Investigation of Water Vapour Resorption / Desorption of Textile Laminates

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The material ability to pass water vapour or perspiration, greatly affects the comfort of the wearer. Therefore, the influence of multifold water vapour resorption/desorption process on the hygienic properties of textiles footwear lining laminates has been investigated. It was shown, that in the first cycle water vapour absorption behaviour can be classified as Fickian. It was observed that the equilibrium water uptake increases with the increase of resorption/desorption cycles.

It was demonstrated, that desorption behaviour of water depends on the textile lining laminates structure. It may be described by the linear or exponential laws. It was found, that the resorption/desorption process cycles influence the water uptake and drying times of laminates and moisture transport properties of the textiles lining laminates are history-dependent.

Keywords: textile laminates, water vapour permeability, water vapour absorption and desorption.

INTRODUCTION

Usually comfort is accepted as one of the most important factors for footwear quality [1 – 3]. However, up to date a reliable measure to assess comfort has not been developed. Comfort has been associated with fit, additional stabilizing muscle work, fatigue, and damping of soft tissue vibrations [1], plantar pressure distribution [4] and subject characteristics such as skeletal alignment [5]. Moreover, comfort of footwear depends on the properties of upper materials, such as softness and flexibility [6].

Besides softness and flexibility, the two most important properties for the foot comfort are permeability and absorption of the upper materials. The material ability to pass water vapour or perspiration, greatly affects the comfort of the wearer. The result of the low permeability is damp or, in extreme case, wet feet. However, high permeability alone is not enough. It must be coupled with high absorption properties because absorption of perspiration by the materials of footwear help to keep the foot dry [6].

Leather has good permeability and absorption properties. Although polymer materials possess reasonable permeability, often equal of conventional side leathers, they lack the good absorption properties of leather. Polymeric upper materials can be made more comfortable if they are combined with an absorbent lining.

The wide range of polymeric membranes gives possibility to create multilayered textile lining materials with unique properties [7 – 10]. The breathable films act as a barrier to liquid water and soil coming from the environment, but are sufficiently permeable to allow significant amounts of perspiration. Two types of breathable polymer membranes – hydrophilic or microporous – are mostly used for textile laminates production [7, 8, 11]. The microporous membranes from polytetrafluorethylene (i. e. *Gore-Tex*) or polyurethane (i. e. *Porelle, Seyntex*) and hydrophilic membranes from polyester (i. e. *Sympatex*) or polyester/polyamid blend (i. e. *Tepor*) are used. Often these membranes are joined with protective layer from polyamide or polyester woven, knitted or non woven fabrics [8, 12, 13].

Microporous membranes are able to "breath" by means of a permanent pore structure with pores approximately of diameter $0.02\,\mu m - 1\,\mu m$ [11, 14]. Such membranes are resistant to water penetration due to markedly higher diameter of water drops ($200\,\mu m$ – $5000\,\mu m$) compared to that of pores of membrane. Strong interaction keeps water molecules in a drop preventing their spreading; so, they are too large to penetrate through the membrane pores. Whereas molecules of water vapour, resulting from sweating, are usually smaller than $0.0003\,\mu m$ and can easily penetrate through the polymer membrane pores and then drift away. Water vapour molecules penetrate through the pores of polymer membrane due to non-activated diffusion (Fig. 1, a). Capillary mechanism of water vapour transmition through pores takes place in this case of microporous membrane [11, 15].

