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Prediction of Stress Relaxation in Laminated Leather Layers

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Laminated leather, obtained by the bonding of the microporous polyurethane film to split leather surface, was used for investigation. Such hybrid leather is resistant to water penetration, but shows high breathable properties. The effect of different nature layers on mechanical properties and viscoelastic behaviour of laminated leather was examined. It was shown that leather backing mainly determines the strength of laminated leather, while polyurethane film – deformability. The combinative strengthening is characteristic for hybrid system due to the repairing of leather surface defects by adhesive layers and dissipation of kinetic energy, which releases during the elementary act of the failure. Generalized Maxwell model, possessing a regular spectrum of relaxation times, successfully describes stress relaxation behaviour of the leather in non-linear regions. The polyurethane film increases the stress relaxation rate in the laminated leather, because rearrangement at the interface of two layers arises. It was obtained that the viscoelastic nature of polyurethane film dominates on the long-term properties of laminated leather.

Keywords: laminated leather, mechanical properties, stress relaxation behaviour, generalized Maxwell model, discrete spectrum of relaxation times.

1. INTRODUCTION

Leather is used for many applications: footwear, gloves, clothing, purses, furniture upholstery, saddles, and a variety of other uses. For each application the leather of different physical and mechanical properties is obtained by means of variation in the processing technology [1].

Tanned leather is usually coated with thin pigmented or lacquer coatings. One of the purposes of such coating is decorative. The coating may also change some physical properties of leather: it may decrease water and air permeability, increase rigidity, etc. [2]. Such changes depend on the coating type and coating formation technology - the coating may penetrate deeply into leather or it may remain on the leather surface [3].

There is also another quite different method to form a surface coating using separate moulded polymeric films. In one case microporous polymeric membranes are laminated to the surfaces of textile, leather, plastic or other; in another - these membranes are sandwiched between an outer material and lining [4, 5]. The range of such membranes is very wide - from waterproof and breathable films to surgical strapping for post-operative cicatrices with an antiviral barrier.

Generally, the leather is covered by a film, which is adhered to the surface by hot pressing [2]. Leather lamination is a mean of creating a product, which has unique properties such as resistance to water, fire, etc.

Phenomenological prediction of the mechanical behaviour of various materials and their systems is a fundamentally important problem for engineering application. To provide information about the viscoelastic properties of materials, various experimental techniques have been used, among which stress relaxation is one of the simplest. Equipment designed for such research has been a continuously improved and versatile extending machine with computer-aided processing of analysis results of the relaxation processes of materials open new experimental opportunities [6 – 8]. The interest of the deformability and relaxation behaviour of leather has been continuously growing. Previous studies concerning stress relaxation in leather have been focused on the effects of heat and humidity [9], pre-stain value [10], parameters of shaping technology [11]. Notwithstanding to abundance of research works performed in practice, there is often a lack of both theoretical and experimental knowledge on relaxation behaviour of leather [6]. Especially it is interesting to investigate viscoelastic behaviour of relatively new system - laminated leather that is composed from materials with quite different nature and properties.

The goal of this investigation is to study and to predict stress relaxation in laminated leather in order to provide the possibility to investigate the time dependence shown by different system layers and, thus, to gain an understanding of their viscoelastic behaviour.

2. THEORETICAL

For materials behaviour description, it is often necessary to fit experimental data to an analytic function. The objective of this process is the determination of the values of parameter that in some sense represent the "best" fit of the approximating function to the experimentally obtained results.

Real polymeric materials are characterised by continuous spectra of relaxation times. However, experimentally it is possible to determine the spectra only roughly. Due to this reason discrete spectra can be used, when relaxation times have certain discrete values [12].

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Macroscopic phenomenological models comprising Hookean spring and Newtonian dashpots have been widely used to represent linear viscoelastic behaviour of various materials [13]. However, behaviour of leather is linear only under small strain. Otherwise, instantaneous strains are practically impossible to be applied. In these cases models representing non-linear viscoelasticity due to the involving non-Hookean and non-Newtonian units are more useful [14, 15]. On the other hand, they are complicated and, therefore, time consuming. So, for the simulation of stress relaxation behaviour of polymeric materials an attempt to adapt generalized Maxwell model, representing linear viscoelasticity [16 – 18], was made. Generalized Maxwell model consists of n Maxwell units, possessing a different relaxation times, and a single elastic Hookean spring with elasticity constant D_0; all of them are coupled in parallel (Fig. 1). Every Maxwell unit consists of Hookean spring with elasticity constant D_i in series and Newtonian viscous dashpot with viscosity constant η_i of fluids inside the cylinders. Ratio η_I/D_i is considered as relaxation time τ_i of a Maxwell i-th element.

