

Chrome-tanned leather shavings as a filler of butadiene–acrylonitrile rubber

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Abstract

The noxious wastes from the tanning industry such as chrome-tanned leather shavings were used as the only filler of rubber mixes containing carboxylated butadiene–acrylonitrile rubber (XNBR) or butadiene–acrylonitrile rubber (NBR), and a dispersing agent Limanol PEV (Schill & Seilacher). The best form addition of leather powder to the rubber mixes is mixed the waste protein with zinc oxide. The leather powder added to the rubber mixes improves the mechanical properties: tensile strength (T_s), elongation at break (ϵ_b) and increase the cross-linking density of carboxylated XNBR and NBR rubber mixes. Satisfactory results of these studies are presented in this work.

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1. Introduction

About 30% of leather substance processed in tanneries is rejected, mainly after the shaving process, in the form of protein wastes containing 3–5% of chromium(III). These wastes are partly utilized, but mainly they are deposited in storage yards, posing a hazard to the environment [1]. The most often proposed technological solution to the problem of waste shavings utilization is the production of secondary or artificial leathers designed for footwear elements, fancy goods or non-woven fabrics as substrates for leather-like materials [1]. Another trend of utilization consists in detanning to recover chromium(III) compounds and processing the recovered collagen into gelatin, adhesives or protein hydrolyzate (fodders, modified polymers, film-forming agents). The methods of leather waste utilization have been reviewed by Przepiórkowska et al. [1].

Taylor et al. [2–6] have patented the conditions of alkaline and enzymatic hydrolysis of chrome-tanned leather wastes to separate protein destruction products and chromium compounds. The authors indicate potential uses of the obtained technical gelatin in cosmetics, sizes, printing inks and photography. On the other

hand, the protein hydrolyzate, due to its high nitrogen content, can be possibly used as fertilizer or additive to fodders, while the recovered chromium may be used in the processes of leather tanning.

In their recent studies, Mu et al. [7] compared the conditions of various alkaline (CaO, MgO, NaOH) and enzymatic (protease–Wenijanf Inc., China) hydrolyses of chrome-tanned shavings to find the most effective process conditions. The authors presented a three-stage hydrolysis. Its first stage resulted in gelatin that, after modification with acrylic monomers by emulsion polymerization, could be used in leather dressing; polypeptides resulted from the second stage, after modification, could be used as retanning agents. Chromium(III)-containing hydrolyzates, after modification, could also be used as retanning agents.

Berry et al. [8] have proposed an interesting procedure to utilize chrome-tanned shavings as a potential source of chromium(III). They hydrolysed chrome-tanned shavings by means of NaOH, CaO, MgO, NH₄OH, followed by enzymatic hydrolysis. The resultant protein hydrolyzate was separated from the chromium(III)-containing precipitate. The chromium deposit was dried for 12 h at a temperature of 140 °C and used to prepare pigments: cobalt-chrome green (CoCr₂O₄) and chrome-stannic pink (CaSnSiO₅ × Cr₂O₅). The obtained pigments were assessed by IR spectroscopy (FT-IR) and X-ray diffraction (XRD).

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Collagen hydrolyzate (Hyskol E), prepared by the enzymatic hydrolysis of chrome-tanned shavings in the presence of organic amines, produced by Kortan Hradek n/Nisou, Czech Republic (nitrogen content 14%) was used for the preparation of biodegradable thermoplastic films of poly(vinyl alcohol)-collagen hydrolyzate (PVA/CH) mixes [9,10]. The tensile strength of PVA/CH mixes is lower and their elongation at break is higher than those of mixes without collagen hydrolyzate. Tests of the biodegradation of the obtained films under oxygen-free conditions showed a positive effect of collagen hydrolyzate on the mineralization rate of PVA/CH mixes.

In the paper [11] has been presented the use of a solid waste generated in the leather industry to effectively remove a liquid waste (tannis) from chromium-tannin wastewater and subsequently use the same for preparation of chemicals needed for the industry itself. The tannin adsorbed shavings were used for the preparation of chromium(III) sulfate. The chromium left behind after near complete removal of tannins was recovered by precipitative techniques and subsequently redissolved in sulfuric acid to generate chromium(III) sulfate. The prepared and recovered chromium(III) sulfate on use in tanning process gave results similar to those of conventional chromium(III) salts, thereby providing a new methodology for the reuse of waste products of the leather industry directly into the leather industry itself.

