# A novel technique for producing conductive polyurethane nanofibrous membrane for flexible electronics applications

**A Shaker[1], Ahmed H Hassanin[1,2], N M Shaalan[1], M A Hassan[1] and Ahmed Abd El-Moneim[1]**

1 Materials Science and Engineering Department, Egypt-Japan University of Science and Technology, New Borg El-Arab, Alexandria 21934, Egypt
2 Textile Engineering Department, Faculty of Engineering, Alexandria University, Alexandria 21544, Egypt
E-mail: ahmed.abdel-baset@ejust.edu.eg

**Abstract.** A novel technique for producing stretchable and flexible conductive polyurethane nanofibrous membrane for flexible electronics applications has been developed. One of the most important challenges in fabricating polymeric membranes for flexible electronics is to enhance its sensitivity and conductivity maintaining its flexibility and stertchability. Wet electrospinning technique was used to fabricate thermoplastic polyurethane (TPU) nanofibers through a coagulant bath of a conductive grade co-polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT: PSS). A Kapton sheet was used as a substrate to load TPU/PEDOT: PSS nanofibers on it. The morphology and stability of the as-spun TPU/PEDOT: PSS nanofibers has been investigated. The fabricated TPU/PEDOT: PSS nanofibrous membrane has showed a well stabilized ohmic behaviour under a wide range of different temperatures up to 90 ℃ as well as different values of tensile strain up to 4.43 %, which makes it suitable for high temperature strain sensing applications.

## 1. Introduction

Flexible and wearable electronic devices have become of a rapidly increasing demand in modern societies. [1-3] It is virtually impossible for conventional rigid electronics to achieve flexibility, stretchability, and deformability into different shapes. [4] There has been rapid progress on fabricating flexible or stretchable strain sensors. Strain sensors with high performance implicate many features, including high sensitivity, stability, stretchablity, response speed, process and production costs. [5-7] High-strain sensors got strong demand in many fields such as biomechanics, physiology and kinesiology applications areas [8, 9]. Recently, nanoscale materials were used to make novel strain sensors. For example, the device based on many typical structures with nanoparticles, nanowires, nanotubes, and graphene have been reported. [10-14]

Electrospinning is a versatile and simple fabricating method of fibers with diameters range of a few micrometers to ten nanometers or less. In conventional electrospinning process, a Taylor cone is used to expel a charged jet and rushes it under an electric field with a driving force onto the ground collector. After the evaporation of solvent, solid fibers with uniform diameter are randomly laid down on the collector [15]. In the past decade, diverse ultrathin fibers extracted from polymer, ceramic, metal, and glass have been synthesized by electrospinning, and their latent applications in optoelectronics, sensors, filters, fiber reinforcement, catalysis, drug delivery, supercapacitors, lithium batteries and tissue engineering have also been broadly investigated [16, 17].

Wet electrospinning is an altering technique of the common electrospinning technique. The modification is based on the usage of a liquid bath collector rather than a solid metallic one. Wet electrospinning was introduced for the first time as a method for producing nanofibrous scaffolds for tissue engineering at the laboratory scale. [18] It is a crafty matter to produce bulky and fluffy membrane using the common electrospinning technique. This task could be accomplished either using distinctive collectors [19] or by using porogen particles, that is, chemical blowing agents, settled in between the nanofibers [20]. Wet electrospinning is a relatively simple and effective method to produce three dimensional (sponge-like) materials without intricated devices and without especial chemical additives. [21]

High electrically conductive nanofibers have been produced from a range of organic conductors, such as polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS), carbon nanotubes, and recently from graphene and graphene oxide. [22] In spite of its high conductivity, these fibers have significant poor deformability, having relatively limited to no elasticity or elastic recovery and cannot be stretched by more than 20% of their original lengths. On the other hand, fibers which are typically produced from elastomers, with very high range of elasticity and deformability are electrically insulating. The combination of high conductivity and high stretchability is considerable in applications requiring strain sensing such as stretchable circuits, wearable bionics and electrochromic textiles. [23]

In this work, stretchable conductive nanofibrous mate was developed with an enhanced range of measured electrical resistance at KΩ scale, where MΩ scale resistance is common for measurements of nanofibrous mats under normal circumstances. [24] The developed nanofibrous mate was produced by wet electrospinning technique where Thermoplastic Polyurethane (TPU) was electrospun into liquid bath which has PEDOT: PSS aqueous solution as a coagulant. Combining between enhanced electrical conductivity supported by PEDOT: PSS co-polymer solution and the stretchability of TPU elastomer in a mate at nanoscale with a stable ohmic behaviour makes it a good candidate for many applications such as supercapacitors, polymeric solar cells and strain gauge sensors.

