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Structure and Properties of Microporous Polyurethane Membranes Designed for Textile-Polymeric Composite Systems

Abstract
The paper presents the results of tests on the structure, basic functional properties and physiological comfort of microporous polyurethane membranes designed for internal barrier layers of textile-polymeric composite systems with various characteristics and practical applications. The membranes tested were prepared at the Institute of Textile Materials Engineering according to the optimised manufacturing technology which we have developed. The tests performed have shown that, depending on the process conditions used, these membranes are characterised by a low thickness of about 50 μm, a very low rigidity and a surface weight of about 40 g/m^2. Such membranes show a high overall porosity, while in addition to the through-micropores passing through the whole membrane thickness, numerous semi-closed pores are found. The uniformity of micropore distribution on the membranes' surface and their different characters are confirmed by means of SEM photographs. The membranes also show a high water-tightness of about 250 cm column of water, practical wind-tightness and a high permeability of water vapour at the same time, under static conditions amounting to about 2000 g/m^2 per 24 h (by the gravimetric method), as well as a low resistance of water vapour flow under dynamic conditions, at a level of 5-8 m^2 Pa/W. A probable mechanism of the water vapour's penetration through the membranes has also been established. Examination of the membranes with a DSC dynamic calorimeter has shown their stability within the range of both elevated and lowered temperatures, and consequently their high suitability for multi-layer composite materials designed for protective clothing used under various climatic conditions which satisfy the requirements of the current European standards.

Key words: *barrier layer, coating, membrane, micro-pore, , micro-porous coating, micro-porous polyurethane membrane, multi-layer textile-polymeric composite system, polymeric mambrane, porosity, protective clothing, resistance of water vapour, textile-polymeric composite system, water vapour penetration, water-tightness, wind-tightness.*

Introduction - review

The basic barrier materials used as so-called internal layers in various high-tech multi-layer textile-polymeric composite systems, designed for various applications, are polymeric membranes, especially polytetrafluoroethylene, polyurethane, polyacrylate, and polyester membranes [4]. Depending on the application and required characteristics of the composite system, the membrane that is its component must also show a suitable set of properties. For example, in the case of composite materials used for various protective clothing and modern sports clothes – which should show excellent barrier properties and, at the same time, good hygienic characteristics and high comfort of use –polymeric membranes with a high water-tightness should be used, to provide effective protection against soaking through and air-non-permeability, while simultaneously showing a high possible permeability for water vapour. This permeability is of importance for the clothing's hygienic value, as it allows human perspiration to be carried away from the skin surface, and secreted (to the extent dependent on the user's activities) beyond the area between the protective clothing and the human body. This prevents (correspondingly to the external conditions and work carried out by the clothing's users) the human body from overcooling or overheating, and consequently protects them against a chill and ensures a good frame of mind and comfort [1,4-7,10-16,18,19].

Hence the membranes designed for such composite materials must be characterised by high water- and wind-tightness, and simultaneously a high possible permeability of water vapour. Additional requirements include a low surface weight and thickness, low rigidity, a high bending strength within the range of temperature of using the given clothing, and resistance of the membrane to the conditions of use and washing. In some cases, resistance to heat at elevated temperatures, non-flammability and resistance to specific organic solvents are also required. All in all, the membrane used as components of specified textile-polymeric systems should provide high protective properties without any deterioration of the other features of the textile components, above all its good hygienic properties and a high permeability of water vapour [1,4,5,10-16].

These properties result from the chemical composition, structure and surface properties of the membranes. Due to the excellent performance properties of these composite systems, the problem of manufacturing appropriate polymeric membranes has been the focus of investigation in many research centres such as W.L Gore Assoc. Int. [21] and the international firm of Akzo-Nobel [22]. Currently, many water-tight and wind-tight membranes are commercially available which also display good water vapour permeability. They are made from various polymers by various techniques and have different performance properties, but information about them is vague and general, often of a largely marketing character, and is treated by their manufacturers as mere know-how [15,16,21,22,24].

