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Investigation of Water Permeability of Thermoplastic Polyurethane (TPU) Electrospun Porous Mat

Aušra BANUŠKEVIČIŪTĖ [*], Erika ADOMAVIČIŪTĖ, Rimvydas MILAŠIUS

Department of Textile Technology, Kaunas University of Technology, Studentų 56, LT-51424 Kaunas, Lithuania

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The aim of this study is to form thermoplastic polyurethane (TPU) mats by electrospinning process on knitted and woven materials, and to determine the water permeability of textile materials before and after mat has been formed on them. TPU granules were dissolved in a mixture of dimethylformamide (DMF) and tetrahydrofuran (THF) (1:1, w/w) solvents. TPU solution of 3 wt.% concentration was prepared. TPU mats were electrospun by "Nanospider^{TM}“, the applied voltage was 65 kV. Selected textile materials were knitted and woven cotton fabrics. Textile materials were covered by 1, 2, 3 and 4 layers of TPU mats. For the experiment four textile support materials such as fleece knitted fabric and three twill weave cotton fabrics were chosen. The water permeability was determined by a water drop method measuring the area of water drop. It was determined that the greater the number of layers on the textile materials with TPU electrospun fiber the thicker will be the mat. The greater number of layers decreases the expansion of water drop area on the textile material.

Keywords: electrospinning, thermoplastic polyurethane, water permeability.

INTRODUCTION

Electrospinning is a fiber spinning technique that produces polymer fibers of nanometer to micrometer size in diameter. These special fibers in nanometer (or micrometer) size diameter have specific improved properties (very large ratio of surface area to volume, small and controllable pore size, superior mechanical performance). These remarkable properties make nanofibers indispensable for much application’s raw material such as medical areas, protective clothing, filtration, nanocomposites, membranes, nanosensors, electrical and optical use [1 – 6].

Polyurethanes are of the most widely used polymers in biomedical, filtration, protective clothes, composites, sensor, actuator and wound healing applications. The application of electrospun mat from PU polymers is quite broad. Thermoplastic polyurethanes (TPU) present a class of polymers that possess a range of very desirable properties: they are elastomeric, resistant to microorganism and abrasion, and have excellent hydrolytic stability. Thermoplastic polyurethane is used in medicine for good compatibility with blood, hydro absorbency, water vapor permeability, stable of water, self-cleaning ability, optical and other [7 – 16].

Yalcinkaya B. with co-authors analyzed the effect of supporting material type on the electrospun PVA fiber properties such as diameter, diameter uniformity coefficient and non-fibrous area percentage [17]. Analyzing the influence of electrodes on PVA nanofibers formed on different support materials and their structure, it was found that the diameter of electrospun PVA nanofibers does not depend significantly on the type electrode and nature of the support material [18]. Analyzing water penetration of textile covered by layer of nanofibers was estimated influence of support material on the some properties water penetration of covered textile [19]. Waterproof breathable fabrics have been developed for use in garments to provide protection of the human body from environmental factors, such as rain, wind and harmful agents, while allowing water vapor to diffuse through. The number of applications for waterproof breathable fabrics continues to increase, ranging from outdoor clothing for leisure and sports to specialized medical and military use [19 – 23]. But there are no many studies about forming microporous mat by electrospinning and investigations of its water permeability properties.

The aim of this study is to form thermoplastic polyurethane (TPU) mats by electrospinning process on knitted and woven materials, and to determine the water permeability of textile materials before and after thermoplastic polyurethane mat has been formed on them.

