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POSSIBILITY OF USAGE OF POLYMERE MEMBRANES FOR PROTECTIVE CLOTHING PRODUCTION

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Abstract. *Workers in chemical industry are, while workong exposed to substances which can cause domages to external tissue or to internal organs. Chemica,l with wich workers come in concact can be in several forms (liquid, mist, vapour, etc.) The damages caused can range from mild skin diseases to more serious chronic ilnesses, such as lung edema or cancer. Therefore, the choice of textile materials and constructions used for protective clothes production is very important.*

INTRODUCTION

Literature data show that no textile material can guarantee a 100% protection against every chemical, even when a completely closed clothing is made out of it. Therefore, manufacturers of protective clothing have the responsibility to make the right choice of textile materials so as to create a barrier fabric with adequately selected characteristics for every single danger.

The choice of materials is often based on laboratory measuerments of penetration or speed of penetration of specific chemicals through a polymere film or the basic fabric. Comparative data for a wide and representative range of chemicals are useful, but they usually relate to older polymere types used in layered and laminated fabrics, where primarily protection and only then comfort were considered [1]. Compurterized data base of permeation and other parameters is useful in selecting textile materials for protective clothing.

The latest research shows that protective clothing must both protect the user against harmful chemical and provide a satisfactory wearing comfort. Protective clothing should support thermo-regulation processes of human body. In order to enable normal

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functioning of these processes, the clothing should be vapour permeable as much as possible, since the "cooling effect" caused by evaporation of sweat is one of the most important mechanisms thet human body thermo-regulation keep in equilibrium. Moisture remaining under the clothing is felt as unplessant, and under certain circumastances, it is also unhealthy. It can cause collapse, even in a moderately warm climate and at moderate physical effort. This characteristic is a serious disadvantage of protective clothing, since its user must have certain comfort over a longer period of time.

In order to enable protective clothing to fulfill its purpose entirely, a lot of research has been in recent years.

Research conducted in this paper was aimed at developing materials that can successfully fulfil two basic tasks: good protection and good permeability in order to take perspiration products away from the underclothing space ("microclimate").

As a result of this research, three kinds of fabric were put on the market: conventional materials treated with hydrophobic finishes, materials consisting of compact polymere layers and materials consisting of microporous layers.

An important momentum to the development of new materials for protective clothing was given by the production of micro-fibres and very thin polymere films-membranes.

Results of this intergrated research were not only new materials but new examination methods as well, standardized as ACCP methods.

Since the largest part of the previous research on the development of new materials is not available, nor is the procedure of polymere membrane building into the protective clothing, the need arised to examine these materials. That was the purpose of this work.

1. POLYMERE MEMBRANE

In recent years, thought not sufficiently, we meet tchnical information on products of a great strategic importance. One of them is vapour-permeable but water-impermeable clothimg. An english term for such clothing is "breathable fabrics" meaning that they enable perspiration products to be taken away from the body, but prevent the penetration of water from the outside.

This double function can be realized through a new construction of fabric, which can separate vapour from liquid, owing to pore dimensions in the fabric.

Polymere membranes have 1.1 to 1.4 milion pores per 1 cm^2. Pore diameter is about 0.2 μm, and that is about 500 times smaller than the finest drop of fog. Fig. 1 shows the functioning principle, i. e. membrane protection [2].

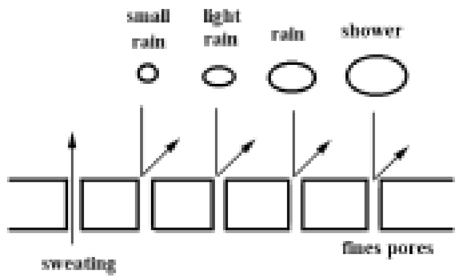

Fig. 1. Scheme of against atmospherials and principe of vapour prmeability and water impermeability

On the basis of this figure, it can be concluded that the penetration of liquid through the membrane is not possible, due to drop dimensions, i. e. small pore diameter. These are the characteristics of a polymere membrane which can be applied on the basic material or on the lining.Howeever, these two ways of membrane application were shown to be ineffective in clothing wearing, since under tension, polymere membranes were worn out and damaged, and at those spots the clothing lost protection against water penetration from outside.

