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INVESTIGATION OF LAMINATED LEATHER RHEOLOGICAL BEHAVIOUR

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Introduction

Relevance of the research. Phenomenological prediction of the mechanical behaviour of various materials and their systems is a fundamentally important problem for engineering application. Recently the multi-component polymeric products from the materials with different nature and properties are widely used into variety applications. One of them, the soft laminated polymeric materials composing microporous or hydrophilic film or membrane, is used for sport, tourist, military and professional clothing products. Such heterogeneous materials often show absolutely new properties and sometimes combine wide range of them, for example, high temperature and chemical resistance, improved permeability properties. On the other hand, the rheological behaviour of laminated materials differs from the rheological behaviour of the separate components. Different elastic properties of laminated materials layers influenced the increase of internal stress and determine the final properties of the composites, too.

One of such soft laminated polymeric materials – microporous film laminated leathers. Microporous polyurethane coat protects leather from various external ambient aggressions very good withal provide good vapour permeability, but in the other hand, it changes leather rheological properties whose are very important in technological aspect. It means that the new manufacture technologies of products from laminated leather are need. Therefore the investigations allowed to predict the behaviour of deformability and relaxation properties of microporous film laminated leather are relevant.

The goal of the work was to investigate the rheological properties of laminated leather and predict the relaxation behaviour in order to select and substantiate the shaping regime.

During the research the following ***tasks*** are approached:

- to determine the peculiarities of mechanical properties of polyurethane (PU) film laminated leather and its layers;
- to investigate the stress relaxation process of laminated leather and its layers and compare with others kinds of leather;
- to chose and adapt the simple and rigorous theoretical model for mathematical description and phenomenological interpretation of investigated materials stress relaxation behaviour;
- to determine the influence of some environment and loading parameters on laminated leather and microporous film relaxation process.

Scientific Novelty and Practical Significance. The substantially different relaxation process of macrolayers with very different structure (leather and microporous elastomeric film) mainly determines the relaxation process of heterogeneous materials (laminated leather). As our investigations have shown, the microporous polyurethane (PU) film substantial changes the intensity and behaviour of stress relaxation process of the microporous PU film laminated leather. Relaxation process of laminated leather was approximated by various mathematical models, but the highest precision of approximation is obtained by generalised Maxwell model. The two stages with different rates of the relaxation process is characteristic for various leathers and PU film were used for prediction of stress relaxation process of this materials till 10 000 s. Stress relaxation of laminated leather and microporous PU film was described by the time-rate analogy, which creates possibility to predicts influence of loading rate on stress relaxation of laminated leather and microporous film in wide interval of relaxation time and loading rate.

The obtained results can be used for prediction of microporous PU film laminated leather relaxation behaviour in order to optimize the leather products technological regimes of formation and increase their shape stability at wearing.

Approbation of the research results. The results of the research were presented in the 10 scientific publications.

Structure of the dissertation. This dissertation consists of: introduction, five chapters, conclusions, list of references and list of scientific publications. The materials of the dissertation are presented in 106 pages, including 60 figures and 13 tables.

Content of the dissertation

Introduction presents the relevance of the research, definition of the research aim and objectives, survey of the scientific novelty and practical value of the dissertation.

Chapter 1. Literature review gives the view of relevant publications related to the theme of dissertation. The information about leather, elastomers and heterogeneous materials structure, environment, and loading parameters influence on their mechanical and relaxation behaviour have been reviewed. The analysis of mathematical description methods of polymeric materials relaxation process has been carried out, too.

Chapter 2 presents the materials and methods of investigations. The leathers of various processing technology (tanning and coating) manufactured in AB "Šiaulių Stumbras" and microporous PU film *Permair* ("*Porvair* plc.", UK) have been used for investigation. The methods of specimens' preparation, tensile properties determination, stress relaxation process and leather shaping investigations are presented. Stress relaxation tests were carried out at 20 % level of deformation and held in this position. The influence of deformation rate on stress relaxation process was determinate by changing loading speed up to 300 mm/min.

Chapter 3 presents the experimental and theoretical investigations.

Investigation of various leathers tensile properties. The mechanical behaviour of tanned leather in great deal depends on leather structure, topographical zone, nature and size of defects, sort and age of cattle, tanning and finishing process, etc. Tanned leather is usually coated with thin pigmented or lacquer coatings. The structure of laminated leather imitates leather with natural grain (Fig. 1).

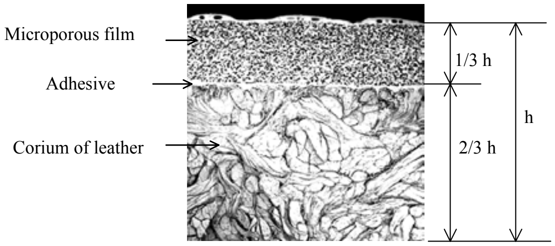


Fig. 1. Microporous PU film laminated leather

It was determined that the tensile strength of laminated leather ($\sigma_t \approx 15.5$ MPa – 22.5 MPa) is close to strength of semifinishing crust leather and is approximately twice higher then this property of elastic leather. Herewith the variation of properties results is lower in compare with values of other types' leathers. That can be explained by influence of homogeneity of synthetic PU film structure on properties of hybrid material. The investigations show the evident dependence of laminated leather tensile properties upon thickness. The difference of values of different thickness laminated leathers (LO_1 and LO_2) is 17% - 36%, the difference of elasticity modulus at break E_{tr} is 36%, and elongations at break ε_{tr} – 23%. It is possible to suppose that the main influence on presented properties of laminated leather has split leather. Therefore, was important to study the mechanical properties of each layer of leather separately and to determine their influence on hybrid leather properties.

Investigation of laminated leather layers tensile properties. Mechanical properties of laminated leather were compared to such properties of semi-finishing products at the different stages of laminate manufacturing: S1 – chrome-tanned split leather 1.2 ± 0.1 mm of thickness, S2 – split leather grounded with acrylic ground (in amount of 20 g/dm^2), S3 – grounded leather coated with adhesive layer (polyurethane water-born dispersion in amount of 12 – 15 g/dm^2) and microporous PU film (PL). 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 moment at σ_1=9.8 MPa is important; this value of stress appears in the leather at the time of its shaping by deformation in order to give the desirable shape. Therefore, elongation ε_1 and elasticity modulus E_1 at 9.8 MPa of stress was determined as well.

It was determined that the influence of grounding on the tensile properties of split leather is very low, while the adhesive layer increases deformation of split leather (Table 1). 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).