Multi-layer textile-polymeric protective materials are produced from various types of water- and wind-tight polymeric membranes that are permeable to water vapour. There are two basic types: microporous membranes (mostly of a hydrophobic character), and hydrophilic

membranes with a compact structure [4,5,11,13,18,21,22,24].

The most frequently used polymeric membranes in textile-polymeric composites systems include [4,21,22,24] the following:

- hydrophobic microporous polytetrafluoroethylene (PTFE) membranes produced by the drawing process under critical conditions from tight or leak-proof membranes, which results in the formation of numerous micro-cracks or micro-porosity; this process is used to produce membranes from PTFE known under the general trade name of Gore-Tex from the American firm W.L. Gore & Assoc.s Inc., as well as many derivative materials for various applications, e.g. Gore-Tex XCR, Gore-Tex Paclite and others [19,21];
- hydrophobic microporous membranes of various polymers produced by the perforation of tight membranes, e.g. by using micro-beams of radiation of high-energy pulsation lasers or electron bombardment [4];
- hydrophobic microporous membranes, mostly polyurethane, produced by the phase separation process (inversion) as a result of selective evaporation of solvent and non-solvent. There are two basic processes: in one of them, which is called wet coagulation, the extraction of solvent is an inductive factor, while the other one involves a phase separation induced by solvent evaporation, defined as thermal coagulation. Porelle membranes of the British firm Porvair [24] are examples of this kind;
- hydrophilic tight membranes, mainly of polyester but also of polyurethane. This group includes the familiar polyester materials made by Sympatex Composites Co. under the trade name Sympatex, as well as polyurethane products BION II from Toyo Cloth [15,16,22].

The types of membranes presented above are generally characterised by high water- and wind-tightness, although they differ in the mechanism of water vapour permeability [4,11-14].

In the case of hydrophobic microporous membranes, this mechanism depends on the porous structure of material. The pores may be:

- open through-pores, where the water vapour penetrates these capillaries, while the diffusion mechanism is of negligible importance, or
- 'semi-open' or semi-closed pores, where water molecules must penetrate the thin films partitioning particular micropores; in this case, the diffusion mechanism plays a very important role.

The mechanism of water vapour permeability through water-tight microporous membranes in the simplest case of open through-pores is schematically shown in Figure 1 [4]. In order to obtain such properties, the dimensions of the micropores in a polymeric membrane should be large enough to provide free water vapour penetration in the molecular form, and simultaneously considerably smaller than the finest water drops. The dimensions of water molecules are about 0.3 nm, while in water vapour they mostly occur in the form of aggregated clusters of sizes of about 1 to 5 nm. On the other hand, the size of the finest water droplets (in liquid phase) is about 100 000 nm, thus being higher by four orders of magnitude [4,13,14].

In the textile industry, the widest application is found for PTFE membranes with a microporous structure, produced by the drawing process, while the most frequently used are polyurethane or polyester microporous membranes made by the process of a controlled phase separation from three- or multi-component systems (pre-polymer, solvent or a mixture of these, and non-solvent). The phase separation is a process in which the homogeneous pre-polymer solution in specified solvents changes into a gel to form a macromolecular network of polymer with a liquid phase dispersed in its structure. Such a solution is unstable, and can be changed into a two-phase system under the influence of various factors; one of the phases so produced is characterised by a high polymer concentration, and the other by a low polymer concentration. The phase that is richer in polymer is solidified after the phase separation to form a microporous membrane. The properties of such a membrane depend on the condition of phase separation and solidification. The phase separation of polymeric solutions can be induced by many factors, with the change in the composition of membrane-forming solution being the most frequently used factor to cause inversion. Considering the factor that causes the phase separation, several methods for producing of microporous polymeric membranes can be distinguished, the most important of which in the case of the membranes used in textile systems is the separation induced by solvent extraction and solvent evaporation. These methods are also known as wet and thermal coagulations. In both coagulation methods, the micro-capillaries are produced by selective removal of the solvent of pre-polymers and non-solvent (water) [4,16,20,23,25].

