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Abstract. This study summarizes the general information about nursing pads and novel electrospun nanofiber mats as potential component for nursing pads. It also compares electrospun thermoplastic polyurethane (TPU), cellulose acetate (CA) and polyethylene oxide (PEO) nanofibers with a polypropylene conventional disposable nursing pad (NP) in terms of hydrophilicity, breathability, air permeability and swelling properties. Nanofiber mats prepared by the electrospinning method have unique properties such as smooth surface, high specific surface area and high porosity with fine pores which will lead to improved wicking properties. These properties make nanofibers potential component for disposable nursing pads. Mean diameters of produced nanofibers were 284.39, 609.70 and 219.30 nm for CA, TPU and PEO, respectively. Water contact angle measurement revealed that these nanofibers show good wettability properties better than commercial nonwoven nursing mat and air permeability results revealed that these nanofibrous mats have considerably adequate permeability. Besides, water vapor permeability results showed these nanofibers still show good breathability despite their compact structure.

1. Introduction

Nursing or breast pads are commonly used by nursing women to prevent milk, which may leak from the woman's breasts, from staining clothing and bed linens when the woman is not nursing [1]. These nursing pads generally divided into two subcategories; reusable pads and disposable pads [2]. Typically, a disposable breast pad contains a multilayered design, including a non-permeable layer for preventing transfer of breast milk from the liner to clothing, an absorbent layer for holding the milk within the liner, and a wicking layer to draw the liquid away from the breast and into the absorbing layer. A non-permeable layer may also be disposed about the outer periphery of the liner so that a reservoir is formed between the outer surface non-permeable layer. An adhesive may be applied to the outer portion of the liner to hold the liner in place in a bra cup [3]. Wicking top layer and the absorbing layer are the most critical part of these disposable pads. Top layer should deliver the absorbed milk immediately to the inner absorbing layer to prevent the discomfort of the mother. Wet nipples also may increase the sensitiveness of the skin.

In that point, nanofiber mats prepared by the electrospinning method have unique properties such as smooth surface, high specific surface area and high porosity with fine pores which will lead to

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improved wicking properties. These properties make nanofibers potential component for disposable nursing pads. Electrospinning method can be applied to synthetic and natural polymers, as well as polymer blends. Polymer solutions could also be loaded with functional nanoparticles, or active agents [4]. A large number of drugs [5-8], vitamins [9,10] could also be immobilized in polymer fibers [11] which make them functional other than casual nonwovens. More than fifty different polymers have been successfully electrospun into ultrafine fibers using this technique [12]. In this study, thermoplastic polyurethane (TPU), cellulose acetate (CA) and polyethylene oxide (PEO) nanofibers were selected and compared with a commercial nursing pad in means of hydrophilicity, breathability, air permeability and swelling properties.

2. Experimental

2.1. Materials

The TPU used in this study was the commercial Pellethane 2103-80AE, which is based on 4,4-methylene bisphenylene isocyanate, polytetramethyleneoxide and 1,4 butanediol, and was provided from Velox (Lubrizol Advanced Materials) and PEO (Polyox WSR N750) with approximate molecular weight of 300,000 was provided from Abalıoğlu Teknoloji as a gift. CA with number average molecular weight (Mn) of ~30,000 g/mol and acetylation degree of 39.8 %wt, acetone, dimethylacetamide (DMAc), N,Ndimethylformamide (DMF) were purchased from Sigma Aldrich Chemical Company. A commercial nursing pad was purchased and top layer of polypropylene mat was removed for comparisons. It is coded as NP through the study.

2.2. The preparation of electrospinning solutions

TPU solution, coded as TPU was prepared by dissolving TPU granules in the concentrations of 9% w/w in DMF at room temperature. Solution was stirred for at least 12h. CA solution, coded as CA was prepared by dissolving CA powder in the concentrations of 16% w/v in acetone/DMAc in the volume ratio of 2:1 at 50 ^{o}C. Solution was stirred for 3h. PEO solution, coded as PEO, was prepared by dissolving PEO powder in the concentrations of 8% w/w in distilled water. Solution was stirred for 2h at 50^{o}C than cooled down to the room temperature and stirred further 2h. Polymer concentration and solvents are given at Table 1.

