The Influence of Laminated Leather Structure on the Water Vapour Absorption and Desorption Behaviour

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In this paper the experimental and theoretical investigations of moisture transfer through microporous film laminated leather are presented. The water vapour absorption and desorption processes of laminated leather are described. Water vapour absorption in the laminated leather and its separate layers may be classified as non-Fickian: sigmoidal – for microporous film and two-stage – for the leather of different structures. Water vapour desorption of leather changes according to the exponential law and for microporous film according to the linear one.

Water vapour absorption/desorption mechanism depends on the leather permeability. Microporous film does not worsen moisture transfer properties of the laminated leather. However water vapour permeability decreases and absorption increases due to the nonporous adhesive layer used for microporous film bonding. The decrease of laminated leather permeability intensifies the formation of capillary moisture or water clusters and increases water accumulation.

Keywords: laminated leather, microporous film, water vapour permeability, absorption, desorption.

1. INTRODUCTION

A laminate is a material constructed by joining two or more layers of material together. The process of creating a laminate is lamination, which in common parlance refers to sandwiching something between layers of plastic and sealing them with heat and/or pressure, usually with an adhesive [1]. The materials used in laminates can be the same or different. An example of laminate made of different materials would be the application of a layer of plastic film – the coating – on one side of leather – the laminated subject.

It is convenient to use microporous films for leather coating. Polymeric microporous coatings are engineered in such a way that they have a very high resistance to a water penetration, yet allow the passage of water vapour. They contain interconnected channels that are much smaller than the finest raindrop, but much large than a water vapour molecule. In Fig. 1 a schematic diagram of a microporous coating is presented [2].
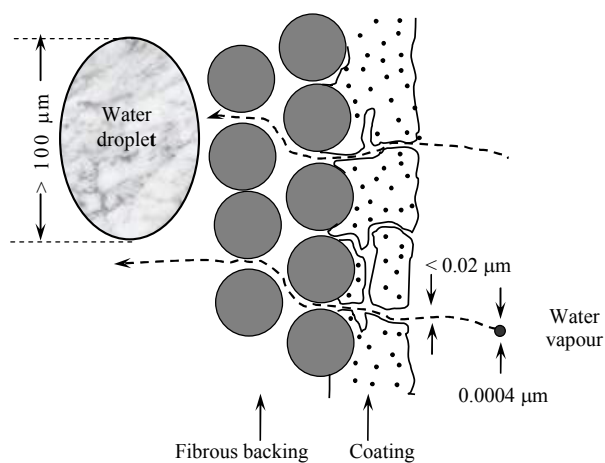

Fig. 1. Schematic diagram of a microporous coating [2]

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Water vapour transfer through multilayered polymeric materials strongly depends on their specific structure and can be very complex [3]. A multi-stage process is characteristic for water vapour molecules penetration through the film of the multilayered structures. It consists of water vapour molecules absorption into the film surface, solubilization into the polymeric matrix, diffusion through the matrix under a concentration gradient and desorption from the membrane into interfacial region of substrate [4].

Generally, depending on the film structure, water vapour transfer through polymeric material can be described as activated or non-activated diffusion [3]. Water vapour activated diffusion depends on the thermodynamic interaction between water and material to be penetrated, the affinity one for the other. Water molecules moved through the films from site to site on different chains of polymers (Fig. 2, a). In the case of nonporous film water molecules occupy free volume among the molecular chains of polymer and move across the film without destroying polymer. Activated diffusion rate is also affected by polymer polarity, crystallinity, chain stiffness, cross-link density, etc. [3].

Water can be either uniformly distributed throughout the polymeric material or heterogeneously located in discrete accumulations or clusters within the polymer [3, 5, 6]. This type of heterogeneous diffusion is known as activated diffusion of water around cluster site (Fig. 2, b). Water molecules can congregate in discrete cluster at polar site and in free volume locations within some polymer films of intermediate polarity under high humidity conditions. H. Leidheiser suggests that activated diffusion, resulting in the clustering of the water within the film, can actually enhance the strength and modulus of the polymer [5, 7].