Basides, this way of application of polymere membranes, caused the apperance of condesate on the inside of the basic material or lining, after a longer wearing period. The condesate reduced the protective function of the clothing as well as working abilites of the user. The condensate was caused by the reduced transport of sweat from the underclothing space into the outer space. For that reason, polymere membranes for protective clothing production should be used as laminates because in that form they can comply with the requirements.

Today for laminates production, i. e. for water-impermeable but vapour permeable clothing production, two types of polymere membranes are mostly used:

- Hidrophilic membrane from modified polyester
- Micro-porous membrane from polytetrafluorethilene

1.1. Hidrophilic membranes obtained from modified polyester

Details conncerning components and their participation in membrane composition are, unfortunately still hidden in complex patent specifications, and remain the secret of polymere producers. So far, it is known that these polymere membranes are obtained from modified polyester. When using clothing made of laminates with this membrane, thermo-physiological characteristics of clothing are insignificatly reduced while other characteristics remain unchaged.

Such a good protective function of the membrane is anabled by its limited swelling in water. Swelling in vapour and water is the result of the basic polymere composition, which is in fact combined (form) copolymere, synthetized from two basic components, dicarbonic acid and glycole:

which represents the basic structural unit, while hydrophile part of the polymere chain consists of polyester line.

The amount of vapour that passes though the membrane dependes on polymere chemical composition, swelling extent and coeficient of diffusion through the membrane. It also depends on the thicknees of the membrane and vapour concetration on the both sides of the membranes, i. e. on the difference between the vapour concentration in the underclothing space above the skin, and the vapour concetration in the outside microclimate.

As a rule, vapour concetrtion above the skin is higher than the concretration on the other side of the membrane, so the vapour is transported through the membrane into the outside space.

The amount of the vapour passed through the membrane expressed as mass/time is proportional to the diameter and number of pores, and inversely proportional to the membrane thickness.

A group of researchers [3] calculated the amount of the vapour passed through W (vapour permeability) from the Hager-Pusselle equation of flow:

$$W = \frac{d^4 \cdot \rho \cdot n \cdot g_c}{1.09 \cdot 10^2 \cdot L}$$

were: d – pore diameter
ρ – density
n – pore number
g_c – gravitation acceleration
L – membrane thickness.

The calculation of vapour concetration under and above the membrane is influenced by air flow, i.e. by heat transfer by convection.

Hydrophilic membrane can be porous, and then vapour transportation is done directly through the pores. Membrane can be closed but hydrophilic, so that vapour transportation is enabled through polymeres. Porous membranes with pores protected with a thin hydrophilic layer are more and more used recently for protective clothing production.In this way, problems characteristic for pore principle are avoided: mechanical features weakening in relation to polymeres, that are not porous. Fig. 2 shows the netting of pore walls.

$$HO - \left[- (CH_2)_n - O \right]_n - H$$

Fig. 2a. Scheme of copolymer molecules arrangement in polymere membrane

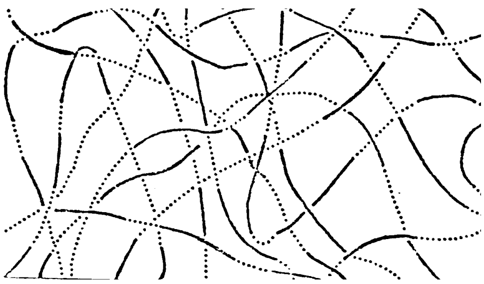

Fig. 2b. Copolyester molecules arrangement in a hydrophilic polymere membrane

Water impermeability of micro-porous system is based on the small dimensions of pores in combination with pore walls [4].

Connecting the membrane with textile materials, so called lamination, in order to obtain membrane laminates can be achived through various procedures:

– appllying the glue from solution by means of pressure
– appllying the glue from in the from of foam
– appllying powder particles
– applying the paste
– connecting with the glue in the foam form
– pappering with flame.

1.2. Micro-porous PTFE membranes

Micro-porous membranes have come out on the market recently. A typical representative is polytetrafluorethilene (PTFE) membrane which has become micro-porous through the procedure of a double-axial orientation.