Another way for the removal of toxic liquid waste chromium(VI) is use of iron treated fleshing, which is solid waste, generated from tanneries [12]. In this study, the performance of iron treated fleshing as an adsorbent to remove chromium(VI) from the aqueous solution has been investigated. An increase of Cr(VI) uptake by iron treated fleshing has been observed with the solution pH of about 4.0, high initial chromium concentration and low sorbent concentration. XPS studies show that the oxidation state of chromium(VI) remains unchanged after loading with iron treated fleshing, and carboxyl groups are involved in binding iron to fleshing. The chromium(VI) loaded iron treated fleshing can also be reused in the leather industry as chrome-iron syntan for leather processing as it contains protein.

Studies on the utilization of arduous wastes such as chrome-tanned leather shavings from the tanning industry have been carried out at the Institute of Polymers [13]. Chrome-tanned waste collagen was used, beside silica, as a filler of rubber mixes containing synthetic 1,4-*cis*-polyisoprene rubber (Cariflex 305) and a dispersing agent (Rokafenol N-8) [14]. The obtained protein-elastomer composites, containing 5 parts by wt. of chrome-tanned leather powder per 100 parts by wt. of rubber, showed slightly lower values of tensile strength than those of an elastomer filled only with silica. Moreover, they were biodegradable and resistant to thermal ageing [14,15]. Satisfactory results of these studies allowed one to continue them with the use of the chrome-tanned leather powder as the only filler of 1,4-*cis*-polyisoprene (Cariflex 305) mixes with Limanol PEV (Schill & Seilacher) [16] as a dispersing agent, because vulcanizates of mixes with ethylene glycol and Rokafenol N-8 had worse mechanical properties than with Limanol PEV. From the performed tests it follows that the vulcanizates of

synthetic 1,4-*cis*-polyisoprene rubber containing 5 parts by wt. of chrome-tanned collagen mixed with 5 parts by wt. of zinc oxide, to which 2 parts by wt. of Limanol PEV per 100 parts by wt. of the rubber were added, show the best mechanical properties. It is most probable that this is due to the ionic mobile lattice nodes. Therefore, further studies are aimed at the use of chrome-tanned leather powder as the sole filler of the mixes of carboxylated butadiene–acrylonitrile rubber (XNBR) and butadiene–acrylonitrile rubber (NBR). To accomplish such an aim, it was decided to determine the procedure of component addition (leather powder, zinc oxide, Limanol PEV) and to assess the effect of collagen on the properties of the above mentioned rubber mixes. The scope of research and testing included:

- (1) Determination of the procedure of chrome-tanned leather powder incorporation into the mixes;
- (2) Preparation of mixes and their vulcanization;
- (3) Testing some properties of the vulcanizates such as equilibrium swelling and mechanical properties during stretching (tensile strength).

2. Experimental methods

- Chrome shavings were subjected to multi-stage disintegration to prepare a powder that was then sieved through a 0.2 mm mesh; chromium(III) content given as Cr₂O₃–0.6%, PN-EN ISO 4684:2006 (U).
- Zeta potential measurement with a Zetasizer 2000; pH control with 0.05 M NaOH and 0.05 M HCl solutions.
- Particles size measurement with a Zetasizer Nano; samples were treated with ultrasound for 1 h.
- Rubber mixes were prepared by using a laboratory mixing mill with roll dimension $D = 20$ mm and $L = 450$ mm. The temperature of the rolls was 303–312 K and the front roll speed $V_0 = 16$ rpm. The prepared mixes were used to draw out sheets with a thickness of 6–8 mm that were then stored at 275–312 K.
- Based on rheometric tests, the kinetics of rubber mixes vulcanization was determined at a temperature about 433 K according to the standard PN-ISO 3417:1994 (vulcameter with an oscillating rotor WG-02). The obtained rheometric curves were used to calculate: $\tau_{0,9}$ is the optimal vulcanization time (min), ΔL the increase in the torque moment (dN m), a_f is the activity of protein filler; based on the equation [14]:

$$\frac{\Delta L}{\Delta L_0} - 1 = a_f \frac{m_f}{m_p} \quad (1)$$

where ΔL is the increase in the torque moment of mix with protein, ΔL_0 the increase in the torque moment of mix without protein, m_f the parts by weights of filler, m_p is the parts by weights of polymer.

- Vulcanization of the mixes was carried out in a vulcanization mold at 433 K for time $\tau_{0,9}$ determined from rheometric measurements.
- Density of vulcanizates in metanol, was tested according to the standard PN-ISO 2781 = AC 1.

