

# Nonwoven PTFE Membranes Fabricated by Electrospinning Method: Preparation and Characterization

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**Abstract.** Polytetrafluoroethylene (PTFE) is one of the promising materials for the purposes of tissue engineering and chemical technology because of its excellent physico-chemical properties and mechanical characteristics. However, conventional methods of PTFE porous membranes production have several disadvantages which limit the number of potential application areas by reason of a insufficient surface-to-volume ratio and poor porosity at small thickness. In the paper the results of using PTFE water suspension with a solution of water-soluble polymer for preparation of porous membranes by electrospinning are reported. The physico-chemical characteristics of membranes were investigated depending on the content of PTFE dispersion in spinning solution. There were found high hydrophobicity and lyophilicity of PTFE electrospun membranes. Main reasons of poor mechanical properties of porous membranes at high content of PTFE suspension in spinning solution are discovered. The ways of mechanical properties improvement and areas of possible applications are proposed.

## 1. Introduction

Materials with good mechanical characteristics and hydrophobic properties are widely used in chemical technology. Materials with similar features are applicable for the purification of gases from particles of organic and inorganic origin, osmotic distillation (OM), membrane distillation (MD), and their varieties. In the case of MD, important qualities are the filtration rate and high temperature gradient across the membrane thickness which can be achieved with high porosity and low thermal conductivity [1].

Polytetrafluoroethylene (PTFE) is a fluoropolymer synthesized by tetrafluoroethylene polymerization at high pressure [2]. Owing to its high chemical and thermal stability, good dielectric, hydrophobic properties, and excellent mechanical characteristics, PTFE is utilized in chemical technology for manufacturing of chemical reactors, chemical-resistant pipes, and membranes for various types of purification [3]. In reconstructive surgery and tissue engineering materials based on PTFE are used as a coating for blood vessels, bile ducts, larynx, implants, walls of heart valves, tissue engineering membranes in dentistry, plastic surgery [4].

The main methods for the manufacture of PTFE-based membranes are biaxial stretching, laser ablation, and the method using pore-forming reagents [5, 6]. The disadvantages of these methods are



difficulties with manufacturing of thin membranes with a high degree of pore interconnectivity, PTFE depolymerization as a result of exposure to high-density laser radiation, usage of environmental-unfriendly plasticizers, and other reagents. Thus, the development of new methods for producing porous PTFE membranes is a necessary challenge.

The electrospinning of polymer solutions or melts is a promising method for production of porous polymer materials [7]. It provides capability to form constructions with high porosity, surface-to-volume ratio, and good mechanical characteristics for various applications: tissue engineering, regenerative medicine, drug delivery, biosensors, and membranes for MD, OD, and water purification [7]. Also, electrospinning makes possible to synthesize highly porous materials at small thickness that is needed for some membrane desalination methods. However, direct formation from PTFE solutions is impossible because of the lack of suitable solvents for PTFE and the high viscosity of its melt. The paper presents the results of the study on the use of PTFE suspensions with the solution of water-soluble fiber-forming polymer – polyvinyl alcohol (PVA) for the formation of membrane by electrospinning method.

## 2. Materials and methods

### 2.1. Preparation of PTFE-PVA precursor membranes by electrospinning

A spinning solution that was used to form nonwoven materials and comprised of a PTFE suspension F-4D (Halopolymer, Russia) and a 9 wt.% aqueous solution of polyvinyl alcohol (PVA) 16-1 (Evrohim, Russia). For investigation 4 groups of materials were formed in such way that the content of the PTFE suspension in the solution was 50, 60, 70, and 80 wt.%. The mixture was processed in an ultrasonic bath (Sapphire 5, Russia) for 10 hours at temperature of  $30 \pm 3$  °C until a homogeneous viscous liquid was obtained.

Nonwoven materials were formed by the electrospinning method on Nanon-01 (MECC, Japan) using a cylindrical collector with length – 200 mm and diameter – 100 mm under following technological parameters: voltage – 25 kV, flow rate – 2 ml/h, the needle – 22 G, the distance between needle and collector was 15 cm.