Hydrophilic membranes are nonporous and transmit water vapour by a molecular mechanism [11, 15]. These membranes can show good permeability depending on their chemical composition and bulk morphologies, whereas they are impermeable to liquid water. The driving force for water vapour transmission process is a difference in water vapour pressure between two sides of the membrane, which gives rise to a concentration gradient within the membrane. Solubility of the water vapour in the membrane also plays an important role [16, 17]. The permeant, that is water vapour, is first adsorbed on the surface of the membrane on the side of highest water vapour concentration. Water molecules occupy free volume among the molecular chains of polymer and move across the membrane without destroying polymer when penetrating through the membrane with nonporous structure. In the case of polymers with active hydrophilic groups water molecules not only fill in the free volume among the polymer molecular chains, but also interact with their active hydrophilic groups (Fig. 1, b). Due to the

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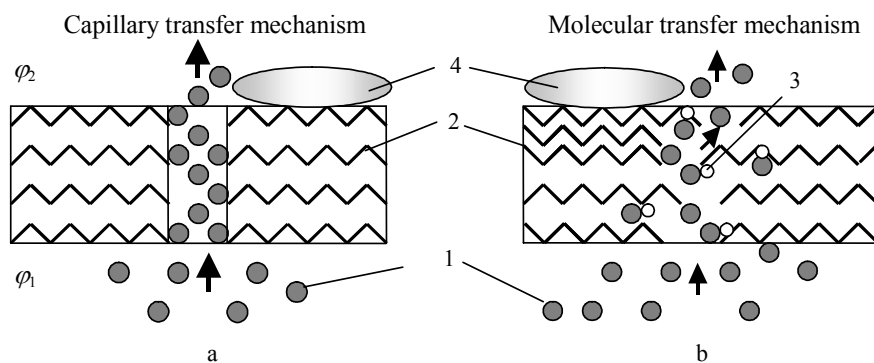
Fig. 1. Water vapour transfer through microporous (a) and hydrophilic (b) membranes: 1 – water vapour molecules, 2 – polymer molecular chains, 3 – active hydrophilic groups, 4 – water drops (φ_1 and φ_2 – relative humidity, $\varphi_1 < \varphi_2$) [17]

moisture gradient they move across the membrane gradually joining the active groups. Then they diffuse across by dissolving in the polymer membrane, which is usually called as activated diffusion. Upon arriving to the opposite surface of the polymer membrane, which has a lower vapour pressure, it is desorbed and enters the surrounding air space as vapour.

With an extensive range of hydrophilic and microporous membranes waterproof, breathable and highly durable multiply textile laminates for lining can be developed in order to keep in equilibrium thermo-regulation processes of feet over a longer period of time [8, 12, 13]. Such laminates are engineered to meet specific requirements in lining materials for military, institutional, industrial, sports and leisurewear footwear.

The structure and properties of materials of textile laminates have great influence on moisture transfer. These properties considerably change when laminates with polymer membranes is used. The breathable polymer membranes improve mechanical properties of materials, their resistance to water, soil, etc., but also worsen the hygienic properties of laminates [9, 10].

During exploitation the process of moisture transmission in materials is multifold. Besides, water vapour transfer through multilayer system depends on its structure. The absorbed moisture has many detrimental effects on the action of the laminate. The water vapour absorption and successive drying influence on the relaxation of polymeric material as well as on its hygienic properties [18]. It is very important to footwear materials to have the ability to absorb the moisture and have high drying rate during the time of wearing. Thus, the investigations of water vapour transfer through multilayer systems and its influence on water vapour resorption/desorption process are in high importance for footwear with good hygienic properties. The mathematical modelling of the diffusion process in multilayered system is very important for full understanding of diffusion mechanisms [18].

Thus, understanding the mechanisms of moisture diffusion and moisture-induced damages is very important in order to improve the long-term durability of multilayer laminates. The aim of this work is to compare the hygienic properties of different textile laminates used for footwear lining by defining their absorption and desorption mechanism.

EXPERIMENTAL

For the investigation three different textiles laminates used for footwear lining were chosen. The structures of investigated laminates are presented in Fig. 2.