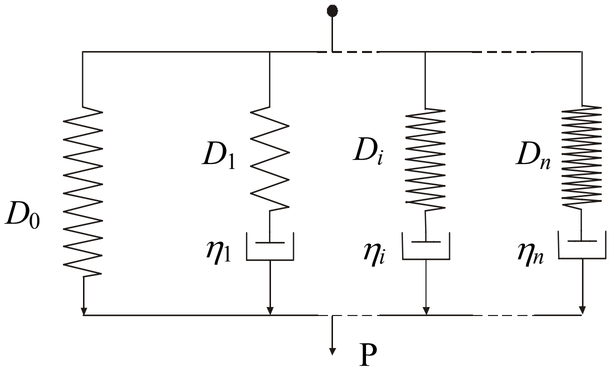


Fig. 1. Generalized Maxwell model for stress relaxation representation

When the generalized Maxwell model is deformed under constant speed $v_t = d\varepsilon/dt$ up to the constant level of its strain $\varepsilon = \varepsilon_t$, the relaxation process can be expressed by the expression [16, 17]:

$$\sigma = D_0\varepsilon_t + \sum_{i=1}^{n}\sigma_i = \\ = D_0\varepsilon_t + v_t\sum_{i=1}^{n} D_i\tau_i\left[1-\exp\left(-\frac{\varepsilon_t}{v_t\tau_i}\right)\right]\exp\left(-\frac{t^*}{\tau_i}\right), \quad (1)$$

where t^* is the time counted from the instant at which the strain reaches the limit strain ε_t, i.e. $t^* = t - \varepsilon_t/v_t$.

The difficulties arise in analysing the relaxation time, because the change of any external factor influences on the change even of two values - relaxation time and its intensity of each model element. Besides it, the number of relaxation times in the spectrum can vary, also. Due to these reasons evaluation of relaxation behaviour becomes complicated.

The above mentioned problems can be eliminated by using regular discrete spectrum proposed in [16]. In this case relaxation times always have constant values, which can be obtained according to the relation:

$$\tau_i = a^{i-1}\tau_1 , \quad (2)$$

where τ_1 is minimal time of relaxation, a is constant ($a > 1$).

It is assumed that the relaxation times of the Maxwell model differ significantly, i.e. $\tau_1 << \tau_2 \ldots << \tau_n$. The number of relaxation times n depends on the time range t^*, which is intended to be covered. In order to ensure that within certain time ranges t^* relaxation is reflected by one Maxwell element solely constant a admitted to be equal to 10.

Elasticity constants of the model can be determined according to method presented in [16, 17]. In the case of $t^* >> \tau_{n\text{-}1}$ stress relaxation process can be described by one Maxwell element:

$$\sigma - D_0\varepsilon_t = \sigma_n = v_t D_n \tau_n G_n \, exp\left(-\frac{t^*}{\tau_n}\right), \quad (3)$$

where $G_n = 1-\exp\left(-\frac{\varepsilon_t}{v_t\tau_n}\right)$.

The value of D_0, which defines the equilibrium stress σ_∞ on the model, can be calculated from Eq. (3) using two experimental values of stress: σ_{n1} that corresponds to the time $t^*_1 \approx \tau_n$ and σ_{n2} – to the time $t^*_2 \approx t^*_u$ (t^*_u is real time of observation) [16]. Thus,

$$D_0 = \frac{\sigma_{n2} - \sigma_{n1}\exp\left(-\frac{t^*_2 - t^*_1}{\tau_n}\right)}{\varepsilon_t\left[1-\exp\left(-\frac{t^*_2 - t^*_1}{\tau_n}\right)\right]} . \quad (4)$$

Correspondingly

$$D_n = \frac{\sigma_{n1} - D_0\varepsilon_t}{v_t\tau_n G_n \exp\left(-\frac{t^*_1}{\tau_n}\right)} . \quad (5)$$

The values of stress σ_n calculated by Eq. (3), are subtracted from experimental values of $\sigma - \sigma_n$ for the whole range of time t^*. For $t^* >> \tau_{n-2}$, using the experimental value of $\sigma_{(n-1)1} \approx \tau_{n-2}$, in a similar way the value D_{n-1} and in turn the values of the other constant D_i are obtained.