### 2.2. Sintering

After formation the precursor membranes were heated to  $360 \pm 10$  °C at a rate of  $5 \pm 1$  °C/h in atmospheric pressure, kept at a given temperature for 5 hours, and then cooled to room temperature at a speed of  $5 \pm 1$  °C/h.

### 2.3. Scanning electron microscopy (SEM)

SEM images allowed determine the average diameter of fibers and specific number of defects. Samples of each type of membranes were fixed onto metallic studs with double-sided conductive tape. A thin gold film was sprayed onto samples in order to provide a contact of the material with the stub and to prevent the accumulation of a negative charge on the samples surface. The morphology and chemical composition of the formed materials were studied using a scanning electron microscope (JEOL JCM-6000, Japan). The average fiber diameter and specific number of defects were calculated using ImageJ 1.5 software (National Institutes of Health, Bethesda, MD, USA).

### 2.4. Porosity

The porosity was determined by measuring the geometric dimensions and weight of the membranes after sintering based on which the calculation was carried out according to the formula:

$$P = \left( 1 - \frac{\rho_{\text{exp}}}{\rho} \right) \cdot 100 \%,$$

where  $\rho_{\text{exp}}$  – calculated mean of density,  $\rho$  – density of PTFE.

### 2.5. Mechanical properties

The investigation of strength and elongation under uniaxial tension was studied according to GOST R 53226-2008 using a tensile testing machine (Instron 3344, USA).

### 2.6. Surface wetting

Surface wetting with water and T-1500 transformer oil (GOST 982-80) was investigated using an optical goniometer (Easy Drop-100, Germany).

### 2.7. FTIR spectroscopy

Chemical structure of the fabricated porous materials before and after sintering was investigated by Fourier transform infrared (FTIR) spectroscopy using Cary 630 spectrometer (Agilent, USA) in the range of 500 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

## 3. Results and discussion

Images of the nonwoven materials surface depending on the weight content of the PTFE suspension in the spinning solution before (left column) and after heat treatment (right column) are shown in figure 1. The initial polymer membranes are formed by randomly interwoven fibers with regular cylindrical shape. On the surface of the fibers there are no defects, such as breaks and cracks, that indicates the optimally selected technological parameters of membrane formation. The interwoven fibers form interconnected pores that is typical for nonwoven materials fabricated by electrospinning [8]. While the content of the PTFE suspension in the spinning solution increases, the average fiber diameter decreases because the solution viscosity lowers (table 1).

