

Composition Polymeric Membranes Based on the VDF-TeFE Copolymer Formed by Electrospinning

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Abstract. The paper presents the results of pilot studies on the formation of non-woven hydrophilic piezoelectric composite polymer membranes based on a copolymer of vinylidene fluoride and tetrafluoroethylene (VDF-TeFE) and polyethenylpyrrolidine (PEP) by electrospinning. Using optical goniometry, the effect of the PEP content on the wetting of the membrane surface with water was established. Using scanning electron microscopy, the influence of the content PEP on the structure of the formed membranes was studied. The effect of an isotonic NaCl solution on the structure of the formed membranes upon their dissolution within 7 days was studied. Based on studies of the chemical composition of the membranes before and after their dissolution, an assumption was made about the possibility of using the developed membranes for targeted delivery of pharmacological preparations for wound healing.

1. Introduction

The first wounds and wound treatments were described 5,000 years ago. Progress that goes beyond the ancient practice of wound care is a recent phenomenon unlike a large number of common technological inventions over the past 100 years. Chronic wound healing is a complex laborious process that is susceptible to external biological attacks (healing time ~ 12 weeks), therefore it is necessary to create a controlled environment for wound healing using an appropriate “barrier”.

Promising materials for creating a “barrier” are nonwoven polymer membranes formed by the electrospinning method [1]. It is known that piezoelectric membranes made of fluorine-containing polymers, under the influence of external mechanical stimuli, can enhance migration, adhesion, and the level of secretion of fibroblast cytokines, the main skin cells [2]. This ability allows piezoelectric fluoropolymer membranes (FPMs) to generate electrical impulses as a result of mechanical action on the tissues surrounding the implant, which allows to stimulate the healing process [3].

The drawback of the FPM, limiting their use as wound dressings, is the high hydrophobicity, significantly reducing the ability of the FPM to absorb exudate (a fluid rich in protein and cellular elements that oozes out of blood vessels due to inflammation and is deposited in nearby tissues). One of the possible solutions to the problem of creating effective FPMs for wound healing is the development of composite membranes based on fluorine and hydrophilic polymers.

In this article, we present the results of pilot studies on the creation by electrospinning of hydrophilic composite membranes based on a piezoelectric fluorine-containing polymer. Studies of the



effect of the content of a hydrophilic component in a composite material on the structure, chemical composition and surface properties of membranes. The results of studies of the dissolution of formed membranes in simulating body fluid are also presented.

2. Materials and methods

A vinylidene fluoride-tetrafluoroethylene copolymer (VDF-TFE) ($M_n 5 \times 10^5$, TFE 7 mol %) and polyethenylpyrrolidine (PEP) ($M_n 3 \times 10^3$) were used to make the FPMs. A mixture of dimethylformamide (C_3H_7NO), dimethyl sulfoxide (C_2H_6OS) and acetone (C_3H_6O), taken in a ratio of 40/40/20 mass %, was used as a mixed solvent of polymers for the preparation of spinning solutions. Spinning solutions containing polymers taken in a ratio of 100; 95/5; 85/15; 75/25; 50/50 mass %, respectively, with a total polymer content in the dope of 7 mass %, were prepared in a sealed glass reactor at a temperature of 40°C and stirring continuously until a uniform, clear, viscous liquid was obtained. A commercially available NANON 01A installation (MECC Co., Japan), equipped with a cylindrical assembly collector with a diameter of 50 mm and a length of 200 mm, was used for the formation of nonwoven materials. The distance between the dope injector (22G needle) and the assembly manifold was 150 mm. The voltage at the injector is 25 kW. The flow rate of the dope solution is 2 ml/hour. Assembly speed 50 rpm.

To study the effect of simulating body fluid on the structure of the formed membranes, membranes 30×30 mm in size were prepared. The resulting membranes were filled with 40 ml of isotonic sodium chloride solution. Samples were kept in solution for 7 days at a temperature of 37±1 °C.

The structure of the formed membranes was studied by scanning electron microscopy (JEOL JCM-6000, Japan). To improve image quality, a thin layer of gold was applied to the sample surface for 2 minutes before examination using a SC7640 magnetron sputtering system (Quorum Technologies Ltd, England). The fiber diameter was determined from the SEM images out of 3 different fields of view using plugin DiameterJ, which located in Image J 1.38 (National Institutes of Health, USA) software.