## 2. Experimental details

### *2.1 Materials*

Thermoplastic Polyurethane (TPU) C95 with a molecular weight of 107,020 g/mol and Polydispersity Index (PDI) of 1.83 was supplied by BASF Corporation, Germany. TPU renders various chemical structures, which enables it to be used for various applications like membranes, filtration, textiles and protective clothing. [25] Dimethylformamide (DMF 98%) was used as a solvent for TPU to prepare the polymer solution. Poly(3,4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT: PSS) is a conductive grade co-polymer, which was supplied by Sigma-Aldrich, USA. This PEDOT: PSS is 1.3 wt.% of the colloidal dispersed polymer in distilled water. A typical Kapton sheet of thickness 75 μm and an area factor of 9.1 m2/kg supplied by UPILEX-Japan was used to be as a substrate for TPU nanofibers mate.

### *2.2 Developed wet electrospinning technique*

TPU was dissolved in DMF at a concentration of 10 wt.% for five hours stirring at 60 ℃, then transferred into 5 ml syringe of electrospinning setup. NANON electrospinning setup was used to fabricate TPU nanofibers. During electrospinning process, a 30 kV direct current voltage was applied to TPU syringe and the collector over which the coagulant bath of PEDOT: PSS was set. A feed rate of 1 mL/h was used at a vertical distance of 10 cm between the needle tip and the collector bath. At the bottom of PEDOT: PSS collector bath, the Kapton substrate was placed. A membrane of average thickness of 60 μm was formed on the top surface of PEDOT: PSS solution which is instantaneously saturated by the conductive polymer solution. A schematic diagram of the wet electrospinning process is shown in Figure 1.

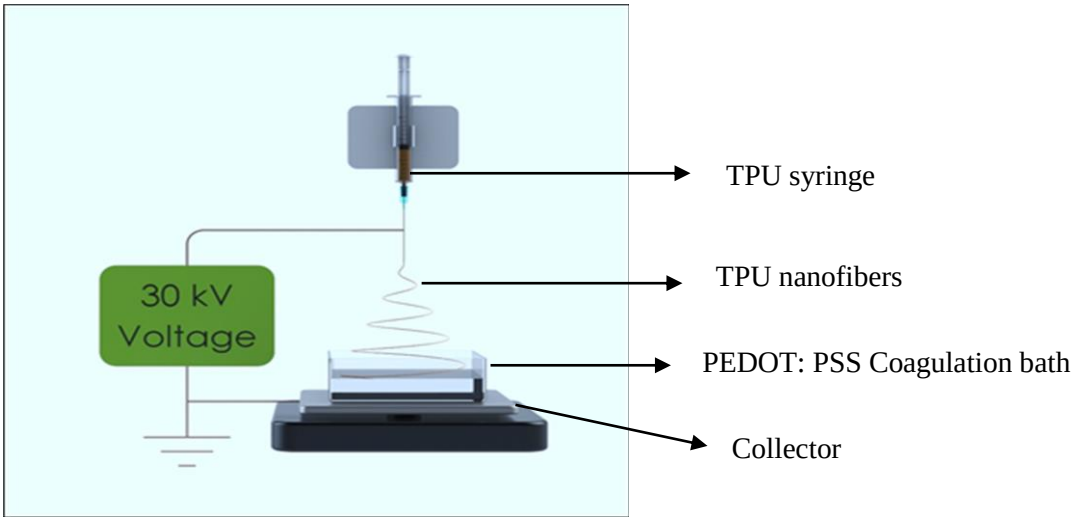


**Figure 1.** A schematic diagram of wet electrospinning technique.

*2.3. Characterization of TPU/PEDOT: PSS nanofibrous membrane*
Morphology of TPU/PEDOT: PSS nanofibrous membrane was investigated using JCM-6000PLUS NeoScope Benchtop scanning electron microscope (SEM). To study the I-V behaviour of the nanofibrous membrane, PHOTO EMISSION TECH. I-V test system was used. Fourier transform infrared (FTIR) spectrometer (Vertex 70, Bruker Scientific Instruments, Germany) and X-ray diffraction (XRD) spectrometer (LabX XRD-6100 Shimadzu, Japan) were used to analyse the TPU/PEDOT: PSS nanofibrous membrane.