Water accumulation will also occur heterogeneously at sites along the coating substrate interface [3]. Water vapour molecules penetrate through the polymeric material by activated diffusion and accumulate at the voids, cavities or defects at the interface between two layers (Fig. 2, c).
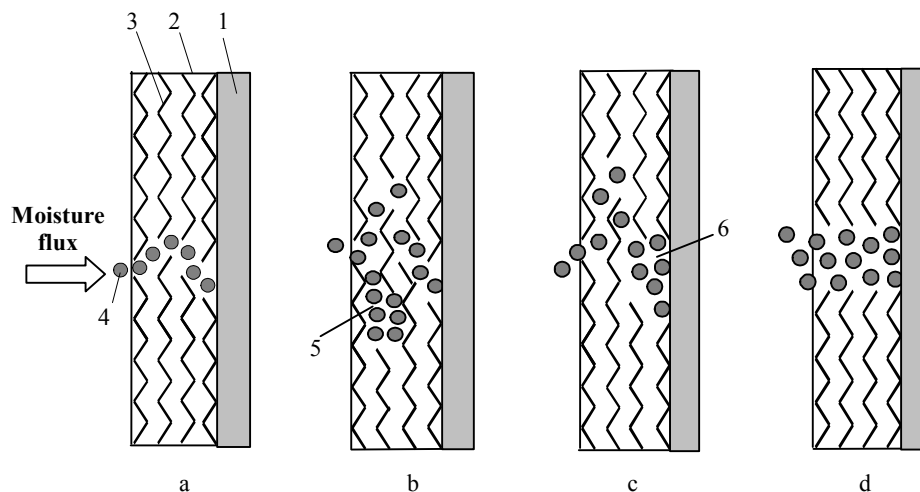
Fig. 2. Water vapour transfer mechanism through the polymeric films of different structure: a – activated diffusion through polymer matrix; b – activated diffusion around cluster site; c – heterogeneous activated diffusion and water accumulation at the interface; d – non-activated diffusion through polymer pore (1 – substrate; 2 – polymeric film; 3 – chains of polymers; 4 – water vapour molecules; 5 – water molecules cluster; 6 – water molecules in voids at the interface) [3]

This accumulation of water effects on wet adhesion failure that will cause changes of mechanical properties due to the polymer film delamination from the substrate surface [4, 7]. The localized accumulation of interfacial water can be increased under the variety of driving forces.

In the case of microporous polymer film water vapour molecules penetrate through the pores due to the non-activated diffusion (Fig. 2, d). The water vapour transfer through multilayer materials is depends on the permeability of their layers. Each of components affects on moisture transfer differently [8 – 10].

Understanding of water vapour transfer behaviour in multilayer material is very important for products with high comfort properties. So, in the present paper water vapour permeation mechanism of microporous film laminated leather was attempt to reveal and the changes in water vapour absorption/desorption behaviour at different stages of laminated leather production was investigated.

2. EXPERIMENTAL

For investigations laminated leather and its separate layers were used. Before lamination split leather was impregnated with acrylic emulsion (ground-coating). Microporous film bonding was performed by water-born polyurethane dispersion (in amount of $12 \text{ g/dm}^2 – 15 \text{ g/dm}^2$) with acrylic hardener (in amount 3.2 % of total weight). Laminated leather was obtained by hot laminating of microporous polyurethane (PU) film to ground-coated split leather surface at the temperature of $70\,°C – 75\,°C$ and pressure of $0.5 \text{ MPa} – 1.0 \text{ MPa}$ for $10\,\text{s} – 12\,\text{s}$. Some characteristics of all investigated materials are given in Table 1.

Before testings all specimens were conditioned in standard atmosphere in accordance with the requirements of LST EN 12222. The water vapour permeability was measured according to ISO 14268 at a constant temperature and relative humidity ($23\,°C \pm 2\,°C$, $50\,\% \pm 5\,\%$). A sample of material was placed over a container, which contained a solid desiccant [4]. The whole set-up was kept upright in a conditioned atmosphere at a temperature of $23\,°C \pm 2\,°C$ and relative humidity of $50\,\% \pm 5\,\%$.