Table 1. Polymer concentration, solvents and solvent ratios

	Polymer concentration (%)	Solvents	Solvent ratio
TPU (w/w)	9	DMF	1
CA (w/v)	16	Aceton/DMAC	2:1
PEO (w/w)	8	Distilled water	1

2.3. Electrospinning

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 mL) with a stainless steel needle (22 gauges, and flat tip), a ground electrode and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). All solutions were electrospun at a voltage of 15 kV and a tip-to-collector distance of 15 cm with a feeding rate of 0.4-0.5 ml/h. A grounded rotating metal drum collector covered by a 90 mesh of plain weave monofilament %100 polyester screen mesh fabric was used as deposition material. Each polymer solution was electrospun for 2 hours.

2.4. The WCA measurements

For determination of hydrophilicity of the nanofiber membranes, the WCA were measured by using CAM 200 contact angle meter (KSV Instruments, Helsinki, Finland). The contact angles with distilled water were measured on the upper surface of the electrospun nanofiber membranes. The measurements were performed by the sessile drop method at ambient temperature. A real-time camera captured the image of the droplet.

2.5. SEM analysis
The morphology of TPU, CA, PEOX nanofibers and nursing pad top layer fibers were observed by a scanning electron microscope (SEM; Phenom G2pro scanning electron microscope). The samples were sputtered by Quorum Q150R S ion sputtering device with a thin layer of gold prior to SEM observation. The mean diameter of the nanofibers was calculated from measurements on SEM images of 5000× magnification by using Image J program. Approximately 50 measurements were carried out from the different parts of each sample.

2.6. Swelling of nanofibrous mats
Swelling of the TPU, CA, PEOX nanofiber and nursing pad top layer mats were measured upon exposure in distilled water for 24 h. The samples were removed from the water and carefully blotted with tissue paper to remove the excess after from the surface. The degree of swelling due to the water uptake was determined and weight loss was calculated at the end after drying for 4 h at 70 ^{o}C in an oven. The percentage of degree of swelling was calculated as follows [13]:

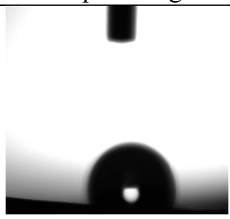
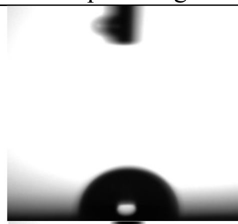
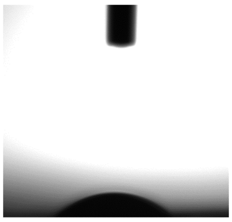
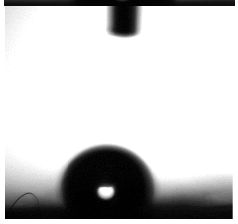
$$\text{Degree of swelling}(\%) = \frac{M - M_d}{M_d} \times 100 \quad (1)$$

where M was the weight of each nanofiber mat sample upon exposure in distilled water for 24 h, M_d was the weight of the samples after swelling and subsequent drying.

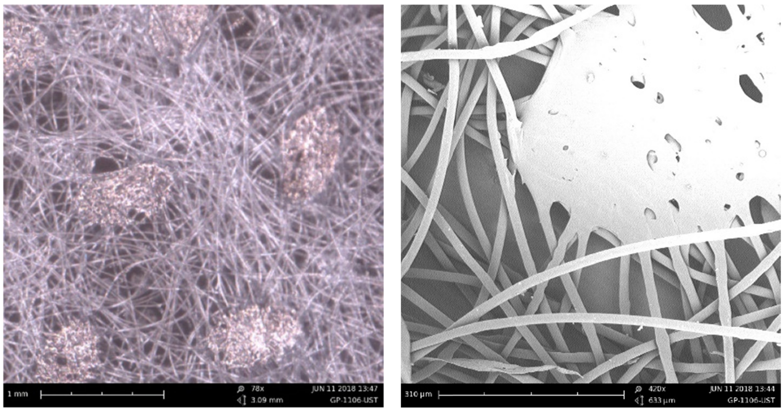
2.7. Characterisation of air permeability and water vapor permeability
Air and water vapor permeability of electrospun nanofibers and NP were tested by Textest FX3300 in accordance with EN ISO 9237 (5 cm^2 surface area and 200 Pa pressure drop) and by SDL-Atlas M261 in accordance with BS 7209, respectively.

