Elena S. Bokova[1],
Grigory M. Kovalenko[1,*],
Maria Pawlowa[2],
Ksenia S. Bokova[1],
Nataliya V. Evsyukova[1]

Modification of Polyurethane Solutions by Means of a Hard Depositor for Fiber Production by the Electrospinning Method

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[1] **The Kosygin State University of Russia, Faculty of Chemical Technology and Industrial Ecology, Department of Polymeric Film Materials and Synthetic Leather,**
Moscow, Russian Federation
* e-mail: gregoryi84@mail.ru

[2] **Kazimierz Pulaski University of Technology and Humanities**
Radom, Poland

Abstract
The article is devoted to fundamental and applied research in the field of the processing of polymer solutions. The purpose of this work was to identify the possibility of using modified solutions of polyurethanes for processing by electrospinning, and also to study the impact of the composition of the moulding solution on the structure and properties of fibrous materials. Nonwoven materials were obtained by electrospinning fibers from PUR solutions using NanospiderTM technology. The transfer of solutions into a metastable state, both in the case of film systems and fibers, leads to a change in the structure of the material: porosity and fiber diameter.

Key words: *fibers electrospinning, polyurethane, polymer solutions processing, solutions modification.*

Introduction

The technology of processing polymers through solutions by the phase separation method in a non-solvent medium is one of the main ways of obtaining fibrous-porous materials and coatings varying in purpose, structure and properties, such as separation membranes, catalyst carriers, highly effective sorbents, grinding materials, as well as various synthetic leathers, including shoe and clothing.

The macro- and microstructure of multilayer composite materials largely depend on the nature of film formation of the polymer in each of its constituent elements. In this regard, knowledge of the basic patterns of the structure of polymer systems and the ability to regulate the type of structures formed are of particular importance and in many ways allow the creation of materials with a predetermined structure and properties.

At present, there are several approaches to the problem of forming porous polymer materials with a predetermined structure and properties. They include empirical, phenomenological and structural [1-3].

The empirical approach has the widest practical application and is based on the definition of characteristics and properties of finished materials. According to this approach, this or that structural feature of the material or its specific properties are first ascertained as a fact, and then subjected to scientific analysis to establish certain relationships between the initial composition of the material and its structure, and properties.

The most graphic illustration of the implementation of this approach, corresponding to the subject of this paper, is the analysis of the fibrous structure of non-woven materials obtained by electrospinning from polymer solutions. Already at the initial stages of the development of this technology, the existence of two extreme cases of such structures differing in the morphology of the fibrous canvas was noted: micro- and nanofibers with a minimum number of defects and uniform distribution along the diameter and electrospraying of the solution (lack of fiber-forming ability).

For a deeper analysis, in order to identify logical relationships and patterns of structure formation, it is necessary to connect the phenomenological and structural approaches.

The phenomenological approach is associated with the availability and application of fundamental knowledge and discoveries that are characteristic of a particular field of research, which, as a rule, arise at the early time stages of studying a particular phenomenon, process, etc. Its merits include the possibility of explaining «post facto» phenomena and their extrapolations to previously known laws and patterns.

The methodology of the structural approach is based on the consideration of various morphological levels in a particular system. At the same time, it is obvious that consideration of a structure is possible and expedient by the example of one class of polymers for materials of the same physical type and specific application.

In the case of processing polymer solutions by the method of phase separation in a nonsolvent medium, the degree of structure formation of macromolecules, i.e. the «prehistory» of a solution, can somehow influence the kinetics of their gelification during phase separation and «transform» in the nature of the porous structure of the finished films, fibers and coatings. Thus the task of creating materials with a predetermined structure can be solved by obtaining structured solutions whose morphology can be preserved by going through the solution → jelly → coating. The spread of structural levels may be quite substantial, since it is necessary to take into account the nuances and possibilities associated with varying the chemical nature of the initial components for polymer synthesis and their ratio, the modification of solutions by various structuring additives, regulation of the phase separation process itself (kinetics) by changing external factors etc.

Thus in work [4] the transformation of solutions of polyurethanes (PUR) into a metastable state was realised by modification of aliphatic alcohols and interpolymer complexes of various nature. These systems were used to produce synthetic leather of a new generation with high hygienic properties. Broadcasting this approach to obtain other final forms of polymeric materials, such as fibers, is an urgent task.

The most suitable technology for the implementation of the above principles is the electrospinning of fibrous materials (EFM), which allows the processing of solutions of a number of polymers in a large number of solvents, enabling a change in process parameters over a wide range, and also providing benefits from the flexibility and simplicity of instrumentation [5, 6].