Table 1. Characteristics of materials at different stages of laminated leather production

Materials	Thickness, mm	Apparent density, mg/mm^3
Microporous PU film	0.43	0.03
Split leather	1.37	0.54
Ground-coated split leather	1.40	0.68
Ground-coated leather with adhesive layer	1.63	0.72
Laminated leather	1.82	0.50

For the determination of water vapour absorption according to ISO 17229 the test piece and an impermeable material (barrier) was clamped over the opened container with water during the test [4]. To determine the influence of the laminated leather structure on the mechanism of water vapour absorption test was proceed until water droplets and moisture spots appear on the material surface (up to 180 h). Water vapour absorption A_i was determined by the changes in weight before and after the test:

$$A_i = \frac{M_i - M_1}{M_1}, \tag{1}$$

where M_1 is the initial weight of sample, M_i is the weight of sample after i time of absorption.

After water vapour absorption test the water vapour desorption (rate of desiccation) of test pieces was determined. In this case damp specimen was dried up to a constant weight in horizontal position in standard atmosphere at a temperature of $23\,°C \pm 2\,°C$ and relative humidity of $50\,\% \pm 5\,\%$. The water vapour desorption was determined at the fixed time interval according to the change of specimen weight by the formula:

$$D_j = \frac{m_j - m_0}{\Delta m},\tag{2}$$

where m_j is the weight of sample after j time of desorption, m_0 is the weight of dry sample after desorption test, Δm is the weight of full desiccated moisture.

3. RESULTS AND DISCUSSIONS

3.1. Structure of laminated leather

The structure of laminated leather was studied by scanning electronic microscopy. The cross-section of laminated leather is presented in Fig. 3. It is evident that laminated leather consists of three layers with different structure – split leather, adhesive layer and microporous polyurethane film.

The adhesive forms nonporous layer of 20 μm – 35 μm thickness (Fig. 3, b). Adhesive wet leather surface not fully and, therefore, tiny microscopic cavities appear at the adhesive and leather interface.

PU film contains interconnecting pores of different diameter – from 2.5 μm up to 37.0 μm (Fig. 4, a, b). The average of pores diameter is $d_p = 5.5$ μm. The structure of the top and bottom of the film is quite different. The bottom of the film has the pores of 3 μm – 20 μm diameter (Fig. 3, c), while the top of film is nonporous due to the coating with protective layer (Fig. 4, d).

3.2. Water vapour permeation mechanism

Multistage permeation process is characteristic for the laminated leather due to different structure of layers. The rate of permeation depends on two independent parameters: the solubility of the penetrant and its ability to pass through the leather layers. In the leather and microporous PU film non-activated diffusion through materials pores and capillaries is primary mechanism of water vapour transfer. In nonporous polyurethane adhesive film water vapour permeation mainly occurs due to activated diffusion.

The changes of water vapour permeability P_{wv} at different stages of laminated leather are shown in Fig. 5, a. As it can be seen the split leather shows the highest water vapour permeability. The ground coating of split leather practically does not worsen the permeability, while
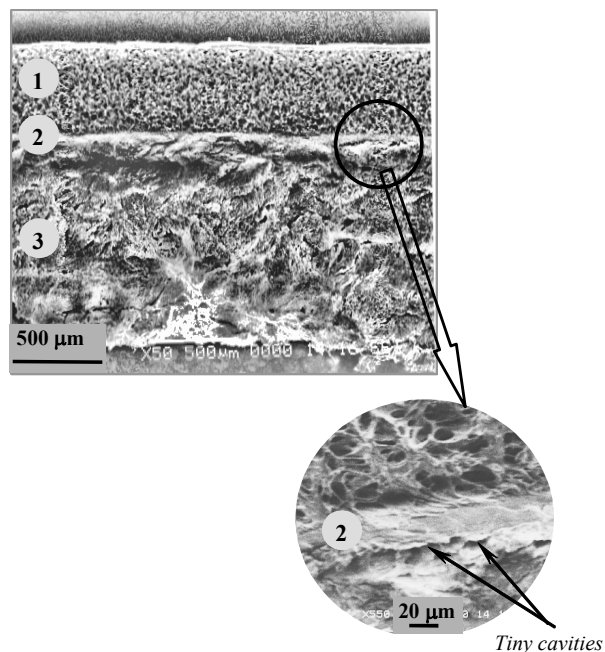

