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Electrospinning of Fibres Using Mixed Compositions Based on Polyetherurethane and Hydrophylic Polymers for the Production of Membrane Materials

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Abstract
In this paper, the possibility of obtaining micro- and nanofibres, as well as nonwoven materials from polyether-urethane solutions using the method of electrospinning, was studied. The conditions and formulation-technological factors for the production of nonwoven fibrous webs from polyetherurethane (PUR) solutions modified with hydrophilic polymers: polyvinyl alcohol (PVA) and polyacrylic acid (PAA) were studied. The effect of hydrophilic polymers on the structure and average fibre diameter is shown. An increase in the indicators of hygienic properties of modified nonwoven materials was revealed with the aim of their further use in membrane bags for clothes and shoes.

Key words: *fibres electrospinning, polyurethane, polymer solutions processing, solutions modification, membrane materials.*

Introduction

The technology of polymer processing through solutions by phase separation in a non-solvent medium is one of the main methods used for the production of fibrous-porous materials and coatings of various purpose, structure and properties, such as separation membranes, catalyst carriers, highly effective sorbents, polishing materials, and synthetic leather of various application, including shoe and clothes leather.

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 structure formation of polymer systems and the ability to control the type of structures formed are of particular importance and allow to create materials with a predetermined structure and properties in a lot of ways. [1, 2].

One of the technologies for the implementation of the above approach is the electrospinning of fibrous materials (ESF), which allows to process solutions of a number of polymers in a large range of solvents and to greatly change the technological parameters, and it also provides flexibility and simplicity of instrumentation [3, 4].

The technology of electrospinning was used in paper [5] to obtain nanofibrous substrates based on hydrophobic poly ε-caprolactone (PCL), hydrophilic polyethylene glycol (PEG) and amphiphilic linear polyetherurethane (PUR). In order to improve the biocompatibility of nanofibres, a thin amine layer was deposited on the nanofibre grids prepared using plasma polymerisation of cyclopropylamine in a radio frequency capacitively coupled discharge. The presence of amino groups on the surface of the substrate nanofibres should contribute to an increase in cell adhesion and proliferation. Infrared spectroscopy confirmed the successful transplantation of chitosan to the surface of PUR. Such processing of PUR nanofibres can open up possibilities of using the material combining the antibacterial properties of chitosan and the excellent stiffness of PUR for wound-healing.

New antibacterial, anti-electrostatic and hydrophilic nanofibres based on a mixture containing thermoplastic polyurethane (TPU) and ionic liquid (IL), hexafluorophosphate 1-butyl-3-methylimidazolium [BMIM] [PF6], were obtained by the authors of paper [6] using the method of electrospinning. The paper studied the effect of IL on the morphology and physical properties of TPU nanofibres. Defective nanofibres with a bead-on-a-filament morphology were obtained by the electrospinning of a pure TPU solution, whereas the addition of 1 wt.% of IL to the spinning solution significantly suppressed the formation of defects during electrospinning, and homogeneous nanofibres were obtained. In addition, the inclusion of IL leads to an increase in the hydrophilic nature of TPU/IL composite fibres compared with hydrophobic TPU nanofibres.

The purpose of this paper is to identify the possibility of using polyether-urethane solutions modified with hydrophilic polymers for processing by the electrospinning method, as well as to study the influence of the composition of a forming solution on the structure and properties of fibrous materials.