Two-ply laminate L1 consists of non-woven polyamide (PA) fabric Cambrelle and thick layer of polyurethane (PU) foam. The patented fibre, Cambrelle® is specially engineered through a process, which spins two types of polyamide (PA) together. The fibre is formed into a non-woven fabric.
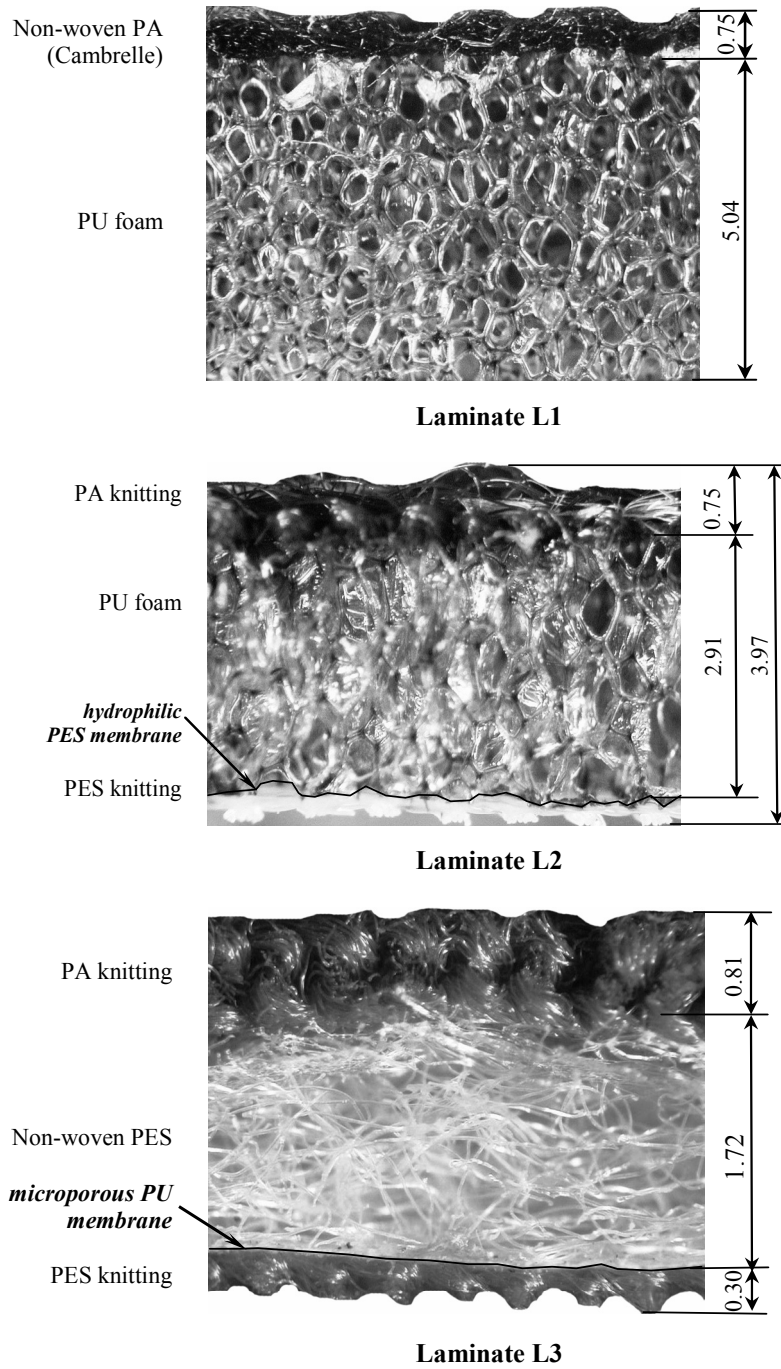
Laminates L2 and L3 consist of 4 layers, one of which is breathable polymeric membrane. Laminate L2 has hydrophilic membrane obtained from modified polyester (PES), while membrane of laminate L3 is from microporous polyurethane (PU). These laminates also consist distinct middle layers, which influences on the laminate water vapour transfer mechanism. The protective layer in both cases is polyester (PES) knitting material.

Water vapour permeability and absorption of the investigated textile laminates L1 – L3 were determined according to the requirements of standard methods. Before all tests specimens were conditioned for at least for 48 h at a standard atmosphere ($T = 23\,°C \pm 2\,°C$, $\varphi = 50 \pm 5\,\%$, i. e. 23/50) in accordance with LST EN 12222: 1997.