MATERIALS AND METHODS

In this study thermoplastic polyurethane (TPU) (Laripur, Coim Group, Italy) solution was prepared by dissolving TPU granules in a mixture of dimethylformamide (DMF) and tetrahydrofuran (THF) (1:1, w/w) solvent. The solution was mixed by magnetic stirring “Yellow line MSH basic” for 48 hours. TPU solution of 3 wt. % concentration was prepared for the test. The distance between “Nanospider^{TM}” electrodes was 15 cm. The applied voltage was 65 kV. Speed of support material was 0.004 m/s. Temperature of electrospinning environment was $T = (20 \pm 2)$ °C, air humidity $\varphi = (40 \pm 2)$ %. TPU mat was electrospun by “Nanospider^{TM}“ (Elmarco, Czech Republic) with a roller electrode. Roller electrospinning method, which has been known as “Nanospider^{TM}” trade name, was used to obtain nano(micro)fibrous structures. Roller electrospinning method consists of the three main parts: rotating roller electrode, high voltage supplier and collector electrode. A slowly rotating roller electrode

[*]Corresponding author. Tel.: +370-620-46972; fax.: +370-37-353989.
E-mail address: *ausra.banuskeviciute@stud.ktu.lt* (A. Banuškevičiūtė)

partially is immersed into the polymer solution tank. Collector is usually grounded and polymer solution is connected to a high voltage supplier. During the spinning process, polymer solution is taken to the surface of the roller because of its rotation. After switched on the high voltage supplier, electrical field occurs between the roller and collector electrodes and large number of Taylor cones are created on the roller electrode surface. The electrospun fibers are transported towards the collector [17, 24]. In this work roller electrode with tines was used. The structure of electrospun mats was determined by using scanning electron microscope (SEM) Quanta 200 (FEI). The Quanta 200 SEM is low-vacuum scanning electron microscope with a tungsten electron source, with three imaging modes (high vacuum, low vacuum and ESEM) to accommodate the widest range of samples of any SEM system. For the experiment four cotton textile support materials for protective clothes such as fleece knitted fabric (sample PM) and three twill weave woven fabrics (samples PAR – twill weave YY1,2, JA – twill weave YY1,3 and MA – twill weave YY1,2) were chosen. The fabrics surface density and thickness was measured in accordance with LST ISO 3801:1998 and ISO 5084:1996, respectively. The parameters of support materials are presented in Table 1.

Table 1. Parameters of the support materials

The sample	Surface density, g/m²	Thickness, mm
PM	340 ±3	1.00 ±0.09
PAR	297 ±3	0.44 ±0.02
JA	282 ±5	0.49 ±0.02
MA	257 ±2	0.40 ±0.02

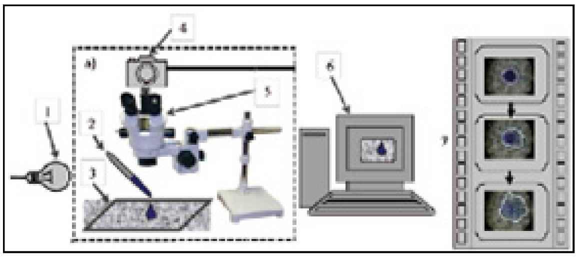


Fig. 1. Test instruments used in the experiment: 1 – light source, 2 – pipette, 3 – textile material, 4 – digital camera, 5 – stereoscope microscope, 6 – computer, 7 – pictures of video record

Textile materials were covered by 1, 2, 3 and 4 layers of TPU mats. The water permeability was determined by water drop method. The expansion of the area of water drop was measured using the chosen time interval (every 10 s). The tests were carried out in accordance with ISO 8655 for a piston-stroke pipette with an air cushion, using a fine balance with a moisture trap approved by the standardisation authorities. One distilled water drop (of 1 µl) was dripped with a pipette (Eppendorf AG, Germany) on the sample, which was put under a SMZ 800 Nicon Stereoscopic Microscope in a free horizontal position. The process of water drop soaking in to the sample was recorded with a Coolpix 4500 Digital Camera. The permeability of water drop was recorded from above. The recorded material was divided in to the pictures according to the time intervals with Paint software (Fig. 1) [20]. The area of water drop expansion was measured with Metric software.

