Influence of UV aging on some rheological properties of footwear leather

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Abstract: In this paper authors described rate of aging behavior processes for upper leather materials, which were measured by changes of rheological properties during determination of extension set. Upper leather samples were exposed to UV rays for 100 and 150 hours in Q-SUN Xenon Test Chamber, which was used to induce property changes associated with the effects of sunlight. Then, the samples have been subjected to mechanical test – determination of extension set due to PN-EN ISO 17236:2005 standard. The main goal of this analysis was to determine of UV aging resistance of these materials. The highest resistance was observed for full grain bovine leather and nubuck as the opposition to box calfs.

Keywords: UV aging, footwear leather, relaxation property, anisotropy.

Zmiana wybranych właściwości reologicznych wierzchnich skór obuwniczych na skutek starzenia pod wpływem promieniowania UV

Streszczenie: Oceniono wpływ procesów starzenia wierzchnich skórzanych materiałów obuwniczych na zmianę ich właściwości reologicznych przy odkształceniu typu relaksacyjnego. Próbki wierzchnich skór obuwniczych naświetlano przez 100 i 150 h w symulatorze procesu przyśpieszonego starzenia Q-SUN Xenon Test Chamber. Oznaczano wydłużenie trwałe naświetlonych próbek według normy PN-EN ISO 17236:2005 i na tej podstawie oceniono ich odporność na starzenie powodowane oddziaływaniem promieniowania UV. Największą odporność wykazywały skóry welurowe oraz nubuk, natomiast najmniejszą – boksy bydlęce.

Słowa kluczowe: starzenie UV, skóry obuwnicze, relaksacja, anizotropia.

Leather and textile materials used to forming the footwear uppers [1], succumb to the aging processes during everyday activities. The intensity of these processes depends on the environmental conditions and time of exposure on aging factors. The basic building block of leather is structural protein of connective tissue – collagen [2]. The collagen fibers are formed into weaves and crosses, which give a complex, irregular lattices, crossing a lot of planes in a three – dimensional space [3–5]. One of many factors, which affect on degradation rate of leather is sun exposition. Aging of fibrous materials is caused primarily by ultraviolet rays. This is an electromagnetic spectrum with wavelength from 200 to 400 nm. Depending on leather surface properties, like nonhomogeneous colour, thickness, brightness, wrinkledness, *etc*. [6], UV radiation may be reflected from the surface or absorbed by the collagen fibers. As a result of the absorption processes, the aging takes place. This adverse process is manifested by deterioration of some mechanical and physicochemical properties of leather material (and leather wastes [7]), like tarnishing, cracks in the leather surface and bleaching visible as colour changes. The main changes in a leather structure occur in grain layer, when the collagen bundles are tight up to grain – corium junction. It is caused by the limited penetration ability of UV rays. One of the most important factor, which increase the degradation rate is exposition time [8, 9] – with the extending, the collagen structures and dyes are decomposed.

For the footwear manufacturers, the most dangerous is the collagen structure degradation, because they are important from the mechanical and hygienic properties of footwear leather point of view, like: thermal insulation properties, water and water vapor permeability, abrasion resistance and adhesion affinity [8].

Over the last two decades a lot of papers were focused on the changes of collagen structures as an effect of UV radiation exposition. In paper [10] the collagen from rat tail tendon degradation was described. It was obtained, that the relative viscosity of collagen increased during the UV irradiation. The time of irradiation was fixed between 0.5 to 8 hours for dose of radiation between 8 and 128 J/cm^2. One of the causes for this are molecular changes induced by ultraviolet light described in paper [11]. In paper [12] authors described the thermal aging of hy-

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drogenated nitrile rubber according to the changes of chemical structures and mechanical properties as tensile strength, elongation at break and Young's modulus.

On the other hand, in paper [13] authors showed changes in a field of thermal parameters of collagen under the action of UV irradiation. Some changes like mass decrement, activation energy and entropy were analysed and described. In paper [14] the negative influence of radiation dose and temperature on colour fastness and some mechanical properties, like tensile strength, crack spreading resistance and bending stiffness were proven. These aspects are very important from the footwear point of view. During the footwear use, the natural aging processes generated by the environmental conditions (sunlight exposition, humidity, temperature and mechanical damages of leather surface) take place.