## 3. Results and discussions

*3.1. Morphology*
Scanning electron microscope (SEM) was used to characterize the morphology of the as-spun TPU/PEDOT: PSS nanofibers. It was noticed that the nanofibers had smooth surface and appeared to be straight with no beads, as illustrated in Figure 2. The average diameter of the nanofibers is approximately 170 nm. It is obvious from morphology of nanofibrous mate that thin layers of PEDOT: PSS was formed between the nanofibers. This can be attributed to using PEDOT: PSS aqueous solution as a coagulant, where the phase inversion process is carried out. In this process, the exchange between the solvent [DMF] and non-solvent [coagulant, PEDOT: PSS aqueous solution] is occurred, which resulting in solidified TPU nanofibers and forming a thin layer of PEDOT: PSS covering the nanofibers and sometimes in between the nanofibers.

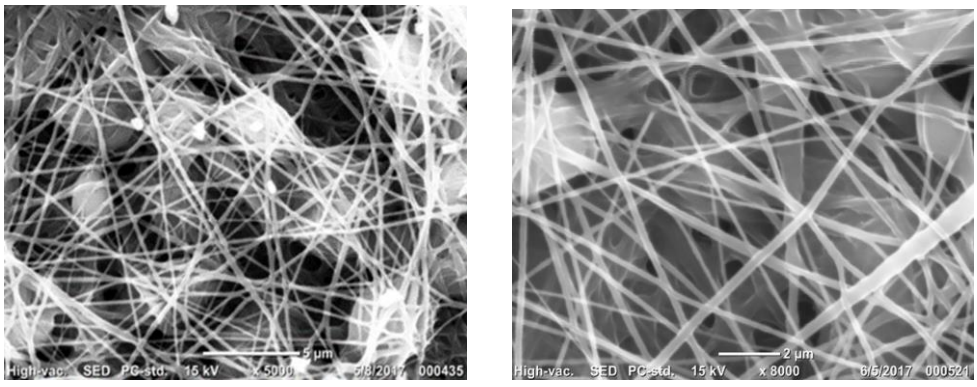


**Figure 2.** SEM images of TPU/PEDOT: PSS nanofibrous membrane.

*3.2. XRD and FTIR analyses*

The XRD pattern of TPU/PEDOT: PSS nanofibrous membrane is shown in Figure 3. TPU has diffraction peaks at 2.4°, 4.9°, 7.4° and 24.7°, and PEDOT: PSS has a diffraction peak at around 25° according to International Centre for Diffraction Data. Jia et al. [26] stated that if there is no interaction or only weak interaction between components in polyblend fibers, there would be two different crystalline peaks for each component. In this study, only one diffraction peak is seen for nanofibrous membrane around 19.0° due to the strong interaction between PEDOT: PSS and TPU. The diffraction peak is seen at 2Θ =19.0° for TPU/PEDOT: PSS nanofibers. The FTIR spectroscopy analyses for TPU, PEDOT: PSS and TPU/PEDOT: PSS nanofibers are shown in Figure 4. The spectra showed all the bonds of the chemical structure of TPU, PEDOT: PSS and TPU/PEDOT: PSS nanofiber composite.

