CHARACTERISATION OF ELECTROSPUN FIBERS MADE OF PVA OR PVAc AND COLLAGEN DERIVATIVE

Maksym Koliada, Olena Ishchenko, Viktoriia Plavan and Volodymyr Bessarabov

Kyiv National University of Technologies & Design, Nemirovich-Danchenko str. 2, 01011 Kyiv, Ukraine
maksym.koliada@gmail.com

Abstract: *One of the greatest potential in electrospun fiber is the area of bioengineering. For many biomedical applications, the materials used have to be biocompatible, thus natural polymers have a distinct advantage over synthetic materials. In this study, electrospinning of collagen derivative (CD) of porcine skin with polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) were carried out. We investigated morphology of the prepared fibers. The optimal distance between syringe needle and collector was 9-12 cm. Obtained nonwoven materials from PVAc and PVA with the addition of Gelatin and Collagen derivative have a diameter of fibers in the range of 0.502-0.894 μm and 0.443-0.895 μm for PVAc:CD and PVA:CD composition respectively.*

Keywords: *collagen, PVA, PVAc, electrospinning.*

1 INTRODUCTION

Leading global trend in the fibers production technology is to reduce the diameter of threads filament to micro- and nanoscale size. Nanofibers became an important group of one-dimensional nanostructures because of their unique properties such as high surface area, high porosity, and their high safety in comparison with other nanomaterials [1, 2]. These abilities improve the quality of products and allow creation of innovative materials. Today there are many methods of ultrafine fibers forming: melt-spinning, aerodynamic spraying molten fibers in the form of a jet of compressed air (melt-blowing), forming a molten mixture of polymers and nanofibers by electrospinning.

Electrospinning has several advantages over other production methods such as the relative ease of use and being cost-effective, production of fibers in a diameter range of lower than 100 nm, easy incorporation of active materials such as drugs, vitamins, antioxidants, metallic nanoparticles, etc. This technology allows obtaining new nanofibers with controlled porous structure. Moreover, organic and inorganic materials, which are temperature sensitive, are resistant to electrospinning process due to the absence of heat [1, 3]. There has been a wide array of polymers used with electrospinning to create structures composed of sub-micron diameter fibers. These include the common synthetic polymers poly(lactic acid) (PLA), poly(glycolic acid) (PGA), polycaprolactone (PCL), polydioxanone (PDO), polyvinylalcohol (PVA) [4], polyvinylpyrrolidone (PVP) and polystyrene (PS). Z.M. Huang et al [5] have given a comprehensive summary of polymers that have been successfully electrospun.

Due to diversity of applications in electrospinning, considerable amount of work is focused on extending the applications and end-uses. Electrospun nanofibers can be used to collect pollutants as filtration materials through chemical adsorption as they have high specific surface area [6, 7]. A wide range of natural polymers including gelatin, collagen, elastin, silk and fibrinogen have also been used, as well as blends of natural and synthetic polymers can be electrospun [8-10]. This method is very suitable to process natural polymers and synthetic biocompatible or bioabsorbable polymers for biomedical applications [11].

Gelatin is widely employed in food industries, cosmetics, pharmaceutical and medical applications due to its biodegradability and natural abundance. In addition, gelatin has shown a great interest in fiber formation via electrospinning technology according to its unique chemo-physical properties such as surface tension along with its viscosity and conductivity [12]. Collagen is the major structural protein of connective tissue such as skin, bone, cartilage, tendons and ligaments. Because of its biological properties and availabilities, it is widely used as a biomaterial with multiple physical forms such as sponges, films membranes, wire and fabrics [13]. Untanned or limed leather can be a source of collagen, gelatin and collagen hydrolysate [14]. Collagen hydrolysate is a polypeptide composite made by further hydrolysis of denatured collagen.

In the present work, we investigated the possibility of application of collagen derivative (CD) in electrospinnable solutions by using the mixture of CD with polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) in suitable ratios.

2 MATERIALS AND METHODS

2.1 Reagents

Polyvinyl alcohol PVA (grade 16/1, Mass portion of acetate groups not more than 0.9-1.7%) was purchased from Himlaborreactiv (Kyiv, Ukraine). Polyvinyl acetate PVAc (dry matter 15%) was supplied from a local market in a form of glue. Food grade, beef-hide gelatin (200 bloom) was supplied from a local market.