In this paper, the impact of UV radiation on stress relaxation for upper footwear leathers was examined. The first signs of statistically significant differences were observed for 100 hours of exposition. Extending the exposure time continued the collagen structures degradation, measured by the relative extension values. The quality of these differences were assessed with use of ANOVA tool.

EXPERIMENTAL PART

Materials and methods of testing

The tests were carried out with use of six leather types. Table 1 describes the basic material characteristics of them.

T a b l e 1. Types and characteristics of leathers used in tests

Sample name	Leather type	Thickness mm	Mass per square meter, g/m^2
W1	Full grain bovine leather	1.8	1678
W2	Full grain bovine leather	2.0	1815
S1	Bovine leather with corrected grain	0.9	802
S2	Box calf bovine leather	1.2	1084
S3	Box calf bovine leather	1.1	1016
N1	Nubuck leather	1.5	1309

The leathers were subjected to UV radiation in Q-SUN Xenon Test Chamber, which reproduces the damage caused by sunlight. The materials were exposed on aging conditions for 100 and 150 hours. After each cycle, the samples were again air – conditioned for 48 hours and tested in order to determine the extension set in according to ISO 17236 with use of MATEST (10 kN) tensile testing machine. The tested pieces (in number of three measuring samples in two directions) were repeatedly extended at a specific rate until the forces reach a predetermined level 20 ± 0.5N. The permanent extension E_s was calculated as a percentage of the original length due to the formula (1):

$$E_s = \frac{(L_1 - L_0)}{L_0} \cdot 100\% \tag{1}$$

where: L_1 – the final distance between the marks [mm], L_0 – initial distance between the two lines [mm]. The lines were marked within 35 ± 5 mm from the each short edge of the test piece with the line parallel to the short edges.

The permanent extension E_s was measured after 60 s, 1 h and 24 h from extending time.

Apart from the permanent extension, the stress and elongation at break were also measured according to the PN-ISO 3376:2012 standard. The tensile strength at break was characterized by the value of breaking load expressed in N/mm^2. Values of this measurement, depend on the several factors, as follows: structure, direction of breaking, thickness and cross – sectional area. On the other hand, the elongation at break (ε_{break}) is a result of a following relation:

$$\varepsilon_{break} = \frac{(L_{break} - L_0)}{L_0} \cdot 100\% \tag{2}$$

where: L_0 – the initial length of the sample, L_{break} – the length of the sample at the moment of break (between clamps).

It is noteworthy, that the value $L_{break} - L_0$ describes the absolute value of the breaking elongation. For the leather materials, the elongation is higher across the samples, and smaller on the length direction. The phenomenon of decreasing of physical properties was observed with use of the strength testing machine Zwick Roell Z010. The tests were carried out with footwear leather samples at a speed test of 50 mm/min.

RESULTS AND DISCUSSION

Due to an anisotropy property of leather materials, all of tests were conducted in two directions: perpendicular and parallel. The sampling procedure was compatible with ISO 2418. Decreasing of reversibility deformation property were noticed in both directions (Figs. 1 and 2). Material, which was less deformation vulnerable was W1, because the noticed deflections ranged from 1.5% for 60 s to 0.5% after 24 hours. In turn, the highest deformations were obtained for S3 leather and ranged to 9.2% (for 60 s), 7.5% (for 1 h) and 6% (for 24 h). The intragroup variabilities for the examined materials lied between 50% for W1 and 21% for S3.

With regard to the perpendicular direction (Fig. 2), the smallest deformations were observed for W1. They were equal to 1.5% (for 60 s), 0.8% (for 1 h) and 0.5% (for 24 h). The highest differences were noticed for S3: 13.2% (for 60 s), 11.8% (for 1 h) and 10.7% (for 24 h). The intergroup