Table 1. Mechanical properties of laminated leather and its layers

Sample	σ_{tr}, MPa	Strain, %:		Elasticity modulus, MPa:	
		ε_1, when σ=9.8 MPa	ε_{tr}, at break	E_1, when σ=9.8 MPa	E_{tr}, at break
S1	20.6±1.9	20±2.0	38±2.6	52.0	55.2
S2	19.1±1.3	21±1.8	38±2.3	47.3	51.4
S3	15.9±1.2	37±2.3	53±3.0	26.7	28.8
PL	7.5±0.2	–	326±14	–	2.3
LO	21.9±1.7	16±1.3	37±2.3	68.8	58.9

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 the low cohesion strength of the medium layer. This effect can be evaluated by the coefficient of the strengthening K_S:

$$K_S = \frac{\sigma_1 - \sigma_0}{\sigma_0}, \tag{1}$$

where σ_l is experimentally obtained value of the tensile strength of laminated system, σ_0 is theoretically calculated tensile strength:

$$\sigma_{t1}\frac{S_1}{S}k_1 + \sigma_{t2}\frac{S_2}{S}k_2 + \ldots + \sigma_{ti}\frac{S_i}{S}k_i = \sigma_0 \tag{2}$$

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 laminated leather mechanical properties shows that the lamination of microporous PU film considerably increases the strength of laminated system: K_S = 14 % - 23 %. It may 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 that releases during the elementary failure.

From the character of σ-ε curve it follows that mechanical properties of different structure layers such as leather and elastomeric PU film differs radically (Fig. 2). The adhesive increases the elongation at break of the split leather about 1.5 times (sample S3 in Table 1). It may be considered that low viscosity elastomeric adhesive penetrates in the leather pores and other gaps, affects as plasticizing agent and repairs the surface defects at the moment of failure under the loading.

The deformation properties of the laminated leather LO are very similar to that 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 (at σ_s=9.8 MPa for LO ε_s=15 %-17 % comparing to 19 %-22 % of S1 and S2). It may be attributed to the interaction between two layers that effects the increase of surfaces layers stiffness.

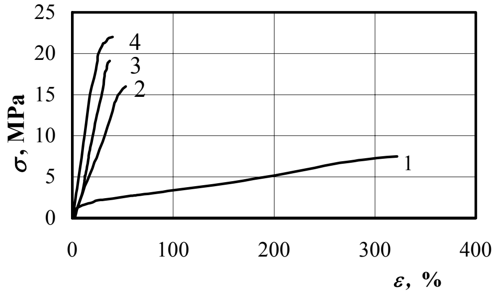


Fig. 2. Stress-strain curves for laminated leather and its layers: 1 – PU film (PL); 2 – split leather with adhesive layer (S3); 3 – grounded leather (S2); 4 – laminated leather (LO)

As can be seen from data, presented in Table 1, for PU film also it is characteristic markedly higher elasticity modulus at low strain, i.e. Young modulus comes up to E_J=18 MPa, when modulus at break - only E_b=2.3 MPa. Thus, as was mentioned above variation of hybrid leather modulus can be explained by the influence of elastomeric PU film on its mechanical behaviour.

The polymeric film has significantly higher elongation at break (higher than 300%) comparing to that of the leather (36 %-40 %). On the other hand, high elastic deformation is characteristic to PU film. It was determined that the residual elongation even after 1 min of relaxation is only 30 %. This property creates problems for laminated leather products formation process and shape stability in wear.

Since the mechanical properties of laminated leather depend on the separate leather layer, it is important to determine the peculiarities of relaxation process of laminated leather and its individual layers (leather split, PU film) contribution on this process.

Mathematical methods for stress relaxation prediction of leather and PU film. For the comparison and modelling it is often necessary to fit experimental relaxation data to an analytic function. The objective of the fitting process is to determine parameter values that in some sense represent the “best” fit of the approximating function to the experimental data.

In order to define the most effective method of mathematical description of stress relaxation in investigated materials four analytical functions were used: power function (Eq. (3)), Kohlrausch equation (Eq. (4)) and two rheological models such us twin Maxwell - Wiechert (Eq. (5)) and generalized Maxwell. Generalized Maxwell model of five Maxwell elements and a single elastic Hookean spring in parallel (Eq. (6)).

$$\sigma = \sigma_\infty + at^b \tag{3}$$

$$\sigma = \sigma_\infty + (\sigma_0 - \sigma_\infty)e^{-mt} \tag{4}$$

$$\sigma(t) = D_s \varepsilon_0 e^{-t/\tau_s} + D_w \varepsilon_0 e^{-t/\tau_w} \tag{5}$$

$$\sigma = \sigma_\infty + \sum_{i=1}^{n} \sigma_i = D_0 \varepsilon_t + v_t \sum_{i=1}^{n} D_i \tau_i \left(1 - e^{-\varepsilon_t / v_t \tau_i}\right) e^{-t^* / \tau_i}\ , \tag{6}$$

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

The regular discrete spectrum, proposed in literature, was used to eliminate influence of external factors on the relaxation time and its intensity. In this case relaxation periods always have constant values, which can be obtained according to the relation:

$$\tau_i = a^{i-1} \tau_1 , \tag{7}$$

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

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.

The value of D_0, which defines the equilibrium stress σ_∞ on the model, can be calculated from Eq. (8) using two experimental values of stress: σ_{n1} that corresponds to the time $t^*_1 \approx \tau_n$ and $\sigma_{n2} - t^*_2 \approx t^*_u$ (t^*_u is real time of observation):

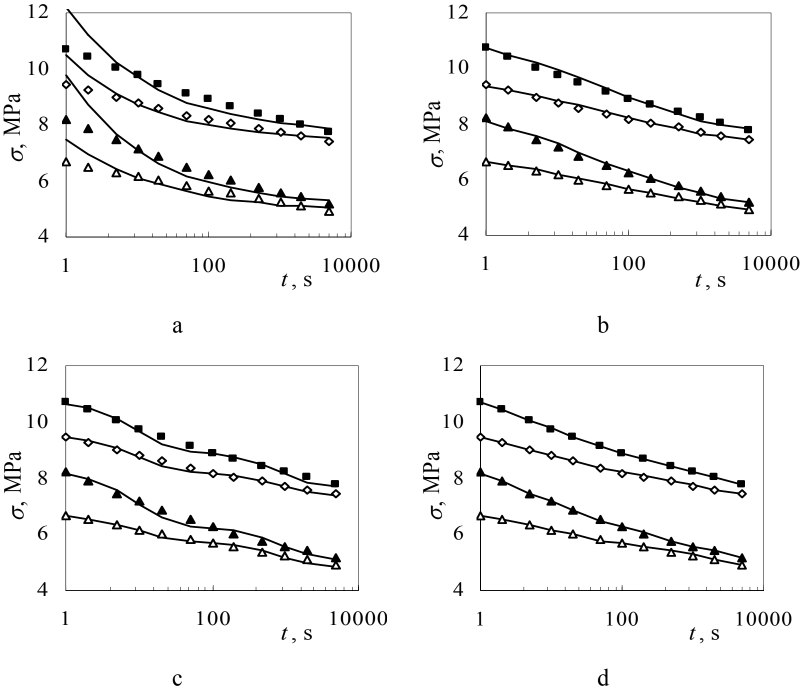
$$D_0 = \frac{\sigma_{n2} - \sigma_{n1} \, exp\left(-\dfrac{t_2^* - t_1^*}{\tau_n}\right)}{\varepsilon_t \left[1 - exp\left(-\dfrac{t_2^* - t_1^*}{\tau_n}\right)\right]} \tag{8}$$

Correspondingly:

$$D_n = \frac{\sigma_{n1} - D_0 \varepsilon_t}{v_t \tau_n G_n \, exp\left(-\dfrac{t_1^*}{\tau_n}\right)} , \tag{9}$$

where $G_n = 1 - e^{\varepsilon_t / v_t \tau_n}$.

