in largest pore size of 3.09 μm for TPU nanofibers. Since PVA nanofibers are significantly thinner than TPU nanofibers, its pore sizes are smaller. Nevertheless, the mesh count of the wires affected the pore size, and the smallest pore size belongs to 90 mesh wire.

In order to evaluate the water vapor and air permeability, the nanofiber webs are transferred onto an interlining and that also simulates lamination process and combine nanofiber web with a textile material. The water vapor permeability of the samples varied between 80% and 90% as well as providing relatively low air permeability values. Significant difference is seen at minimum amount of thicker TPU nanofiber web (1h collection), which has the highest air permeability value. With increasing nanofiber amount, air permeability decreased dramatically. In case of air permeability, finer nanofibers are much affected from the character of deposition material.

Authors' Contribution

The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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