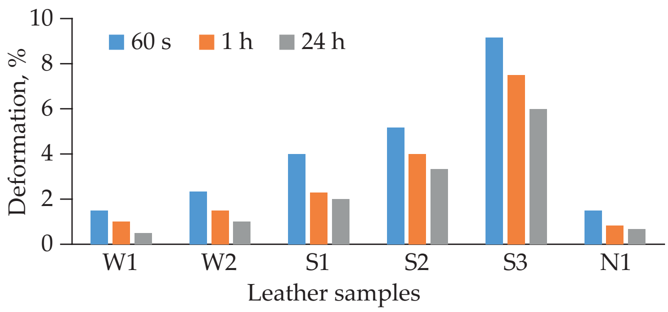

Fig. 1. Deformation of samples in the parallel direction for 100 h irradiation cycle

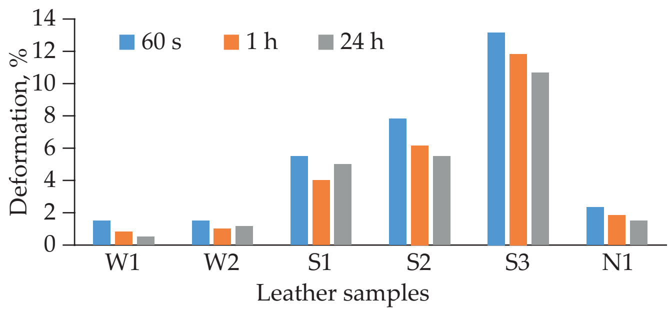

Fig. 2. Deformation of samples in the perpendicular direction for 100 h irradiation cycle

variabilities lied between 54% for W1 to 11% for S3. It shows, that the changes affected by time, were sighted off especially for W1 in contrast to S3.

In order to identify the exposure time on anisotropy property, the following measure K_A was defined:

$$K_A = \frac{R_S}{R_D} \tag{3}$$

where: R_S – the result of the measurement of mechanical property for sample taken across of roll of tested material, R_D – the result of the measurement of mechanical property for sample taken along of roll of tested material.

Material W1 was characterized by strong isotropy, which was manifested by value of K_A close to 1 obtained for t_1 = 60 s and t_3 = 24 h.

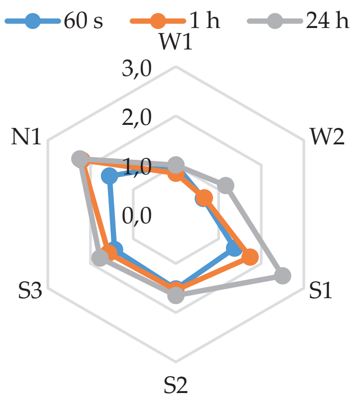

Fig. 3. Anisotropy phenomenon as a dependence of time after the force removal for 100 h irradiation cycle

In the case of materials characterized by higher anisotropy, the largest values of deformations were obtained after 24 hours for S1 (2.5) and N1 (2.3) (Fig. 3). In addition, it is worth to notice, that for N1, the qualitatively change between 1 h and 24 h, was small. It was reflected by small changes in K_A – from 2.2 to 2.3. Globally, the smallest anisotropy property was observed for t_1 = 60 s.

In case of extended exposure time to 150 hours, the qualitatively changes were highlighted, both in parallel (Fig. 4) and perpendicular direction (Fig. 5). After 150 hours UV irradiation, the highest UV radiation resistance, was observed for full grain bovine leathers W1 and W2. In these cases, the picked up differences were in the range 10% for W1 and t_1 = 60 s and W2 for t_3 = 24 h in comparison to materials irradiated for 100 hours.

Leather S3 turned out to be the weakest – the differences reached the 68% level for t_2. Similar situation took place for nubuck leather N1 and time t_1 after removing the test piece from the tensile tester. The differences of deformation parameter reached a level of 47% in comparison to samples irradiated for 100 hours.

The trend to differences remained also in perpendicular direction (Fig. 5). The largest changes were observed for grain leather W1 – the maximum difference for extensions amounted to 75% for t_3 period. In cases of W2, S1 and S3, the deformations were negligible and for the majority of periods were close to zero in comparison to irradiation period of 100 hours. It means that in this direction, the viscosity properties of collagen structures were stable after increased dose of irradiation.