In the thermal coagulation process, the set of 'solvent and non-solvent of pre-polymer' should be selected so that these liquids can be partially mixed in the proportions used to be able to dissolve the pre-polymer. The base of coats of this type may for example be a one-component urethane pre-polymer in the form of a solution in a proper organic solvent, e.g. methylethylketone (MEK), toluene or various solvent mixtures.After being alkalised, such polymers are capable of absorbing considerable amounts of water to form a stable oil-in-water emulsion that is used as a coating paste in the direct or reversible coating processes. Once such a coat is applied onto a suitable carrier, it is dried under conditions of multi-stage gradual thermal treatment, during which a microporous structure is formed. The solution of polymeric products in the composition of the coating paste is metastable; the phase division is not self-acting, but occurs under the influence of the change in solvent concentration. This change results from the selective evaporation of organic solvent/solvents due to the lower evaporation temperature in relation to the non-solvent, water. The proceeding process of organic solvent (or mixture) evaporation leads to an increased water content in the coat, until the moment when the polymer is precipitated and coagulated. The further evaporation of solvent residue and water results in gouging micro-capillaries in the partially-formed coat structure to create micro-porosity. The microporous coat structure obtained this way is then sta-

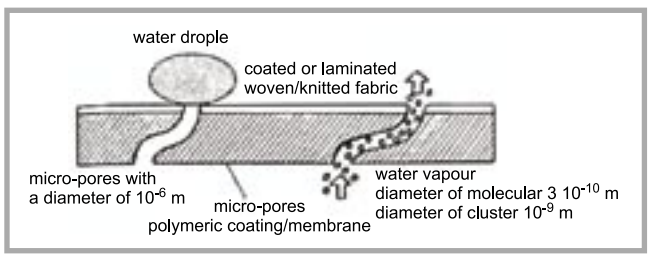

Figure 1. *Principle of water vapour permeability in a textile product with a hydrophobic microporous coat of open through-pores.*

bilised by polymer cross-linking, which takes place under conditions of an appropriate thermal treatment [1,4,16,20,23].

Research into microporous polyurethane membranes

Basic process conditions

Studies on the technology of producing polyurethane microporous hydrophobic membranes by the process of thermal coagulation were undertaken long ago at the Institute of Textile Materials Engineering (ITME). The choice of this specific method was on the one hand justified by the membranes' good performance properties, and on the other by the fact that no substantial machinery investments were necessary and the existing installations in Polish textile plants could be used. The commercial availability of indispensable polymeric products and other additives is also of crucial importance, as are reasons of patent.

However, as shown by preliminary trials, this technique has turned out to be difficult in realisation, despite its relative simplicity, and the preparation of stable, high-quality coats/membranes proved to be difficult to accomplish. The preparation of coats/membranes of a stable and high quality which also display the required properties depends on the proper selection of numerous specific process parameters and their optimised values. These parameters relate to the preparation of coating pastes as well as to the conditions of coating, drying and final thermal treatment of the coats, and they must be adapted to the characteristics of the used polymeric products and additives, as well as to the technical capabilities of existing equipment for the coating process. Such basic process conditions include the following [1]:

- type of polymeric products and various additives used for the preparation of coating pastes, and appropriate selection of their characteristics and quantitative proportions of components,
- the composition of the coating paste, quantitative relations of the membrane-forming polymeric products, addition of solvent/solvents and the non-solvent, water,
- the optimised process of coating paste preparation, and the proper sequence of component addition,
- the selection of paste composition and dry solid content, as well as the rheological properties of pastes in relation to the used coating technique (direct or reversible coating), and the process of coat application,
- the selection of coating conditions (single- or multi-layer coating, application with doctor blade, roller or template, contents of particular layers, total content of pastes),
- the selection of the multi-stage convection drying process, during which the microporous structure of membranes is formed;
- in the case of two-stage reversible coating, the conditions of transferring the coats from an indirect carrier onto a textile one, and
- the conditions of the final thermal treatment, during which polymer is cross-linked and the microporous structure of the membrane are stabilised.