2.2 Electrospinning

The electrospinning set-up (Figure1) consisted of a syringe pump to deliver electrospinning solution to the spinneret – stainless steel blunt needle (0.5 mm inner diameter) at a flow rate approx. 0.5 ml/min. Electrospinning of the various solutions was performed using an applied voltage of 30 kV and a spinneret-to-collector distance 9-12 cm. Electrospun samples were collected using a stainless steel plate covered with polytetrafluoroethylene (PTFE) film substrate in the form of nonwoven matrices. The temperature within the setup was maintained at 25±1°C. The spinning geometry was upwards, this allows obtaining of nonwoven materials without drops of electrospinning solution on the sample. Obtained matrices after sufficient drying were peeled off from the collector with the aid of a surgical knife and transferred on the clean slide glass until subjected to characterization.

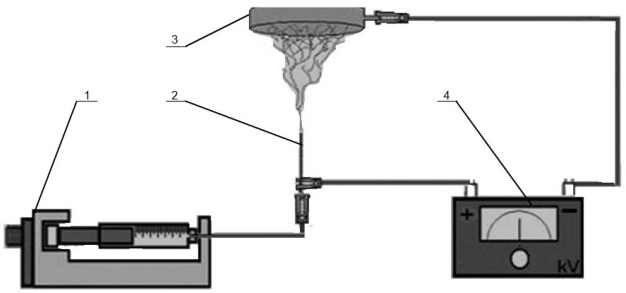

Figure 1 Capillary type electrospinning setup (1-syringe pump, 2-needle, 3-collector, 4-hight voltage power supply)

2.3 Obtaining of collagen derivative

Preserved pig skin was purchased from local slaughterhouse in Kyiv, Ukraine. After it was fleshed, unhaired, neutralized and washed as by conventional technology of leather production beamhouse processes, the dermis of the skin was cut into small pieces (1x1 cm). Collagen derivative (CD) was then extracted from the pieces by acid hydrolysis using 0.1 M acetic acid. Ratio skin:acid 1:3, duration 6 hrs., at 70-75±1°C. The obtained collagen solution was then neutralized with a 25% solution of Na_2CO_3, (pH=4.0±0.5, dry matter 9.75%, ash 1.46%).

2.4 Preparation of electrospun solutions

PVA (10% solution) and PVAc (10% solution) was prepared by stirring for 40 minutes on a water bath. Afterwards, PVA or PVAc was incorporated into the CD or gelatin (Gel) solution; the dispersion was maintained at 25-30°C for 30 min under stirring until complete dissolution. Table 1 displays the test combinations chosen for this study (PVA:CD; PVAc:CD and PVA:Gel; PVAc:Gel).

Table 1 Composition ratio details on PVA, PVAc, collagen derivative and gelatin used for electrospinning

Sample	PVA, PVAc	Collagen Derivative, Gelatin
1	9	1
2	8	2
3	7	3
4	6	4
5	5	5

2.5 Morphological characterization

The morphology and diameters of the produced fibers were examined by using a light microscope Biolam-C11. Fiber diameter analysis was carried out by randomly counting 100 fibers per experiment using software (ImageJ, 1.51 P). The diameter values of the obtained fibers were statistically analyzed by using the Minitab-18 program (Minitab Inc., USA).

3 RESULTS AND DISCUSSION

Experimental ratios for both PVA and PVAc composition are 9:1, 8:2 and 7:3. Table 2 shows the experimental results of the performed runs for PVAc combinations. The optimal distance between syringe needle and collector was 9-12 cm. While increasing the CD content takes place drop formation, which leads to impossible electrospinning formation. This requires further studies of rheology characteristics of compositions, the inner diameter of needle and distance between syringe needle and collector.