Tiny cavities

Fig. 3. The cross-section of laminated leather: 1 – microporous film; 2 – adhesive layer; 3 – split leather
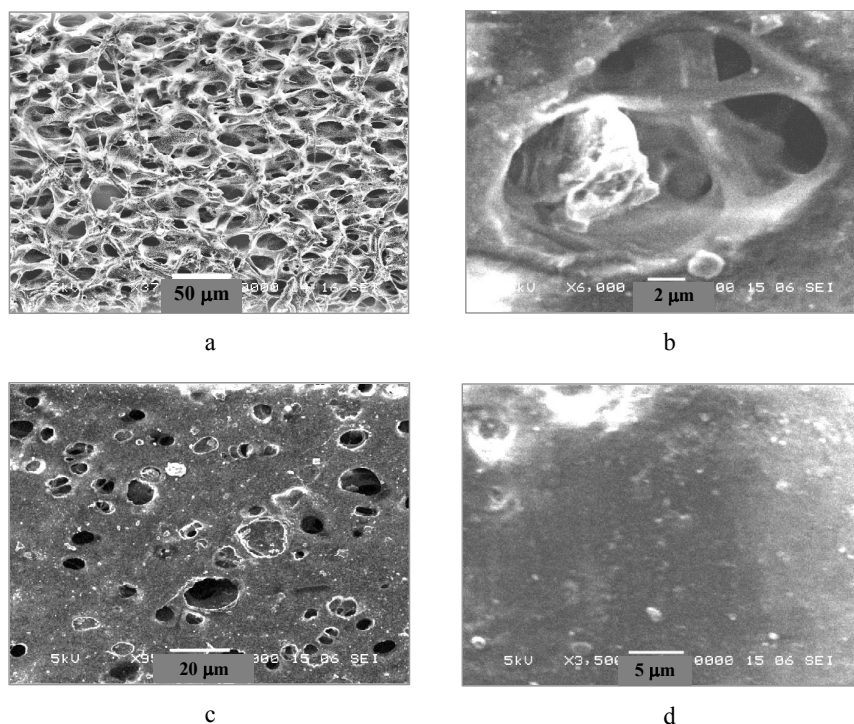

a

b

c

d

Fig. 4. Structure of microporous polyurethane film: a – cross-section; b – the view of connecting pores; c – bottom of the film; d – top of the film
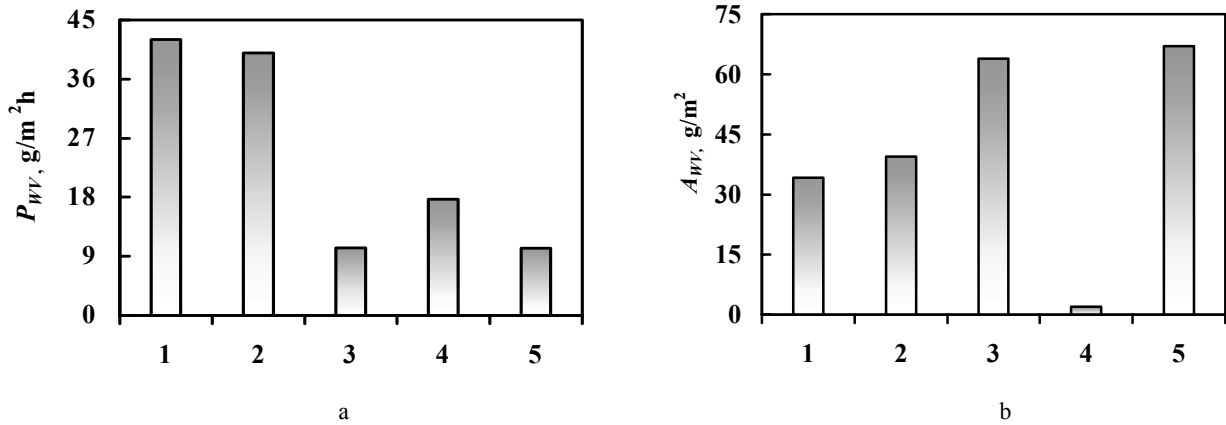
Fig. 5. Water vapour permeability (a) and absorption (b) of laminated leather at different stages of its production: 1 – split leather; 2 – ground-coated split leather; 3 – ground-coated split leather with adhesive layer; 4 – microporous PU film; 5 – laminated leather

adhesive layer reduces the P_{wv} four-times (from 40 g/(m^2 × h) down to 10.3 g/(m^2 × h)). The water vapour permeability through microporous PU film is significantly lower than that for split leather (18 g/(m^2 × h) compared to 40 g/(m^2 × h) – 42 g/(m^2 × h)).