Experimental

Materials

As objects of study, polyether urethane (PUR) of the Vitur TM-1413-85 brand (NVP VLADIPUR LLC, Vladimir, Russia) was used, obtained from the interaction of 4,4′-diphenylmethane-diisocyanate and polyethylene butylene glycol adipate with an NCO:OH ratio of 1:1, and average molecular weight of 40 kDa. To prepare the forming compositions, 15% solutions of polyether-urethane in N, N – dimethyl formamide (DMF) were used. Hydrophilic polymers were used as modifiers of PEU solutions: polyacrylic acid (PAA) with a molecular weight of $2 \cdot 10^5$ (Russia), polyvinyl alcohol (PVA)

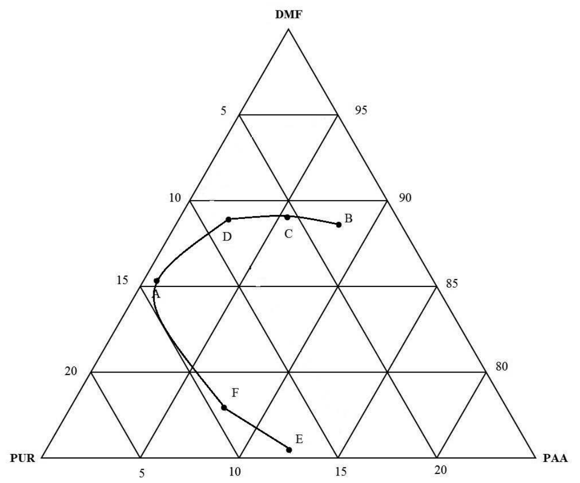

***Figure 1.** Phase diagram PUR:PAA:DMF. Composition of mixture: A – 1% PAA, 84% DMF, 15% PUR; B – 7.5 % PAA, 90% DMF, 2.5% PUR; C – 5% PAA, 90% DMF, 5% PUR; D – 2.5% PAA, 90% DMF, 7.5% PUR; E – 15% PAA, 70% DMF, 15% PUR; F – 25% PAA, 60% DMF, 15% PUR. T = 25 ± 2 °C.*

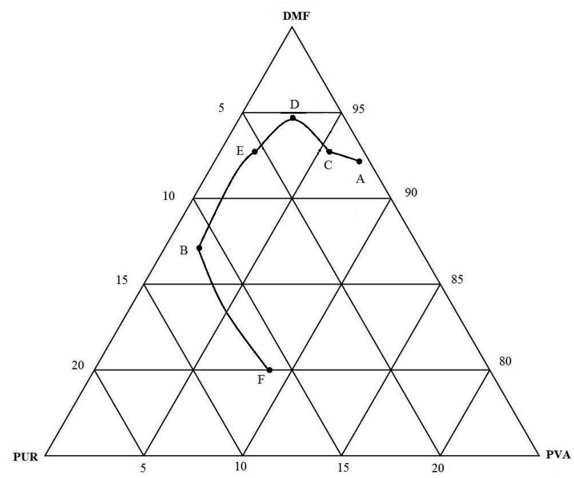

***Figure 2.** Phase diagram PUR:PVA:DMF. Composition of mixture: A – 5% PVA, 94% DMF, 1% PUR; B – 10% PVA, 89% DMF, 1% PUR; C – 7.5% PVA, 90% DMF, 2.5% PUR; D – 5% PVA, 90% DMF, 5% PUR; E – 2.5% PVA, 90% DMF, 7.5% PUR; F – 11.25% PVA, 85% DMF, 3.75% PUR. T = 25 ± 2 °C.*