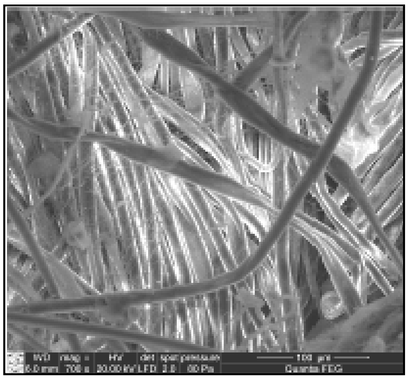
Diameter of pores was measured to determine the density of the mat. The greatest diameters of TPU mat pores were measured with software Metric. The highest average diameter of pores was determined by inscribing a circle in a pore (Fig. 2).

RESULTS AND DISCUSSION

The micro porous mat was formed on knitted and woven textile materials by electrospinning method using 3 wt.% concentration TPU solution. By increasing number of layers the size of pores among fibers in the mat decreases and the TPU porous mat became thicker. During the experiment it was determined that the thicker mat stops the water drop and does not let it spread on the support materials.

Table 2. Highest average diameter of TPU mat porous

Sample	The number of layers of TPU mat	Highest average diameter of pores of TPU mat, µm	The number of layers of TPU mat	Highest average diameter of pores of TPU mat, µm
PM	1	778.2	4	677.4
PAR	1	726.2	4	546.8
JA	1	777.4	4	445.2
MA	1	631.0	4	336.8



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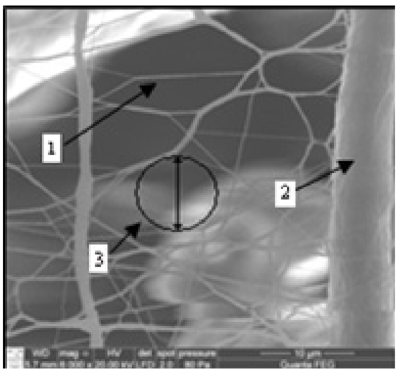

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Fig. 2. SEM images of electrospun TPU mats when support material is knitted fabric PM: a – 1 layer of TPU mat (scale 100 µm), b – 1 layer of TPU mat (scale 10 µm), 1 – support materials fiber, 2 – electrospun fibers, 3 – diameter of TPU mat porous

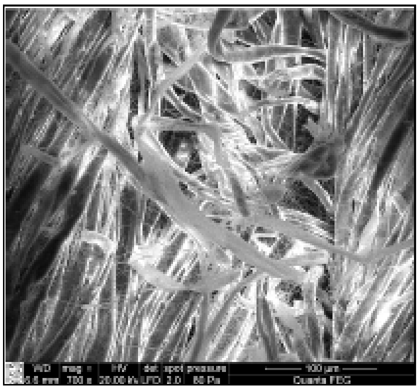
The data given in the Table 2 show that when the number of TPU porous mat layers was increased to 4 layers the highest diameter of pores decreased by 13 % (sample PM), 25 % (sample PAR), 43 % (sample JA), and 47 % (sample MA).

Fig. 2 (sample PM) and Fig. 3 (sample JA) showed the structure of TPU electrospun micro porous mats with 1 layer. Fig. 4 (sample PM) and Fig. 5 (sample JA) showed the structure of TPU electrospun micro porous mats with 4 layers.

Dotti F. with co-authors researched and determined that the thickness of nanofibers layer and the pore size can be control by the electrospinning process. The pores size was measured using Opera Plus v6.12 software [3].

New waterproof breathable materials should be targeted to this area of need in order to provide consumers with materials offering enhanced barrier and comfort performance.

As is seen from Figs. 2 – 5, the number of layers and support material influence on electrospun TPU mat structure, and herewith can influence on water permeability of the covered material.