3. Results and Discussion
Water contact angle measurement (WCA) is used to determine the hydrophility of the produced nanofiber mats. The contact angles between water droplets and the TPU, CA, PEOX nanofiber mats and NP were measured and pictures were taken after 0.128 s. The average WCA values of the right, middle and left are reported in Table 2. It also shows the droplet images after the water droplets were placed on the surface of TPU, CA and PEO nanofibrous mats and NP. It can be seen that the water contact angle of TPU and NP are the highest which are 119.8^{o} and 109.50^{o} respectively. These WCAs reveal the hydrophobic characters of TPU and NP. Since CA has an acetylation degree of 39.8%, it is more hydrophobic than PEOX with WCA of 86.21^{o}. PEOX is the most hydrophilic mat with WCA of 29.53. When we compare the new developed nanofiber mats with NP, TPU nanofibers show similar, CA nanofibers show better, PEO nanofibers show very high wetting tendency. However, the reason for high wetting tendency of PEO is that, it is soluble in aqueous environment and in case of water contact it loses its integrity which restricts its usage.

Table 2. Water contact angle (°) and droplet images of TPU, CA, PEO nanofibers and NP mat

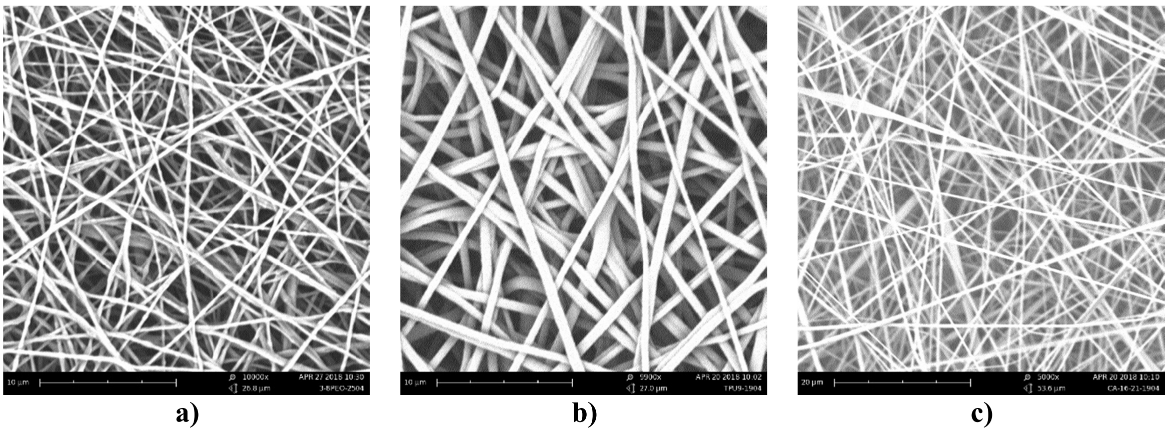
Mat Code	WCA (°)	Droplet image	Mat Code	WCA (°)	Droplet image
TPU	119.80		**CA**	86.21	
PEO	29.53		**NP**	109.50	

The surface morphology of electrospun TPU, CA and PEO nanofibers and NP were investigated by SEM imaging. In Figure 1 two different magnifications of SEM images are given for NP. Spot weldings of binding agent could be seen approximately with 1 mm distance from each other. From the measurements of 26 fibers, mean diameter of the NP was calculated as 14.65µm. SEM images of TPU, CA and PEO nanofibers are given in Figure 2. According to these images bead free, smooth nanofibers were produced and mean diameters were calculated as 284.39, 609.70 and 219.30 nm for CA, TPU and PEO, respectively. Finest nanofibers were obtained with 8% of PEO solutions.



a) **b)**

Figure 1. SEM images NP with a magnification of a) 78x b) 420x



a) **b)** **c)**

Figure 2. SEM images a) CA, b) TPU and c) PEO

Table 3 lists the diameters of TPU, CA, PEO nanofibers and NP fibers, results of their air permeability and water vapor permeability results.