These optimised process conditions were determined during systematic studies [1-3,5,10,11], which allowed the production of membranes of good and stable quality. The basic determinants of this quality include the character and uniformity of the microporous structure and the thermal properties of membranes which define their barrier, as well as water- & wind-tightness and physiological properties such as water vapour permeability, strength parameters, suitability for combining with textile carriers and other components of the multi-layer composite systems, and the resistance of these systems to conditions of use and repeated washings.

Detailed process conditions are included in the ITME know-how [1]. These have been developed on the basis of systematic studies on the effect of process parameters of known thermal coagulation methods on the properties of membrane materials. Thus, these studies were carried out to optimise and to accurately define the general process conditions included in the information provided by various pre-polymer manufacturers, indicating crucial parameters of the product's quality. The production of polyurethane membranes according to these optimised conditions results in products with a high quality standard and performance properties similar to those of known world-leading products for similar types and applications, such as Porelle of Porvair Ltd. [24]. According to the comparative research data published by CIBA, this kind of membrane is characterised by a water-tightness of 250-300 cm of water column, and a water vapour permeability of 1200 g/m^2 per 24 h or a water vapour resistance (R_{et}) of 7 m^2 Pa^{-1} W^{-1} [23]. The highest water vapour permeability, and consequently the lowest water vapour resistance, is shown by the microporous PTFE Gore-Tex membranes, with an R_{et} value ranging from 2.1 to 2.5 m^2 Pa^{-1} W^{-1} [21,23]. However, it should be mentioned that hygienic properties reported by the manufacturers of these products, such as water vapour permeability or resistance of polymeric membranes, refer to various testing conditions that are often completely unspecified. On the other hand, it is known that the value of water vapour resistance is considerably affected by such test conditions as temperature, relative humidity of air or membrane thickness. Hence the data included in the companies' information is difficult or even impossible to compare [1,2,4,12,14,16].

The basic criterion for the process optimisations as implemented was to obtain the assumed parameters of water-tightness and water vapour permeability that must be met within the range of ambient temperatures corresponding to the conditions of using the composite fabric for specified applications [1,11].

The microporous polyurethane membranes produced under such optimised conditions were tested to determine their structure and physical, chemical & performance properties, as well as the most probable mechanism of water vapour penetration.

Test methods for the final products

Considering the flaccidity of microporous membranes, most of the tests were carried out on membranes laminated with standard textile carriers, using the following test methods [1-3]:

- thickness determined according to standard PN-EN ISO: 1999 [27], with the use of an MO34A type digital thickness gauge, from SDL Int. Ltd. (England);
- surface weight determined by the gravimetric method according to standard PN-ISO 3801:1993 [26];
- disruptive strength (ball test) determined according to standard PN-P-04738:1978 using an apparatus for disruption with a ball, installed in an Instron TM tensile testing machine (England);
- tensile strength determined according to standard PN-EN ISO 13937:2002 part 3., with the use of a ZW-2.5/TNiS type 1120 tensile testing machine, from Zwick GmbH (Germany);
- resistance to repeated bending determined in accordance with standard