The visual examination of the theoretical curves permits to conclude that Kohlrausch method and generalized Maxwell one only successfully describe stress relaxation behaviour in the non - linear regions of leathers (Fig. 3, *b, d*). Power function and Maxwell - Wiechert model representing approximating functions fit to the experimental data in worse manner (Fig. 3, *a, c*).



a b

c d

Fig. 3. Stress relaxation of various leathers approximated by different theoretical models: a –according to Eq. (3), b – according to Eq. (4), c –according to Eq. (5), d – according to Eq. (6); ■ – hydrophobic, ◊ – elastic, ▲ – laminated *Permair*, and Δ-S – split leathers experimental data

The same tendency is observed in the case of microporous *Permair* film: experimentally determined and predicted stress relaxation behaviour changes in the same manner using Kohlrausch and generalized Maxwell models.

Adequacy of the approximating curves to the experimental data may be evaluated by the magnitude of inadequacy dispersion. The next consideration is the selection of a measure of the error between approximating function and the experimental data. One convenient measure is the Euclidean norm of the deviations at the *N* data points. However, since the stress decays over several orders of magnitude, this error measure artificially weights the error at short time higher than that at long times. An error measure, which avoids this defect, measures the deviations between the natural logarithms of the stresses:

$$e = \sum_{i=1}^{N}\left(ln[\sigma(t_i)] - ln\left[\sigma^{teor}(t_i)\right]\right)^2 \qquad (10)$$

Comparison of the congruity of the used analytical functions to the experimental data showed that according to the values of inadequacy dispersion s and measure error e the “best” fit to the experimental data shows Eq. (4), which represents generalized Maxwell model, possessing a regular spectrum of relaxation times (analogous values of inadequacy dispersion and measure error of Kohlrausch model are considerable higher). So, the description of the relaxation processes by generalized Maxwell model, applying a regular spectrum of relaxation periods, may be considered as the most suitable method for non - linear behaviour of leathers and its polymeric layers at various conditions of testing (rate, temperature, adhesion between layers, etc.).

Evaluation and comparison of relaxation processes of various leathers. The various types of leather were used for investigations: hydrophobic (H) (PU pigment coated hybrid-tanned bovine leather with fat content not less than 14%), elastic (E) (soft and elastic chrome-tanned cowhide leather with PU pigmented coating), and two kinds of laminated leather with microporous PU film (LO_1 and LO_2) with different thickness of split leather. The specimens were stretched up to 20 % and held in this position up to 5000 s.

It was determinate that stresses of laminated leathers are low than these of hydrophobic and elastic leathers (Fig. 4).

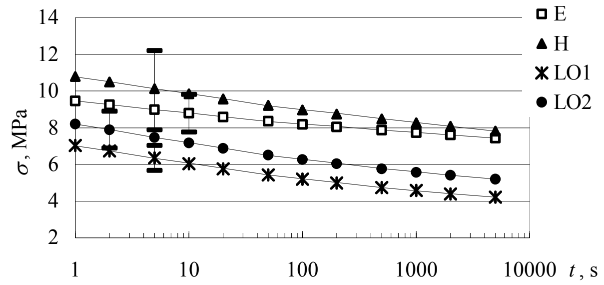


Fig 4. Stress relaxation of investigated materials (— theoretical dependences by generalised Maxwell model (Eq.6))

It was noticed that the rate of stress relaxation of laminated leathers are higher comparing to that of other leathers. After 5000 s it decreases until 50 % (Fig. 5). It can be stated that behaviour of laminated leather relaxation differs from these process of another type of leathers.

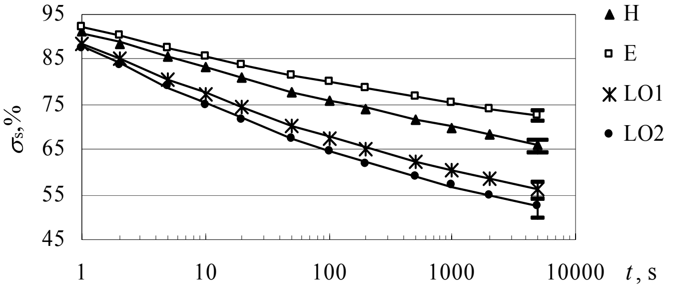


Fig 5. Relative stress relaxation curves of investigated materials (— theoretical dependences by generalised Maxwell model (Eq.6))

Investigation of relaxation process of laminated leathers layers. The load-elongation and recovery behaviour of leather and polyurethane film, which are used in laminated leather manufacturing, show considerable differences, which arise mainly from the differences in their layers structure. Under the loading the structural elements of leather shift with respect to each other. Due to it stress reduces and a residual strain is closely connected to the leather topographical zone, nature and size of defects, sort and age of cattle, etc. Meanwhile, elastomers are characterised by strong reversible deformation that impedes the fixation of given shape. So, the layers of laminated leather have very different structure, which influenced on relaxation properties. The behaviour of relaxation depends on both components.

The spectrum of short relaxation time of laminated leather is higher than in the case of various split leathers, because of higher rate of initial part of relaxation (Fig 6).

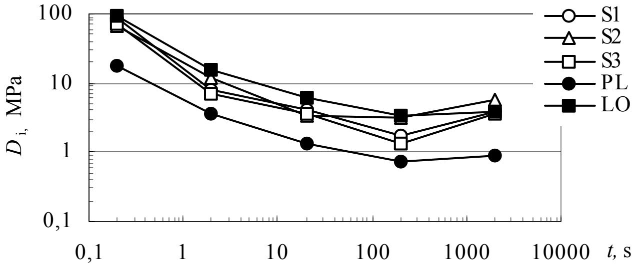


Fig 6. Regular discrete spectrum of laminated leather and its layers by generalised Maxwell model

The values of initial relaxation σ_0 of microporous PU film are 9 times lower than values of laminated leathers. The values of constants D_i are low, too. Notwithstanding, regular discrete spectrum of film is lower than spectrum of leathers, but the character of dependences on time is very similar to laminated leather and differs from all split leathers.