This membrane has fine cells with pores whose distribution is very narrow. PTFE membranes are water resistant.Membrane is plastic material with no elasticity, which means that it is very sensitive to extension. For that reason, in prodiction of quality clothing, a laminate is used, since a membrane in a laminate is mechanically protected.

There are several procedures for micro-porous membrane production [5]:

– mechanic fibrillation
– polymere dissolution in a solvent
– phase separation
– solvent extraction
– bombardment (collision) with electrons
– ultraviolet radiation-electronic bombardment
– coating through foam pushing

Mechanical fibrillation is a process of a certain polymere of crystal or semi-crystal character and biaxial extension which produce microscopic ruprures throughout the membrane, which gives appropriate micro-structure for barrier layers against water.

Fibrillated polyolefines are, for this purpose, shaped into thin membranes of hard PTFE, which are transformed into more elastic membranes through extension and thermic treatment. In extended form, breaking strenght is three times greater.

Membrane structure consist of PTFE particles conected with one another with numerous fine fibrilles.

Polymere dissolution ia carried out in a suitable solvent which is mixed with water and then, in that form, applied onto the textile base (backing) to form laminates. Initial structure is developed by pasing through a coagulation bath, where solvent is removed by means of water. This method is a pre-condition for porosimetric technic [6].

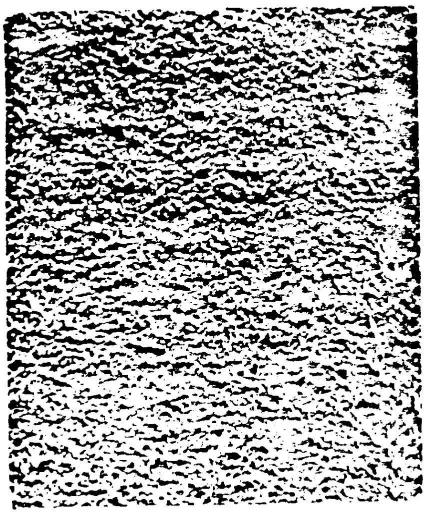

Fig. 3. Micro-porous membrane Appearance

For certain fabrics (backing), micro-porous aluminium layers can be used, in order to improve heat isolation by re-flecting the heat from the user’s body. However, it is still unreliable, since it is difficult to determine the amount of heat surplus that can be taken by metallized laminates, having in mind that heat loss through the clothing is performed

through conduction and convection processes, and not through radiation [7].

Fig. 3. shows one of the membranes from this group.

Phase separation is a process of coating of polymere from the mixture of easily evapourable solvent and part of the non-solvent, having higher boiling point [8]. Micro-porous membranes are obtained

Delicately distributed, salts or other components dissolved in water, can be shaped into a polymere [9]. However, this proces is quite complex and time consuming and therefore infrequently used.

Production of protective clothing fabrics using electron bombardment is used for hard coated fabrics, which, in order to becime micro-porous, must be subjected to the bombardment of polymere coating by electronic rays.

The proces goes like this: coated fabrics are placed between two electrodes that produce electrons of high voltage. Electrons perforate the coating without damaging the fabric lying underneath. Electrons can be focused in a discrete radiation, which produces over a billion pores per 1 cm^2. Pore diameter ranges from 0.1 μm to 0.2 μm.

Electron bombardment perforation method produces the structure in which surfaces are connected by uninterupted pores or cylindric capillaries, as is shown in Fig. 4. However, this method was not a great commercial success.

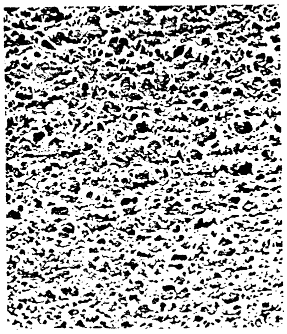

Fig. 4. Porous membrane whose pores were made by electron bombardment

UV-EB proces of plastic films hardening enables bombardment of films by ultra-violet radiation. For this purpose, Sunbeam proces for micro-porous films and membranes production using monomere connection with electronic rays or ultra-violet light, is mostly used.

This technology with low surface energy gives membranes with good chemical stability.