In the last decade nonwoven nanofibre materials have been actively used in textile and light industry. Such cloths are used as membranes, in particular for the production of «smart» sportswear and footwear. Membrane materials should have high hygienic properties and meet a number of water permeability and durability requirements, thus nonwoven webs are part of a single composite membrane package.

Nanofibers for textiles are obtained from a wide range of polymers, but the most common are polyamide and polyurethane [7]. Literature has sufficient data on the process of electrospinning non-woven fibers from spinning solutions based on polyurethane. A number of works describe the use of modified solutions of the above polymer in order to change the properties of the spinning solution as well as the structure and properties of the resulting nonwoven webs. However, most often non-woven polyester matrices are used as materials for medicine and biotechnology.

Thus in article [8] the authors created a non-woven nanocomposite from a solution of polyurethane modified with carotene oil, using electrospinning technology. Studies have shown that the nanofibers have a smaller diameter (702 ± 130 nm) than those obtained from an unmodified PUR solution (969 ± 217 nm). Analysis of infrared spectroscopy confirmed the interaction between carotene oil and PUR in the form of a hydrogen bond. It was also proved by the authors that non-woven webs of the modified PUR solution are more hydrophobic (the wetting contact angle is 119°). The composite materials developed from PUR-carotene oil compositions are recommended for potential application in tissue engineering.

Non-woven nanofibrous composites from PUR solutions were obtained in [9] for use as small-diameter vascular grafts. The low hydrophilicity and hemocompatibility of polyurethane predetermined the need for modification of spinning solutions of PEU with polyethylene glycol (PEG) and phosphatidylcholine.

Electrospinning technology was used in [10] to produce nanofibre substrates based on hydrophobic poly ε-caprolactone (PCL), hydrophilic polyethylene glycol (PEG) and amphiphilic linear polyurethane. To improve the biocompatibility of nanofibres, a thin amine layer was deposited on the nanofibrous meshes prepared by plasma polymerisation of cyclopropylamine in a radio frequency capacitive discharge. The presence of amino groups on the surface of the substrate nanofibers should promote the adhesion and proliferation of cells. Infrared spectroscopy confirmed the successful transplantation of chitosan onto the surface of PUR. This treatment of PUR nanowires can open up the possibility of using wound healing material that combines the antibacterial properties of chitosan and excellent PUR stiffness.

The purpose of this work was to identify the possibility of using modified solutions of polyurethanes for processing by electrospinning, and also to study the impact of the composition of the molding solution on the structure and properties of fibrous materials.

Scientific novelty:

- the conditions for obtaining micro- and nanofibres, as well as non-woven materials from solutions of injection polyurethane in dimethylformamide, were developed and scientifically justified by the method of electroforming.
- conditions, prescription and technological factors for the production of non-woven fibrous webs by electrospinning from true and metastable solutions of polyurethane modified by a rigid precipitator – water were investigated;
- it is proved that if the quality of the solvent deteriorates with the addition of water, the diameter of fibers obtained decreases and the fiber distribution interval along the diameter increases;

Practical significance: technological solutions for obtaining non-woven nanofibre webs from solutions of polyesterurethane for use as membrane materials in the design of sportswear and footwear packages were developed.

Experimental

Materials

As a research object, polyurethane of the brand Vytur TM-1413-85 (VLADIPUR Ltd., Vladimir, Russia) was used as a reaction product of 4,4'-diphenylmethane diisocyanate and polyethylene butylene glycol adipinate at a ratio of NCO: OH of 1: 1, with a weight-average molecular weight of 40 kDa. 15%, 20%, and 25% polyurethane solutions in N, N-dimethylformamide were used to prepare moulding compositions. Distilled water was used as the modifying additive («hard» precipitator) during electrospinning.

Methods

The dynamic viscosity of the spinning solution was determined by a viscometer – Brookfield DV-II-Pro (USA), and the specific volumetric electrical conductivity – using a conductivity meter: Expert-002 (Russian Federation). Studies of the structure of fibre-bonded and individual fibres were carried out on a scanning electron microscope – Hitachi TM 1000 (USA). Nonwoven materials were obtained by electrospinning fibers from PUR solutions using Nanospider™ technology.

Results and discussion

At the first stage of the work, it was necessary to identify the principal possibility of obtaining fibers from a solution of polyurethane in dimethylformamide.