The different character of stress relaxation behaviour can be observed in relative stress - time dependences (Fig. 7).

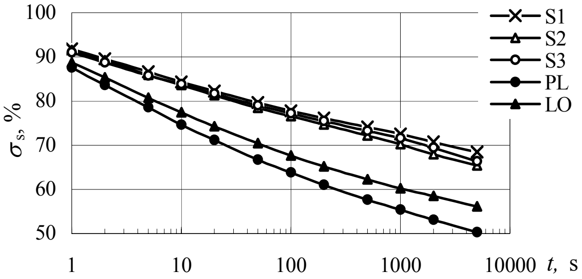


Fig 7. Relative stress relaxation curves of laminated leather and its layers

As is seen, the coating of split leather with acrylic ground and PU adhesive do not influenced markedly on relaxation process, while this process for laminated leather is different and similar to that of microporous PU film. Although stress occurring in PU film is the lowest, intensity of their variation after removing load 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.

So, the film substantial changes relaxation properties of leather: the intensity and behaviour of stress relaxation process differ from that of leathers and are close to micropores PU film.

The investigation of stress relaxation of soft polymeric materials by description with two linear equations. Evaluation of dependence of relative stress $\sigma_S = \sigma/\sigma_0$ on the time ($\sigma_S - \lg t$) the marked moment of relaxation rate changing can be observable. It can be named as "break-point" of relaxation process and determined as point of intersection of two linear equations. This "break-point" is determinate by the calculation a lowest maximum relative error δ_{max} between experimental and theoretical values. The dependences $\delta_{max} - \lg t$ are calculated changing the time value for intersection point and the "break-point" of stress relaxation process is determinate.

It was obtained that the rate of stress relaxation after 50 s – 100 s changed markedly for all investigated materials. The "break-point" of all split leather semimanufactures S1, S2, S3, hydrophobic and elastic leather is observable after 50 s ± 5 s, while for microporous PU film and laminated leather the first period of relaxation is twice longer and "break-point" is observable only after 100 s. Besides the "break-points" of last materials are more observable (Fig. 8), i.e. the changes of rate of stress relaxation more than for another leathers. The reason of such phenomena can be explained by the relaxation processes in microporous PU film.

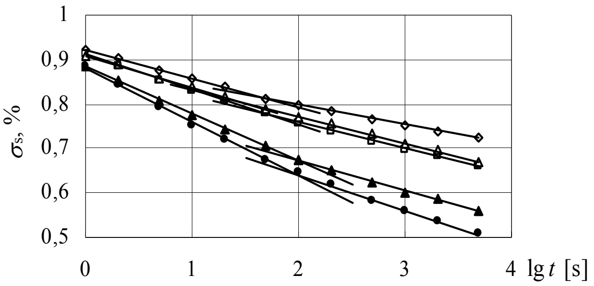
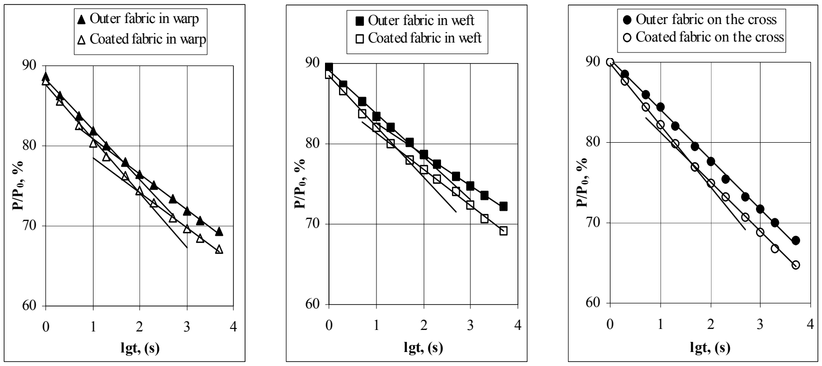


Fig 8. Relative stress relaxation curves of investigated materials: ●– microporous PU film and leathers: ▲– laminated, □– hydrophobic, ◊– elastic and Δ– split S3

The analogous investigations were carried out with three-ply textile laminate *Gore – Tex* fabric, which also consist of microporous film. The results obtained showed that stress relaxation processes in all directions (in weft, in warp and on the cross) are more intensive for laminate (in comparison with uncoated fabric) (Fig. 9). The influence of microporous film on the relaxation properties of laminate is high expressed, especially on the cross by 45 ° angle (Fig. 9, c). In this case the deformation of woven fabric structure arises and the fabric structure changing becomes.



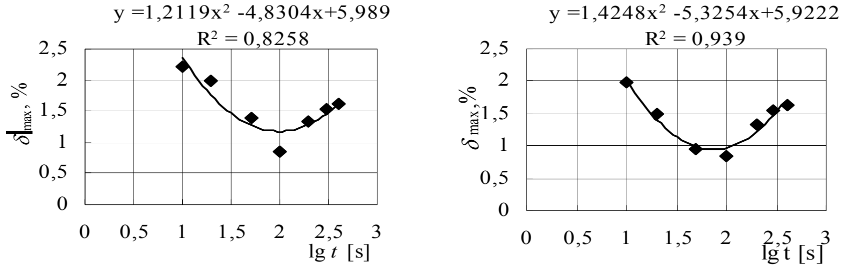
a b c

Fig 9. Relaxation curves P/P_0 of polyester fabric and three-ply laminate

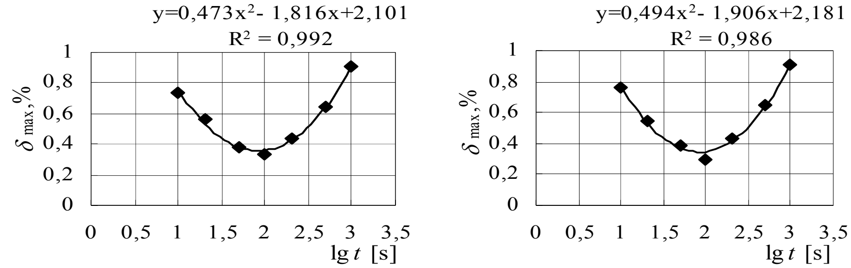
For this reason the stress relaxation curve of woven fabric do not have a “break-point”, while in three-ply laminate case the film constrained the woven fabric structure changing and relaxation process become with “break-point”.

So, the influence of microporous *Gore – Tex* film on three-ply textile laminate is the same as the influence of the microporous PU film on laminated leather: the rate of stress relaxation of laminates is higher than of unlaminated materials and have a high expressed “break-point” of relaxation process. These results confirm hypothesis about domination of one kind of polymeric material viscoelastic properties on relaxation process of hybrid material.

