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FLUOROPOLYMER MEMBRANES WITH PIEZOELECTRIC PROPERTIES FOR ORAL MUCOSA REGENERATION

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ФТОРСОДЕРЖАЩИЕ ПОЛИМЕРНЫЕ МЕМБРАНЫ С ПЬЕЗОЭЛЕКТРИЧЕСКИМИ СВОЙСТАМИ ДЛЯ РЕГЕНЕРАЦИИ СЛИЗИСТОЙ ОБОЛОЧКИ ПОЛОСТИ РТА

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Abstract. *В настоящей работе представлены результаты исследований структуры и свойств двух типов полимерных мембран для регенерации слизистой оболочки ротовой полости, изготовленных из политетрафторэтилена (ПТФЭ) и сополимера винилиденфторида с тетрафторэтиленом (ВДФ-ТеФЭ). Методом атомно-силовой микроскопии исследована структура и пьезоэлектрические свойства мембран. Показано, что оба типа мембран сформированы хаотично переплетающимся между собой ультратонкими волокнами, при этом волокна ВДФ-ТеФЭ мембран обладают выраженными пьезоэлектрическими свойствами. В сравнительном эксперименте на лабораторных животных установлена высокая способность ВДФ-ТеФЭ мембран регенерировать слизистую оболочку ротовой полости.*

Introduction. Wounds of the oral mucosa occur in 42 % of the population throughout life, therefore, in modern surgical practice, their healing is an urgent problem. Traditionally, Gore-Tex® paraelectric fluoropolymer membranes are used to close wound defects [1]. Membranes made of copolymer of vinylidene fluoride and tetrafluoroethylene demonstrate piezoelectric properties, which makes it possible to provide physiotherapeutic treatment of a wound defect under the membrane without electric current sources. However, there are few comparative studies of membranes with paraelectric properties and membranes with piezoelectric properties. The purpose of the study is to provide a comparative analysis of membranes with paraelectric properties made from polytetrafluoroethylene (PTFE) and membranes with piezoelectric properties made from a copolymer of vinylidene fluoride and tetrafluoroethylene (VDF-TeFE).

Research methods. For PTFE membranes producing, a spinning solution was obtained by mixing a polyvinyl alcohol (JSC Vekton, Russia) 10 % aqueous solution with a PTFE (JSC Halopolymer, Russia) aqueous suspension in a 50:50% wt. ratio of solution and suspension. For VDF-TeFE membrane making, a 6 % wt. solution was prepared of a copolymer of vinylidene fluoride and tetrafluoroethylene (JSC Halopolymer, Russia) in a mixed solvent. Mixed solvent consisted of acetone (JSC EKOS-1, Russia) and dimethylformamide (JSC EKOS-1, Russia) in a ratio of 85:15 % wt., respectively. Composite membranes were formed on a rotating assembly manifold using a NANON-01A electrospinning facility (MESS, Japan). After that, the composite PTFE membrane was quenched in a muffle furnace [2] and the composite VDF-TeTE membrane was crystallized in a muffle furnace [3].

The topography and piezoelectric properties of the membrane-forming fibers were studied by piezoelectric force microscopy (PFM) using an Ntegra Prima atomic force microscope (NT-MDT, Russia). To study the surface topography, the microscope was equipped with an NSG10/Pt cantilever (NT-MDT, Russia). To study the piezoelectric properties of fibers, the microscope was equipped with an NSG30/Au cantilever (NT-MDT, Russia). The measurements of the piezoelectric response were carried out in a quasi-static regime at the frequencies 20 kHz with the 10 V amplitude of a.c. excitation signal. Studies of the polymer membranes effect on the oral mucosa regeneration were carried out on laboratory animals, namely, Wistar rats. Graphic images were processed using Axio Vision (Carl Zeiss, Germany) and Image, version 1.52u (USA).

Results. Topography, d33 coefficient, phase image and piezoelectric amplitude distribution of these fibers are presented in Figure 1.

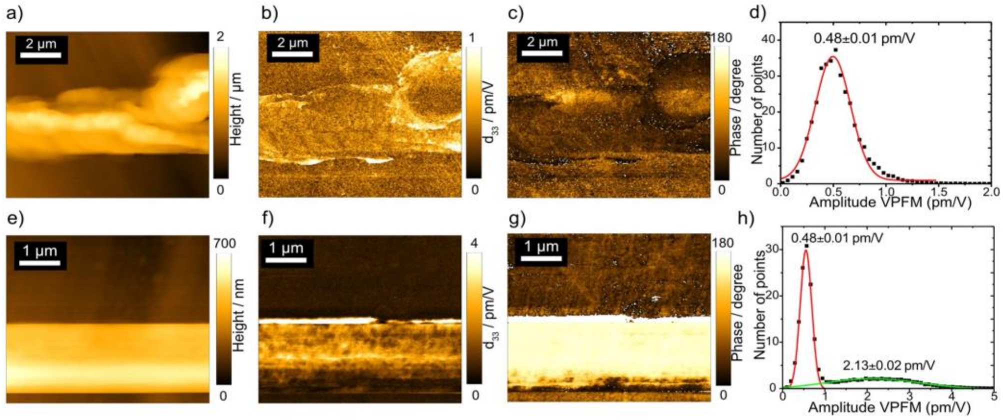

Fig. 1. Vertical PFM images of PTFE and VDF-TeFE fibers: (a) Topography, (b) VPFM amplitude, (c) VPFM phase images and (d) VPFM amplitude distribution of PTFE fiber; (e)Topography, (f) VPFM amplitude, (g) VPFM phase and (h) VPFM amplitude distribution of of VDF-TeFE fiber