However, the microporous PU film shows significantly higher water vapour permeability than other polymeric films used for leather coating, i. e. (0.3 – 0.5) g/(m^2 × h). The mean free path of water vapour molecules through polymer is $\lambda = 0.1$ μm at the pressure of 0.1 MPa, and $\lambda = 1$ μm – 2 μm at the pressure of 0.01 MPa [11]. Meanwhile, the water vapour molecules permeate through PU film pores according to the capillary model as a result highest water vapour permeability.

On the other hand, the PU film has higher water vapour permeability compared to that of split leather coated with adhesive layer. Similar value of P_{wv} is characteristic for PU film laminated leather. Consequently, it can be supposed that adhesive layer forms nonporous barrier, which significantly reduces water vapour permeability of laminated leather. It is supposed that diffusion of water vapour molecules through the adhesive layer occurs through the free volume of polymer by gradually joining to active polyurethane active groups (carboxylic, ester or amide). Therefore, the water vapour transfer proceeds according to the activated diffusion when water vapour molecules interact with these groups [12, 13]. However, it causes the decrease of water vapour permeability.

Lamination of leather also changes water vapour absorption. As it can be seen from data presented in Fig. 5, b, water vapour absorption A_{wv} of PU film is low – only 2 g/m^2 in comparison with that of split leather (34.2 g/m^2). Water vapour absorption of split and ground-coated leathers is high due to the interaction of leather with water molecules. The water vapour absorption in ground-coated split leather depends upon water concentration, when water molecules interact with active groups of collagen and active carboxylic groups of acrylic ground.

However, the coating of split leather surface with adhesive layer increases water vapour absorption almost twice compared to that of unlaminated leather (Fig. 5, b). It allows to confirm the decrease of surface permeability after the split leather coating by adhesive. As it was assumed earlier [4], the most critical location of water is the interface of leather and adhesive, i. e. the cavities formed due to the insufficient wetting of leather surface by the adhesive. Water vapour permeation rate in the adhesive layer depends on the amount of carboxylic, ester groups, and, to less extent, on the amide groups of urethane. The water clusters may form in PU adhesive layer at high humidity conditions because in polyurethanes water cluster size (MCS) is MCS = 1.5, when $\varphi = 90$ % [14].
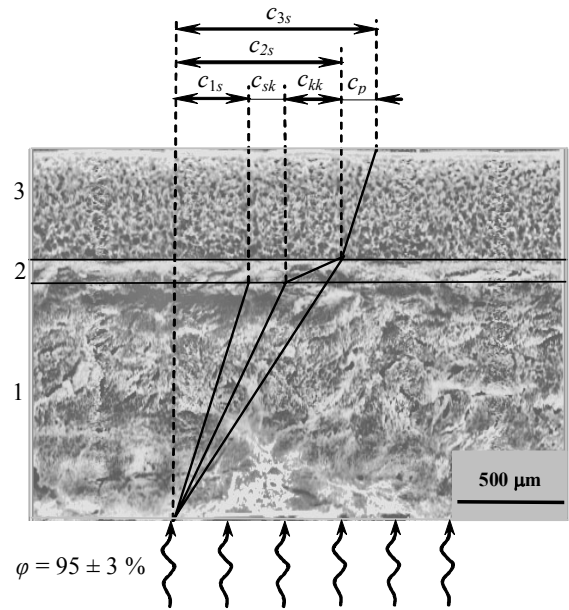

Fig. 6. Changes of water concentration in the laminated leather layers: 1 – ground-coated split leather; 2 – adhesive layer; 3 – microporous film (c_{1s} – water concentration in ground-coated split leather; c_{2s} – water concentration in leather with adhesive layer; c_{3s} – water concentration in laminated leather; c_{sk} – water concentration due to the capillary water formation in the leather micropores; c_{kk} – water concentration due to the water solubility and water clusters formation in the adhesive layer; c_p – water concentration due to the water solubility in film)