On the other hand, the allocation of “break-point” of relaxation process has practical application for shortening of experimental stress relaxation investigation time. It was determined that shortening of stress relaxation investigations till 2000 s using “break-point” determination method do not increases the relative error δ while shortening till 500 s or 1000 s increases relative error δ (Figure 10 and 11).



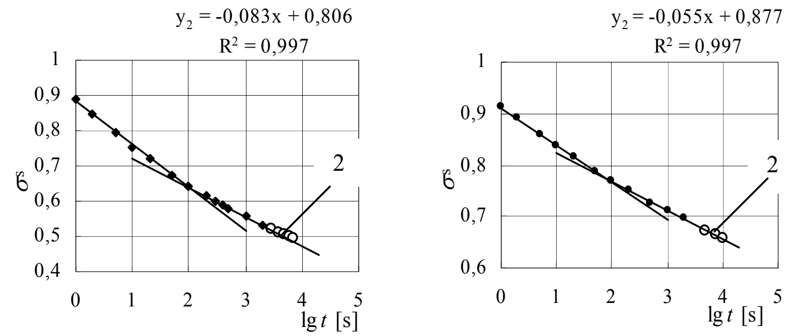
Microporous PU film, when t_n=7000 s Microporous PU film, when t_n=2000 s



Split leather S3, when t_n=10000 s Split leather S3, when t_n=2000 s

Fig 10. Dependences of maximum relative error δ_{max} between experimental and calculated data during stress relaxation

So, it is possible to state that experimental investigation till 2000 s is sufficient time for “break-point” localisation of soft polymeric materials stress relaxation and prediction of stress values even till 10000 s, i.e. 5 time longer than experimental investigations were carry out (the relative error $\delta < 2$ %).



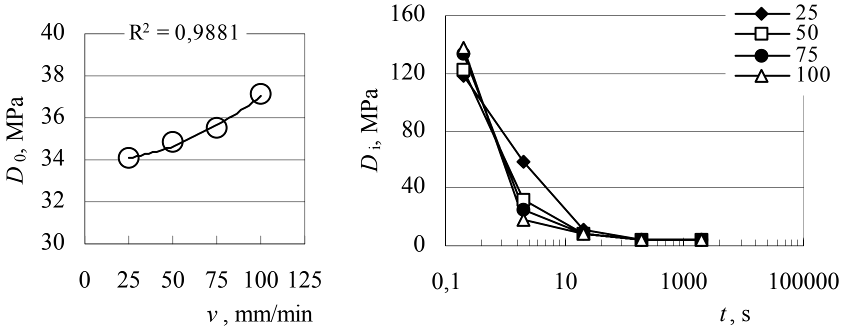
a b

Fig 11. Prediction of stress relaxation with "break-point" localisation: a – microporous PU film, b – split leather S3; ● – experimental values for two linear equations determination

Influence of loading speed on laminated leather and microporous PU film stress relaxation. It was determinate that the initial rate of stress relaxation grows by linear dependence, the rate increases up to 100 mm/min:

$$d\sigma / dt = 0{,}0099 \cdot v + 0{,}4245\ , (R^2 = 0{,}995). \qquad (11)$$

It was determined that rate of stress relaxation apparently differ in the process initial part only (by increasing rate of loading from 25 mm/min up to 100 mm/min values of constants D_4 and D_5 vary marginally) (Fig. 12). Later this difference declines and after 1000 s stresses of all samples actually relax by the same rate.

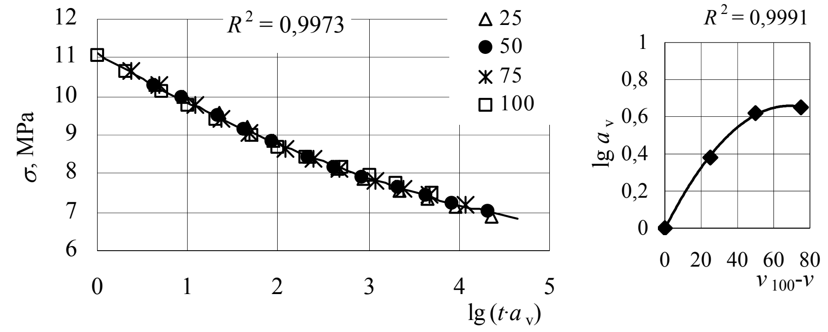


a b

Fig. 12. Dependence of generalized Maxwel model constant D_0 (a) and discrete spectrum of relaxation times (b) on loading speed of laminated leather

Using method of time-rate analogy the master curve of stress relaxation of laminated leather was obtained (Fig. 13). By this curve it is possible specify laminated leather stress changing in the wide time period - twice higher than it was analysed:

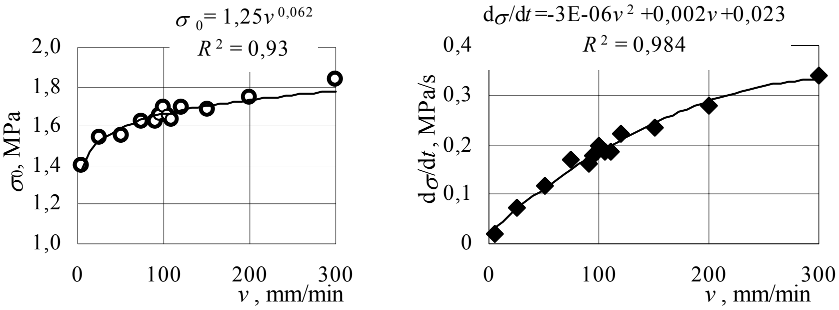
$$\sigma = 0{,}0948\left(lg\left(t \cdot a_V\right)\right)^2 - 1{,}3583\, lg\left(t \cdot a_V\right) + 11{,}103 \qquad (12)$$



a b

Fig. 13. Master curve of stress σ of laminated leather (a) and dependence of shift factor a_V on loading speed of laminated leather (b)

In previous investigations it was found that stress relaxation of strained laminated leather depends on the rheological properties of microporous PU film. So, it is important to analyse the influence of loading rate on stress relaxation of this PU film. It was determined that increasing loading rate from 5 mm/min up to 300 mm/min, initial stress σ_0 (Fig. 14, a) increases as well as increases initial rate of relaxation (Fig. 14, b).