Water vapour permeability was measured according to LST EN ISO 14268 at the same constant temperature ($T = 23\,°C \pm 2\,°C$) and relative humidity ($\varphi = 50 \pm 5\,\%$). A circular specimen of textile laminate was placed over a jar, which contain a solid desiccant, i.e. silica gel [10]. This unit was placed in a strong flux of air in a conditioned atmosphere at a temperature of $23\,°C \pm 2\,°C$ and relative humidity of $50\,\% \pm 5\,\%$ for 16 h. Then the container was weighed in order to determine the mass of moisture that has passed through the test piece and has been absorbed by the desiccant. The permeability of water vapour was calculated according to:

$$P = \frac{7639M}{d^2 \cdot t},\qquad(1)$$

where M was calculated as $M = M_2 - M_1$, M_1 and M_2 are respectively the initial and final mass of the container (M_2 was determined after 16 hours of test), d is the average diameter of the neck of the container, t is the duration between weighing equal to 16 hours. The test result was average of six measurements. Variation of the found results was not higher than 7 %.

Non-woven PA (Cambrelle)

PU foam

0.75

5.04

Laminate L1

PA knitting

PU foam

hydrophilic PES membrane

PES knitting

0.75

2.91

3.97

Laminate L2

PA knitting

Non-woven PES

microporous PU membrane

PES knitting

0.81

1.72

0.30

Laminate L3

Fig. 2. Cross-sections of the textile laminates (dimensions are given in mm)

Water vapour absorption was measured according to LST EN ISO 17229. For the determination of water vapour absorption an impermeable material, the specimen were clamped above the opening of a container, which contains 50 ml of water, for the duration of test [10]. The duration of water vapour absorption was determined as the absorption time up to constant weight of the damped specimen. The water vapour absorption A_{ij} of the laminate at the determined time was defined as the mass difference before and after the water vapour absorption:

$$A_{ij} = \frac{M_{ij} - M_{i1}}{M_{i1}},$$ (2)

where M_{i1} is the initial mass of specimen in i cycle, M_{ij} is the mass of specimen in i cycle after j time of absorption. The test result was the average of six measurements. Variation of the found results was not higher than 10 %.

After each water vapour absorption test, water vapour desorption (rate of desiccation) of the laminates was investigated, as well. In this case damp specimen after absorption test was dried up to a constant weight in a horizontal position at standard conditions ($T = 23\,°C \pm 2\,°C$, $\varphi = 50\ \% \pm 5\ \%$). In this case the weight of specimen was monitored until its constant weight was obtained. Then the same specimen was used in the subsequent absorption test. The same procedure was followed in several cycles. The

water vapour desorption was determined at a fixed time interval as the change of specimen weight using:

$$D_{il} = \frac{m_{il} - m_{id}}{\Delta m_i}, \tag{3}$$

where m_{il} is the mass of specimen in cycle i after time l of desorption, m_{id} is the mass of dry specimen after desorption in cycle i, Δm_i is the mass of full moisture desiccated in cycle i of desorption.
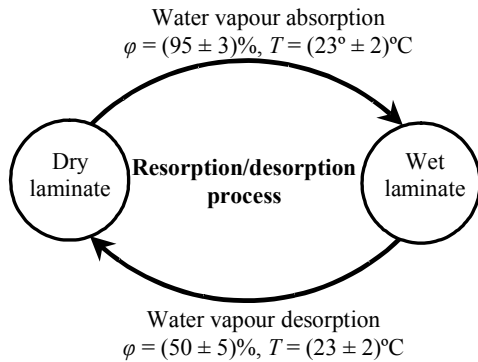
Water vapour absorption
$\varphi = (95 \pm 3)\%$, $T = (23° \pm 2)°C$

Dry laminate — **Resorption/desorption process** — Wet laminate

Water vapour desorption
$\varphi = (50 \pm 5)\%$, $T = (23 \pm 2)°C$

Fig. 3. Schematic representation of resorption / desorption test

The resorption/desorption process for all textile laminates was carried out by the repetitive water vapour absorption and desorption cycles (Fig. 3).