Coating through foams pushing in a mechanical way which are applied on aappropriate textile backing gives coatings. These coatings usually have large surface of pores, which become more compact through pressure cylindres rolling which produce micro-porous fabrics with small liquid permeability.

In other methods, surface pores in formed membranes are connected with a huge net of microscopic openings and passages. Air and vapour pass through these openings but liquid drops cannot.

PTFE membranes have a perfect symetric structure with uniform pores, including the ones on the surface. In each PTFE membrane production process, the basic task of the membrane should be always borne in mind: membrane protective function must be impaired during clothing exploatation.

PTFE membrane scope of application, has so far been, in clothing production.

2. EXAMINATION RESULTS

2.1. Results of laminate examination to vapour permeability

In the experiment, laminates of various structures and membrane thicknesses were examined. The following parameters were varied: membrane thickness, laminate backing surface covered with glue and hydrophobness of laminate carrier treatment, in order to determine the influence of these parameters on vapour permeability and water impermeability of the clothing made with laminates.Howeever it must be borne in mind that realization of double function of polymere membranes, i. e. laminates, that are built into clothing as inter-lining, must not impair:

– appearnce
– feeling
– thermo-physical features.

Laminate L-1 is made of a membrane consisting of 100% PES built in a backing consisting of 100% cotton in knit from. Polymere membrane thickness for this laminate is 10 μm.

Laminate L-2 is made of membrane consisting of 100% PES built in a backing consisting of 100% cotton in knit from. Polymere membrane thickness for this laminate is 15 μm.

Laminate L-3 is made of membrane of 100% PTFE, built in a carrier in the felt from. Polymere membrane thickness for this laminate is 20 μm.

Laminate L-4 is made of membrane of 100% PTFE, built in a carrier in the felt from. Polymere membrane thickness for this laminate is 25 μm.

Such a choice was made for two reasons. The first one was the fact those laminates constitued almost 94% of the laminates present on the market, and the second one was the desire to thoroughly examine the basic laminate parameters that influenced vapour permeability and water impermeability, i. e. their influence on achiving compatibility between thermoplastic and non-thermoplastic materials.

The amount of vapour passed through the membrane expressed as mass/time, is proportional to the product of diffusion coefficient and the difference between vapour pressure, and reciprocal to the membrane thickeness value. Air flow influenced the equalization of the vapour concentrations under and above the membrane. In order to make laboratory conditions more similar to conditions in practice, examinations were performed on three surfaces: original surface, five times washed surface and dry cleaned surface.

In order to confrim these conclusions, comparative values of membrane permeability for vapour are given in Fig. 5.

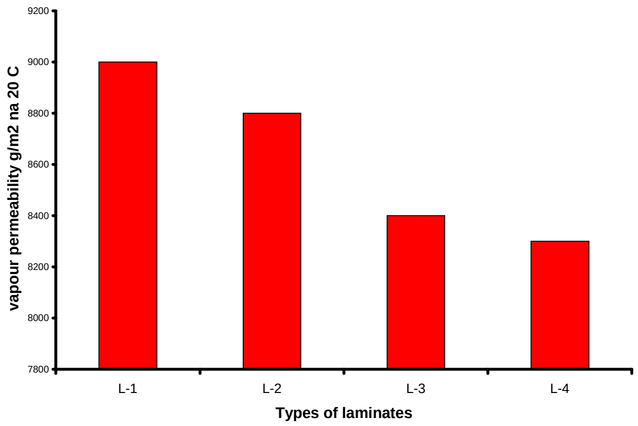

Fig. 5. Comparative values of vapour permeability of the examined laminates

It can be seen that vapour permeability of all laminates is approximately the same. It only varies in dependence on the laminate thickness, which is shown in Fig. 6.