Thus, water vapour absorption in leather with adhesive layer c_{2s} depends upon water concentration in ground-coated leather c_{1s}, upon the capillary water formation c_{sk} in the leather micropores and upon water

concentration due to the water solubility and water clusters formation c_{kk} in polyurethane adhesive layer (Fig. 6):

$$c_{2s} = c_{1s} + c_{sk} + c_{kk}. \qquad (3)$$

As shown in Fig. 5, b, water vapour absorption of laminated leather is close with that of adhesive coated split leather. It may be supposed that water vapour absorption increases due to the separate water molecules solubility in microporous polyurethane film. Therefore, as it can be seen from Fig. 6, water vapour absorption in laminated leather c_{3s} depends upon water concentration in adhesive coated leather c_{2s} and upon water concentration c_p due to the water vapour solubility in microporous film:

$$c_{3s} = c_{2s} + c_p. \qquad (4)$$

Thus, lamination of split leather by microporous PU film does not worsen moisture transport properties, while adhesive layer, used for this film bonding to the leather surface, acts as nonporous barrier and decreases water vapour permeability by increasing its absorption capacity.

3.3. Water vapour absorption desorption mechanism

Different permeation of the laminated leather components possesses different absorption kinetics during exposure to humid conditions. The water vapour absorption in laminated leather and its separate layers (split leather and microporous coating film) as a function of the square root of time are presented in Fig. 7 and Fig. 8. In all investigated cases water vapour absorption can be classified as non-Fickian [15, 16]. For ground-coated leather and laminated leather the two-stage water vapour absorption behaviour is characteristic (Fig. 7). In this case the absorption is composed of two parts: fast Fickian absorption A_F and slow non-Fickian absorption A_N. As it can be seen, the curves are Fickian from beginning absorption roughly until 48 h. After saturation the absorption curves are extended through non-Fickian part. Ultimately, in non-Fickian stage the saturation in all leather samples is reached approximately at the same time as in the film, i. e. after 160 h.

It was determined that Fickian absorption in leather (ground-coated or laminated) can be expressed by equation:

$$A_F(\tau) = k_g \, \tau_i^{0.5} - k_p, \qquad (5)$$

where $\tau_i = t_i^{1/2}$ is the time after i period of absorption, k_g is the constant of absorption rate and k_p is constant of absorption equilibrium. Values of these constants are presented in Table 2.

Table 2. Values of the water vapour absorption constants of Eq. (5)

Component	k_g, kg/(kg·h$^{1/4}$)	k_p, kg/kg	Determination coefficient R^2
Ground-coated split leather	1.02×10^{-2}	4.4×10^{-4}	0.978
Laminated leather	2.06×10^{-2}	-1.58×10^{-4}	0.951

Hydratation moisture is supposed to form in ground-coated leather at the first stage, when water vapour molecules interact with leather peptide and ionized groups as well as, carboxylic groups of acrylic ground [13, 17]. It was stated that lamination of split lather by microporous PU film increases the absorption rate – the water vapour constant of absorption rate k_g of laminated leather is twice higher than that of the ground-coated split leather. It can be supposed that the absorption rate in the laminated leather increases due to the water molecules interaction with the active groups of PU adhesive. However, it can not cause such considerable increase of absorption. As far as the microporous PU film almost does not absorb moisture at the beginning of absorption (48 h), its influence on the water vapour absorption of laminated leather in Fickian stage is very negligible.

In Fickian stage the laminated leather the water vapour absorption saturation level reaches after 40 h – 48 h. It can be seen from the values of equilibrium constants k_p in Table 2, that due to the water vapour condensation in micropores at the layers boundary the laminated leather absorbs water vapour slower compared to that of ground-coated split leather.

The non-Fickian sorption process of laminated and ground-coated leather proceeds in similar manner and can be described by the exponential function:

$$A_N(\tau) = \left(k_{N1} \cdot e^{-\tau} + k_{N2} \right)^{-1}, \qquad (6)$$

where k_{N1} and k_{N2} are relaxation constants (Table 3).

Table 3. Values of non-Fickian absorption constants of Eq. (6)

Component	k_{N1}, (kg·h$^{1/2}$)/kg	k_{N2}, kg/kg	Determination coefficient R^2
Ground-coated split leather	28832.8	9.89	0.989
Laminated leather	10517.1	8.11	0.922

The values of water vapour absorption constant k_{N1} for laminated leather is more than twice lower than that of ground-coated split leather (Table 3). Capillary water, which formation started in Fickian stage, is continued accumulate in non-Fickian stage. The surplus of water molecules also accumulates in PU adhesive layer causing the water clusters formation. These processes can influence on the laminated leather water vapour absorption mechanism in non-Fickian stage.