The extending of irradiation time, was influenced on the anisotropy curves shape (Fig. 6). In comparison to

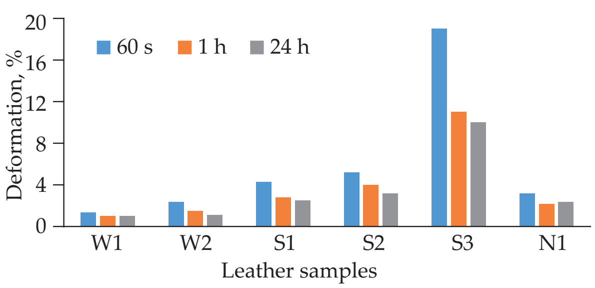

Fig. 4. Deformation of samples in the parallel direction for 150 h irradiation cycle

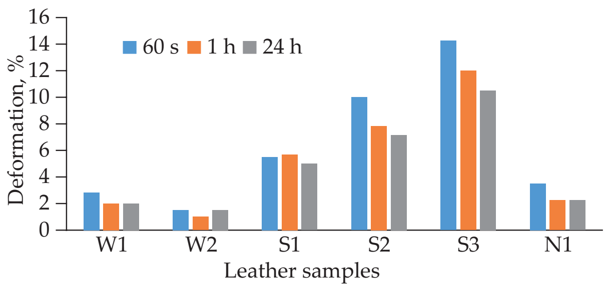

Fig. 5. Deformation of samples in the perpendicular direction for 150 h irradiation cycle

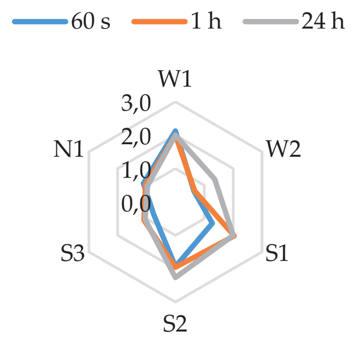

Fig. 6. Anisotropy phenomenon as a dependence of time after the force removal for 150 h irradiation cycle

100 hours, the areas appointed by the anisotropy curves turned to be narrowed. It was caused by a fact, that for materials W2, S3 and N1 the anisotropy coefficient K_A reached values close to unity. So the anisotropic properties became nullified.

In order to identify the character of the differentiation, the ANOVA analysis was implemented. For the confidence level $\alpha = 0.05$, the hypothesis H_0 of equality of extensions means for three different times after removing the piece from the tensile tester versus the alternative hypothesis H_1, which says that means are not all equal. This analysis indicated, that the differences exist and were statistically significant. The ANOVA analysis was conducted after the checking the normality and homogeneity of variances assumptions in examined homogeneity groups:

– Group I – measurements at 100 hours of irradiation, for the time points t_1, t_2, t_3 in a parallel direction;

– Group II – measurements at 100 hours of irradiation, for the time points t_1, t_2, t_3 in a perpendicular direction;

– Group III – measurements at 150 hours of irradiation, for the time points t_1, t_2, t_3 in a parallel direction;

– Group IV – measurements at 150 hours of irradiation, for the time points t_1, t_2, t_3 in a perpendicular direction.

The achieved results were given at the Table 2.

The results of ANOVA procedure (F > Test F) gave a qualitative information about influence of material type on the UV resistivity. In order to verify the influence power, the Tukey post – hoc procedure based on the honest significant difference (HSD) was carried out. The results of this, were collected in the Tables 3 and 4.

In order to identify the impact of exposure time on the rheological properties, the coefficient of variation (CV) was calculated according to the following formula:

$$CV = \frac{S}{\bar{X}} \cdot 100\% \quad (4)$$

where: $\bar{X}$ – arithmetic mean of measurement results for time 100 and 150 h, S – standard deviation.

T a b l e 2. ANOVA results (differentiation factor – material type)

Compared groups	*SS* total	*df*	*F*	*p*-value	Test *F*
G1–G3 (t_1)	270.35	11	5.32	0.03000	4.39
G1–G3 (t_2)	103.59	11	16.21	0.00200	4.39
G1–G3 (t_3)	82.66	11	9.07	0.00900	4.39
G2–G4 (t_1)	229.20	11	59.87	0.00004	4.39
G2–G4 (t_2)	181.47	11	59.04	0.00005	4.39
G2–G4 (t_3)	138.90	11	57.00	0.00005	4.39

df – degrees of freedom, *F* – the ratio produced by dividing the mean square for the model by the mean square for error, *SS* – sum of squares.