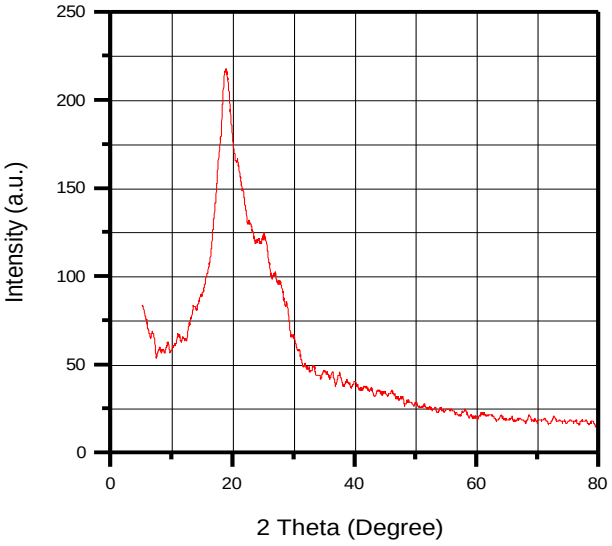


**Figure 3.** XRD pattern of TPU/PEDOT: PSS nanofibrous membrane.

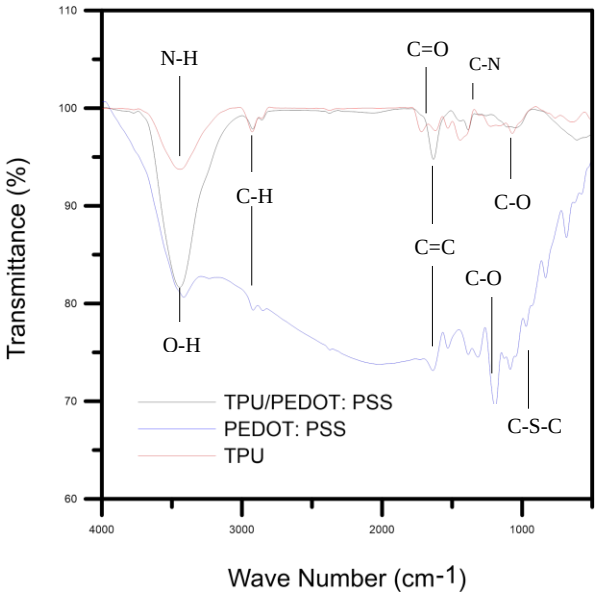


**Figure 4.** FTIR of TPU, PEDOT: PSS and TPU/PEDOT: PSS nanofibers.

*3.3. I-V Characterization*

Figure 5 shows I-V characterization curves of the as-spun TPU/PEDOT: PSS nanofibrous membrane. The I-V behaviour of produced nanofibrous membrane under different temperatures is illustrated in a semi-log plot as seen in Fig. 5(a) whereas Fig. 4(b) shows the I-V behaviour of the produced nanofibrous membrane under different strains in normal plot. From Fig. 5(a), it is clear that the membrane has showed a stabilized and symmetric ohmic behaviour at different values of temperature ranging from room temperature to 90 ℃ at zero strain. On the other hand, current-voltage characteristics of the TPU/PEDOT: PSS nanofibrous membrane have shown the normal linear trends under different percentages of tensile strain at room temperature. The produced mate, by the current developed technique, has demonstrated an ohmic behaviour irrespective the applied strain and the current decreases in a monotonic way with increasing the applied strain as shown in Fig. 4(b).

Based on the calculated conductivity obtained from these curves, Figs 4 (a) and (b), the as-spun TPU/PEDOT: PSS nanofibrous membrane has provided a great enhancement in the electrical conductivity compared to previous studies [24]. For instance, in this study, the TPU/PEDOT: PSS nanofibrous membrane has a KΩ resistance and the average value of the electrical conductivity was 0.08 S $Cm^{-1}$. However, according to other published work [24], a MΩ scale for electrical resistance of nanofibrous membranes is usually common under similar conditions of strains and temperature. This can be attributed to the fabrication technique which using PEDOT: PSS aqueous solution as a coagulant, where the phase inversion process is carried out, and in turn, thin layer of PEDOT: PSS is covering the nanofibers and sometimes in between the nanofibers.