The value of constant D_1, corresponding to the shortest relaxation time τ_1, can be obtained from the equation

$$\sigma_1 = \frac{\sigma_{1e}}{v_1\tau_1 G_1} , \quad (6)$$

where σ_{1e} is the rest of the experimental values of stress for $t^* = 0$ after subtraction of the calculated values of σ_2 from the experimental values of $\sigma - \sigma_\infty - \sigma_n - \cdots - \sigma_3$. In such way for $t^* = 0$ the calculated and experimentally determined values of stress fit ideally.

3. EXPERIMENTAL

Materials. Hybrid leather - *Permair* leather - used in these studies was a commercial grade product. For investigation the semi-finished products at the different stages of *Permair* leather manufacturing were used, also.

The characteristics of investigated materials are presented in Table 1.

Table 1. Characterisation of materials

Sample	Material	Materials characterisation
S1	Split leather	Chrome-tanned leather 1.2 ± 0.1 mm of thickness
S2	Ground coated split leather	Split leather grounded with acrylic ground STUCO in amount of 20 g/dm^2
S3	Ground coated leather with adhesive layer	Grounded leather coated with polyurethane adhesive layer in amount of 12 – 15 g/dm^2; content of acrylic hardener in the adhesive composition – 3.2 %
S4	*Permair* film	Microporous polyurethane (PU) membrane 0.4 ± 0.05 mm of thickness
S5	*Permair* leather	Hybrid leather: micro-porous polyurethane membrane laminated to split leather surface by adhesive

After the leather has been tanned, then it is split from both sides to the uniform thickness (S1). Such leather is grounded with unpigmented acrylic ground (S2). The grounding layers penetrate the surface of the corium and bond leather inner layers. The polyurethane water-born dispersion with acrylic hardener was used for the bonding of microporous polyurethane film (S3). The polyurethane film consists of interconnected pores with diameter of 5 μm (S4). Such film is resistant to water penetration, because usually diameter of water drops is 500 – 5000 μm (diameter of small drops – 200 μm). Forces of strong interaction keep water molecules in a drop preventing their spreading. Therefore, such drops are too large to penetrate through the membrane pores. Whereas molecules of water steam, resulting from sweating, are usually smaller than 0.0003 μm. So, they penetrate through the membrane pores easily and then drift away.

The hybrid leather was obtained by the lamination of the polyurethane film to the split leather surface by hot pressing at the temperature of 70 – 75 °C and pressure of 0.5 – 1.0 MPa for 10 – 12 s (S5).

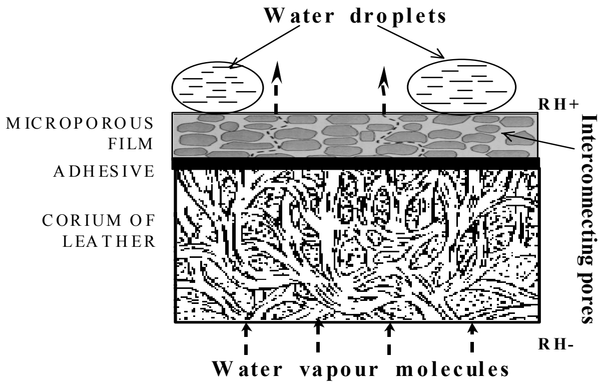


Fig. 2. General scheme of *Permair* leather structure and action

The general scheme of *Permair* leather structure and its action is presented in Fig. 2. *Permair* leather is resistant for a long-term water impact as well as for many chemical materials; it has absolutely no reaction with the road salt (NaCl); it may be characterised by high wear resistance and may be used at low temperatures (down to –25 °C).

Samples. The test pieces were cut in the shape of dumb-bell and the dimensions in accordance to the requirements described in standard ISO 3376:1976 (length of l_1 =5 0 mm, width of $b = 10$ mm). All specimens were conditioned for at least 48 h at a standard atmosphere (temperature $T = 20 \pm 2$ °C, humidity $\varphi = 65 \pm 5$ %) in accordance with EN 12222:1997.

Tensile test. Mechanical properties – tensile strength and elongation – of investigated leather were determined by means of universal tensile testing machine FP-10/1 (Germany) with crosshead speed of 100 ± 10 mm/min in accordance with ISO 3376:1976. Foe each experimental point 15 – 25 specimens of leather and not less than 10 specimens of polymeric film were tested.