EDS (JEOL JED 2300, Japan) carried out the study of the chemical composition of the membranes. Semi-quantitative chemical composition was assessed using the method of three corrections (ZAF-corrections): in the average atomic number, absorption and fluorescence.

The wetting of the surface of the materials with water until dissolution was investigated by the “sedentary drop” method using an optical goniometer (Easy Drop-100, Germany). For this, a drop of deionized water with a volume of 3 µl was placed on the membrane surface. The measurement of the contact angle was carried out three minutes after the contact of the liquid and the membrane.

3. Experiment results

It was revealed that membranes prior to dissolution with a PEP content in the range from 0 to 25 mass % are formed by interwoven fibers with a normal diameter distribution, have well-developed interconnected porosity (Figure 1, Table 1), while an increase in PEP content leads to a decrease the average diameter of the fibers (d_{av}) forming the membrane by more than 20% (Table 1). The decrease in d_{av} of the fibers forming the membrane is due to a decrease in the viscosity of the dope with an increase in the content of PEP. An increase in the PEP content to 50 mass % causes significant changes in the structure of the fibers forming the membrane, the fibers are grouped into bundles, while the bundles have a pronounced directivity (Figure 1 e) and d_{av} decreases by more than 25% from the level of control values. Probably, the reason for the change in the membrane structure in this case, in addition to reducing the viscosity of the dope solutions, is a significant change in the electrophysical characteristics (dielectric constant, conductivity, dipole moment) of the dope solution.