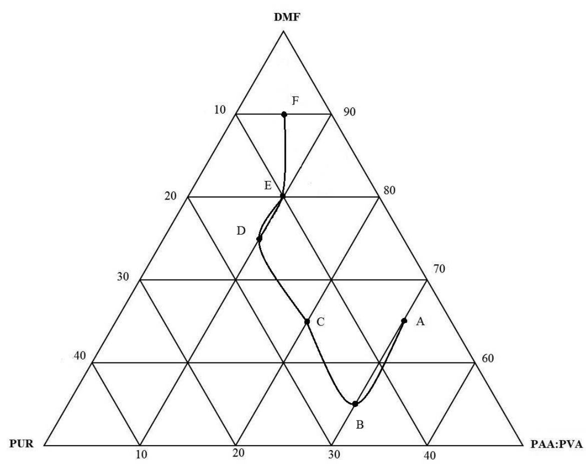

***Figure 3.** Phase diagram PUR:(PAA+PVA):DMF. Ratio PAA:PVA = 1:1. Composition of mixture: A – 13% (PAA:PVA), 85% DMF, 2.5% PUR; B – 15.5% (PAA:PVA), 79% DMF, 5.5% PUR; C – 7.5% PVA, 85% DMF, 7.5% PUR; D – 7.5% (PAA:PVA), 90% DMF, 2.5% PUR; E – 5.5% (PAA:PVA), 92% DMF, 2.5% PUR; F – 2.5% (PAA:PVA), 95% DMF, 2.5% PUR. T = 25 ± 20 °C.*

***Table 1.** Electrospinning process parameters of composition PUR: (PAA:PVA(1:1)) = 3:1. **Note:** η* – dynamic viscosity, æ* – electrical conductivity, U* – voltage, Q* – volume flow.*

Characteristics of solution		Electrospinning process parameters		Characteristics of electrospinning process	Average diameter of fibres, nm
η*, Па·с	æ*, Sm/m	U*, kV	Q*, sm³/sec		
0.61	0.22	38-44	$3.5 \cdot 10^{-4}$	Steady spinning	100-250

***Table 2.** Indicators of hygienic properties of a nonwoven material obtained from compositions based on PUR and hydrophilic polymers at T = 25 ± 2 °C.*

Indicator	Property values of nonwoven material	
	PUR	PUR:(PAA:PVA)
Hygroscopicity,%	0.93 ± 0.001	5.65 ± 0.001
Water yielding capacity,%	0.93 ± 0.001	1.05 ± 0.001
Water vapour permeability, mg/(sm^2 · h)	2.5 ± 0.001	2.43 ± 0.001
Sorptive capacity, g/g	0.035 ± 0.001	0.175 ± 0.001

with a molecular weight of $8{,}4 \cdot 10^4$, containing acetate groups – about 10% «Celvol» (USA).

Methods

The dynamic viscosity of the spinning solution was determined by a viscometer – Brookfield DV-II-Pro (USA), and the specific volumetric electrical conductivity by 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). The water vapour permeability of nonwovens was determined by means of a C330H Water Vapor Transmission Rate Test System (China). The water vapour sorption, hygroscopic properties, and moisture yielding capacity of nonwoven materials were determined by a DVS Adventure AZO Materials device (UK). Nonwovens were obtained by the electrospinning of fibres from PEU solutions using Nanospider ™ technology.

Results and discussion

It is known [7] that the modification of polyether urethane solutions with compositions based on hydrophilic polymers, in particular collagen hydrolysate, makes it possible to obtain film structures with controlled heteroporosity and high hygienic properties.

As previously noted in paper [8], the possibility of obtaining fibres and nonwoven materials from PUR solutions of the Vitur TM-1413-85 brand was established. It was discovered that non-woven cloths with an average diameter of fibres from 200 to 600 nm with a minimum number of defects could be obtained from a 15% forming solution.

The task of the present study was to obtain nonwoven materials by the electrospinning of compositions based on polyether-urethane solutions modified with hydrophilic polymers to make elements of membrane modules in clothing.

In this paper we studied mixed compositions based on PUR solutions with the addition of various amounts of PAA and PVA and their mixtures. To find the ratio of components that is optimal for electrospinning, the method of phase diagram analysis was used.

When constructing phase diagrams (***Figure 1-3***), it was proven that PUR is limitedly compatible with both PVA and PAA, as well as with their mixed composition.

Based on the analysis of phase diagrams, for the production of nonwoven materials by the electrospinning method, the systems with the ratio: PUR: (PVA:PAA (1:1)) = 3:1 were chosen.

Fibres were obtained at an ambient temperature of 22 °C and humidity of 65%, and the distance from the surface of the moulding solution to the support was 13 cm (***Table 1***).