(a) (b)

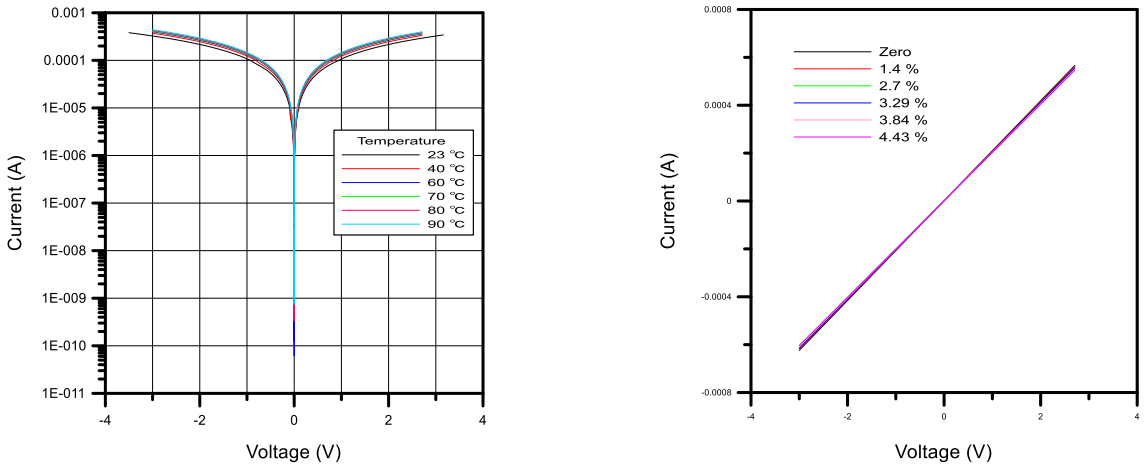


**Figure 5.** I-V characterization curves the as-spun TPU/PEDOT: PSS nanofiber membrane under (a) different temperatures (b) different strains.

## 4. Conclusions

In summary, the fabricated TPU/PEDOT: PSS nanofibrous membrane showed a great enhancement in electrical conductivity at KΩ scale rather than common MΩ scale in the previous studies. The mat demonstrates an ohmic behaviour irrespective the applied strain and the current decreases in a monotonic way with increasing the applied strain. On the other hand, current-voltage characteristics of the TPU/PEDOT: PSS nanofiber membrane under different percentages of tensile strain demonstrate an ohmic behaviour irrespective the applied strain and the current decreases in a monotonic way with increasing the applied strain. The experimental results are showing that the producd nanofibrous membrane is a promising candidate for strain sensing applications.

## 5. References

[1] Chen X, Zheng X, Kim J.-K, Li X and Lee D.-W 2011 *J. Vac. Sci. Technol.* B **29** 0601
[2] Chen Z, Ren W, Gao L, Liu B, Pei S and Cheng H M 2011 Nat. Mater 10 424