The topography of PTFE fibers is different from that of VDF-TeFE fibers. PTFE fibers have domains with different shapes and the diameter of fiber is about 774 ± 5 nm (Fig. 1 a). Vertical PFM (VPFM) amplitude of PTFE is almost the same as aluminum foil (Fig. 1 b, c and d), however, on the edge the authors observed some piezoelectric response, which could be related to the defects on the edge of PTFE. In consequence, VPFM amplitude of these fibers is different (see Fig. 1 f). As it is shown in the Fig. 1 f and 1 g, the vertical piezoelectric amplitude d33 of VDF-TeFE is firstly experimentally demonstrated in this article and can reach up to 4 pm/V, therefore, the piezoelectric response of the presence of contrast of VPFM amplitude in Fig. 1 f is related to polydomain with the size of tens of nanometers in VDF-TeFE. The contrast in the VPFM phase images is related to different polarization directions. Fig. 1 h shows the distribution of d33 coefficient, and the average d33 coefficient of aluminum foil and fibers, which was fitted by Gaussian distribution, equals 0.48 ± 0.01 and 2.13 ± 0.02 pm/V.

Figure 2 shows the results that were obtained for the area of the oral mucosal defect under the membrane, depending on the type of membrane used on days 3, 7 and 12 of the experiment.

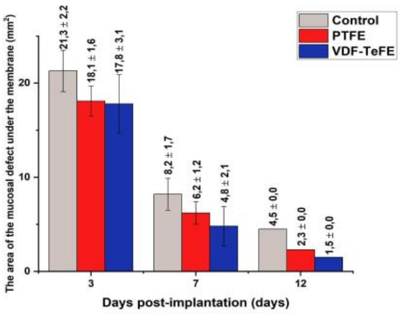

Fig. 2. The area of the oral mucosal defect under the membranes on days 3, 7 and 12 of the experiment

The area of the oral mucosal defect is greater on the third day after surgery in the control group than in the groups where the wound defects were covered with membranes and equals 21.3 ± 2.3 mm^2. There were no statistical differences in wound closure with membranes (Fig. 2). On the seventh day after the operation, the area of the oral mucosal defect in the control group was 8.2 ± 1.7 mm^2. The area of the oral mucosal defect is 6.2 ± 1.2 mm^2 in the group where the wound defect was closed with a PTFE membrane, which is 29% more than the area of the oral mucosal defect in the group where the wound defect was closed with a VDF-TeFE membrane. On the twelfth day after the operation, a scar was formed at the site of the oral mucosa defect. The area of the scar in the control group is 4.5 mm^2, 2.3 mm^2 in the group where the wound defect was closed with a PTFE membrane, and 1.5 mm^2 in the group where the wound defect was closed with a VDF-TeFE membrane.

Conclusion. A comparative analysis was carried out for membranes made from polytetrafluoroethylene and membranes made from a copolymer of vinylidene fluoride and tetrafluoroethylene. The use of polymeric membranes to close wound defects accelerated the regeneration process and reduced the severity of the inflammatory response compared to the treatment method, when the wound defect remains open. However, membranes made from PTFE do not demonstrate electrical activity and are less effective when used as a material for closing wound defects of the oral mucosa. Membranes made from VDF-TeFE exhibit piezoelectric properties and are more efficient.

REFERENCES

1. Godin, M. S., Waldman, S. R., & Johnson Jr, C. M. (1995) The use of expanded polytetrafluoroethylene (Gore-Tex) in rhinoplasty: A 6-year experience. Archives of otolaryngology–head & neck surgery, no. 121, 10, pp. 1131–1136.
2. Melnik, E., Stankevich, K., Zinoviev, A., Poletikina, E., Andreev, A., Buznik, V., & Bolbasov, E. (2022) Effect of heat treatments and aggressive media on mechanical properties of porous polytetrafluoroethylene membranes fabricated via electrospinning. Jour. Fl. Chem., no. 264.
3. Konyaeva, A.D., Varakuta, E.Yu., Leiman A.E., Bolbasov E.N., & Chernova, U.V. Osobennosti neovaskulyarizatsii ranevogo defekta slizistoy obolochki polosti rta v khode yego regeneratsii pri zakrytii polimernoy p'yezoelektricheskoy membranoy (Peculiarities of neovascularization of a oral mucosa wound defect during its regeneration with a polymeric piezoelectric membrane). Byulleten' eksperimental'noy biologii i meditsiny, vol. 174, no. 12, pp. 780–785.