Table 2 Parameters of PVAc electrospinning

Sample	PVAc	Collagen Derivative, Gelatin*	Distance between electrodes [cm]	Formation stability
1	9	1	9-10	+
2	8	2	10-12	+
3	7	3	10	+
4	6	4	9	±
5	5	5	9-10	-
1*	9	1	10-12	+
2*	8	2	12	+
3*	7	3	12	+

* PVAc:Gelatin compositions

Ratios 6:1 and 5:5 performed insufficient electrospinning, the fibers were short and teared on small pieces even after reducing the distance

between electrodes (ex. >9 cm). Compositions containing gelatin were unstable by mean of rheology (gelation occurs), temperature 25-30°C is too low to maintain them sufficient and runny. Higher viscosity causes beads.

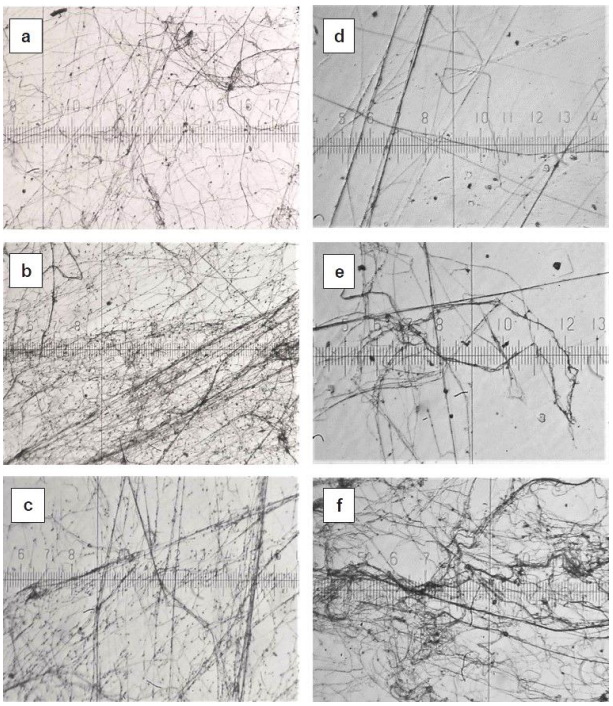

Figure 2 Representative microphotographs of the electrospun solutions a,b,c – PVAc:CD; d,e,f – PVAc:Gel of the ratios 9:1, 8:2, and 7:3 respectively

It has been well know that the concentration of polymer solution, applied voltage and conductivity affects bead formation, bead density, morphology of the electrospun fibers, and average diameter of the fibers [2, 15]. A comparison of CD and Gelatin with respect to ability to spin fibers and electrospinning process conditions showed that CD could spin fibers and gave practically defect-free (drops, thickenings) nanofibers. Mixed compositions containing Gelatin were rather difficult to process by this method because of the poorly disperse solutions and unstable in time viscosity that plugged the capillary orifices.

The morphology of electrospun PVAc containing CD or Gelatin shows in Figure 2. It is clear from the figure that no phase separation has been observed in the same time the homogeneity of the obtained fiber can be easily observed. According to the obtained data (Figure 3) PVAc:CD composite shows the increasing of the beads diameter size. A network of fibers could be observed along with beads. The fiber density increased as well as the fiber networking.

High-density fibers for both addition of Gelatin or CD along with beads were observed at ratio PVAc:CD/Gel and PVA:CD/Gel as 7:3. Therefore, for more accurate evaluation of the fibrous material morphology, additional studies were performed on light microscope Biolam-C11. Figure 3 shows diameter ranged between 0.496-1.443 μm and 0.502-0.894 μm for PVAc:Gel and PVAc:CD respectively.

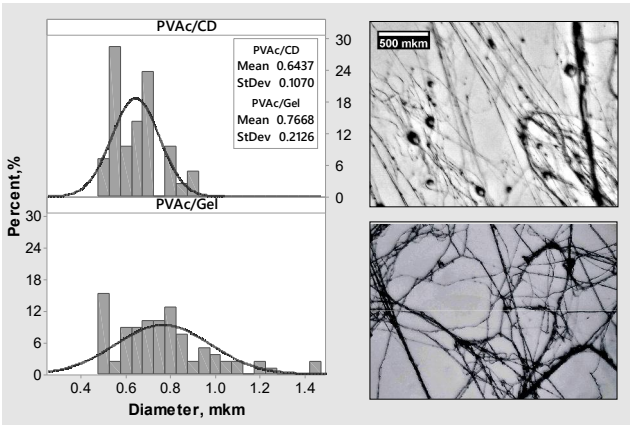

Figure 3 Images and bar graphs of diameter ranges of electrospun PVAc/CD and PVAc/Gel fibers – 7:3 ratio