T a b l e 3. The results of post-hoc Tukey test for groups G1–G3

Compared groups	Treatment pairs	Tukey HSD *p*-value	Tukey HSD interference
G1–G3 (t_1)	W1-S3	0.032	$p < 0.05$
	W2-S3	0.044	$p < 0.05$
	S3-N1	0.045	$p < 0.05$
G1–G3 (t_2)	W1-S3	0.002	$p < 0.01$
	W2-S3	0.003	$p < 0.01$
	S1-S3	0.007	$p < 0.01$
	S2-S3	0.022	$p < 0.05$
	S3-N1	0.003	$p < 0.01$
G1–G3 (t_3)	W1-S3	0.009	$p < 0.01$
	W2-S3	0.011	$p < 0.05$
	S1-S3	0.028	$p < 0.05$
	S3-N1	0.016	$p < 0.05$

T a b l e 4. The results of post-hoc Tukey test for groups G2–G4

Compared groups	Treatment pairs	Tukey HSD *p*-value	Tukey HSD interference
G2–G4 (t_1)	W1-S2	0.002	$p < 0.01$
	W1-S3	0.001	$p < 0.01$
	W2-S1	0.027	$p < 0.05$
	W2-S2	0.001	$p < 0.01$
	W2-S3	0.001	$p < 0.01$
	S1-S3	0.001	$p < 0.01$
	S2-S3	0.011	$p < 0.05$
	S2-N1	0.004	$p < 0.01$
	S3-N1	0.001	$p < 0.01$
G2–G4 (t_2)	W1-S1	0.030	$p < 0.05$
	W1-S2	0.003	$p < 0.01$
	W1-S3	0.001	$p < 0.01$
	W2-S1	0.018	$p < 0.05$
	W2-S2	0.002	$p < 0.01$
	W2-S3	0.001	$p < 0.01$
	S1-S3	0.001	$p < 0.01$
	S2-S3	0.006	$p < 0.01$
	S2-N1	0.005	$p < 0.01$
	S3-N1	0.001	$p < 0.01$
G2–G4 (t_3)	W1-S1	0.013	$p < 0.05$
	W1-S2	0.027	$p < 0.01$
	W1-S3	0.001	$p < 0.01$
	W2-S1	0.015	$p < 0.05$
	W2-S2	0.003	$p < 0.01$
	W2-S3	0.001	$p < 0.01$
	S1-S2	0.002	$p < 0.01$
	S1-N1	0.032	$p < 0.05$
	S2-S3	0.007	$p < 0.01$
	S2-N1	0.006	$p < 0.01$
	S3-N1	0.001	$p < 0.01$

T a b l e 5. Values coefficients of variation (*CV*) within groups G1, G2, G3, G4 for materials W1, W2, S1, S2, S3, N1

Group	*CV*, %					
	W1	W2	S1	S2	S3	N1
G1–G3 (t_1)	44	1	1	17	6	28
G1–G3 (t_2)	58	1	25	17	1	14
G1–G3 (t_3)	47	7	16	4	35	79
G2–G4 (t_1)	8	1	5	1	49	51
G2–G4 (t_2)	1	1	14	1	27	63
G2–G4 (t_3)	47	7	16	4	35	79

In the Table 5 the values of coefficient of variations for groups of materials were given.

High level coefficient of variation for some samples, gives a feedback, that 100 and 150 hours of irradiation exposure is sufficient for catch the differences in viscosity properties of examined upper leathers. In some cases (for W1, S3, N1), the values are greater than 40%, which is confirmation of data volatility between 100 and 150 hours of irradiation. In order to pick up the explicit trend, which could gave the possibility of forecasting rheological property, the sampling density should be enhanced and the exposure time prolonged. Additionally, the set of aging factors should spiked with other elements like temperature and humidity. Such action could be taken for automotive, furniture or garment leathers [15–17].