Table 3. The Diameters, Air Permeability Results of Water Vapor Permeability and Thickness of TPU, CA, PEO nanofibers, NP fibers and blank 90 mesh PES fabric

	Nanofiber Diameter *(nm)*	Air Permeability *(L/m^2s)*	Water Vapor Permeability *(g/m^2day)*
TPU	609.70± 140.03	42.78	655.85
CA	284.39 ± 143.01	46.44	637.88
PEO	219.30± 42.82	26.16	637.88
NP	14.65± 1.44	4006	691.78
90 mesh		4740.00	664.83

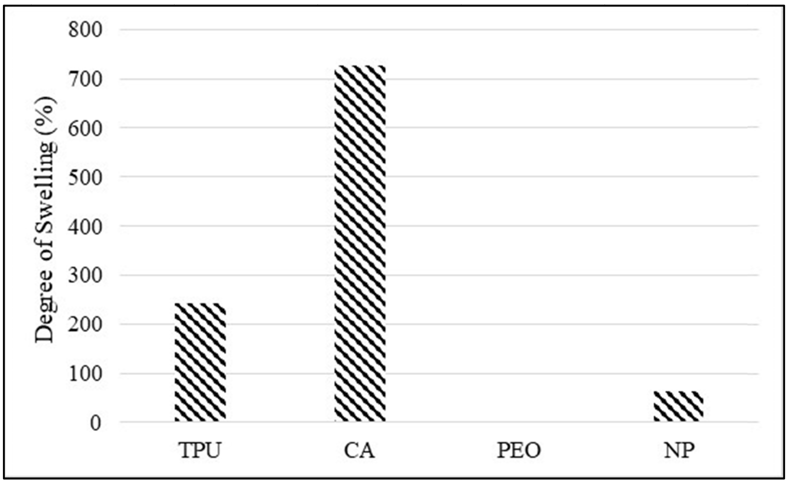


Figure 3. Swelling of TPU, CA, PEO nanofibers and NP mat

Swelling percentages of TPU, CA, PEO nanofibers and NP mat in distilled water for 24h are given in Figure 3. Due their hydrophobic characters TPU nanofibers and NP mat show lower swelling percentages as ~244% and ~63%, respectively. CA nanofibers showed considerable high swelling percentages of ~726% because of its hydrophilic structure and showed no weight loss while PEO nanofiber mats totally dissolved immediately after putting the mat into the water. The results showed that electrospun CA nanofiber membranes could be preferred when better hydrophilicity and swelling are required. Whenever more elastic and rigid mats are required TPU nanofiber mats could also be used with tolerable swelling.

Differences in air permeability was analyzed by one-way analysis of variance (ANOVA) followed by a Duncan test for pairwise comparison. There was a statistically significant difference between the air permeability of TPU, CA, PEO nanofibers and NP mat as determined by a one-way ANOVA ($p < .001$). Nanofibrous mats exhibited very low air permeability when compared to the NP mat and base fabric (4740 /m^2/s). The pores of micrometer dimensions for TPU, CA and PEO nanofiber mats, which are quite smaller than those in NP and the base fabric, would be too small to allow air flow at a prescribed pressure differential; thus result in very low air permeability [14]. Duncan post hoc test revealed that the air permeability values of TPU, CA and PEO nanofibers were found to be in same subset despite the differences in fiber diameter and statistically significantly lower than NP mats. Nano diameters of TPU, CA and PEO nanofibers decreased the air permeability values which would provide a barrier effect for the skin.

In case of water vapor permeability, polymer type or fiber diameters did not have a significant effect, all TPU, CA and PEO nanofiber mats showed similar results and they were not statistically different from each other ($p < .001$). Nanofibrous mats gave very high water vapor transmission like NP mat (691.78 g/m^{2}day) and base fabric (664.83 g/m^{2}day). Fine pores allowed water vapour transmission in all cases (Figure 2). According to this result (Figure 4), electrospun TPU, CA and PEO nanofibrous mats can be considered to have high water vapor transmission values despite their different hydrophilic characters. Water vapor transport properties of electrospun nanofibrous mats are excellent and indicate that layers based on electrospun fiber technology will be thin, lightweight, and very ‘‘breathable’’ with respect to allowing cooling to take place through a barrier material [15].