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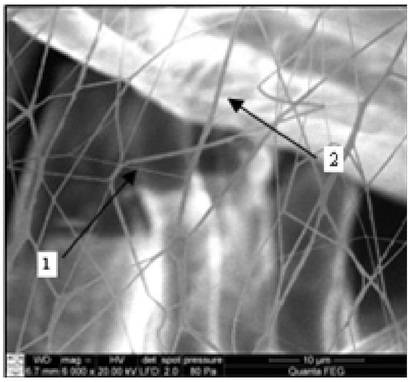

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Fig. 3. SEM images of electrospun TPU mats when support material is woven fabric JA: a – 1 layer of TPU mat (scale 100 μm), b – 1 layer of TPU mat (scale 10 μm), 1 – support materials fiber, 2 – electrospun fibers

The sample PM, which is not covered with TPU mat, has the area of water drop expansion from 0.5215 cm^2 (10 seconds have passed since the water drop was dripped on the sample) to 0.7937 cm^2 (50 seconds have passed since the water drop was dripped on the sample when water drop will not spread). When the sample is covered with 4 layers of TPU mat, the area of water drop expansion is from 0.2163 cm^2 (10 seconds have passed since the water drop was dripped on the sample) to 0.3548 cm^2 (40 seconds have passed since the water drop was dripped on the sample). In this case the 4th layer not only decreased the

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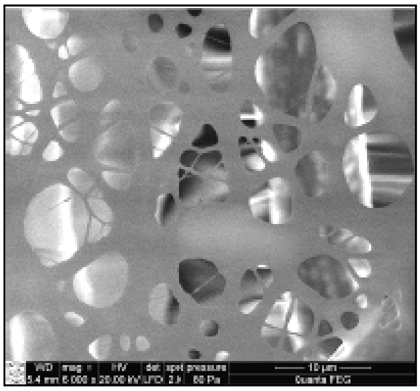

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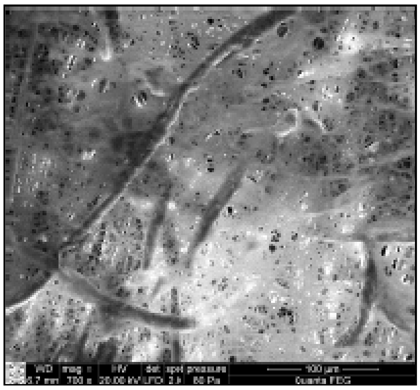
Fig. 4. SEM images of electrospun TPU mats when support material is knitted fabric PM: a – 4 layers of TPU mat (scale 100 μm), b – 4 layers of TPU mat (scale 10 μm)



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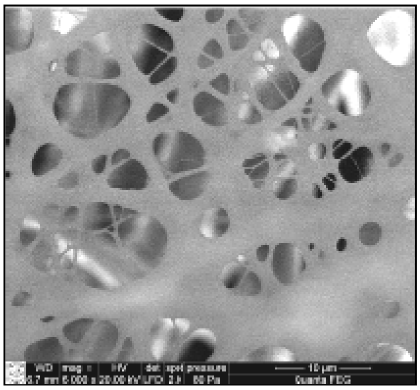

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Fig. 5. SEM images of electrospun TPU mats when support material is woven fabric JA: a – 4 layers of TPU mat (scale 100 μm), b – 4 layers of TPU mat (scale 10 μm)

area of water drop but it also shortened its permeability time by 10 seconds.

Kang Y. K. with co-authors analyzed the resistance to water penetration of electrospun polyurethane mat. The resistance to water penetration was determined by ISO 811 resistance to water penetration-hydrostatic pressure test. The control fabric was chosen for polyester/nylon blended fabric. Electrospun PU mat/fabric showed better resistance to water penetration than control fabric [8].

Kang Y. K. [8] and Lee S. [19] also have presumption that the level of water resistance may possibly be improved by controlling the fiber/pore size and electrospun mat thickness.

So, our investigations show good correlation with results obtained by other authors.

In Figures 6 – 9 the date of average values with relative errors of measurements are given.

Fig. 6 showed that the sample have been covered with 2 TPU mat layers the difference between areas of the water drop is decreasing. Covering the sample PM with 1 layer its water permeability decreased by 23 %, after the 2 layer the water permeability decreased by 25 % more, after the 3 layer it decreased only by 4 % and after the 4 layer – by 3 % (after 50 s). As it is seen from Fig. 6 that 2 TPU mat layers give the optimal results.