PN-EN ISO 7854 test method A, using a Bally-Test flexometer;
- thermal properties of the membranes tested by the DSC method, using a dynamic DSC-204 calorimeter from Netsch (Germany);
- water-tightness determined by measuring the water column pressure at which water penetrates through the tested fabric, according to standard PN-EN 20811:1997 [29], with the use of a Penetrometer FX 3000 from Textest A.G. (Switzerland);
- water vapour permeability under static conditions, determined by the gravimetric method, measuring the quantity of water vapour in grams, passed through the sample surface under specified conditions according to test procedure NJC/2/95-IIMW [32]. Silica gel was used as drying agent, under the following climatic conditions: T = 37 °C; RH = 90%; v = 1 m/s; t = 24h.
- resistance of water vapour flow under dynamic conditions, tested with the use of a Sweating Guarded Hotplate M259B from SDL Int. Ltd., whose basic element consists of a special microporous plate that simulates human skin. Measurements were carried out according to standard PN-EN 31092: 1998/Ap1:2004 [2,31], while the resistance of water vapour flow, $R_{et,}$ was defined according to this standard as a quotient of the difference in pressures of water vapour between both sides of the material, and the difference resulting from this in the flow of evaporation heat through a unit surface according to the pressure gradient;
- air permeability was determined according to standard PN-EN ISO 9237: 1998 [28], using a Textest FX 3300 apparatus from Textest A.G. (Switzerland).
- total porosity (open through-pores), the fractional distribution of pores and the average and maximum pore diameters, measured using a capillary porometer from PM (USA).
- microphotographs of membrane surfaces, taken by means of a scanning electron microscope JSM 550 LV from JOEL. The membranes were tested under a high vacuum, using a detector of secondary electrons. Based on the microphotographs of the membrane surface, with the use of the WSxM program for image analysis (Nanotec Freeware, Spain), the total porosity was assessed (the percentage content of the surface occupied by pores in relation to the surface of the tested area), as well as the average distance between the middle points of the adjacent pores and fractal measure, which provides information about the pore shape. Using the analysis of the surface image, the histograms of surface area and pore perimeter were worked out.
- resistance of the membranes to the conditions of repeated washing (5 washings) in water according to PN-EN ISO 6330:2002. [30], procedure 5A (40 °C). Considering the high flaccidity of membranes and their natural susceptibility to 'sticking' in a bath under conditions of intensive mechanical effects, tests were carried out with model multi-layer systems containing membranes designed for sports clothing. After washing, the systems were tested again to assess the changes in water-tightness and the resistance of water vapour flow and heat, in relation to the corresponding parameter measured before washing. Tests were carried out with the use of a Wascator FoM 71 MP LAB automatic washing machine from Electrolux (Switzerland).

Test results - Features of the obtained membranes

The tests performed showed that the polyurethane hydrophobic microporous membranes produced under optimised process conditions are characterised by the following features [1]:
- low thickness of about 35-50 μm (depending on coating process);
- very low rigidity and good resistance to repeated bending (no visible changes after 10 000 bending cycles);
- a surface weight of about 40 g/m^2;
- good and stable barrier properties – water-tightness at a level of about 250 cm, and practically total wind-tightness;
- good hygienic properties: high water vapour permeability (tested by the gravimetric method under static conditions at a level of > 2000 g/m^2 per 24 h), relative resistance of water vapour flow under dynamic conditions at a level of 5-8 m^2 Pa/W. It should be added that according to the classification system developed by the German Hohenstein Institute, membranes with R_{et} < 6 m^2 Pa/W are considered as products with very good (the highest) hygienic properties, those with R_{et} < 13 m^2 Pa/W as good membranes, while passable membranes show R_{et} = 13-20 m^2 Pa/W; when R_{et} > 20 m^2 Pa/W, the hygienic properties of membranes are unsatisfactory [18]. The appearance of the surface of microporous membranes and the uniformity of pore distribution are shown in the SEM photograph (Figure 2).

Analysis of the abundant photo material has shown that the micropores are generally uniformly distributed on the membrane surface. The SEM photographs of membrane cross-section show that the shape of micropores is variable along their length and their arrangement is multi-directional.

This variable arrangement suggests that the pores inside the membranes form a complicated network of micro-capillaries, of which only some portion is visible on the membrane surface, while the pores are of through- and non-through character, as illustrated in Figure 3 [1].

- The porosity tests show that the size of pores, their distribution on the membrane surface and the degree of its coverage with pores for the membranes produced under the optimised conditions we developed present themselves as follows [1]:
  - the average diameter of micropores is about 2 μm (ranging from 1 to 3 μm), while only a small portion of pores show higher diameters of 8-9 μm;
  - the coverage of membrane surface with pores amounts to 50%;

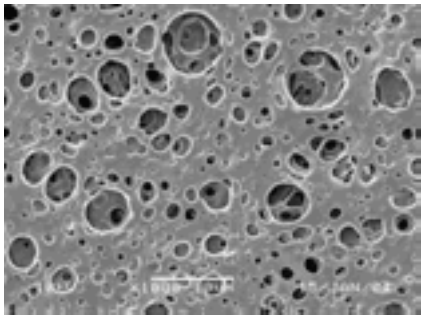

Figure 2. *SEM photograph of the surface of the polyurethane micro-porous membrane (back side adhering to the carrier), magnification × 1000 [1].*