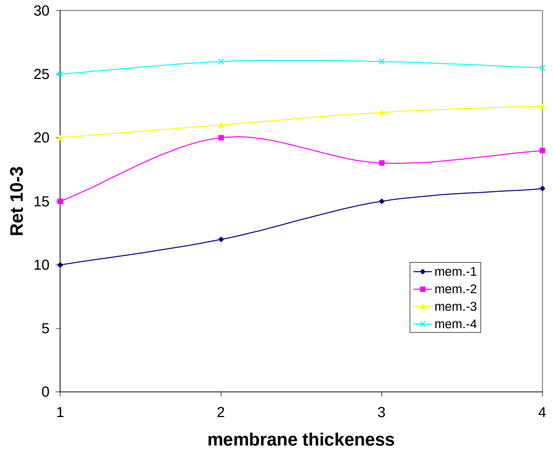

Fig. 6. Influence of the membrane thickness on laminate vapour permeability

Fig. 6 shows that vapour permeability is higher if a laminate polymere membrane is thinner. The experiment showed that appart from this factor, laminate backing surface also influenced the laminate vapour permeability, as it is shown in Fig. 7.

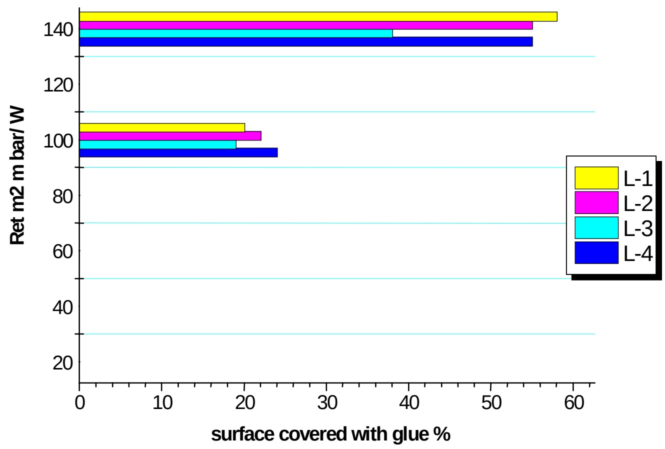

Fig. 7. The influence of carrier serface covered with glue of the examined laminates on vapour permeability

2.2. Results of laminate examination to water permeability

In order to make laboratory examinations similar to the conditions in practice, examinations were performed for friction resistance, flexion and extension, since during wearing, laminates in protective clothing are exposed to such strains in the areas of elbows and knees. These examinations were carried out together with the examinations to laminate water impermeability.

Fig. 8. shows comparative values of laminate water impermeability in dependence on the convexity height.

convexity height	sample	obtained values, mbar
30 mm	L-1	135
30 mm	L-2	138
30 mm	L-3	130
30 mm	L-4	134

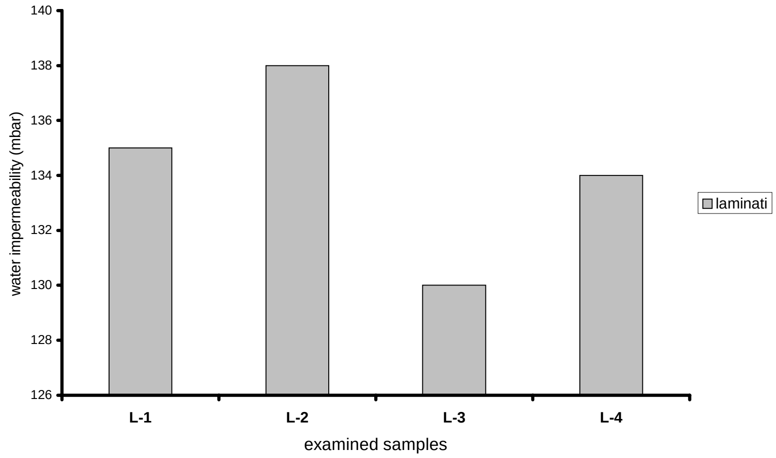

Fig. 8. Comparative values of laminate water impermeability in dependence on the convexity height.

The results obtained showed that all examined laminates had good ability of mambrane extension, since heigh convexities were achived without any damages to the membrane.

Examination of laminates water resistance in dependence on the strain caused by rubbing, both in a dry state, gave good results shown in table 1.

Table 1. Comparative values of laminate examinations in dependence on abrasion

laminate	at the number of revolutions of a working element		
	1000	5000	10000
L-1	134 mbar	132 mbar	131 mbar
L-2	137 mbar	135 mbar	133 mbar
L-3	137 mbar	134 mbar	133 mbar
L-4	138 mbar	135 mbar	133 mbar

Examination of flexion resistance under real codition gave results adequate to the requirements of wearing the clothing made of the examined laminates more than five seasons of wearing with unimpaired water permeability, the value of which is given in DIN 61539.