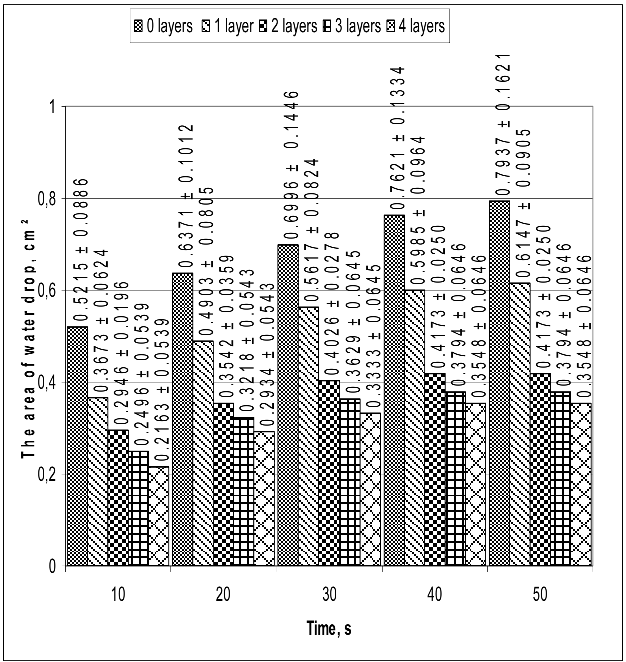

Fig. 6. The area of water drop on knitted support material (PM) which is covered by layers of TPU electrospun mat

The next layers do not have significant influence on the water permeability of the covered textile.

The sample PAR, which is not covered with TPU mat, has the area of water drop expansion from 0.1885 cm^2 (10 seconds have passed since the water drop was dripped on the sample) to 1.2816 cm^2 (50 seconds have passed since the water drop was dripped on the sample). The sample covered with 4 layers of TPU mat has the area of water drop expansion from 0.1261 cm^2 to 0.5124 cm^2. It is stated that in this case the time of water drop expansion has shortened by 10 seconds.

The sample PAR has been covered with one TPU mat layer, there is no change in water drop area expansion after 10 seconds, but after 50 seconds the area has decreased 61 % comparing with the sample which is not covered with TPU mat (Fig. 7).

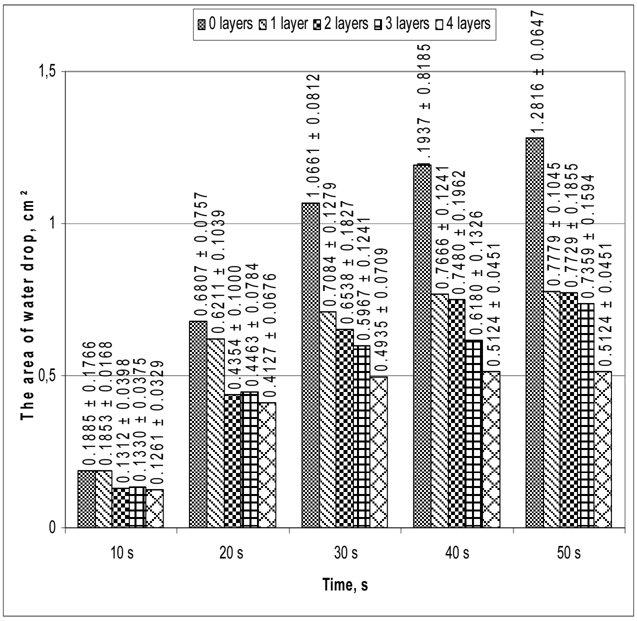

Fig. 7. The area of water drop on woven support material (PAR) which is covered by layers of TPU electrospun mat

Water permeability decreased even by 39 % of the sample PAR with 1 TPU mat layer (after 50 s). This sample has been covered with 2 layers its water permeability decreased only by 1 % and the 3 layers decreased its water permeability by 2 % more. It can be stated that one layer of TPU porous mat is enough to keep water penetrating into the textile material. The results differ from previous, when the sample PM was investigated.