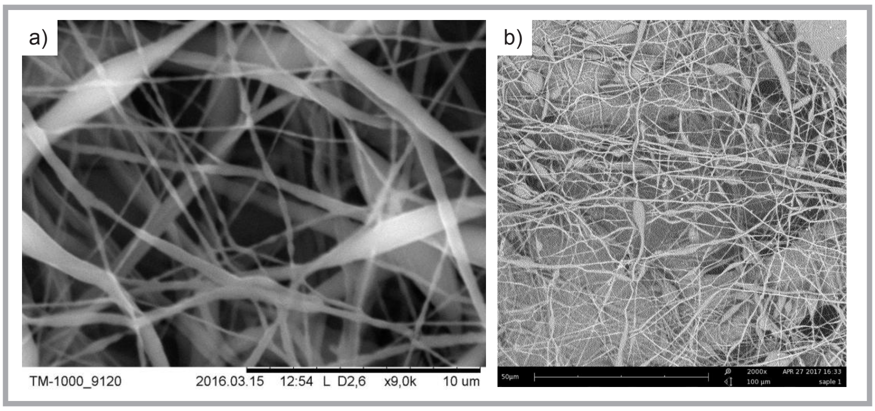

Figure 4. *Micrographs of fibres obtained by the Nanospider^{TM} method from forming solutions: a) solution PUR in DMF and b) solution PUR:(PAA:PVA (1:1)) = 3:1. Increased to a scale of 9000.*

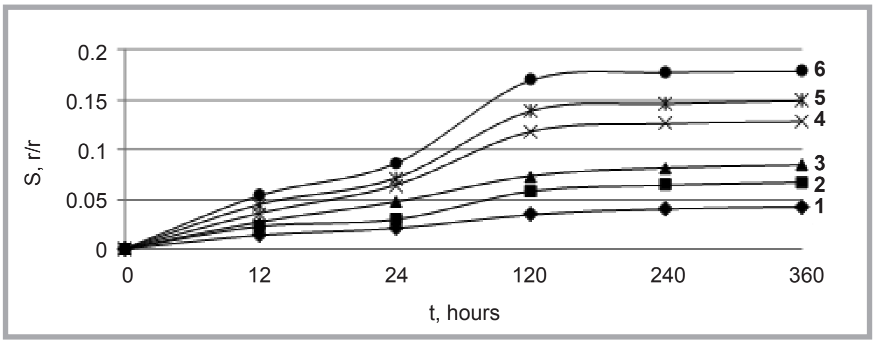

Figure 5. *Kinetics of water vapour sorption by a sample of nonwoven material obtained from a composition based on PUR, PAA and PVA at the ratio of components PUR:(PAA:PVA (1:1)) = 3:1 at a different relative humidity: 1 – 9.7%, 2 – 35.4%, 3 – 46.5%, kr. 4 – 58.6%, 5 – 88%, 6 – 100%.*

Figure 4 shows a micrograph of nonwoven materials obtained from pure (***Figure 4.a***) and modified (***Figure 4.b***) PUR solutions.

It is obvious that when a PUR solution is modified with hydrophilic fillers, the average fibre diameter sharply decreases and the fibre diameter distribution interval increases, which confirms the data in [6].

Figure 5 shows the results of determining the kinetics of water vapour sorption by nonwoven materials (***Figure 5***), and ***Table 2*** – the main indicators of hygienic properties.

Conclusions

In summary, it was shown that the transition of solutions into a metastable state, as in the case of using a hard non-solvent – water [8] and that of partially compatible solutions of hydrophilic polymers, leads to a change in the structural characteristics and properties of the fibres (porosity, fibre diameter, hydrophilic property). It is proven that in the modification of hydrophilic polymers, PUR solution increases the indicators' hygienic properties. Such a structure of the material predetermines the use of nonwovens as components of membrane stacks for clothing and footwear.

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