Stress-relaxation test. Stress relaxation tests were conducted using a universal tensile testing machine FP-10/1 at the standard atmosphere 20/65. Specimens were stretched at a speed 100 ± 10 mm/min up to strain level of 20 % and held in this position. The stress was recorded as a function of time (from 1 s up to 5000 s). Few relaxation times were chosen ($\tau_1 = 0.2$, $\tau_2 = 2$, $\tau_3 = 20$, $\tau_4 = 200$, $\tau_5 = 2000$) for experimental data approximation. In all cases 10 specimens were tested and average value reported.

4. RESULTS AND DISCUSSION

4.1. Mechanical properties

Mechanical properties of laminated *Permair* leather and its semi-finishing products are presented in Table 2. Such properties as tensile strength σ_t , elongation at break ε_b and elasticity modulus at break E_b were determined. Besides, in the footwear manufacturing the case at $\sigma_s = 9.8$ MPa is important. This value of stress appears in the leather in its shaping by deformation. Therefore, elongation ε_s and elasticity modulus E_s at 9.8 MPa of stress was determined as well.

Table 2. Mechanical properties of the laminated leather and its layers

Sample	σ_t, MPa	Strain, %:		Elasticity modulus, MPa:	
		ε_s	ε_b	E_s	E_b
S1	20.6 ± 1.9	20 ± 1	38 ± 2	52.0	55.2
S2	19.1 ± 1.3	21 ± 1	38 ± 2	47.3	51.4
S3	15.9 ± 1.2	37 ± 2	53 ± 3	26.7	28.8
S4*	7.5 ± 0.2	–	326 ± 14	–	2.3
S5	21.9 ± 1.7	16 ± 1	37 ± 3	68.8	58.9

* Microporous polyurethane film tensile strength is lower than 9.8 MPa; only Young modulus can be determined ($E_Y = 18$ MPa at $\varepsilon_Y \approx 8$ %).

From Table 2 it is evident that mechanical properties of the microporous PU film laminated leather depend on the nature of layers from which the system is composed. The tensile strength σ_t of semi-finished leathers S1-S3 is in the range of 16 – 22 MPa. The differences in the leather strength properties can be related not only to the finishing procedure, but also to initial properties of the sample, topographical zone of leather, defects, etc. Meanwhile, the value of σ_t of the hybrid leather is higher ($\sigma_t \approx 22$ MPa), although it is laminated with low strength PU film ($\sigma_t \approx 2.3$ MPa). It can be attributed to the combinative strengthening of laminated system, when the tensile strength of hybrid system is higher than that of the separate layers even at low cohesion strength of the medium layer [19]. This effect can be evaluated by the coefficient of combinative strengthening K_s:

$$K_s = \frac{\sigma_1 - \sigma_0}{\sigma_0}, \tag{6}$$

where σ_1 is experimentally obtained value of the tensile strength of a laminated system, σ_0 is theoretically calculated tensile strength.

Thus, in the instant of a highest strength layer failure, the strains of layers with lower strength do not reach the limitary values yet. So, influence of these layers on the system resistance to failure is determined not by the tensile strength of separate layers of hybrid system, but by tensile strength that is reached at the instant of corresponding strains, which develop in the instant of the failure of a highest strength layer. Therefore, tensile strength of laminated material should be compared not with total value σ of system constituents, but with their contribution to the materials resistance to failure. So,

$$\sigma_{t1}\frac{S_1}{S}k_1 + \sigma_{t2}\frac{S_2}{S}k_2 + \cdots + \sigma_{ti}\frac{S_i}{S}k_i = \sigma_0\ , \tag{7}$$

where σ_{ti} and S_i are the tensile strength and the cross-section of i-th layer, respectively; k_i is the ratio of elasticity modulus of i-th layer with highest modulus.

The evaluation of *Permair* leather mechanical properties shows that the lamination of microporous PU film considerably increases the strength of laminated system ($K_s = 14 - 23$ %). It can be attributed to the leather surface defects "repairing" by the adhesive layer. Another possible explanation of these results may be related to the effect of "defects locking", i.e., to the dissipation of kinetic energy, which releases during the act of elementary failure [19].