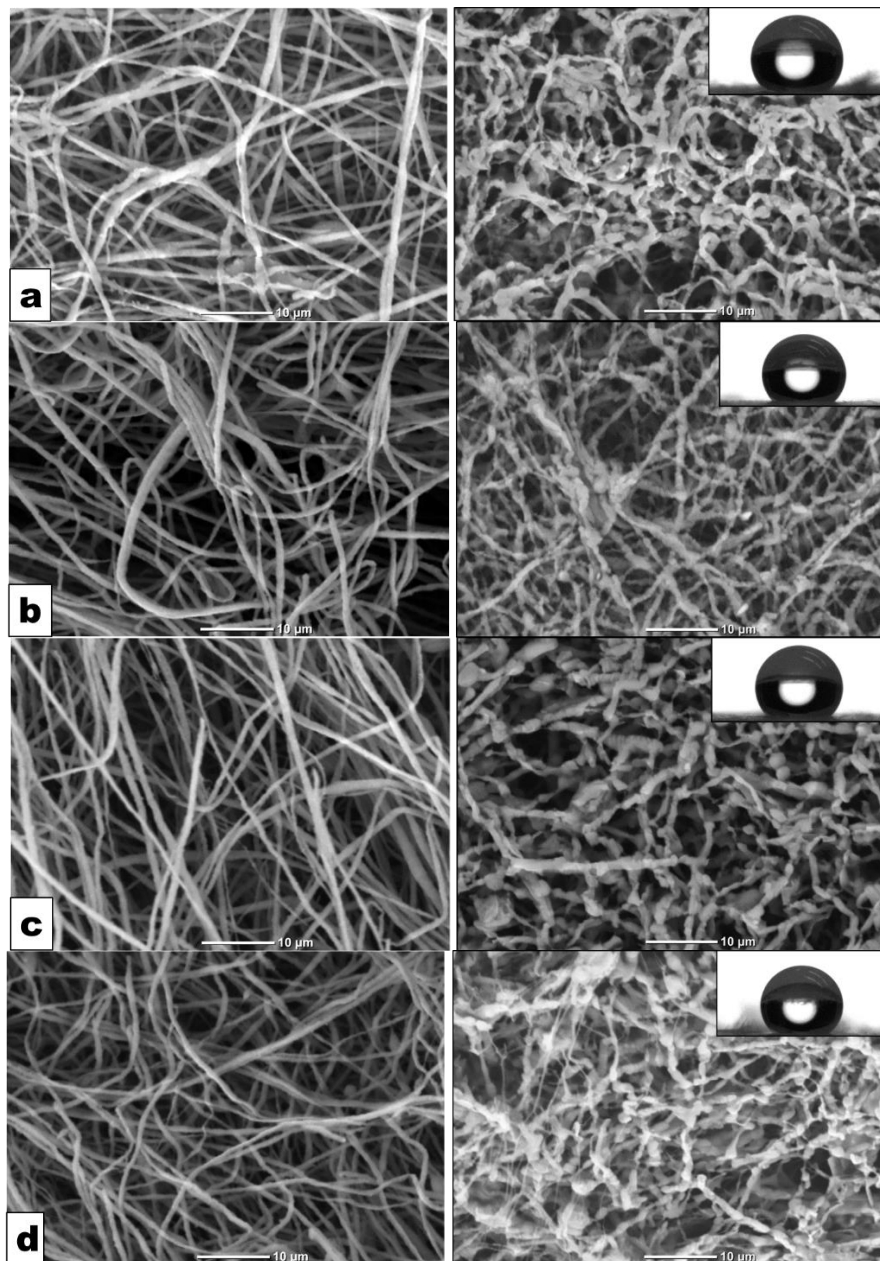
Heat treatment of samples at temperature of 360 °C leads to changes in the morphology of the fibers that form the polymer membrane (figure 1). Thickening and cracking occur on the fibers surface. The number of these changes per unit length of fiber increases with raising content of the PTFE suspension in the solution (table 1). The porosity of the obtained membranes also does not change depending on the content of the suspension and is equal to 83±2%.

**Table 1.** Physico-chemical properties of PTFE porous materials depending on PTFE suspension content in spinning solutions.

Content of PTFE suspension wt. %	Viscosity mPa·s	Average fiber diameter $\mu\text{m}$		Specific number of defects, $\mu\text{m}^{-1}$	Mechanical properties	
		before sintering	after sintering		Tensile strength MPa	Elongation %
50	414±12	0.96±0.18	1.02±0.18	0.45±0.06	0.45±0.02	115±16
60	332±10	0.94±0.14	0.90±0.17	0.64±0.09	0.31±0.04	113±8
70	217±6	0.89±0.16	0.95±0.19	0.71±0.06	0.13±0.01	63±5
80	136±4	0.77±0.16	0.96±0.18	0.93±0.08	0.06±0.01	43±4

The formation of defects in the fiber is explained by the following main reasons. The first is the decomposition of PVA, surfactants, and the removal of water from the fiber bulk during heat treatment. The removal of volatile impurities leads to the formation of voids between the particles of PTFE. The filling of these cavities is obstructed even at elevated temperatures in consequence of the high PTFE melt viscosity. Secondly, PTFE is a semi-crystalline polymer which crystallinity during crystallization from the melt is determined by the cooling rate, while the maximum crystallization rate is observed at 310-315 °C. Considering that the cooling rate of the samples after sintering was 5±1 °C/h, favorable conditions were selected during the cooling process for the formation of the crystalline phase in PTFE. Since the crystalline phase occupies a smaller volume than the amorphous phase, significant stresses

appear in the polymer that stimulate the defects formation in polymer fibers. At the same time, formed during the destruction process the low molecular weight products of PVA and surfactants can diffuse into the structure of PTFE and have a plasticizing effect thereby complicating the crystallization process. Thus, fewer defects and, as a result, better physico-mechanical properties are observed for membranes obtained from spinning solutions with a low concentration of PTFE suspension, since the amount of plasticizer in these samples is greater (table 1).