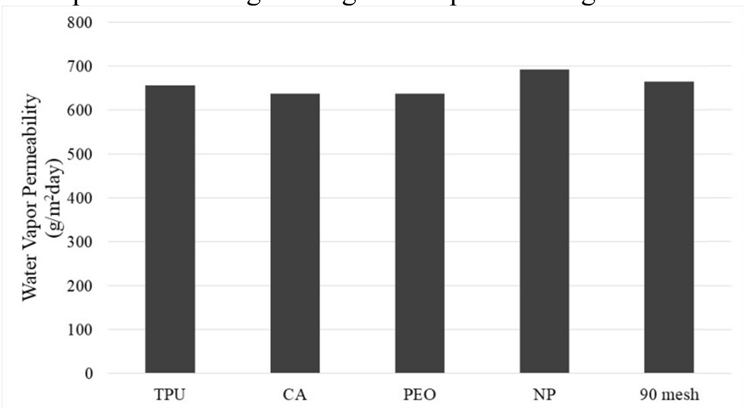


Figure 4. The effect of collection period (h) on water vapor permeability (g/m^{2}day)

4. Conclusion

Nanofiber mats prepared by the electrospinning method have smooth surface, high specific surface area and high porosity with fine pores which could improve wicking properties of a top layer of a disposable nursing pad. Electrospinning method can be applied to synthetic and natural polymers, as well as polymer blends with various active ingredients. In this study, CA, TPU and PEO nanofibers were selected and compared with a commercial nursing pad in means of hydrophilicity, breathability, air permeability and swelling properties. It was seen from the WCA measurement that when compared with NP, the new developed TPU nanofibers have similar, CA nanofibers have better, PEO nanofibers have very high wetting tendency. However, high solubility of PEO restricts its usage. Nano diameters of TPU, CA and PEO nanofibers decreased the air permeability values which would provide a barrier effect for the skin. In case of water vapor permeability, polymer type or fiber diameters did not have a significant effect, all TPU, CA and PEO nanofiber mats showed pretty high water vapor permeability results. Fine pores allowed water vapour transmission in all cases which indicates that layers based on electrospun fiber technology will be thin, lightweight, and very ‘‘breathable’’ and could be a potential candidate for disposable nursing pads.

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5. References

[1] Spiezio C L, Spiezio M, 2004, Disposable Nursing Breast Pad with Medication, US 2004/0058619 Al
[2] Hebert C A, 2000, Nursing Pad Bra Liner, US6074272A
[3] Foley R M, Nanna K A, Thomas S, 2006, Medicated Breast Pad, US 2006/0052033 Al
[4] Greiner A, and Wendorff J H 2007 Angewandte Chemie International Edition. 46(30) 5670-5703.
[5] Zeng J, Yang L, Liang Q, Zhang X, Guan H, Xu X and Jing X 2005 J. Control. Release 105(1)

43-51.
[6] Taepaiboon P, Rungsardthong U and Supaphol P 2006, Nanotechnology 17 2317-2329.
[7] Akduman C, Özgüney I and Akçakoca Kumbasar E P 2016 Materials Science and Engineering: C 64 383-390.
[8] Kenawy E R, Bowlin G L, Mansfield K, Layman J, Simpson D G, Sanders E H and Wnek G E 2002 J. Control. Release 81 57–64.
[9] Taepaiboon P, Rungsardthong U and Supaphol P 2007 Eur. J. Pharm. Biopharm. 67(2).387-397.
[10] Sheng X, Fan L, He C, Zhang, K, Mo X and Wang H 2013 International journal of biological macromolecules 56 49-56.
[11] Sen R, Zhao B, Perea D, Itkis M E, Hu H, Love J and Haddon R C 2004 Nano letters. 4(3) 459-464.
[12] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 Composites science and technology 63(15) 2223-2253.
[13] Cay A, Kumbasar EPA, Keskin Z, Akduman Ç and Urkmez A Ş 2017 *J Matter Sci* **52(20)** 12098-12108
[14] Lee S, and Obendorf S K 2007 *Fibers and polymers* **8(5)** 501-506.
[15] Akduman C, Oglakcıoğlu N, Kumbasar E P A and Sarı B 2018 *J Fashion Technol Textile Eng* **S4** 015