Stress-strain curves ($\sigma - \varepsilon$) of the laminated leather and its layers at the different stages of manufacturing are shown in Fig. 3. From the character of $\sigma - \varepsilon$ curve follows that mechanical properties of different layers such as leather and elastomeric PU film differ radically. The polymeric film has significantly higher elongation at break (higher than 300 %) comparing to that of the leather (36 – 40 %). However, the adhesive increases the elongation at break of the split leather about 1.5 times (sample S4 in Table 2). It may be considered that low viscosity elastomeric adhesive penetrates in to the leather pores and other gaps, affects as plasticizing agent and repairs the surface defects under the loading.

The deformation properties of the laminated leather S5 is very similar to those of the split or grounded leathers. However, it should be pointed out that at the beginning the deformability of the hybrid leather is slightly lower (for S5 at $\sigma_s = 9.8$ MPa elongation $\varepsilon_s = 15 - 17$ % comparing to 19 – 22 % of S1 and S2). It may be attributed to the interaction between two layers, which results on the increase of surfaces stiffness of contacted layers.

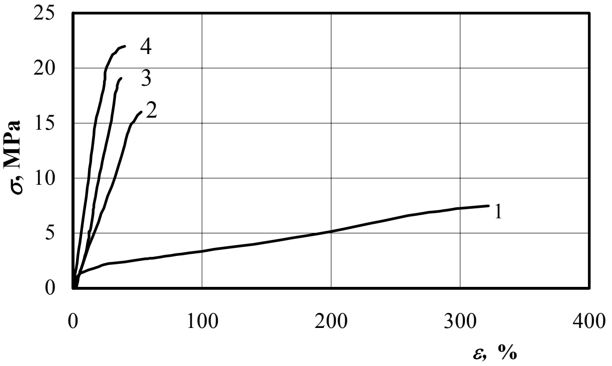


Fig. 3. Stress-strain curves for laminated leather and its layers: 1 – PU film S4; 2 – split leather with adhesive layer S3; 3 – grounded leather S2; 4 – laminated leather S5

Elasticity moduli at break E_b of all leather samples are considerably higher than that of PU film (Table 2). Moreover, in the case of split leather without or with ground coating or adhesive layer modulus E_b is slightly higher than that determined at the shaping stress $\sigma_s = 9.8$ MPa; whereas for the hybrid leather the opposite phenomenon is observed. In this case E_b is significantly higher than E_s (68.8 MPa and 58.9 MPa, respectively). As can be seen from the data, presented in Table 2, for PU film the markedly higher elasticity modulus at low strain is characteristic, also. In this case Young modulus is $E_Y = 18$ MPa, while modulus at break E_b reaches only 2.3 MPa. Thus, above mentioned variation of hybrid leather modulus can be explained by the influence of microporous PU film on its mechanical behaviour.

4.2. Stress relaxation behaviour

It is interesting to determine the stress relaxation behaviour in the waterproof and breathable film laminated leather - relatively new material used in the manufacturing of footwear for professional use, sport and active leisure.

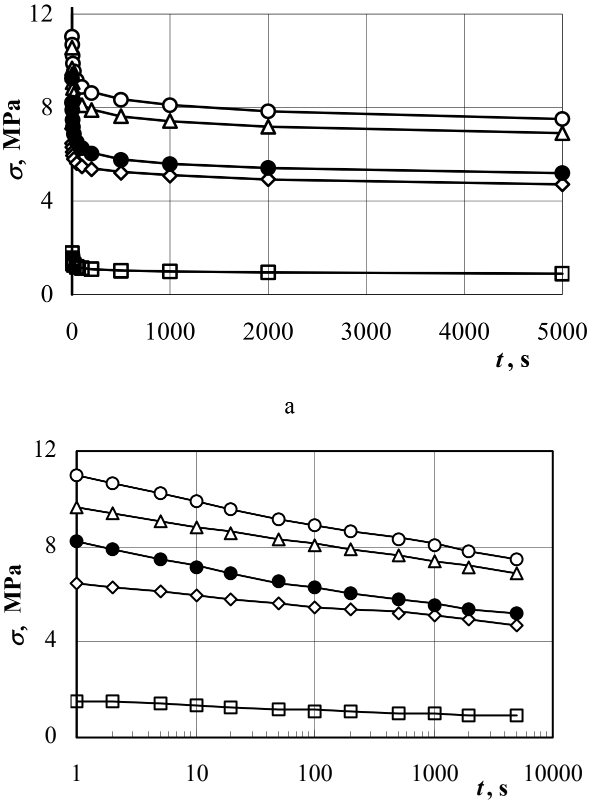
The load-elongation and recovery behaviour of leather and polyurethane film, which are used in *Permair* leather manufacturing, shows considerable differences, which arise mainly from the differences in the layers structure (Fig. 4). Under the loading the structural elements of leather shift with respect to each other. Consequently, stress reduces and residual strains are closely connected to the leather topographical zone, nature and size of defects, sort and age of cattle, etc. Meanwhile, elastomers are characterized by strong reversible deformation that impedes the fixation of given shape.