[3] Choong C L, Shim M B, Lee B S, Jeon S, Ko D S, Kang T H, Bae J, Lee S H, Byun K E, Im Jeong Y J, Park C E, Park J J and U. I. Chung 2014 *Adv. Mater* **26** 3451
[4] Lee J, Kim S, Lee J, Yang D, Park B C, Ryu S and Park I 2014 *Nanoscale* **6** 11932
[5] Li X, Zhang R, Yu W, Wang K, Wei J, Wu D, Cao A, Li Z, Cheng Y, Zheng Q, Ruoff R S and Zhu H 2012 *Sci. Rep.* **2** 870
[6] Liang H-W, Guan Q-F, Zhu Z, Song L-T, Yao H-B, Lei X and Yu S-H 2012 *NPG Asia Mater.* **4** 19
[7] Mannsfeld S C, Tee B C, Stoltenberg R M, Chen C V, Barman S, Muir B V, Sokolov A N, Reese C and Bao Z 2010 *Nat. Mater* **9** 859
[8] Park M. A. A. P. S. L. S. R. I. 2014 *Acs Nano* **8** 5154
[9] Park M, Im J, Shin M, Min Y, Park J, Cho H, Park S, Shim M B, Jeon S, Chung D Y, Bae J, Park J, Jeong U and Kim K 2012 *Nat. Nanotechnol* **7** 803
[10] Hu D, Wang Q, Yu J, Hao W, Lu H, Zhang G, Wang X and Qiu L 2016 Highly Stretchable Strain Sensors Using an Electrospun Polyurethane Nanofiber/Graphene Composite *Journal of Nanoscience and Nanotechnology* **16** 6 pp 5839-5842
[11] Sayed S, Gamil M, Fath El-Bab A M R and A. El-Moneim A 2015 Laser Reduced Graphene Oxide Film on Flexible Substrate for Strain Sensing Applications: Temperature Effect on Gauge Factor *Key Engineering Materials* **644** pp 115-119
[12] Gamil M, Nageh H, Bakrey I, Sayed S, Tabata O, Nakamura K, Fath El-Bab A M R and A. El Moneim A 2014 New Flexible Graphene-based Strain Gauge Sensor *Sensors and Materials* **26** 9 pp 699–709
[13] Sayed S, Fath El-Bab A M R, Nakamura K and A. El-Moneim A 2016 Development of Graphene Film on Flexible Poly-ethylene Terephthalate Substrate Using High Power Laser: Temperature Dependency of Gauge Factor for Graphene-based Strain Sensor *Sensors Review* **36** 2 pp 140-147
[14] Gamil M, Nakamura K, Fath El-Bab A M R, Tabata O and A. El-Moneim A 2014 Investigation of a New High Sensitive Micro-Electromechanical Strain Gauge Sensor Based on Graphene Piezoresistivity *Key Engineering Materials* **605** pp207-210
[15] Long Y Z, Yu M, Sun B, Gu CZ and Fan Z Y 2012 Recent advances in large-scale assembly of semiconducting inorganic nanowires and nanofibers for electronics, sensors and photovoltaics *Chem. Soc. Rev.* **41** 12 pp 4560–4580
[16] Schiffman J D and Schauer C L 2008 A review: electrospinning of biopolymer nanofibers and their applications *Polymer Rev.* **48** 2 pp 317–352
[17] Agarwal S, Wendorff J H and Greiner A 2008 Use of electrospinning technique for biomedical applications *Polymer* **49** 26 pp 5603–5621
[18] Ali A A and Al-Asmari A Kh 2012 Wet-electrospun CuNP/carbon nanofibril composites: Potential application for micro surface-mounted components *Applied Nano - science* **2** pp 55–61
[19] Luká D, Sarkar A, Martinová L, Vodsed'álková K, Lubasová D, Chaloupek J, Pokorn P, Mike P, Chvojka J and Komárek M. 2009 Physical principles of electrospinning (electrospinning as a nano-scale technology of the twenty-first century) *Textile Progress* **41** pp 59–140
[20] Zhong S, Zhang Y and Lim C T 2012 Fabrication of large pores in electrospun nanofibrous scaffolds for cellular infiltration: A review *Tissue Engineering Part B: Reviews* **18** pp 77–87
[21] Kostakova E, Seps M, Pokorny P and Lukas D 2014 Study of polycaprolactone wet electrospinning process. *Express Polymer Letters* **8** 8
[22] Seyedin M Z, Razal J M, Innis P C and Wallace G G 2014 Strain - Responsive Polyurethane/PEDOT: PSS Elastomeric Composite Fibers with High Electrical Conductivity
[23] Park M, Im J, Shin M, Min Y, Park J, Cho H, Park S, Shim M-B, Jeon S, Chung D-Y, Bae J, Jeong U and Kim K 2012 *Nat. Nanotechnol* **7** 803
[24] Liu N, Fang G, Wan J, Zhou H, Long H and Zhao X 2011 Electrospun PEDOT: PSS–PVA nanofiber based ultrahigh-strain sensors with controllable electrical conductivity *Journal of Materials Chemistry* **21** 47 pp18962-18966

[25] Polat Y, Pampal E S, Stojanovska E, Simsek R, Hassanin A, Kilic A, Demir A and Yilmaz S 2016 Solution blowing of thermoplastic polyurethane nanofibers: A facile method to produce flexible porous materials *Journal of Applied Polymer Science* **133** 9
[26] Jia Y T, Gong J, Gu X H, Kim H Y, Dong J and Shen X Y 2007 *Carbohydr Polym* **67** 403

**Acknowledgements**
This work was supported by Central Research Laboratories and Technology Management Department at Egypt-Japan University of Science and Technology, Alexandria, Egypt. The work was fully funded by Ministry of Higher Education (MOHE) of Egypt. Thanks are also for Eng. Enas Mostafa for her kind experimental and analytical effort in this work.