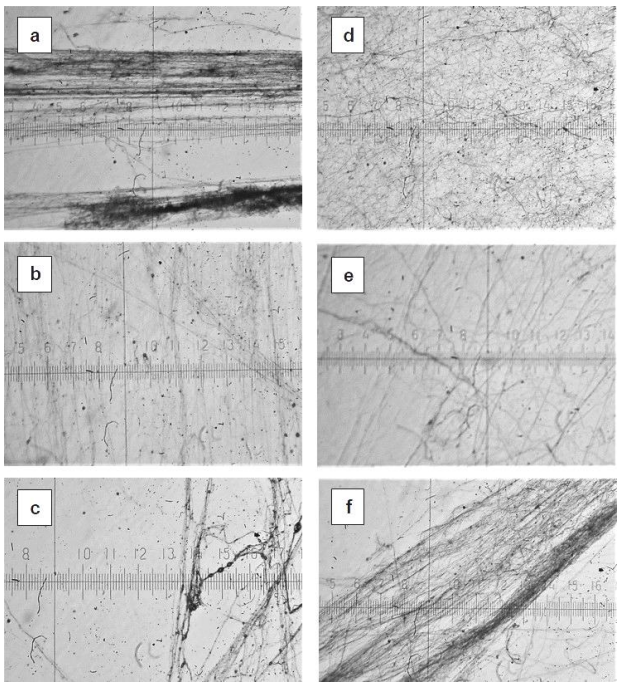

Figure 4 Representative microphotographs of the electrospun solutions a,b,c – PVA:CD; d,e,f – PVA:Gel of the ratios 9:1, 8:2, and 7:3 respectively

Table 3 shows the experimental results of the performed runs for PVA combinations with Gelatin and CD. The resulting fibers also showed that the incorporation of the CD into the composition not only decrease the average diameter but also reduced the diameter distribution of the electrospun fibers from 0.766 μm and 0.773 μm for PVAc:Gel, PVA:Gel, to 0.643 μm and 0.606 μm for PVAc:CD PVA:CD respectively, as shown in Figures 3 and 5.

Table 3 Parameters of PVA electrospinning

Sample	PVA	Collagen Derivative, Gelatin*	Distance between electrodes [cm]	Formation stability
1	9	1	9-10	+
2	8	2	10	+
3	7	3	10	+
1*	9	1	10	+
2*	8	2	12	+
3*	7	3	12	+

* PVA:Gelatin compositions

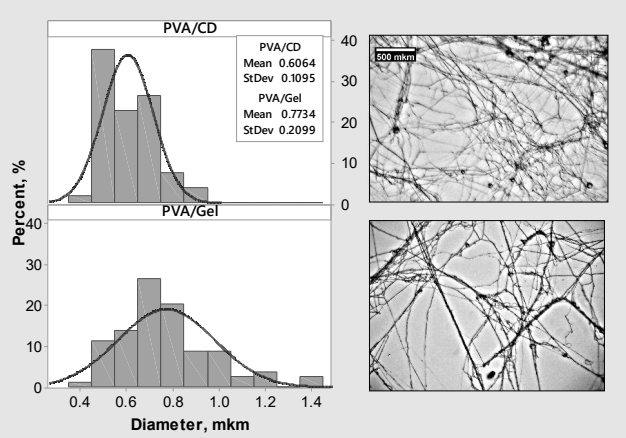

Figure 5 Images and bar graphs of diameter ranges of electrospun PVA:CD and PVA:Gel fibers – 7:3 ratio

4 CONCLUSION

Described the features of the structure (diameter – up to 1 μm) and properties of nonwoven polymeric materials obtained by electrospinning method. Obtained nonwoven materials from PVAc and PVA with the addition of Gelatin and Collagen derivative have a diameter of fibers in the range of 0.502-0.894 μm and 0.443-0.895 μm for PVAc:CD and PVA:CD composition respectively. The optimal distance between the electrodes ranges between 9-12 cm for established voltage of 30 kV for both compositions. We studied the influence of Gelatin and Collagen derivative on the morphological characteristics of fibers. It had been shown that adding of CD in compositions with PVA and PVAc leads to obtaining fibers with diameter >0.500 μm of 38% and 26% (of whole volume) respectively. Application of collagen derivative allows expanding the applications of final nonwoven polymer materials due to the wide range of reactive groups of collagen and their incorporation with other modifiers such as drugs, vitamins, antioxidants etc.