The water vapour desorption processes of ground-coated and laminated leathers have the same character (Fig. 7). These leathers reach their initial weight gradually after 24 h of drying. The drying rate is higher at the beginning of desorption process. Ground-coated split leather half of absorbed moisture evaporates after 30 min, while laminated leather twice longer – after 60 min. The second part of moisture is removed approximately after 23 h, independently on leather structure.

Desorption process of these leathers can be described by the exponential law:

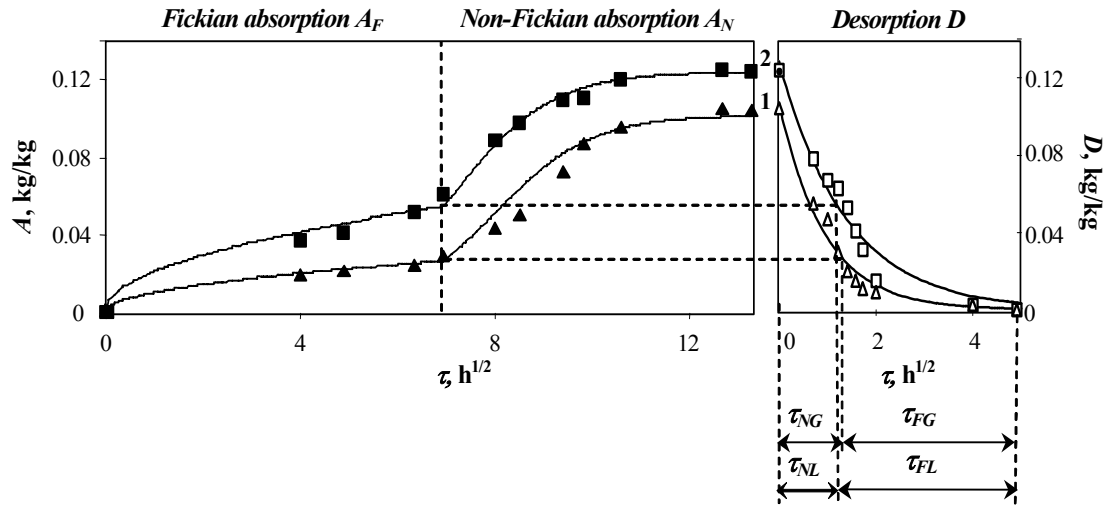$$D(\tau) = k_v \cdot e^{-\frac{\tau}{k_d}}, \qquad 0 \le \tau \le 4,9. \qquad (7)$$

Fig. 7. Dependence of ground-coated leather (1) and laminated leather (2) water vapour absorption A and desorption D upon the exposure time
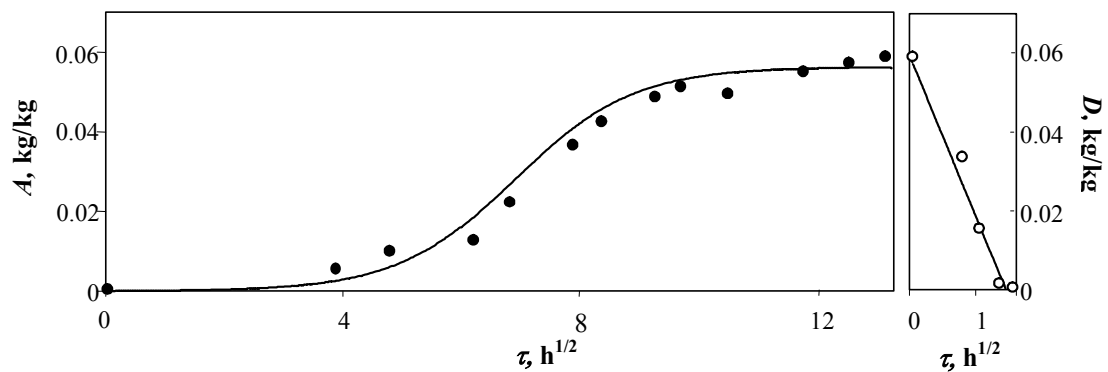

Fig. 8. Dependence of the water vapour absorption (A) and desorption (D) of the microporous PU film upon the exposure time

In order to find out the absorption and desorption dependencies upon the finishing level of laminated leather Fickian and non-Fickian desorption rates (v_F and v_F, respectively) were determined according to the declination of the desorption curves (Fig. 7 and Fig. 8). The average values of desorption rate is presented in Table 4.