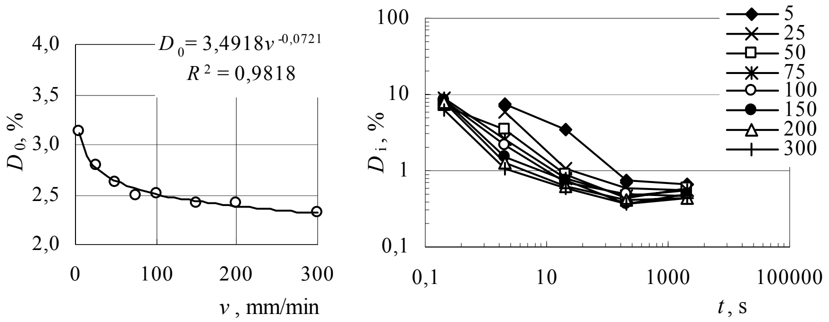


a b

Fig. 14. Dependence of initial stress σ_0 (a) and rate of stress relaxation during the first second of process dσ/dt (b) on loading speed of microporous PU film

After evaluation of engineering stress σ_s variation on time it was determined that due to increase of loading rate relaxation increases as well.

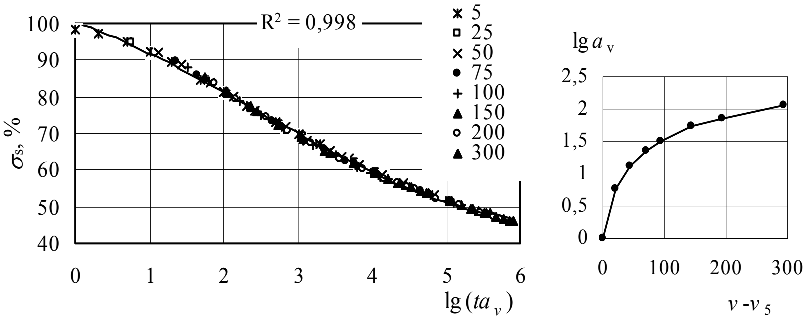
Therefore, appeared stresses of the film samples strained on higher rate at the same time relax more intensively. It was determined that taking into consideration results of relative stress σ_s mathematical approximation, the values of constants D_0 (Fig. 15, a), as well as D$_2$, D_3, D_4 and D_5 (Fig. 15, b) of rheological generalized Maxwell model has regularly decreases as loading rate increases.



a b

Fig. 15. Dependence of generalized Maxwell model constant D$_0$ (a) and discrete spectrum of relaxation times (b) on loading speed of microporous PU film

Using method of time-rate analogy obtained master curve of variation relative stress σ_s of microporous PU film (Fig. 16).



a b

Fig. 16. Master curve of relative stress σ_s in microporous film (a) and dependence of shift factor a_V on film straining speed (b)

The equation, described by least square method, specifies stress relaxation behaviour depending on loading speed in wide range of time:

$$\sigma_S = 0{,}243(lg(ta_V))^3 - 1{,}785(lg(ta_V))^2 - 7{,}001 lg(ta_V) + 100{,}84 . \qquad (13)$$

Influence of parameters, intensifies stress relaxation, on laminated leather shaping. The quality of leather products is satisfying only when product after shaping keep this obtained shape. The shape stability of leather was evaluated according to the change in the area of biaxially deformed by punch leather specimen before and after shape fixation:

$$\varepsilon_d = (h_2 / h_1)^2 \times 100, \tag{14}$$

where h_1 and h_2 are height of punched circular segment of leather straight and after appropriate time of loading, respectively.

The laminated leather specimens after shaping were exposed 10 min at 18 °C ± 2 °C temperature and after affected by various treatments of shaping (Table 2).

Table 2. Parameters of laminated leather treatment

Treatment mode	Heating	Cooling
I	$T = 120 \pm 2$°C; $\tau = 5$ min	No cooling
II	1.H_2O vapour $T = 80$°C, $\tau = 30$ s 2.Heat air stream $T = 100$°C, $\tau = 60$ s	No cooling
III	$T = 120 \pm 2$°C; $\tau = 5$ min	H_2O stream $T = 10 \pm 2$ºC; $\tau = 2$ min
IV	$T = 140 \pm 2$°C; $\tau = 5$ min	$T = -7 \pm 2$°C; $\tau = 20$ min
V	$T = 140 \pm 2$°C; $\tau = 15$ min	No cooling
VI	$T = 140 \pm 2$°C; $\tau = 15$ min	$T = -16 \pm 2$°C; $\tau = 20$ min

The changes of the shape stability coefficient of laminated leather during exposure up to 140 h on the treatment mode after punching are presented in Fig. 17. It is evident that shape stability significantly depends on the treatment parameters. When temperature on leather surface (determined by contact thermometer PT with sensor HD 9214) increases more than 1.5 times (from 19,5 ºC ± 1 C ° up to 30 ºC ± 1,5° C) (V and VI treatments in Table 2), the well-marked increases of residual deformation of punching is obtained.

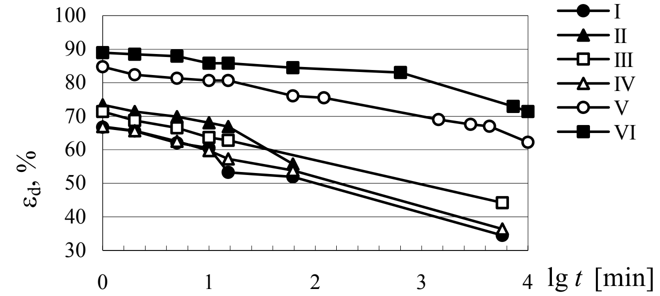


Fig 17. Dependence of laminated leather relative shape stability change during time upon treatment mode

On the other hand, the drastic cooling cycle does not influence on shape stability so significantly as heating temperature and its impact duration.

Conclusions

1. The rheological properties of laminated leather depend on both leather and microporous polyurethane film properties.
2. The strength of laminated leather mainly determines leather bottom laeyer. Combined strengthening is characteristic for laminated leather. Split leather lamination with low cohesive strength microporous PU film reinforces the system up to 23 %.
3. The microporous PU film substantially changes relaxation properties of leather: the intensity and run of stress relaxation process differ from that of leathers and are close to stress relaxation process of microporous PU film.
4. The mathematical approximation of laminated leather relaxation processes by Kohlraush equation is more precise than approximation by power equation or equation of twin Maxwell-Wichert model. Notwithstanding, only changeable parameter of Kohlraush equation decreases possibility of the results interpretation when different objects of investigations or changing loading parameters are compared. The highest precision of modelling is obtained by generalised Maxwell model, herewith even six constants of equation can be used for more widely phenomenological interpretation of relaxation process.
5. It was determined that relaxation process of various leathers and PU film can be divided into two stages definable by different intensity. The position in time scale of this slowup of laminated leather relaxation process, named as "break-point", depends on viscoelastic properties of the microporous film.
6. Localisation of the relaxation curve "break-point" makes possibility to reduce the stress relaxation tests fivefold (up to 2 000 s). It was determined that in this case it is possible to predict behaviour of stress relaxation of various leathers and microporous film up to 10 000 s with suitably precision ($\delta < 2$ %).
7. It was obtained that loading speed influence on relaxation process of laminated leathers and PU film:
    - the increase of laminated leathers loading speed increases the initial relaxation rate according to linear dependence only in initial stage (up to 100 s). Afterwards the stress relaxation rate does not depend on loading speed (the constants D_4 and D_5 of discrete spectrum have close values);
    - the loading speed influences on stress values and relaxation behaviour of microporous PU film – the stresses and the intensity of stress relaxation increases as the loading speed increases.