It is supposed that stress in polymeric materials becomes steady after 1000 s of relaxation [20]. From Fig. 4, *a* it seems that stresses in all investigated samples become nearly constant after 5000 s of relaxation. However, the transfer of experimental results into the '$\sigma -$ log t' scale demonstrates that the process is still in progress both in the leather and polyurethane film (Fig. 4, *b*).

The attempt to obtain satisfactory prediction of long-term viscoelastic behaviour of the hybrid leather using generalized Maxwell model (Fig. 1) was made. Using the experimental data, presented in Fig. 4, the stress relaxation behaviour was described by Eq. (1).

Calculation of elasticity constant D_0 of a single spring of Maxwell model by the method proposed in [16], leads to conclude that stress σ_{5000} comprises 98 – 99 % of the stress equilibrium value σ_∞.

Although D_0 of the microporous polyurethane film has the lowest value (6 – 10 times lower comparing to that of tested leathers), it has no practical impact on D_0 value of hybrid leather – it is in the same level as in the cases of semi-finished leathers (Table 3).



a

b

Fig. 4. Stress relaxation in the laminated leather and its layers (○, Δ, ●, ◊, □ – experimental points; —— – theoretical curves by Eq. (1)): ○ – S1, Δ – S2, ◊ – S3, □ – S4, ● – S5; a – σ – t ; b – σ – log t

Table 3. Elasticity constant D_0 (MPa) of Maxwell model

Samples				
S1	S2	S3	S4	S5
28.48	34.15	23.23	4.38	25.63

Changes of elasticity constant D_i during the relaxation time, determined by the approximation of stress relaxation curves by regular spectrum of discrete relaxation periods, are presented in Fig. 5. As can be seen, the intensity of the shortest time of relaxation for the PU film also markedly differs from that of leathers (values of D_1). However, in the next periods the elasticity constants of all materials to be tested become similar.

Fig. 4 compares the predicted and measured stress relaxation data. The theoretical stress relaxation curves were obtained by inlaying in Eq. (1) the calculated values of elasticity constants D_0 and D_i. It is evident that theoretical prediction is excellent. On the other hand, constants D_0 and D_i may be used partially for the interpretation of the relaxation process as well.

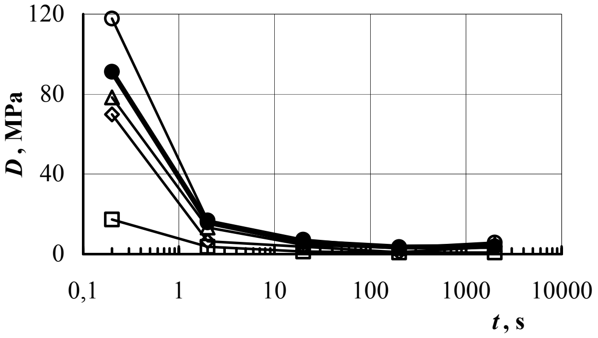


Fig. 5. Dependence of constants D_i of Maxwell model of laminated leather layers on relaxation period τ_i. (Curves description as in Fig. 4)

The inadequacy dispersion and the error of measurement [21] were used for the evaluation of adequacy of the theoretical stress changes to the experimental data. The accuracy data of the stress relaxation behaviour evaluation in the materials analysed are presented in Table 4. The comparison of the predicted and measured stress relaxation data shows that theoretical prediction by the generalized Maxwell model, which represents linear viscoelasticity, successfully describes leather behaviour in the non-linear regions.