5 REFERENCES

1. Noruzi M.: Electrospun nanofibres in agriculture and the food industry: a review, J. Sci. Food Agr. 96(14), 2016, pp. 4663-4678, doi: 10.1002/jsfa.7737
2. Ramakrishna S., Fujihara K., Teo W.E., et al.: An introduction to electro- spinning and nanofibers, New Yersey, World Scientific, 2005
3. Haghi AK.: Electrospinning of Nanofibers in Textiles, Oakville, CRC Press, 2011
4. Ishchenko O.V., Plavan V.P., Kovalchuk O.V., et al.: The preparation of biocompatible polymeric fibers by electrospinning method, Technology Audit and Production Reserves 4(4(30)), 2016, pp. 22-26, doi: 10.15587/2312-8372.2016.76522
5. Huang Z.M., Zhang Y.Z., Kotaki M., et al.: A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites science and technology 63(15), 2003, pp. 2223-2253, doi: 10.1016/S0266-3538(03)00178-7
6. Emo B., Eberlin C.T., Hixon K.R., et al.: A study on the potential of doped electrospun polystyrene fibers in arsenic filtration, Journal of Environmental Chemical Engineering 5(1), 2017, pp. 232-239, doi: 10.1016/j.jece.2016.11.039
7. Zhao R., Li X., Sun B., et al.: Branched polyethylenimine grafted electrospun polyacrylonitrile fiber membrane: a novel and effective adsorbent for Cr (VI) remediation in wastewater, J. Mater. Chem. A 5(3), 2017, pp. 1133-1144, doi: 10.1039/C6TA09784G
8. Engel E., Michiardi A., Navarro M., et al.: Nanotechnology in regenerative medicine: the materials side, Trends in biotechnology 26(1), 2008, pp. 39-47, doi: 10.1016/j.tibtech.2007.10.005
9. Kwak H.W., Shin M., Lee J.Y., et al.: Fabrication of an ultrafine fish gelatin nanofibrous web from an aqueous solution by electrospinning, International Journal of Biological Macromolecules 102, 2017, pp. 1092-1103, doi: 10.1016/j.ijbiomac.2017.04.087
10. Mendes A.C., Stephansen K., Chronakis I.S.: Electrospinning of food proteins and polysaccharides, Food Hydrocolloids 68, 2017, pp. 53-68, doi: 10.1016/j.foodhyd.2016.10.022
11. Babitha S., Rachita L., Karthikeyan K., et al.: Electrospun protein nanofibers in healthcare: A review, International journal of pharmaceutics 523(1), 2017, pp. 52-90, doi: 10.1016/j.ijpharm.2017.03.013
12. Oraby M.A., Waley A.I., El-Dewany A.I., et al.: Electrospun gelatin nanofibers: effect of gelatin concentration on morphology and fiber diameters, J. Appl. Sci. Res. 9(1), 2013, pp. 534-540
13. Sionkowska A., Skrzyński S., Śmiechowski K., et al.: The review of versatile application of collagen, Polymer. Adv. Tech. 28(1), 2017, pp. 4-9, doi: 10.1002/pat.3842
14. John Sundar V., Gnanamani A., Muralidharan C., et al.: A. Recovery and utilization of proteinous wastes of leather making: a review, Rev. Environ. Sci. Biotechnol. 10(2), 2011, pp. 151-163, doi: 10.1007/s11157-010-9223-6
15. Park J.Y., Shim W.G., Lee I.H.: Modeling and optimization of electrospun polyvinylacetate (PVAc) nanofibers by response surface methodology (RSM), J. Nanosci. Nanotechnol 11(2), 2011, pp. 1359-1363, doi: 10.1166/jnn.2011.3420