RESULTS AND DISCUSSIONS

In this work the influence of polymeric membrane on moisture transport properties of textile lining laminates for footwear was investigated. The water vapour permeability and absorption were determined. Obtained data are presented in Fig. 4. It is evident that two-ply laminate L1 shows significantly higher water vapour permeability as compared to that of four-ply laminates L2 and L3 (Fig. 4, a). The water vapour permeability of laminate L1 is approximately 80 % higher than that of laminates L2 or L3 (13.9 mg/cm^{2}h for L1 compared to that of 2.4 mg/cm^{2}h and 3.2 mg/cm^{2}h for L2 and L3, respectively). Thus, the increase of the layer number in the laminate structure decreases is ability of water vapour transfer.

On the other hand, absorption properties of all investigated textile laminates are similar and permeability P for all textiles laminates varies in the range from 5.7 mg/cm^2 up to 7.9 mg/cm^2 (Fig. 4, b). As it can be seen, the lowest water vapour absorption is shown by the

laminate L3 with non-woven middle layer including the microporous PU membrane.

The internal climate, next to the skin, can be described as warm and damp because human body is generats heat and moisture. The external climate in the case of low temperature is much drier and cooler. Consequently, the water vapour is driven from inside to outside. In wearing moisture transport – water vapour diffusion, absorption and desorption – continuously take place. For evaluation of hygienic properties of the footwear materials, it is very important to know their moisture transport properties after a long period of exposure in humid conditions. Therefore, the test of water vapour absorption and desorption was carried out. For the investigation, comparable lining laminates with the middle PU foam layer were chosen: two-layer laminate L1 without breathable membrane and four-layer laminate L2 with a hydrophilic PES membrane.

In this case the water vapour absorption was carried out by keeping laminates in humid conditions ($T = 23 °C \pm 2 °C$, $\varphi = 95 \pm 3$ %) for a long time (up to 120 h) till the constant weight was reached. Water vapour absorption kinetics for laminates L1 and L2 is presented in Fig. 5. Generally, the water vapour absorption kinetics is presented by plots of absorption rate A_{ij} as a function of time or square root of time ($\tau = t^{1/2}$).

As it can be seen from Fig. 5, the character of water vapour absorption for laminates L1 and L2 is quite similar. However, the water vapour uptake rate of the laminate L2 is markedly higher. This laminate reaches maximal weight 1.5 times faster than laminate L1. According to the character of presented absorption plots (Fig. 5) it may be assumed that the water vapour absorption of both laminates may be classified as Fickian and can described by an exponential law [19 – 22]. It was obtained that Fickian water vapour absorption of laminates L1 and L2 may be extrapolated by:

$$A_i(\tau) = k_{ig} \exp(-\tau) - k_{ip}; \ R^2 = 0.96, \tag{4}$$

where $\tau = t^{1/2}$ is the time of absorption, k_{ig} is the constant of absorption rate, k_{ip} is the constant of absorption equilibrium.