Table 4. The inadequacy dispersions s^2_{ad} and measurement error e of stress relaxation evaluation by Maxwell model

Sample	s^2_{ad}	e
S1	$6.3\cdot10^{-4}$	$1.1\cdot10^{-5}$
S2	$2.2\cdot10^{-4}$	$2.0\cdot10^{-6}$
S3	$5.2\cdot10^{-4}$	$1.8\cdot10^{-5}$
S4	$1.9\cdot10^{-5}$	$1.3\cdot10^{-5}$
S5	$3.8\cdot10^{-4}$	$1.0\cdot10^{-5}$

In order to demonstrate the intensity of reduction of stress in materials the rate of stress relaxation can be used [12, 15]. Fig. 6 shows values of σ/σ_0 as a function of time t (where σ_0 is a maximum stress at the instant $t = 0$, i.e., the instant at which the desired strain is reached, and σ is a stress at subsequent times t) for all investigated samples. The rate of stress relaxation decreases in time for both the laminated leather and its layers. It was observed that stress relaxation rate of semi-finished leathers is lower than in the case of laminated leather or film, and practically did not depend on their finishing. Although stress occurring in PU film is the lowest, the intensity of stress decreasing is highest; already after 5 s stress in the film reduces in 22 %, while in split leathers – only in 11 – 14 %. It may be supposed that polymeric film increases the stress relaxation rate of the laminated leather.

In all cases experimental points in the curves $\sigma/\sigma_0 - t$ appear to lie on the two straight lines. The first line refers to a greater slope and applies for the short times, while the second line is for longer times. The initial relaxation may arise due to rearrangement or reorientation in the material structure.

The differences of the mechanism of stress relaxation of various materials may be estimated by the location of the intersection of lines. It should be pointed out that the location of intersection of two lines depends on the materials nature and represents the changes over time, at which the mechanism operating at short time exhausted.

It is obvious that the rearrangements in the leather do not depend on the finishing processes (Fig. 6). So, the intersection of lines for all semi-finished leathers is observed approximately at the same time – $t_l \approx 500$ s. Meanwhile, for PU film this time equals only $t_f = 100$ s. So, combining elastic leather with viscoelastic PU film the changes in hybrid system long-term behaviour may be expected. It confirms results, presented in Fig. 6: PU film reduces the time of initial relaxation in the laminated leather. Due to that the position of lines intersection of the laminated leather curve decreases from 500 s down to $t_h = 200$ s. It follows, by similar reasoning, that initial relaxation region arises due to the rearrangement or reorientation at the leather and polyurethane film interface.

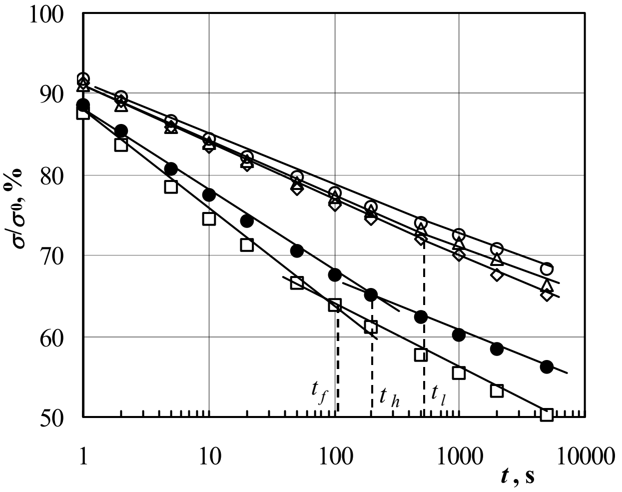


Fig. 6. Relative stress relaxation curves for laminated leather and its layers. (Curves description as in Fig. 4)

Thus, the estimation of the contribution of polyurethane film on the stress relaxation indicates that viscoelastic nature of the film dominates principally on the long-term properties of the hybrid leather. The shape stability of laminated leather will considerably differ from common finished leathers. It may be noticed in the stage of design and manufacture of leather products.

CONCLUSIONS

Mechanical properties and viscoelastic behaviour of microporous polyurethane film laminated leather depend on the structure of the layers from which it is composed. Polyurethane film provides leather with the entire complex of high performance parameters such as resistance to water and high breathable features. At the same time it changes system properties and behaviour under the loading.

Leather backing mainly influences on the mechanical behaviour of the hybrid system, while polymeric film – deformability. For laminated leather combinative strengthening is characteristic due to the repairing of leather surface defects by adhesive layer and kinetic energy dissipation during failure.

The linear viscoelastic model such as generalized Maxwell model can be used to predict non-linear stress relaxation behaviour at constant strain levels up to about 20 %. For this purpose regular discrete relaxation time spectrum can be used. It is expected that this method can be applied for the prediction of creep behaviour of laminated leather.