It was established that the process of electrospinning from PEU solution with a 25% concentration is stable using a point electrode, but electrospinning with the use of a cylindrical electrode is pulsating in nature and leads to the production of defective fibers (the presence of thickenings, drops, etc.), which is clearly illustrated by the micrographs of the samples obtained (***Figure 1.a, 1.b***).

The electrospinning process from a solution of 20% concentration (using both types of electrodes) also leads to the formation of defective fibers (the fibers dry out too quickly and do not have time to fix themselves onto the substrate). The resulting fibrous structure is characterised by local inhomogeneities in the form of pear-shaped thickenings and dried droplets (***Figure 2.a, 2.b***). When electrospinning, a non-woven material with a small number of defects is formed from a 15% PUR solution. The diameter of fibers obtained from this solution averaged from 300 to 500 nm (***Figure 3.a, 3.b***).

The parameters of the process of electrospinning true PUR solutions at a temperature of 24° C, 66% humidity, and distance from the surface of the moulding solution to the substrate of 13 cm were determined experimentally (***Table 1***).

Thus the possibility of obtaining fibers and nonwoven materials from PUR solutions (Vytur TM-1413-85 brand) was established. It was found that non-woven fabrics with a minimum number of defects can be obtained from a moulding solution with a concentration of 15%.

Based on the purpose of the work, it was necessary to obtain fibrous materials from the metastable polymer solution. The conversion of the polyester-urethane solution to a metastable state was carried out by adding a hard precipitator – water. It is known from literature sources that the maximum water content in PUR solutions is 3-5% [4]. We were interested in obtaining fibers from solutions of PUR in DMFA containing water as a modifying additive, which would influence the formulation and technological parameters of the electrospinning process, as well as the structure of the fibers obtained.

In our work, by the method of turbidimetric titration, the maximum water concentration in the PUR-DMFA moulding solution was determined as 6%. It was found that the itration of a concentrated solution of PUR with a «hard» precipitator – water, is not possible due to instantaneous phase separation. Based on this, a number of PUR solutions were prepared in DMFA with the same polymer concentration of 0.2%, but with a different water content, namely a water content of 1%, 3% and 6% of the total volume of the solution, in order to study the effect of the "hard" precipitant in PUR solutions for the process of electrospinning and the properties of the finished non-woven materials.

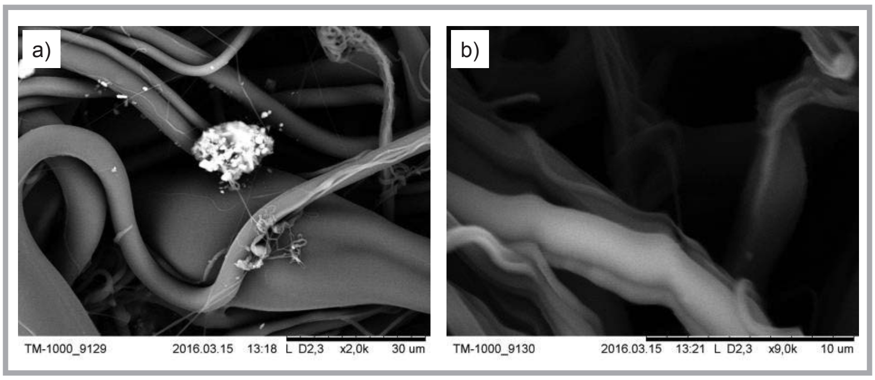

Figure 1. *Microphotographs of fibers obtained by the Nanospider™ method from PUR solution with a concentration of 25%: a) 2,000 times increase, b) 9,000 times increase.*

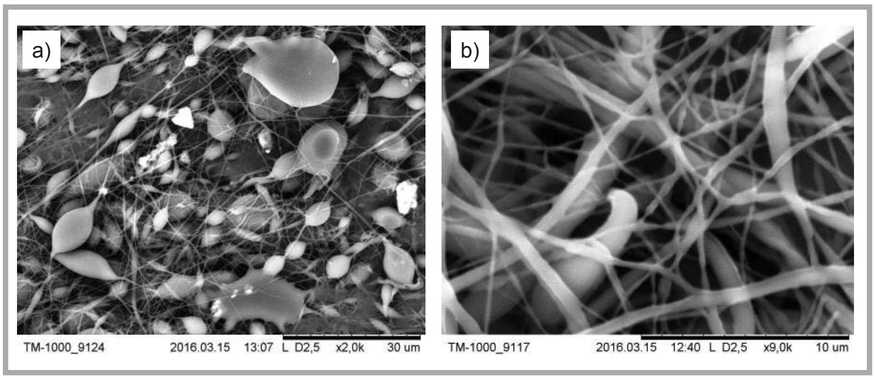

Figure 2. *Microphotographs of fibers obtained by Nanospider™ method from a solution of PUR with a concentration of 20%: a) 2,000 times increase, b) 9,000 times increase.*