During footwear wearing moisture sorption and subsequent desorption of lining materials are multiple. It is known [18] that water vapour absorption and desorption influence on polymer materials relaxation as well as on their hygienic properties. Therefore, in this work the laminates water vapour absorption / desorption cycle was repeated by several times (not less than 3).
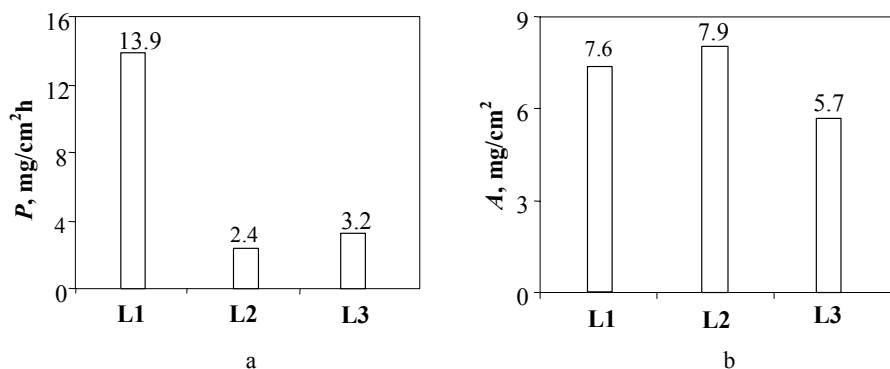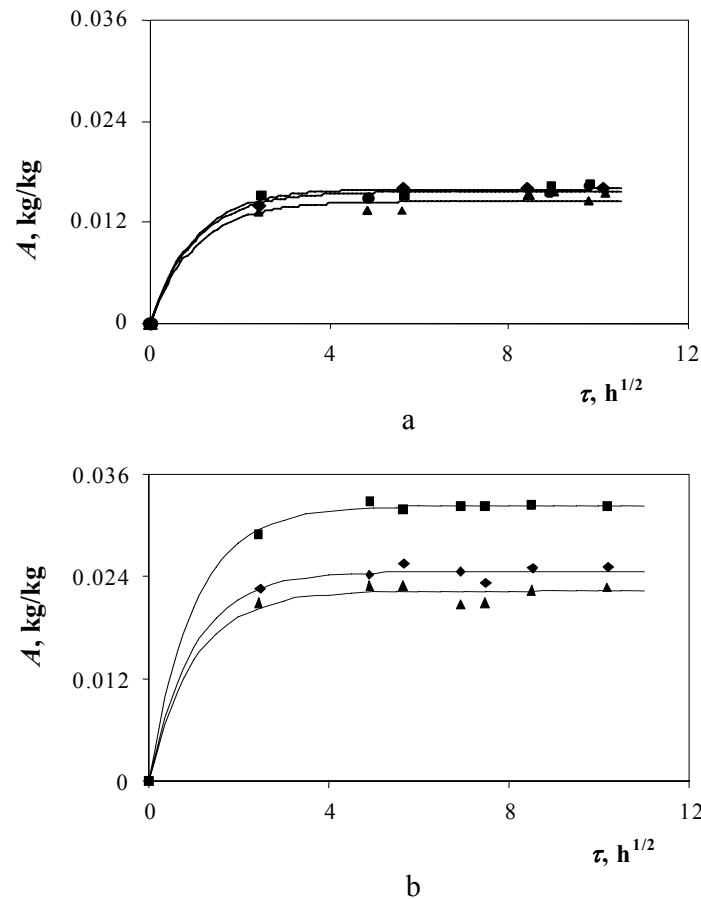

a

b

Fig. 4. Dependence of the water vapour permeability (a) and water vapour absorption (b) on the laminates L1 – L3

Fig. 5. Water vapour absorption kinetics for laminates L1 (a) and L2 (b): ▲ – cycle I; ♦ – cycle II; ■ – cycle III

As it can be seen from Fig. 5, the water vapour absorption depends on the laminates type and cycle number – curves in each cycle have a different slope and maximal values. However, the equilibrium of water vapour absorption achievement does not depend on the cycle number and in all the cycles it occurs after approx. 80 h for both laminates (Fig. 5). The rate of water vapour absorption increases with the increase of cycle number. Water vapour uptake in cycle II for both laminates increases in similar value – 13 % for laminate L1 and 12 % – for L2 (Fig. 5). Whereas in the cycle III, water vapour uptake is higher, especially for the laminate L2 (up to 31 %).

From Fig. 5 it is also evident that the dependence between the water vapour absorption of two-ply laminate L1 and the resorption/desorption cycle number is not significant. Thus, resorption / desorption process practically do is not influence the properties of the laminate with a simple structure.