Stress relaxation rate is markedly higher in the polymeric film than in the leather. The film increases laminated leather stress relaxation rate due to the rearrangement or reorientation at the leather and polyurethane film interface. So, the viscoelastic nature of the film dominates on the long-term properties of the hybrid leather.

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REFERENCES

1. **Thorstensen, T. C.** Practical Leather Technology, 4th ed. New York, Shoe Trade Publishing, 1993: 340 p.
2. Coatings Technology Handbook, 2nd ed. Ed. by **D. Satas, A. A .Tracton**. New York, Marcel Dekker Inc., 2001: 902 p.
3. **Sarkar, K. T.** Retanning, Dyeing and Finishing of Leather. New York, Shoe Trade Publishing, 1996.
4. Proline Ihr Hautnaher Schutz, Lainiere de Picardie, *Laminated Textiles Department*, France, 2000.
5. **Hurten, J., Spijkers, J.** Laminierung von Sympatex Membranen *Adhasion Kleben & Dichten* 1 – 2 1997: pp. 34 – 36.
6. **Wolf, H.** Spanungs - und Dehnungsrelaxation an Leder *Leder- und Hautemarkt* 12 1998: pp. 33 – 37.
7. **Burmistrov, A. G., Kocherov, A. V.** Evaluation of Materials Quality by Computer-aided Complex “Relax” *Leather and Footwear Manufacturing* 1 1998: pp. 17 – 19 (in Russian).
8. **Burmistrov, A. G., Chiursin, V. I., Manukian, A. M.** Automatic Control of Deformation Properties of Leather by Means of the Apparatus “Relax” *Leather and Footwear Manufacturing* 4 2000: pp. 27 – 30 (in Russian).
9. **Bukin, A. N., Kalita, A. N.** Influence of Heating and Temperature of Footwear Materials on their Relaxation Behaviour *Knowledge of Universities. Technology of Light Industry* 2 1981: pp. 37 – 40 (in Russian).
10. **Gvoziakaja, V. A., Adigezalov, L. I., Shvarc, A. S.** Influence of Pre-strain on the Relaxation Properties of Chrome-tanned Leather *Leather and Footwear Manufacturing* 8 1981: pp. 58 (in Russian).
11. **Kravchenko, A. D.** Influence of Stress Relaxation in Chrome-tanned Leather on the Footwear Shape Stability and use Properties *Leather and Footwear Manufacturing* 2 1972: pp. 46 – 50 (in Russian).

12. **Pahl, M., Gleisle, W., Laun, H. M.** Praktische Reologie der Kunststoffe und Elastomere. Dusseldorf, VDI-Verlag GmbH, 1995.
13. **Fried, J. R.** Polymer Science and Technology. New York, Prentice Hall, 1995.
14. **Nitta, K., Suzuki, K.** Prediction of Stress-Relaxation Behavior in High Density Polyethylene Solids *Macromolecular Theory of Simulation* 8 (3) 1999: pp. 254 – 259.
15. **Saha, N., Banerjee, A. N.** Stress-Relaxation Behavior of Unidirectional Polyethylene-Carbon Fibers: PMMA Hybrid Composite Laminates *Journal of Applied Polymer Science* 67 1998: pp. 1925 – 1929.
16. **Vitkauskas, A.** Regular Discrete Relaxation Time Spectrum of Textiles *Materials Science (Medžiagotyra)* 2 (2) 1996: pp. 65 – 71.
17. **Vitkauskas, A.** Influence of Alternating Rate of Extention on Stress Relaxation in Textile Yarns *Materials Science (Medžiagotyra)* 3 (1) 1997: pp. 52 – 57.
18. **Kothari, V. K., Rajkhowa, R., Gupta, V. B.** Stress Relaxation and Inverse Stress Relaxation in Silk Fibres *Journal of Applied Polymer Science* 82 2001: pp. 1147 – 1154.
19. **Gul, V. E.** Structure and Strength of Polymers. Moscow, Chimija - 1978, 170 p. (in Russian).
20. **Guillemenet, J., Bistac, S., Schultz, J.** Relationship between Polymer Viscoelastic Properties and Adhesive Behaviour *International Journal of Adhesion & Adhesives* 22 2002: pp. 1 – 5.
21. **Macosko, C.W.** Rheology: Principles, Measure Elements, and Application. New York, VCH Publishers Inc., 1994.