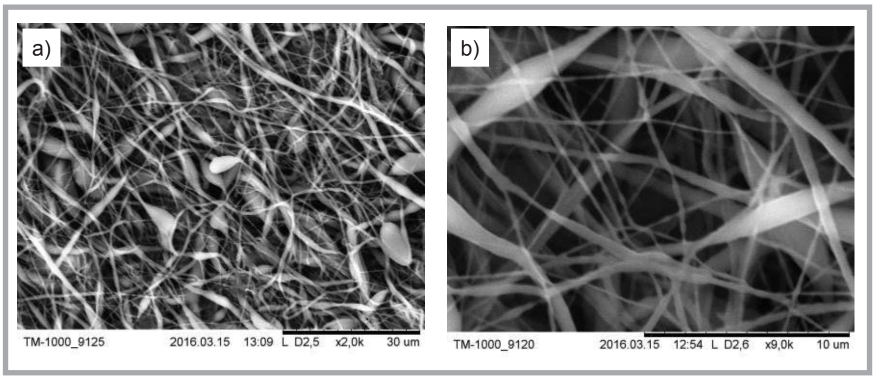

Figura 3. *Microphotographs of fibers obtained by the Nanospider™ method from PUR solution with a concentration of 15%: a) 2,000 times increase, b) 9,000 times increase.*

Table. 1. *Parameters of the process of electrospinning of true PUR solutions of different concentration.* ***Note:*** ** C – solution concentration, η – dynamic viscosity, æ – electrical conductivity, U – tension, Q – volume flow.*

Characteristics of PUR solution			Electrospinning process parameters		Characteristics of the electrospinning process	Average fiber diameter, nm
C*, %	η*, Pa·s	æ*, Cm/m	U*, kV	Q*, cm³/sec		
15	0.4	0.11	19-30	$3.5 \cdot 10^{-4}$	Stable electrospinning	200-350
20	0.7		26-40		Stable moulding with fiber defects	300-600
25	1.3		30-47		Unstable moulding	> 600

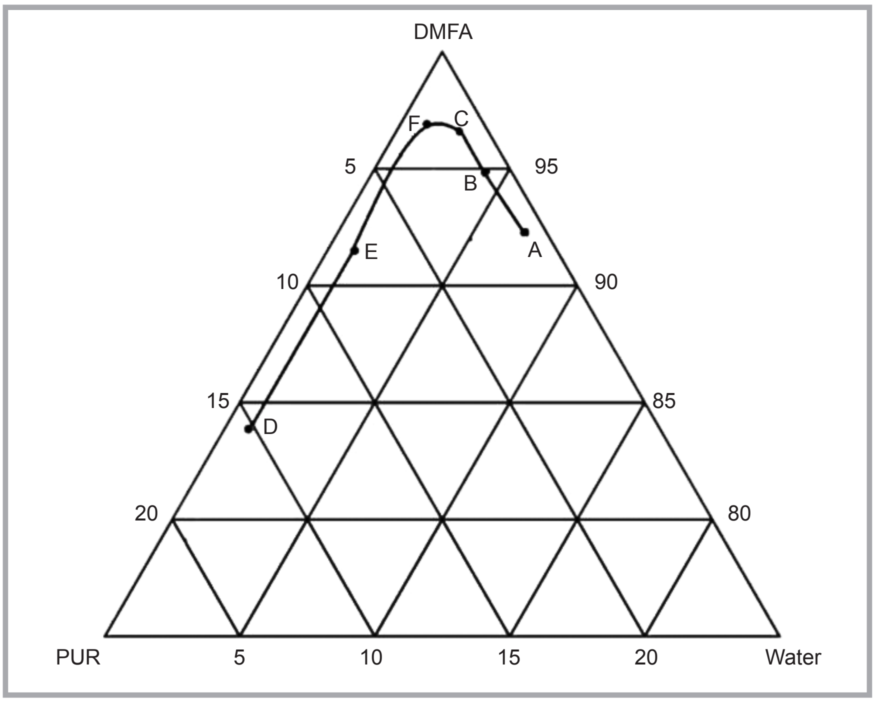

Figure 4. *Diagram of the phase state of the PUR-DMFA-water system (T = 22 ± 2 °C).*