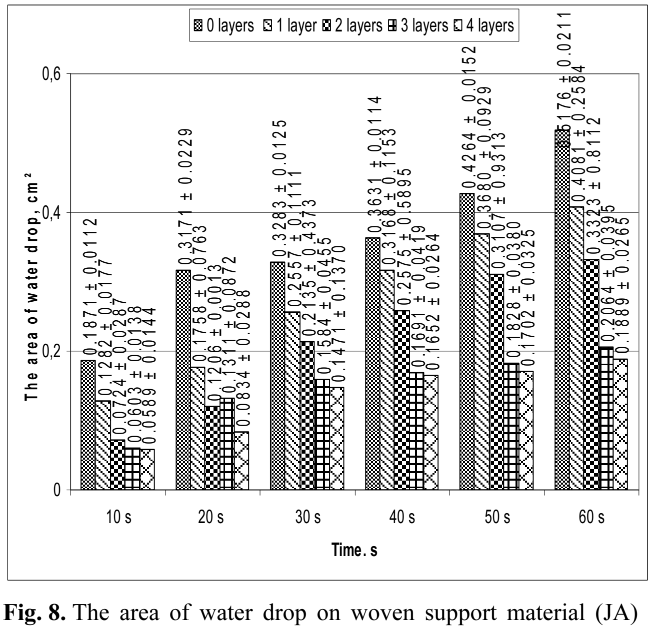

Fig. 8. The area of water drop on woven support material (JA) which is covered by layers of TPU electrospun mat

Fig. 8 shows how the area of water drop changes on the sample JA. The area of water drop, which is not covered with porous mat, expansion is from 0.1871 cm^2 (after 10 s) to 0.5176 cm^2 (after 60 s). The sample has been covered with TPU mat 1 layer, has the area of water drop expansion from 0.1282 cm^2 (after 10 s) to 0.4081 cm² (after 60 s) and after 4 layers – 0.0589 cm^2 (after 10 s) ÷ 0.1889 cm^2 (after 60 s).

The sample JA would be sufficient to cover with TPU mat 3 layers, because the 4 layers has not significant influence on the area of water drop. It is evident from the calculated results. The area of water drop expansion is from 0.0603 cm^2 ÷ 0.2064 cm^2 then is 3 TPU mat layers and 0.0589 cm^2 ÷ 0.1889 cm^2 then is 4 TPU mat layers. So the results differ from those of the previously investigated materials. That can be explained by pore size of each material – lower pore size, lower water drop expantion.

Water permeability of the sample JA with 1 TPU mat layer decreased by 21 %, with 2 layers by 15 % more, with 3 layers by 24 %, while the 4 layer decresed its water permeability only by 3 % (after 60 s). It can be stated that in this case 3 layers of electrospun TPU porous mat are enough to stop the permeability of water drop.

The sample MA, which is not covered with TPU mat, has the area of water drop expansion from 0.5360 cm^2 (10 seconds have passed since the water drop was dripped on the sample) to 1.5194 cm^2 (40 seconds have passed since the water drop was dripped on the sample). The sample having been covered with TPU mat 1 layer, the area of water drop expansion is from 0.4457 cm^2 to 1.4398 cm^2. Whereas then the sample with 2 layers TPU mat the area of water drop is about 2 times lower compared with the sample which is covered with TPU mat 1 time (Fig. 9). Similar results are when the support material is covered with 3 or 4 layer of TPU mat.