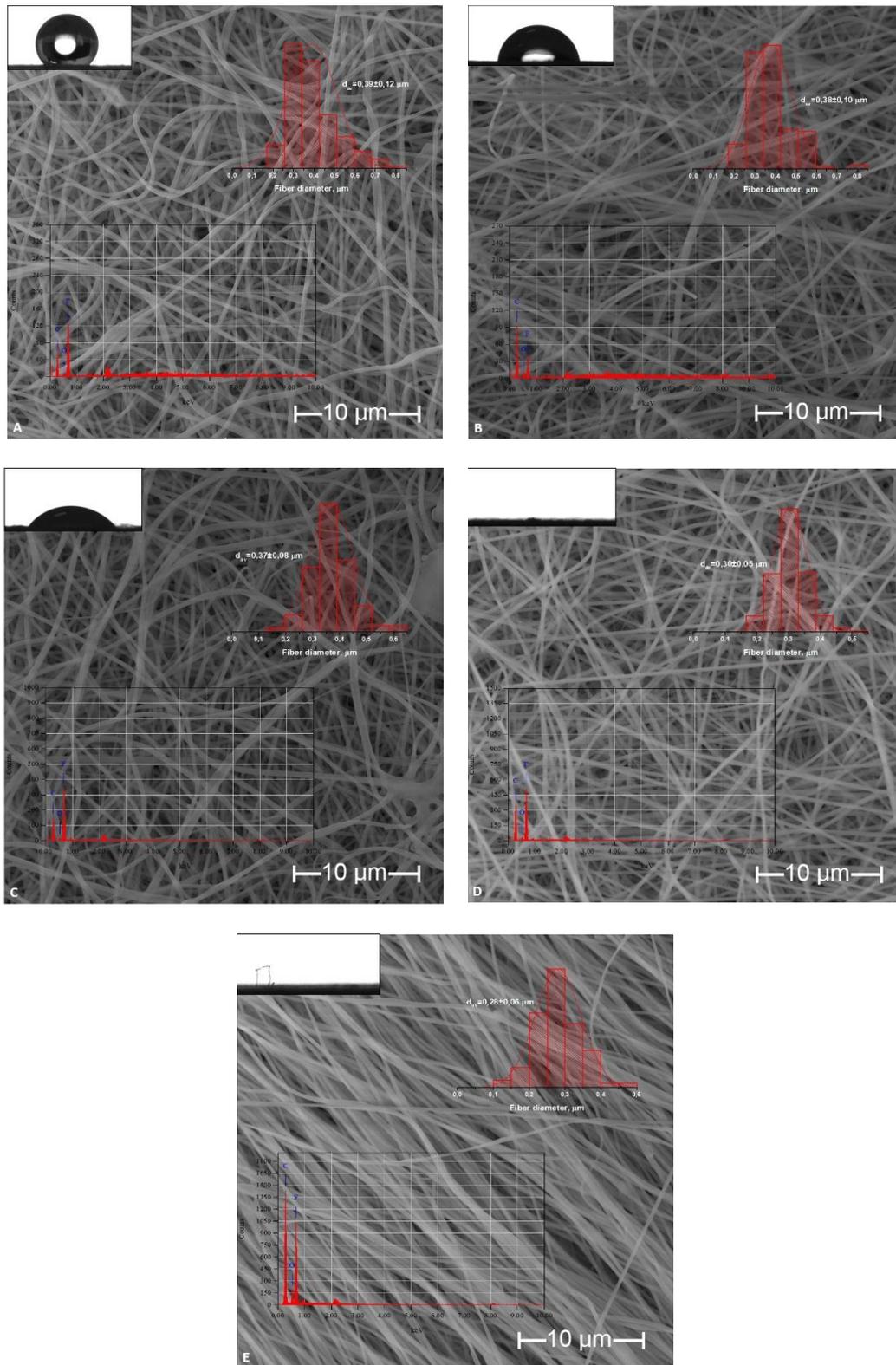


Figure 1. SEM images of samples: a) pure VDF-TeFE; b) VDF-TeFE containing 5% PEP; c) VDF-TeFE containing 15% PEP; d) VDF-TeFE containing 25% PEP; e) VDF-TeFE containing 50% PEP before dissolving.

An increase in the PEP content in the spinning solution leads to changes in the chemical composition of the membranes, increasing the oxygen content by a factor of ~ 21 compared to the control membrane. In this case, the contact angle of the membrane surface with water changes from 125 (super-hydrophobic surface) to 0 (full wetting, absorption of a drop of water into the membrane), which is associated with an increase in oxygen-containing groups on the membrane surface.

Table 1. Physical properties of samples.

PEP content (%)	Average diameter before dissolving (μm)	Average diameter after dissolving (μm)	Contact angle before dissolving (deg)
0	0.39 \pm 0.12	0.37 \pm 0.08	125 \pm 7
5	0.38 \pm 0.10	0.36 \pm 0.09	46 \pm 5
15	0.37 \pm 0.08	1.07 \pm 0.56	20 \pm 4
25	0.30 \pm 0.05	0.97 \pm 0.42	0
50	0.28 \pm 0.06	2.17 \pm 1.32	0

Exposure of membranes in an isotonic NaCl solution for 7 days causes structural changes in the formed membranes depending on the content of the hydrophilic component. Thus, the effect of an isotonic solution does not cause structural changes and significant changes in the average fiber diameter in membranes based on pure VDF-TeFE copolymer and in membranes with a PEP content of 5 mass% (Figure 1 a, b, Figure 2 a, b). With an increase in the PEP content in the composite membrane to 15%, the diameter of the fibers forming the membrane increases by more than 2.5 times compared with the membrane before immersion in an isotonic solution (Figure 1, Figure 2, Table 1). In this case, the fibers begin to “stick together” at the contact points (Figure 2 c). At a PEP content of 25 mass %, the average fiber diameter after dissolution increases by more than 3 times, while the membrane morphology is similar to membranes with a PEP content of 15 mass % (Figure 1 e, Figure 2 e, c). The greatest changes in the structure of the fibers forming the membrane are observed at a PEP content of 50 mass %. In this case, the average fiber diameter increases by more than 7.5 times. If, before immersion in an isotonic solution, the composite membrane was formed by separate directional fibers of the fiber, then after exposure to the solution the fibers stick together not only at the contact points, but also along the length of the fiber, which leads to a loss of fiber orientation and the formation of enlarged fibrous structures.

Table 2. Chemical composition of samples.