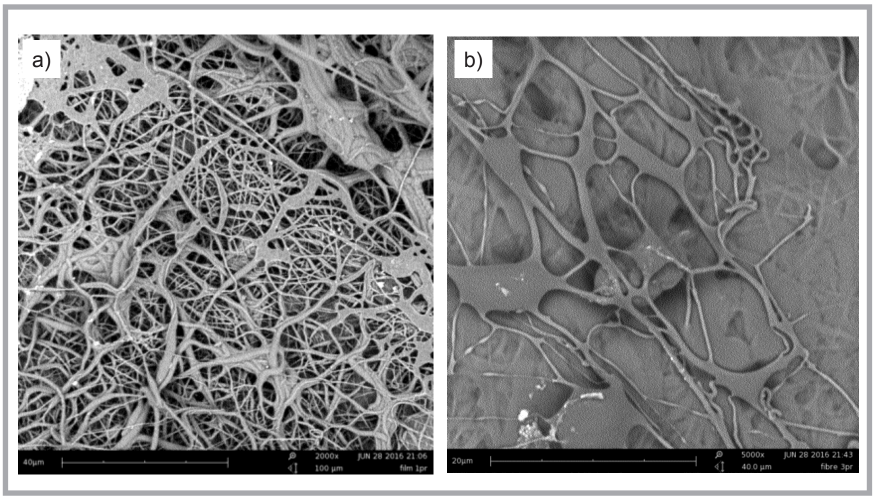

Figure 5. *Micrographs of a nonwoven fabric obtained from a modified solution of PUR in DMFA: a) 1% water, b) 3% water. (2,000 times increase).*

By the method of constructing phase diagrams on cloud points (***Figure 4***), it was shown that a composition with a 6% water content is a two-phase system in which a phase separation process occurred, whereas solutions with a water content of 1% and 3% are single-phase systems; however, they are in a metastable state.

It was shown that the formation of a solution containing 1% water is stable, continuous and uniform, where the influence of the precipitator is invisible and does not significantly affect the course of the electrospinning process (***Figure 5***).

The process of forming PUR solution containing 3% water is also stable. However, when analysing microphotographs, a large number of films were detected in the interfiber space (***Figure 5***). This behaviour of the polymer solution can be explained by its transition to a metastable state. This increases the viscosity of the solution, and the formation of the polymer jet undergoes changes. In the electric field between electrodes, while the elementary jet is stretched into fiber, film systems are formed due to phase separation and the removal of the solvent. It can be assumed that such a fibrous film structure will have a greater strength and rigidity than fibrous materials obtained from unmodified polyurethane solutions.

The work determined parameters of the process of the electrospinning of metastable PUR solutions containing water as a modifying additive at a temperature of 25 °C, humidity of 67%, and distance from the surface of the moulding solution to the substrate of 14 cm.

It should be noted that when the PUR solution is modified with water, the average diameter of fibers decreases sharply and the fiber distribution interval along the diameter increases, which is confirmed by the literature data [8].

Conclusions

Nanofibres and nonwoven materials were obtained from a solution of Vytur TM 1483-85 polyurethane, as well as from modified PUR compositions containing water. It was proved that the transformation of a solution of polyurethane into a metastable state leads to a decrease in the fiber diameter, and an increase in a new type of non-woven nanofibrous system containing film inclusions.

Table 2. *Parameters of the process of electrospinning of PUR metastable solutions (C = 15%) with different water content.* ***Note:*** ** η – dynamic viscosity, æ – electrical conductivity, U – tension, Q – volume flow.*

Solution characteristics			Electrospinning process parameters		Characteristics of the process of electrospinning	Characteristics of the electrospinning process, nm
Water content, %	η*, Pa·s	æ*, Cm/m	U*, kV	Q*, cm³/sec		
1	0.40	0.11	20-31	$3.7 \cdot 10^{-4}$	Stable electrospinning	100-300
3	0.39	0.13	22-33		Electrospinning is preceded by film formation on the electrode. Stable moulding with minor defects in fibers	70-250

It is obvious that, irrespective of the processing technology of polymers (film-formation by phase separation in a nonsolvent or electrospinning), one can speak of general approaches to modification. The transformation of solutions into a metastable state, both in the case of film systems and fibers, leads to a change in the structure of the material in terms of porosity and fiber diameter. This material structure predetermines the use of cloths as part of membrane bags for clothing and footwear.

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