8. It was determined that stress relaxation of laminated leather and microporous PU film can be described by the time-rate analogy. The power equations obtained make possibility to predicte loading speed influenc on stress relaxation of laminated leather and microporous film in wide range of time and rate (up to 24 h for laminated leather and 11 days for PU film).
9. The microporous PU film considerably changes the laminated leather shaping properties. To increase the shape stability of laminated leather products it is necessary to use more drastic treatment parameters: higher temperature of fixation, higher lasting and more effectual cooling methods that are more close to treatment parameters of the synthetic leathers.

List of Publications on the Theme of Dissertation

Article in journal from ISI (Institute of Scientific Information) list

1. R. Milašius, D. Milašienė, V. Jankauskaitė. Investigation of Stress Relaxation of Breathable-Coated Fabric for Clothing and Footwear // Fibres & Textiles in Eastern Europe. ISSN 1230-3666, 2003, Vol. 11, No. 2, p. 53-55.

Articles in Other Periodical Reviewed Scientific Journals

1. D. Milašienė, V. Jankauskaitė, R. Arcišauskaitė. Prediction of Stress Relaxation in Laminated Leather Layers // Materials science (Medžiagotyra). ISSN 1392-1320. Kaunas: Technologija, 2003, Vol. 9, No. 1, p. 73 – 79.
2. V. Jankauskaitė, D. Milašienė, A. Vitkauskas. Differences in Viscoelastic Properties of Chrome-tanned Leather upon Surface Coating // Light Industry – Chromium In Leather, Prace Naukowe. ISSN 1642-5251. Radom, Politechnika Radomska, 2003, Nr. 22, p. 180-184.
3. D. Milašienė, V. Jankauskaitė. Comparable Evaluation of Methods for Stress Relaxation Prediction in Leather // Mechanika. ISSN 1392-1207. 2003, Nr. 4 (42), p. 11-18.

Articles in Proceedings of International Scientific Conferences

1. D. Milašienė, V. Jankauskaitė, R. Arcišauskaitė. Peculiarities of Viscoelastic Properties of Laminated Leather for Footwear // International Conference "Baltic Textile &Leather". ISBN 9955-09-479-6. Kaunas: Technologija, 2003, p. 200-204.
2. D. Milašienė, V. Jankauskaitė. Stress Relaxation Behaviour of Polymeric Film Laminated Leather // Proceedings of Baltic Polymer Symposium 2003 Jurmala. ISBN 9984-32-535-0. Riga, RTU, 2003, p. 158 – 162.

Articles in Proceedings of Lithuanian Scientific Conferences

1. D. Milašienė, G. Radžiūnaitė, V. Jankauskaitė, R. Arcišauskaitė. *Permair* odos formavimo savybių ypatumai // Vartojimo reikmenų technologijos ir dizainas: Konferencijos pranešimų medžiaga.-Kaunas:Technologija, 2001, 10-16 psl.
2. D. Gapševičiūtė, D. Milašienė, V. Jankauskaitė. *Permair* odos atskirų gamybos stadijų pusgaminių stiprumo ir deformacinių savybių tyrimas // Gaminių technologijos ir dizainas: Konferencijos pranešimų medžiaga.-Kaunas: Technologija, 2002, 32-37 psl.
3. D. Milašienė, V. Jankauskaitė, G. Arcišauskaitė. Deformavimo priešistorės įtaka dubliuotų sistemų įtempių relaksacijai // Gaminių technologijos ir dizainas: Konferencijos pranešimų medžiaga.-Kaunas: Technologija, 2002, 38-41 psl.
4. D. Gapševičiūtė, D. Milašienė, V. Jankauskaitė. Deformavimo priešistorės įtaka įtempių relaksacijai mikroporingoje *PERMAIR* dangos plėvelėje // Gaminių technologijos ir dizainas: Konferencijos pranešimų medžiaga.-Kaunas: Technologija, 2003, 189-193 psl.

Information about the Author of Dissertation

Born in 1965 07 23 in Kaunas, in 1983 graduate Jonava 1th secondary school. In 1983 – 1989 engineering studies at Kaunas Polytechnical Institute, Faculty of Light Industry, diploma of Leather Products Technology Engineering. In 1989 – 1993 engineer at Faculty of Mashines Production of Kaunas Polytechnical Institute. In 2000 – 2004 doctoral's degree studies (Materials engineering) at Kaunas University of Technology. From 2004 junior research assistant at Faculty of Design and Technologies.

Reziumė

Tiriamoji problema. Pastaraisiais metais ypač populiarūs tampa daugiakomponenčiai polimeriniai gaminiai, sudaryti iš labai skirtingų savybių medžiagų. Tokie junginiai dažnai pasižymi visiškai naujomis tiek technologinėmis, tiek eksploatacinėmis savybėmis. Viena tokių hibridinių medžiagų grupė yra minkštieji polimeriniai laminatai, sudaryti iš odos ar tekstilės ir mikroporingų ar hidrofilinių polimerinių plėvelių (membranų) sluoksnių. Laminatų reologinė elgsena apkrovimo metu skiriasi nuo ją sudarančių medžiagų įprastinės elgsenos. Taigi, tokių daugiasluoksnių medžiagų reologinių savybių tyrimai yra labai svarbūs parenkant naujus technologinius gamybos režimus. Nežymus vieno iš komponentų savybių pasikeitimas gali ženkliai pakeisti viso laminato reologines savybes, todėl svarbu ištirti kiekvieną tokią naują medžiagą.

Darbo aktualumas. Natūralios odos laminavimas atsparia vandeniui, bet laidžia prakaito garams mikroporinga poliuretanine (PU) plėvele suteikia odai visą kompleksą labai gerų eksploatacinių savybių, tačiau apie 1/3 visos hibridinės medžiagos storio sudaranti plėvelė keičia ir technologiškai labai svarbias natūralios odos reologines savybes. Dėl šios priežasties reikalingos ir naujos gaminių formavimo technologijos, todėl yra aktualūs mikroporinga plėvele laminuotos odos deformacinių ir relaksacinių savybių tyrimai, leidžiantys prognozuoti medžiagos elgseną formavimo ir eksploatacijos metu.

Darbo tikslas. Ištirti mikroporinga PU plėvele laminuotos odos ir atskirų jos sluoksnių reologines savybes, siekiant prognozuoti šios odos relaksacinę elgseną gaminių formavimo metu.