Table 4. The rates of water vapour desorption

Component	v_F, kg/(kg·h$^{1/2}$)	v_F, kg/(kg·h$^{1/2}$)
Ground-coated split leather	7.4×10^{-3}	5.6×10^{-2}
Laminated leather	14.6×10^{-3}	5.9×10^{-2}

From Table 4 it is evident that moisture absorbed at Fickian stage is removed at the lower rate than that absorbed during non-Fickian. The value of desorption rate v_F in Fickian stage of ground-coated split leather is about 7.5 times lower than value v_N in non-Fickian stage, while in the case of laminated leather – only in 4 times. It allows to suppose that during Fickian absorption in the leather hydratation moisture is formed with longer duration of removal. The same phenomenon was observed in the case of nonporous leather coating [6, 16].

The water vapour absorption and desorption in microporous PU film has quite different mode than in leather (Fig. 8). The free film is subjected to the penetrant activity at both sides. The transfer process in the film is Fickian, but due to slow establishment of equilibrium at the surface of the film water vapour absorption kinetics appears anomalous [15].The saturation level in the film is reached after 160 h of exposure at the humid conditions.

As it can be seen from Fig. 8, the water vapour absorption kinetics is more similar to sigmoidal model – non-Fickian behaviour. The microporous film water vapour absorption curve is S-shaped, showing the point of inflection roughly after 40 h of exposure.

The water vapour absorption of microporous PU film can be expressed by exponential function:

$$A_{Sig}(\tau) = \left(17.76 + 178632 \cdot e^{-\tau}\right)^{-1}, \quad 0 \leq \tau \leq 13.3. \tag{8}$$

Such character of water vapour absorption kinetics often is characteristic to polymers with microporous structure with low water vapour solubility [15, 18]. At the beginning of process (till 24 h) the film almost does not absorb moisture ($A = 0.011$ kg/kg). It can be supposed that at this stage the water vapour concentration increases due to separate water molecules solubility in polymer structure. Film exposure in the humid conditions intensifies water vapour absorption after 40 h until saturation level – after 160 h. When the water molecules concentration reaches critical value the water vapour condensation can begin in the smallest film pores and the capillary water can appear.

The water vapour desorption of microporous PU film also has quite different character compared to leather. The

water vapour desorption of the film proceeds lineary ($R^2 = 0.984$):

$$D(\tau) = 1 - 0.0125\tau. \tag{9}$$

PU film removes all absorbed moisture in short period (~ 2 h), which is close to desorption period τ_N of non-Fickian absorption. It can be affirmed that in microporous PU film only separate water molecules or capillary water can exist. The average of microporous film water vapour desorption rate is $v_N = 3.4 \cdot 10^{-2}$ kg/(kg $\times$ h$^{1/2}$).

Thus, water vapour absorption process for coated leather differs at different stages of absorption and moisture of different type appears. Coating with nonporous film or lamination with microporous film (when the water vapour permeability decreases) intensifies the water vapour absorption.

CONCLUSIONS

1. Water vapour transfer through the laminated leather depends on the properties of composed layers. Microporous coating film does not worsen moisture transfer of laminated leather, while adhesive layer, used to bond this film, decreases the water vapour permeability and increases its absorption due to the formation of nonporous barrier.

2. Water vapour absorption in the laminated leather and its separate layers can be classified as non-Fickian – sigmoidal for microporous film and two-stage for leather samples.

3. Fickian water vapour absorption of leather increases until equilibrium according to the power dependence. The intensity of the absorption depends on water vapour transfer mechanism in the coating film and water vapour molecules localized interaction with active polar groups of the leather and coating.

4. Non-Fickian water vapour absorption of leather increases according to the exponential law. The intensity of absorption depends on the capillary water formation at the leather and adhesive interface and water clusters formation in polyurethane adhesive layer.

5. The water vapour absorption mechanism depends on the permeability of leather. With the decrease of the coating permeability capillary moisture or water clusters formation becomes more intensive and increases water accumulation in leather.

6. The water vapour desorption of leather changes according to the exponential law, while of the microporous film – according to the linear dependence.

Acknowledgments

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