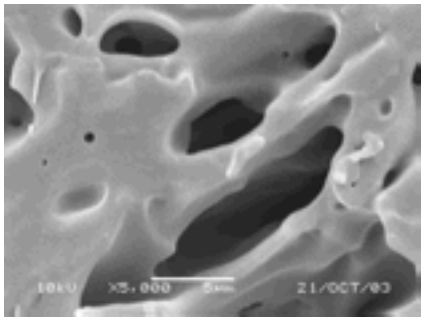

Figure 3. *SEM view of micro-pores in the cross-section of membrane, magnification × 5000 [1].*

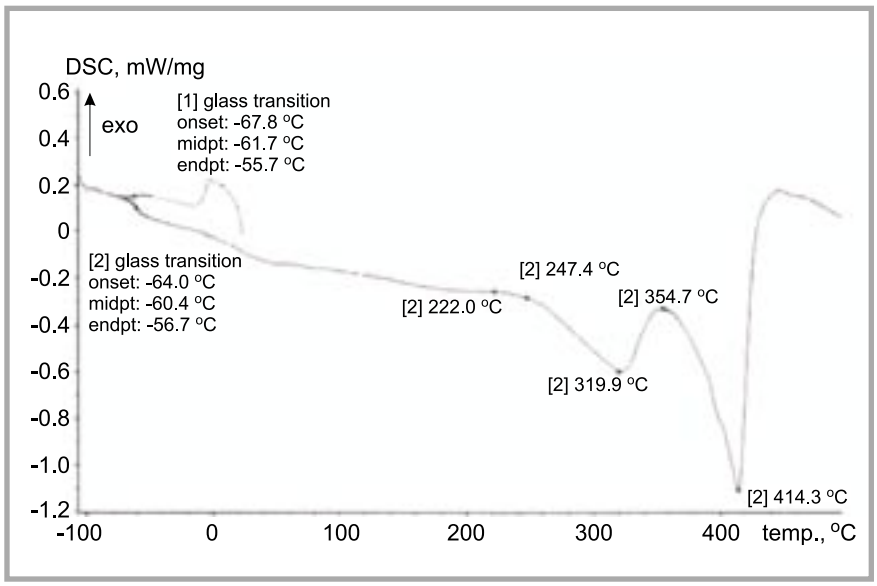

Figure 4. *DSC curve of micro-porous polyurethane membrane [1].*

- the total porosity, ε_o, i.e. the pore content in the volume unit, is at a level of 35%.

- When analysing the results of water vapour permeability and comparing them with the results of porosity tests and SEM photographs of membrane surfaces and their cross-sections, we can conclude that not all the openings (craters) visible in the SEM photographs correspond to open through-micropores, and that at least a portion of them have a closed structure, while individual pores are separated with thin partitions through which water molecules diffuse. Hence, the mechanism of the penetration of water vapour through the hydrophobic polyurethane microporous membranes is complex: in addition to a simple transport of water molecules through micro-capillaries, there is also diffusion [1,10].
- The measurements of the membranes' thermal properties performed with a DSC dynamic calorimeter have shown that their thermal stability ranges from -60 °C to +299 °C; these results confirm the suitability of the produced membranes for use in multi-layer clothing systems to be used under various climatic conditions. This is illustrated by the DSC curve of an example microporous membrane shown in Figure 4 [1].

As follows from the above results of tests on the microporous polyurethane membranes, as produced under the developed and optimised process conditions, and included in the know-how, the basic performance properties of these materials such as barrier and hygienic properties (water-tightness and water vapour resistance) are at the same level as those of world-renowned products of similar types [24], such as those from Porelle of Porvair, and similar to those of tight polyester membranes of the Sympatex type (lower water-tightness and better hygienic properties, as well as lower water vapour resistance) [23]. It should be mentioned that according to information available from Sympatex Composites GmbH, the three-layer composite systems containing Sympatex membranes as the middle layers are characterised by the water vapour resistance R_{et} = 6 – 15 m^2 Pa/W depending on the type of textile component materials [23].