Water vapour absorption of laminates L1 and L2 in all resorption/desorption cycles changes according to the same exponential law (Eq. 4) with different values of absorption constants (Table 1). Comparing data presented in Table 1 for the different absorption cycles, it is obtained that for the laminates higher diffusivity and water uptake is characteristic in the cycles II and III.

The constant k_{ig} characterizes the water vapour absorption rate. From the data given in Table 1 it can be stated that absorption rate for both laminates increases with the increase of cycle number. For the laminate L1 this con-stant has close values in cycles II and III and it is approximately 8 % higher than in the cycle I. The changes of absorption rate constant values are more remarkable for four-ply laminate L2. In this case the absorption rate con-stant k_{ig} value is higher approximately 10 % for the cycle II and approximately 44 % for the cycle III as compared to that of the cycle I. It may be supposed that water vapour absorption rate increases due to the changes in the lami-nates structure during water vapour sorption and drying process. Due to absorbed moisture in the cycle I, the lami-nate structure becomes more opened and accessible for the additional water vapour penetration [18]. Therefore, water vapour absorption uptake in cycle II and III for both laminates increases. Besides, water vapour absorption of the textile laminates is history-dependent.

Table 1. Dependence of absorption constants of Eq. (4)

| Cycle | Water vapour absorption constants at different cycles for laminate: | | | |
| | L1 | | L2 | |
	k_{ig}, kg/kgh$^{1/2}$	k_{ip}, kg/kg	k_{ig}, kg/kgh$^{1/2}$	k_{ip}, kg/kg
I	0.0145	0.0144	0.0223	0.0222
II	0.0156	0.0156	0.0246	0.0246
III	0.0158	0.0160	0.0322	0.0322

Another constant – water vapour absorption equilibrium constant k_{ip} also increases with the increase of resorption/desorption cycle number ($k_{Ip} < k_{IIp} < k_{IIIp}$). With the increase of the testing cycle number, the equilibrium of water vapour absorption is reached more rapidly. It is supposed that relaxation processes that take places in laminates after the first resorption/desorption cycle accelerates the achievement of water vapour absorption equilibrium state during the following cycles [19, 23].

The linings used for footwear must not only possess high ability to pass and absorb water vapour but also ability to remove accumulated moisture. Therefore, the changes of laminates water vapour desorption in several resorption/desorption cycles were investigated, as well. The data of water vapour desorption for laminates L1 and L2 are presented in Fig. 6. As it can be seen, both laminates show high rate of desiccation. Initially in the cycle I of absorption (up to 10 min) drying rates of laminates L1 and L2 are markedly higher. However, further drying rate slows down and laminate reaches its constant weight after approximately 60 min.
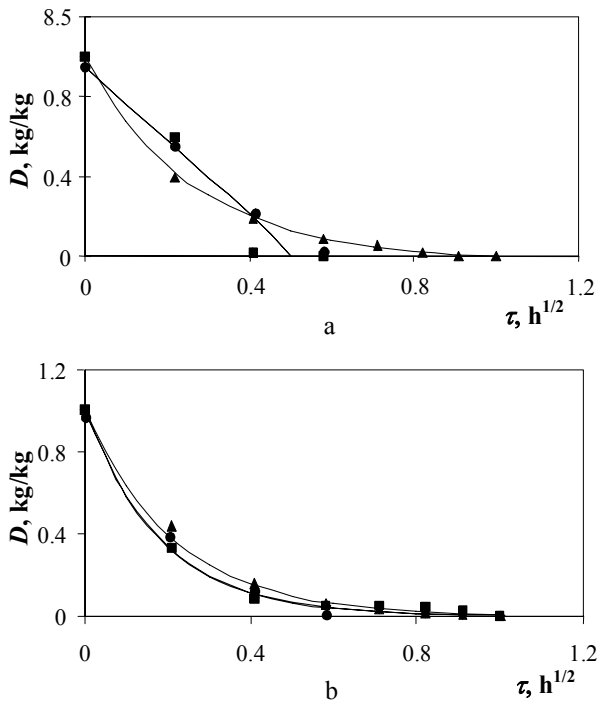