Šiam tikslui pasiekti buvo iškelti tokie **uždaviniai**:

- nustatyti mikroporinga PU plėvele laminuotos odos ir atskirų jos sluoksnių stiprumo ir deformacinių savybių ypatumus;
- ištirti įtempių relaksacijos procesus laminuotoje odoje ir ją sudarančiuose sluoksniuose bei palyginti su šiais procesais kitų tipų odose;
- parinkti nesudėtingą, tačiau pakankamai tikslų teorinį modelį tiriamų medžiagų įtempių relaksacijos matematiniam aprašymui ir fenomenologiniam šio proceso interpretavimui;
- nustatyti kai kurių aplinkos ir apkrovimo parametrų įtaką relaksaciniams procesams laminuotoje odoje ir mikroporingoje plėvelėje.

Darbo mokslinis naujumas ir praktinis vertingumas. Relaksacinius procesus tokioje heterogeninėje medžiagoje kaip laminuota oda didele dalimi lemia iš esmės skirtingi relaksaciniai procesai jos makrosluoksniuose - natūralioje odoje ir polimerinėje dangos plėvelėje. Iš kitos pusės, daugiasluoksnes hibridines medžiagas sudarančių fazių paviršinių sluoksnių tarpusavio sąveika ir jų struktūros pokyčiai taip pat turi įtakos visos daugiasluoksnės medžiagos reologinėms savybėms. Literatūroje nerasta duomenų apie relaksacinių procesų laminuotose odose specifiką, ją lemiančias priežastis, bei poveikių šiems procesams galimybes. Darbe atlikti mikroporinga poliuretanine plėvele laminuotos odos įtempių relaksacijos tyrimai, nustatyta deformavimo greičio įtaka relaksaciniams procesams tiek laminuotoje odoje, tiek mikroporingoje poliuretaninėje plėvelėje. Parinktas nesudėtingas, tačiau pakankamai tikslus teorinis modelis - apibendrintas Maksvelo reologinis modelis - minkštųjų polimerinių medžiagų įtempių relaksacijos matematiniam aprašymui ir interpretavimui.

Atlikti tyrimų rezultatai gali būti pritaikyti prognozuojant mikroporinga poliuretanine plėvele laminuotos odos relaksacinę elgseną formavimo metu bei optimizuojant šio proceso technologinius režimus.

Publikacijos. Disertacijos tema paskelbta 10 publikacijų.

Darbo apimtis. Disertacijos apimtis 106 puslapiai. Diseratcją sudaro įvadas, trys skyriai, išvados, literatūros sąrašas, publikuotų mokslinių darbų sąrašas, 60 paveikslių, 13 lentelių.

Išvados

1. Laminuotos odos reologines savybes lemia tiek odos, tiek mikroporingos poliuretaninės plėvelės savybės.
2. Laminuotos odos stiprumą lemia natūralios odos savybės. Dėl kombinuoto sustiprėjimo efekto skeltinės odos laminavimas nedidelio kohezinio stiprumo mikroporinga poliuretanine plėvele sustiprina laminuotą odą iki 23 %.
3. Mikroporinga poliuretaninė plėvelė keičia relaksacines natūralios odos savybes: laminuotos odos įtempių relaksacijos intensyvumas ir eiga skiriasi nuo šių procesų įvairiose odose ir yra artimesni relaksaciniams procesams mikroporingoje poliuretaninėje plėvelėje.
4. Tirtų minkštųjų polimerinių medžiagų relaksacijos procesų matematinis aprašymas Kolraušo lygtimi tikslesnis, nei aprašant tiek laipsnine, tiek sudvejinto Maksvelo-Vicherto modelio lygtimis. Tačiau kintantis tik vienas Kolraušo lygties parametras sumažina tyrimų rezultatų interpretavimo galimybes, lyginant skirtingus tyrimo objektus ar keičiant deformavimo sąlygas. Modeliuojant apibendrintuoju Maksvelo modeliu relaksacijos procesų visose tirtose medžiagose aprašymo tikslumas yra geriausias, o net šešios šios lygties konstantos gali būti panaudojamos ir platesnei fenomenologinei relaksacijos proceso interpretacijai.
5. Nustatyta, kad įvairiose odose ir poliuretaninėje plėvelėje vykstantį įtempių relaksacijos procesą galima padalinti į du skirtingo intensyvumo etapus. Laminuotos odos relaksacijos greičio ryškų sumažėjimą apibūdinančio „lūžio taško" padėtį laiko ašyje lemia mikroporingos plėvelės klampiaelastinės savybės.
6. Relaksacinės kreivės „lūžio taško" lokalizavimas, panaudojant teorinius tyrimus, leidžia įtempių relaksacijos stebėjimo trukmę sutrumpinti 5 kartus (iki 2 000 s). Nustatyta, kad šiuo būdu iki 10 000 s galima gana tiksliai ($\delta < 2$ %) prognozuoti įvairių odų ir poliuretaninės plėvelės įtempių relaksacijos eigą.
7. Ištyrus deformavimo greičio įtaką laminuotos odos ir mikroporingos poliuretaninės plėvelės įtempių relaksacijai, nustatyta, kad:
   - didinant laminuotos odos deformavimo greitį, pradinis įtempių relaksacijos greitis didėja pagal tiesinį dėsnį tik pradinėje proceso stadijoje (iki 100 s). Toliau įtempių relaksacijos greitis beveik nepriklauso nuo odos deformavimo greičio (diskretinio spektro D_4 ir D_5 konstantų vertės yra labai artimos);
   - deformavimo greitis turi didelės įtakos mikroporingoje poliuretaninės plėvelės pradinių įtempių dydžiui bei relaksacijos

proceso eigai - didinant deformavimo greitį įtempiai laipsniškai didėja, didėja ir įtempių relaksacijos intensyvumas.

8. Nustatyta, kad laminuotos odos ir mikroporingos poliuretaninės plėvelės įtempių relaksacijos procesams, kintant deformavimo greičiui, galima taikyti laiko-greičio analogiją. Gautos laipsninės lygtys leidžia prognozuoti deformavimo greičio įtaką įtempių relaksacijai laminuotoje odoje ir mikroporingoje poliuretaninėje plėvelėje plačiame laiko ir greičio diapazone (iki 24 h laminuotai odai ir iki 11 dienų plėvelei).
9. Mikroporinga poliuretaninėa plėvelė esminiai keičia natūralios odos formuojamumo savybes. Norint padidinti gaminių iš laminuotos odos formos stabilumą, būtina naudoti griežtesnius formos fiksavimo režimus: aukštesnę fiksacijos temperatūrą, ilgesnę trukmę ir efektyvesnius vėsinimo metodus, tai yra naudoti formavimo režimus, kurie artimesni sintetinių odų formavimo režimams.

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