Summary

- Based on the tests and measurements of the hydrophobic polyurethane microporous membranes produced by the method of phase separation induced with solvent evaporation, relationships have been established between the microporous structure and the surface's morphology & performance properties: water- and wind-

Table 1. *Basic barrier and physiological properties of exemplary materials for component layers and the composite materials .*

Layer	Composition of the composite system	Properties of component materials				Properties of the composite material			
		Water-tightness, cm water column	Air permeability, mm/s	Resistance of water vapour R_{et}, m^{2}Pa/W	Thermal resistance R_{ec}, m^{2}K/W	Water-tightness, cm water column	Air permeability, mm/s	Resistance of water vapour R_{et}, m^{2}Pa/W	Thermal resistance R_{ec}, m^{2}K/W
External	- PES woven fabric	259	62,8	4,38		278	0.0	35.89	0.113
Middle	- M.H.M. *) on PES knitted fabric		0	7.51					
Internal	- Polar knitted fabric		874	22.90	0.092				
External	- PES woven fabric	253	67.0	5.28		275	0.0	44.38	0.219
Middle	- M.H.M. *) on PES knitted fabric		0.0	7.55					
	- PES nonwoven		2491.0	26.00	0.180				
Internal	- Polar knitted fabric		1415,0	3,35					
External	- PES woven fabric/hydrophobic micro-porous coat	234	2,8	6,33		249	2,4	37,66	0,153
Internal	- Polar knitted fabric		896.0	22.90	0.092				
External	- PES woven fabric/hydrophobic micro-porous coat	237	2.6	6.33		245	2.3	37.39	0.196
Middle	- PES nonwoven		2350.0	26.00	0.180				
Internal	- PA woven fabric		1420,0	3,35					

*Note: *) M.H.M. - micro-porous hydrophobic membrane.*
Test methods: water-tightness: according to standard PN-EN 20811:1997 "Textiles. Determination of water-tightness. Hydrostatic pressure method"; air permeability: according to standard PN-EN ISO 9237:1998; resistance of water vapour flow under dynamic conditions (measured by the method of "sweating plate" according to standard PN-EN 31092:1998.Ap1.2004. "Textiles. Determination of physiological properties."); thermal resistance according to standard PN-EN 31092:1998. Ap1:2004.

tightness, resistance of water vapour flow and water vapour permeability on the one hand, and the process conditions of membrane production on the other hand.

- In order to assess the performance stability of the membranes produced, analogous tests were also performed with membranes subjected to repeated washings (5 cycles). These tests showed only a slight drop in the membrane's water-tightness, and almost complete stability of the remaining performance & hygienic parameters, including water vapour permeability.
- The tests and measurements performed allow the effect of various process factors on the structure and performance properties of the polyurethane microporous membranes to be assessed, which allows this structure and properties to be optimised and adapted to their intended conditions of use.
- A probable mechanism of water vapour flow through the polyurethane microporous membranes has been determined; the comparison of the diffusion coefficients of water vapour in porous membranes of about 10^{-3} cm^2/s with the coefficients of water vapour in polyurethane amounting to 10^{-6} cm^2/s and in air of 10^{-1} cm^2/s, as well as the complex nature of the water molecules' path in the porous membrane, leads to the conclusion that the flow of water vapour takes place in pores, and shows a diffusive character.

Conclusions

The tests performed on the performance and hygienic properties of the produced microporous membranes, and on the multi-layer textile-polymeric composite systems that contain those membranes, allowed us to confirm the suitability of these membranes for the production of modern high-tech materials, as shown by the test results of the microporous membranes and coats, as well as other components material and the model composite systems obtained from them and listed in Table 1. These systems fully meet the requirements for this type of fabric as presented in the current European standards, including EN 343:1998 'Protective clothing. Protection against rain.' [33] and PN-EN 14058 'Protective clothing. Sets of clothing protecting against cold' [34].

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