PEP content (%)	Before dissolving					C/F
	Elements (mass %)					
	C	O	F			
0	43.86 \pm 0.62	0.41 \pm 0.25	55.67 \pm 0.51			0.79
5	43.60 \pm 1.58	1.90 \pm 1.04	54.50 \pm 1.14			0.80
15	46.02 \pm 1.07	3.03 \pm 0.06	50.95 \pm 1.02			0.90
25	49.18 \pm 0.37	4.08 \pm 0.82	46.74 \pm 0.61			1.05
50	52.90 \pm 0.44	8.64 \pm 1.76	38.45 \pm 2.12			1.38
PEP content (%)	After dissolving					C/F
	Elements (mass %)					
	C	O	F	Na	Cl	
0	41.85 \pm 1.50	0.52 \pm 0.21	56.59 \pm 0.76	0.64 \pm 0.67	0.39 \pm 0.51	0.74
5	43.01 \pm 1.21	2.78 \pm 1.29	53.99 \pm 1.85	0.18 \pm 0.12	0.04 \pm 0.04	0.80
15	45.23 \pm 0.58	2.80 \pm 0.08	50.49 \pm 0.56	0.62 \pm 0.20	0.85 \pm 0.53	0.90
25	46.05 \pm 0.79	3.89 \pm 0.59	49.32 \pm 0.27	0.25 \pm 0.17	0.27 \pm 0.21	0.93
50	49.43 \pm 1.10	6.43 \pm 1.05	42.76 \pm 0.09	0.67 \pm 0.02	0.72 \pm 0.13	1.16