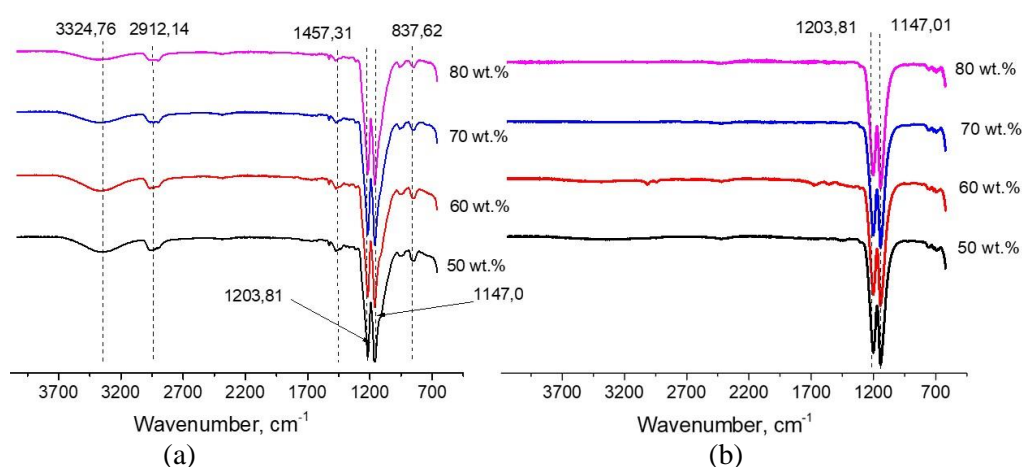


**Figure 1.** SEM images of nonwoven materials formed from spinning solutions with a suspension of PTFE from a) 50 to d) 80 wt. % (left column – precursor materials, right column – after sintering).

A study of the surface wetting of the formed porous materials indicates that, regardless of the suspension content, all formed membranes are hydrophobic, while the value of the contact angle of the surface for wetting with water is  $\sim 125^\circ$  and does not significantly change when the content of the PTFE suspension in the spinning solution is varied (figure 1). Before sintering membranes completely absorb

water droplets placed on the surface. In this case, a drop of transformer oil deposited on the membranes surface, regardless of the content of the PTFE suspension, is completely absorbed into the membrane after 2-3 seconds that indicates the high lyophilic properties of the formed membranes.

Confirmation of the removal of water and PVA from PTFE membranes after sintering was approved by FTIR spectroscopy, results of which are presented in figure 2. In the FTIR spectrum of PTFE precursor membranes (figure 2a) the highest absorbance is observed at 1203 and 1147  $\text{cm}^{-1}$  that corresponds to asymmetric and symmetric stretching of C-F<sub>2</sub> in PTFE [9]. At 3325, 2912, 1457, and 838  $\text{cm}^{-1}$  the stretching of O-H, asymmetric stretching of C-H<sub>2</sub>, asymmetric bending of C-H<sub>2</sub>, and stretching of C-C, respectively, are detected that correlate with the presence of PVA in the precursor membranes [10, 11]. After sintering process (figure 2b) the strong absorbance peaks at 1204 and 1147  $\text{cm}^{-1}$  are only observed that approve full decomposition of PVA.



**Figure 2.** FTIR spectra of PTFE porous materials: (a) – spectrum of precursor materials, (b) – spectrum of materials after sintering.

## Conclusion

In conclusion, porous materials based on PTFE were fabricated by electrospinning with sintering of precursor membranes. It was demonstrated that the obtained materials have high porosity with pore interconnectivity, as well as good mechanical characteristics. High hydrophobicity and lipophilicity of the obtained membranes because of the low surface energy of PTFE and high porosity of the membrane were found [12]. After sintering process the full decomposition of PVA and surfactant was observed. The combination of high hydrophobicity and porosity allows to utilize obtained membranes as selective ones, for example, for cleaning oils from water contaminants.

## Future outcome

The improvement of the mechanical properties of PTFE membranes is associated with a decrease in the crystallinity of the membranes because of the optimization of heat treatment and the synthesis of composite membranes based on PTFE and carbon nanotubes.

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