Fig. 6. Water vapour desorption of laminates L1 (a) and L2 (b): ▲ – I cycle; ● – II cycle; ■ – III cycle

The investigations show that water vapour desorption process of laminates L1 and L2 during cycle I may be described by the exponential law [24]:

$$D_i(\tau) = k_{1i} \exp\left(-\frac{\tau}{k_{2i}}\right); \ R^2 = 0.964 , \qquad (5)$$

where k_{1i} and k_{2i} are the desorption constants, τ is the time of water vapour desorption.

The values of constants k_{1i} and k_{2i} of function (Eq. 5) in the cycle I are presented in Table 2.

However, as it can be seen from Fig. 6, a, for the laminate L1 water vapour desorption in the cycles II and III proceeds according to the different law. In this case the water vapour desorption process can be described by a linear function:

$$D_i(\tau_i) = k_{3i} - k_{4i}\tau_{il} ; \ R^2 = 0.93 , \qquad (6)$$

where k_{3i} and k_{4i} are the constants of water vapour desorption in the i-cycle. Values of the constants k_{3i} and k_{4i} are presented in Table 2.

For the laminate L1 in the cycle I, water vapour desorption proceeds more slowly than in the cycles II and III. The moisture after the cycles II and III is evaporated from the laminates during the first 10 minutes of drying. Therefore, it can be stated that interaction of the moisture absorbed during the cycle II and III with the laminate material is weaker. Thus, drying rate is higher. Non-woven polyamide fabric Cambrelle and thick layer of polyurethane foam of laminate L1 have microporous structure. Therefore moisture penetrates through the pores of laminate two layers at higher rate.

Meantime, the character of water vapour desorption of laminate L2 remains the same during resorption/desorption process, and drying of laminate proceeds according to the same exponential law (Eq. 5). As it can be seen from Table 2, the water vapour desorption rate in the cycles II and III is lower than in the cycle I. During further cycles the laminate absorbs more moisture. Therefore, longer drying time is needed for moisture elimination from the laminate layers. It can be supposed that the third layer (hydrophilic membrane) of laminate influences the drying process. Moisture evaporates from top and bottom laminate with different desorption rates and this determines the exponential character of water vapour desorption process.

Thus, the investigation shows that the multifold resorption / desorption process of textiles laminates is history-dependent. Resorption / desorption changes the absorption ability of textile laminates.

Table 2. Dependence of the desorption constants of Eq. (5) and Eq. (6)

Cycle	Laminate L1				Laminate L2	
	k_{1i}, kg/kg	k_{2i}, kg/kgh$^{1/2}$	k_{3i}, kg/kg	k_{4i}, kg/kgh$^{1/2}$	k_{1i}, kg/kg	k_{2i}, kg/kgh$^{1/2}$
I	1.0009	4.628	–	–	1.0006	4.627
II	–	–	0.989	1.823	0.9995	5.495
III	–	–	0.991	1.836	0.9987	5.376

CONCLUSIONS

Water vapour permeability depends on the structure and type of textile laminates. However, water vapour absorption values are close for all investigated laminates. The character of water vapour absorption behaviour does not depend on the laminate structure and type, but water uptake rate is significantly influenced by the laminate structure. The Fickian behaviour is characteristic for the water vapour absorption. Its increase with time can be expressed by the exponential law.

Water vapour resorption / desorption process of the textiles laminates is history-dependent. The laminates ability of moisture uptake increases with the increase of resorption/desorption cycle number. The drying of the laminates proceeds faster after the first cycle of water vapour absorption, but after further resorption / desorption cycles the drying time increases. After the first resorption/desorption cycle water vapour desorption behaviour can be described by the exponential law, while after subsequent cycles it depends on the lining laminate structure.

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