In order to qualitative description of aging processes into the leather structure, the relaxation analysis for leathers before aging was done. The results were compared with aging materials with use of T-test. At the level of confidence α = 0.05, the null hypothesis H_0, which states that any differences in relaxation results are purely due to random and not systematic errors as an opposition to the alternative hypothesis H_1. The results of this procedure were placed into the Table 6.

The comparison between samples before aging and after aging, the statistically significant differences were observed in most cases. In order to present a complete picture of qualitative changes, the anisotropy factor was

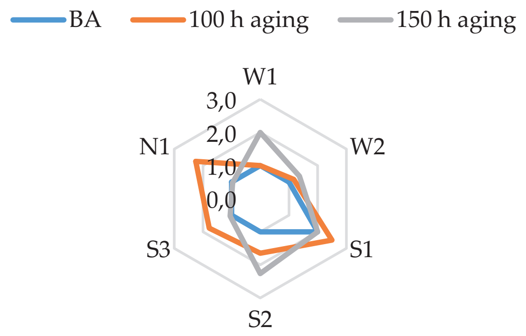

Fig. 7. Anisotropy coefficient before (BA) and after aging during 100 and 150 hours

T a b l e 6. The T-test procedure of qualitatively comparison between leathers before aging (BA) and after 100 h and 150 h aging

Paralell direction			
Relaxation time: 60 s			
Compared samples	T-value	*p*-value	Significance
BA/100 h	-2.004	0.04	Yes
BA/150 h	-1.630	0.07	No
Relaxation time: 1 h			
BA/100 h	2.324	0.02	Yes
BA/150 h	-2.202	0.03	Yes
Relaxation time: 24 h			
BA/100 h	-2.303	0.02	Yes
BA/150 h	-2.248	0.02	Yes
Perpendicular direction			
Relaxation time: 60 s			
Compared samples	T-value	*p*-value	Significance
BA/100 h	-1.052	0.16	No
BA/150 h	-1.432	0.09	No
Relaxation time: 1 h			
BA/100 h	-1.404	0.10	No
BA/150 h	-1.856	0.04	Yes
Relaxation time: 24 h			
BA/100 h	-1.892	0.04	Yes
BA/150 h	-2.475	0.02	Yes

T a b l e 7. Magnitude of changes in values in stress and elongation at the point of break expressed in a terms of tangent coefficients of gradient lines

Sample name	Stress at the point of break		Elongation at the point of break	
	Parallel	Perpendicular	Parallel	Perpendicular
S1	-3.05	-2.95	-0.50	-5.35
S2	-3.15	-1.75	-7.15	-11.00
S3	-1.80	-0.65	-2.15	-4.00
W1	-1.70	-1.83	-2.50	-3.35
W2	-9.05	-1.47	-1.85	-9.50
N1	-7.15	-4.25	-10.35	-6.15

calculated. This parameter was fluctuated depending on the UV radiation time. The most visible were observed for time t = 24 hours (Fig. 7).

For this time (t = 24 h), the anisotropy properties were extended to a wider area in comparison to before aging (BA) case (blue line).

According to the breaking stress and elongation at break, the differences also occurred dependently on the aging time. In order to determine impact of the UV radiation aging, the lines between results before aging and after aging were drawn. The tangent coefficients (Table 7), which described the maximum gradient of these lines, showed the magnitude of aging process.

Based on the monotonicity of tangent function, the highest values described the biggest differences and small values – the opposite. In case of stress at the point of break, the maximum values were observed for W2 (-9.5) in a parallel direction and for N1 (-4.25) in a perpendicular direction. The changes of values for W2 in a parallel direction were placed from 36.5 N/mm^2 before aging to 18.4 N/mm^2 after 150 hours. On the other hand for N1, the maximum stress at break fluctuated between 20.3 N/mm^2 for standard sample and 11.8 N/mm^2 after 150 hours irradiation. Moreover, the intra group diversity was placed on a strong level 71% and 59% for along and across directions, respectively. For the elongation parameter, the maximum values were obtained for N1 (-10.35) in a parallel direction and for S2 (-11.00) in a perpendicular direction. The differences were varied from 59% to 38% (for N1) and from 73% to 51% (for S2). The intra group diversity was equal to 93% and 45% for measures done along and across the samples, respectively. Values obtained in this paper confirm the sensitivity of following parameters, like stress at break or elongation to the UV radiation. It corresponds to results obtained in papers [18, 19].