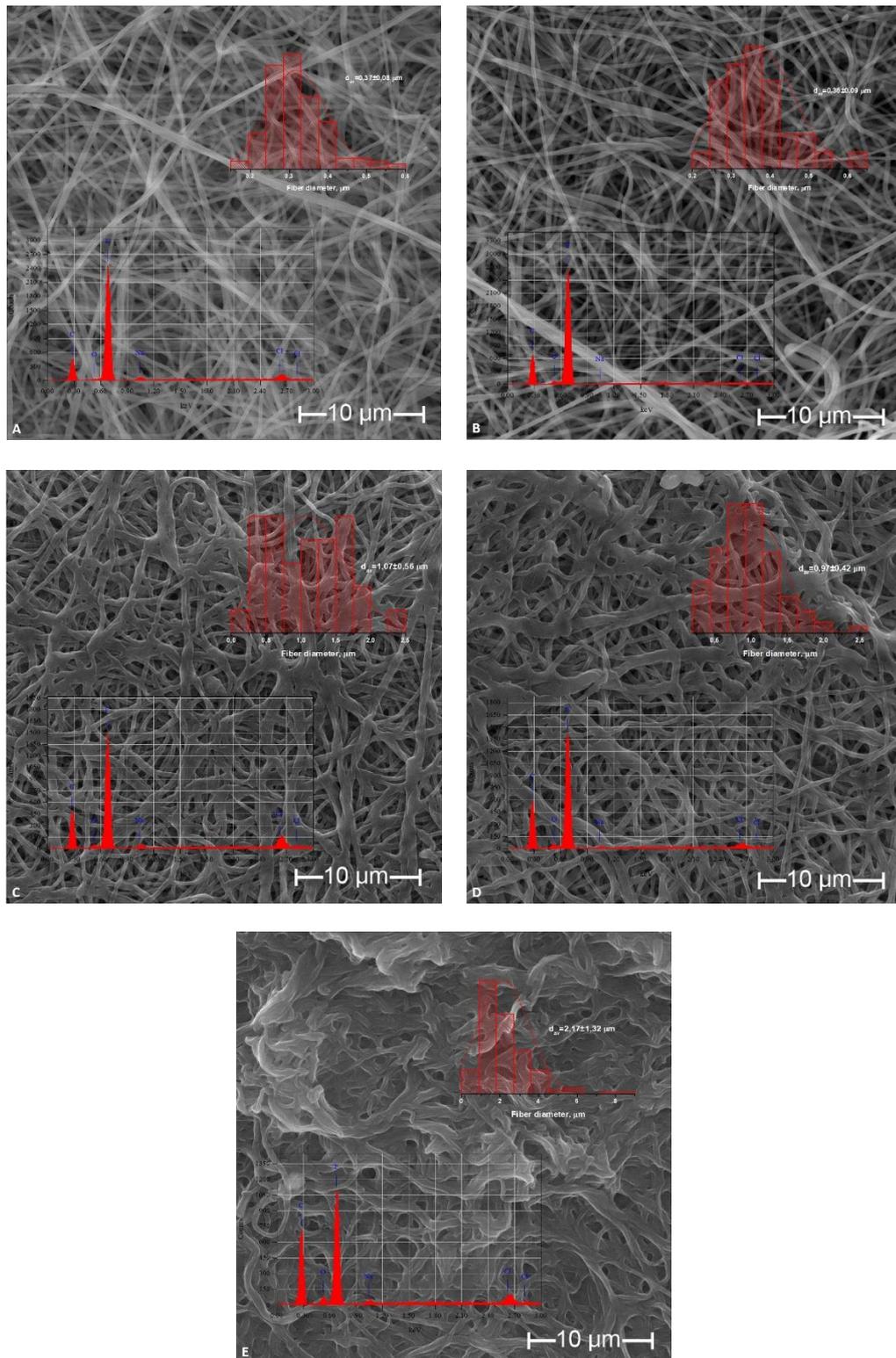


Figure 2. SEM images of samples: a) pure VDF-TeFE; b) VDF-TeFE containing 5% PEP; c) VDF-TeFE containing 15% PEP; d) VDF-TeFE containing 25% PEP; e) VDF-TeFE containing 50% PEP after dissolving.

The interaction of membranes with isotonic NaCl solution also causes changes in the chemical composition of the membranes (Table 2). Thus, membranes formed from pure VDF-TeFE copolymer

retain their chemical composition, which is due to the high hydrophobicity and chemical resistance of the VDF-TeFE copolymer, which prevents the dissolution of the membrane. The presence in the membranes based on the VDF-TeFE copolymer of elements of an isotonic Na and Cl solution is due to the crystallization of these elements on the membrane surface, since the membrane floated on the solution surface during the entire interaction time. When the PEP content in the composite membrane is 5 mass %, no significant changes in the chemical composition of the membranes after interaction with the solution are also observed. This is due to the fact that the concentration of the hydrophilic component is not significant and the hydrophilic component is evenly distributed in the matrix of the hydrophobic component of the composite. Under these conditions, the interaction of water and PEP is possible only on the surface of the fibers forming the membrane; therefore, the output of PEP into the solution is significantly limited. When the PEP content in the composite is 15 mass %, the concentration of PEP on the surface of the fibers increases, however, most of the molecules are still firmly bound to the polymer matrix, which complicates their migration to the solution. At the same time, part of the “free” polymer chain of PEP is capable of sorbing water from the solution, which leads to an increase in fibers diameter with a constant C/F ratio. When the PEP concentration in the composite is 25 mass %, conditions arise when the PEP molecules are able to leave the fibers, which leads to a decrease in the C/F ratio, while the concentration of PEP molecules capable of absorbing water from the solution increases both on the surface and in the volume of the fibers, which is also leads to an increase in the diameter of the fibers forming the membrane. The greatest difference in C/F ratios before and after interaction with an isotonic solution is observed in composites with a PEP content of 50 mass %, which is due to the largest number of PEP molecules capable of leaving the polymer fibers. Also in these composites there is the largest number of PEP molecules capable of absorbing water, which also explains the largest changes in the morphology of these membranes.

4. Conclusion

The possibility of creating composite polymer hydrophilic membranes based on a copolymer of vinylidene fluoride with tetrafluoroethylene and polyethenylpyrrolidine (PEP) by the electrospinning method has been shown for the first time. It was established that an increase in the concentration of PEP in the composite material allows one to change the contact angle of the membranes with water from 125 to 0 degrees. Using scanning electron microscopy, it was found that with an increase in the concentration of PEP, the fibers forming the membrane decrease from 0.39 ± 0.12 to 0.28 ± 0.06 μm . It was found that significant changes in the average diameter of the fibers forming the membrane during the interaction of the membrane with an isotonic NaCl solution are observed at a PEP concentration of 15 mass %. The study of the chemical composition of the membranes by EDX revealed a decrease in the C/F ratio after dissolution, which suggests the use of the developed membranes for targeted delivery of pharmacological preparations.

Acknowledgments

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References

- [1] Ambekar R S and Kandasubramanian B 2019 Advancements in nanofibers for wound dressing: A review *Eur. Polym. J.* **117** 304–36
- [2] Guo H-F, Li Z-S, Dong S-W, Chen W-J, Deng L, Wang Y-F and Ying D-J 2012 Piezoelectric PU/PVDF electrospun scaffolds for wound healing applications *Colloids Surfaces B Biointerfaces* **96** 29–36
- [3] Wang A, Liu Z, Hu M, Wang C, Zhang X, Shi B, Fan Y, Cui Y, Li Z and Ren K 2018 Piezoelectric nanofibrous scaffolds as in vivo energy harvesters for modifying fibroblast alignment and proliferation in wound healing *Nano Energy* **43** 63–71