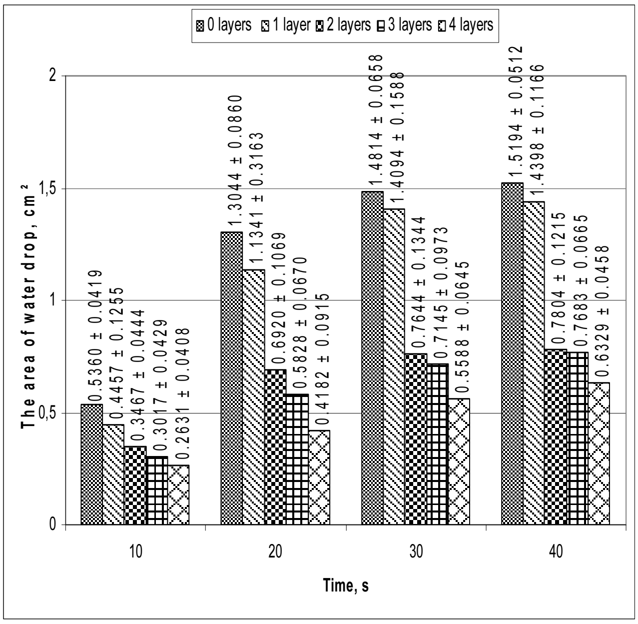

Fig. 9. The area of water drop on woven support material (MA) which is covered by layers of TPU electrospun mat

The sample MA having been covered with 1 TPU mat layer its water permeability decreased even only by 5 % (after 40 s), while after 2 layers its permeability decreased even 44 %. The sample having been covered with the 3 and 4 layers its water permeability decreased accordingly by 1 % and 8 %. So in this case 2 layers of electrospun TPU porous mat are enough for optimal water permeability.

Lee's S. and co-authors analyzed water resistance to water penetration of densely woven fabric, PTFE (microporous polytetrafluoroethylene membrane laminated fabric) and a hydrophilic nonporous PU coated fabrics. The experiment exhibit that densely woven fabric has very low resistance to water penetration, whereas microporous PTFE membrane laminated fabrics provide the highest resistance to water penetration. PU coated fabrics exhibit about midrange resistance to water penetration [19]. So, like in our investigation, it has been noted the significant influence of support material on water permeability.

Analysis of all materials covered by electrospinning show, that water permeability properties depend not only on number of layers, but also from the type of support material. Having analyzed the sample covered with electrospun TPU porous mat we can state that water permeability could depend not only on the number of mat layers. Results can be influenced by the properties and parameters of support materials such as electrical resistance, surface density, weave and et al. So, our investigations show that the support material is very important parameter for the properties of covered textile, even if support material does not have influence on diameter of fibres, it can influence the size of pores.

The investigations of support materials electrical resistance and other properties influence on electrospinning process will be the aim of our further investigations.

Ideal materials covered with electrospun mat should prevent penetration of water, while allowing the release of moisture vapor and air to provide thermal comfort.

CONCLUSIONS

Electrospun porous mat can be formed on knitted and woven materials by electrospinning method using 3 wt.% concentration TPU solution.

The greater number of layers of TPU mat on the textile material formed the thicker mat and decrease diameter of the highest porous. Diameter of the highest porous of 4 layers TPU mat decreased to 13 % (sample PM), 25 % (sample PAR); 43 % (sample JA) and 47 % (sample MA) in comparison with porous of 1 layer TPU mat.

It has been noticed, that the greater number of layers decreases not only the expansion of water drop area on the textile material but herewith decreased the water drop permeability of textile materials.

The experiments showed that 2 or 3 layers with TPU porous mat on the textile materials give optimal results for decreasing of water permeability of samples. The area of water drop of sample PM uncovered with TPU mat was 0.7937 cm^2, after 2 layers the area decreased by 0.4173 cm^2, of sample PAR – 1.2816 cm^2 ÷ 0.7729 cm^2, of sample JA – 0.5176 cm^2 ÷ 0.3323 cm^2 and of sample MA – 1.5194 cm^2 ÷ 0.7804 cm^2.

The behavior of water permeability depends on support material and this phenomena can depend on parameters of support materials.

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