In order to make a discussion of the obtained results, it should be underlined, that the rate of aging processes depends on the leather type. Full grain bovine leathers (W1 and W2) are characterized by interwoven collagen fibers that are diameter ≤ 5 μm [20]. So this layer preserve the strongest corium layer, lied beneath the grain leather, where the diameters of fibers are close to 100 μm. This is a main cause, that these types of leather are protected from the loss of tensile properties. The similar situation is observed for nubuck leather (N1). In this case the grain layer was gently removed, but the sanding was very shallow [21]. On the other hand, the boxing leathers are produced from the light raw materials from young cows, bullocks or heifers [22]. The collagen fibers orientation in the calf leather is locally non-uniform, so this is the cause of significant changes in tensile properties [23]. The leather characteristics are also effected by type, sex and age of individuals [24]. It was shown that type, sex and age of animal may cause the statistically significant influences on such parameters as: thickness, breaking force, tensile strength and extension. Moreover, the time followed by leather destruction depends on the lot of other factors, like initial acidity, salt content, relative humidity of storage room or presence of air pollutants [25]. Influence of all this factors must be taken into account in order to describe of aging processes nature.

The analysis of relaxation process for footwear lathers is one of the most important factor to determine the quality of leathers. The good relaxation property ensures a tight fit of the upper and shape retention in wear. Moreover, the plasticity property adjusts the leather to the shape of the foot and increases a mechanical comfort [26]. Today in order to determine collagen structures, the wide spectrum of techniques as: small angle X-ray scattering [27–30], differential scanning calorimetry [31], scanning electron microscopic analysis [32] are used. These abovementioned techniques could give the indicators of leather quality from the molecular level point of view. The aspects of collagen structures of footwear materials (both uppers as linings and insoles) is important from a comfort sensation point of view, examined in previous papers [33, 34].

CONCLUSIONS

The results made in this paper, described the aging process of upper leather. This issue was taken, because it is important from a footwear manufacturer point of view, because the upper leathers are subjected to some aging factors, including UV irradiation. During the production, preservation, cleaning processes or wearing, the footwear is posed to a lot of external fatigue forces, which can caused the multidirectional deformations of different values and durability.

Studies, which were carried out in this paper, showed that for upper leathers, the relaxation property manifested by the reduction of stress with time under a give extension is a desirable feature for footwear. Because leather is not a homogeneous material [35], [36], the direction of cutting and combining each upper elements is very important in footwear manufacturing practice. Knowledge about the aging phenomenon and influence of aging processes on some rheological properties decides about making tougher and more comfortable shoes. Radiation dosage, which was equivalent to 100 and 150 hours of radiation, had a significant effect on the relaxation property, which is very important from a mechanical comfort of footwear point of view. The effect of UV irradiation influence was observed as:

– Changes in deformation values observed for irradiation period – in both directions. For parallel cutting samples the changes were registered in a following intervals: 1.5–9.2% for 60 s, 0.8–7.5% for 1 h, 0.5–6% for 24 h measured after 100 hours of UV irradiation and 1.3–19% for 60 s, 1–4% for 1 h, 1–10% for 24 hours measured for samples irradiated of 150 hours. For perpendicular cutting the changes ranged as follows: 1.5–13.2% for 60 s, 0.8–11.8% for 1 h and 0.5–10.7% for 24 h measured after 100 hours of irradiation and 2.8–14% for 6 s, 1–12% for 1 h, 1.5–10.5% for 24 h measured for samples irradiated of 150 hours.

– Changes in anisotropy coefficients – the area limited by anisotropy curves became narrowed for 150 hours in comparison with 100 hours. The anisotropy coefficient values changed as follows: 0.6–1.6 for 60 s, 0.7–2.2 for 1 h, 1.0–2.5 for 24 h, when the samples were irradiated for 100 h and 0.6–2.1 for 60 s, 0.7–2.0 for 1 h and 1–2.3 for 24 h for samples irradiated for 150 hours.

– Values of stress at break and breaking elongation obtained in this paper confirm the sensitivity of these parameters to the UV radiation.

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