Table 2 shows comparative results of laminate water impermeability examinations in dependence on the holding time of a flexed sample.

Table 2. Comparative results of laminate water impermeability examinations in dependence on the holding time of a flexed sample.

laminate	flexion duration	
	2 weeks	5 weeks
L-1	134 mbar	132 mbar
L-2	137 mbar	133 mbar
L-3	137 mbar	133 mbar
L-4	138 mbar	133 mbar

2.3. Examination results of membrane laminates to water permeability under pressure

Fig. 9 shows the results of measurements of laminate fastnees to water under pressure.

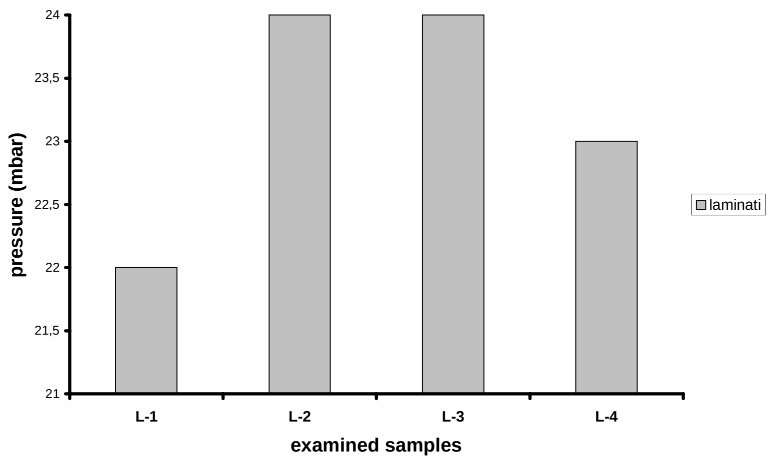

Fig. 9. Laminate fastness to water under pressure

The graphs show that measuring procedure made it possibile to diferentiate between membrane types of the examined laminates, which means that water resistance under pressure depends not only on the membrane type but also on the laminate structure.

2.4. Results of mambrane laminates axamination to air permeability

Air permeability was carried out on all four laminates, and the examination results are given in tables 3. The experiment was performed under following conditions: maximum amount of air flow at the pressure of 20 mbars was 3001 (m^2s), underpressure was 20 mbars, and the dimensions of the examined samples were 50 cm^2.

Table 3. Laminate L-1 resistance to air permeability

No.	sample	air permeability l/ (m^2s) for laminates			
		L-1	L-2	L-3	L-4
1.	original surface	0	0	0	0
2.	five times washed surface	0	0	0	0
3.	after dry cleaning	0	0	0	0
		0	0	0	0

Results show that examined laminates have no air permeability.

CONCLUSION

On the basis of the examinations it can be concluded:

Laminates consisting of polymere membranes and textile carrier, can be built in protective clothing as inter-lining, and they represent a new generation of textile materials.

Owing to their features, laminates enable transportation of sweat in the form, of vapour, from the under-clothing space into the outside, thus establishing equilibrium between the body of the user and the enviroment.

At the same time, clothing made of membrane laminates provide good protection against chemical in a drop form or aginst liquid.

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MOGUĆNOST UPOTREBE POLIMERNIH MEMBRANA ZA IZRADU ZAŠTITNE ODEĆE

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Radnici u hemijskoj i srodnim industrijama u toku rada izloženi su supstancama, koje mogu izazvati oštećenja na spoljašnjem tkivu ili unutrašnjim organima. Hemikalije sa kojima radnici

dolaze u kontakt postoje u nekoliko oblika (tečnost, magla, para i slično). Posledice koje izazivaju kod radnika mogu biti od blagih kožnih oboljenja ili drugih povreda do težih hroničnih kao što je plućni edem ili kancer. Zato je važan izbor tekstilnih materijala i konstrukcija (dizajn) za izradu zaštitne odeće namenjenu za ovu industriju.