- The equilibrium swelling in toluene, toluene and ammonia vapors was determined at a temperature of $298\text{ K} \pm 1\text{ K}$ for 48 h according to the standard PN-74/C-04236.
- Concentration of the effective chains ν_e , to the vulcanizates of carboxylated butadiene–acrylonitrile rubber (M1, M2) in toluene, toluene and ammonia vapors was calculated according to the Flory–Rehner’s equations [17]:

$$\nu_e^T = -\frac{\ln(1 - V_T) + V_T + \mu V_T^2}{V_o(V_T^{1/3} - (V_T/2))} \quad (2)$$

ν_e^T is the concentration of the effective chains in toluene calculated from the measurement of equilibrium swelling in toluene (mol/cm^3), V_T is the volumetric content of elastomer in the sample under test in toluene:

$$V_T = \frac{1}{1 + Q_w^T(\rho_{\text{XNBR}}/\theta_T)} \quad (3)$$

Q_w^T is the equilibrium swelling in toluene (was assigned separately to the M1 and M2), ρ_{XNBR} the density of the XNBR vulcanizates (without protein M1 = 0.8236, with protein M2 = 0.8161 (g/cm^3)), θ_T the density of toluene 0.8623 (g/cm^3), V_o is the molar volume of toluene (mol/cm^3): $V_o = M_T/\theta_T$, M_T is the molar mass of toluene (g/mol),

$$\nu_e^{T/\text{NH}_3} = -\frac{\ln(1 - V_{T/\text{NH}_3}) + V_{T/\text{NH}_3} + \mu V_{T/\text{NH}_3}^2}{V_o(V_{T/\text{NH}_3}^{1/3} - (V_{T/\text{NH}_3}/2))} \quad (4)$$

ν_e^{T/NH_3} is the concentration of the effective chains calculated from the measurement of equilibrium swelling in toluene and ammonia vapors (mol/cm^3), V_{T/NH_3} is the volumetric content of elastomer in the sample under test in toluene and ammonia vapors:

$$V_{T/\text{NH}_3} = \frac{1}{1 + Q_w^{T/\text{NH}_3}(\rho_{\text{XNBR}}/\theta_{T/\text{NH}_3})} \quad (5)$$

Q_w^{T/NH_3} is the equilibrium swelling in toluene and ammonia vapors (was assigned separately to the M1 and M2), θ_{T/NH_3} the density of toluene and ammonia vapors 0.8669 (g/cm^3), V_o is the molar volume of toluene and ammonia vapors (mol/cm^3): $V_o = M_{T/\text{NH}_3}/\theta_{T/\text{NH}_3}$, M_{T/NH_3} is the molar mass of toluene and ammonia vapors (g/mol),

- Concentration of the effective chains ν_e , to the vulcanizates of butadiene–acrylonitrile rubber (M3, M4) in toluene, in toluene and ammonia vapors was calculated similarly, as to the vulcanizates of carboxylated butadiene–acrylonitrile rubber and were taken into consideration the quantities: Q_w^T is the equilibrium swelling in toluene, assigned separately to the M3 and M4, Q_w^{T/NH_3} the equilibrium swelling in toluene and ammonia vapors (assigned separately to the M3, M4), ρ_{NBR} is the density of the NBR vulcanizates (without protein M3 = 0.7767, with protein M4 = 0.7947 (g/cm^3)).
- Huggins’ parameter, parameter of polymer–toluene interaction calculated based on the equation:

$$\mu = \mu_o + \beta V_T \quad (6)$$

where V_T is the volumetric content of elastomer in the sample under test in toluene, μ_o the slope of the straight line describing the relationship $\mu = f(V_T)$, to the XNBR rubber: $\mu_o = 0.487$, $\beta = 0.228$ and to the NBR rubber: $\mu_o = 0.479$, $\beta = 0.164$.

- Huggins’ parameter, parameter of polymer–toluene and ammonia vapors interaction calculated based on the equation:

$$\mu = \mu_o + \beta V_{T/\text{NH}_3} \quad (7)$$

V_{T/NH_3} is the volumetric content of elastomer in the sample under test in toluene and ammonia vapors, μ_o the slope of the straight line describing the relationship $\mu = f(V_{T/\text{NH}_3})$, to the XNBR rubber: $\mu_o = 0.483031$, $\beta = 0.320372$ and to the NBR rubber: $\mu_o = 0.502$, $\beta = 0.282$.

- The density of cross-linking in toluene, toluene and ammonia vapors to the carboxylated rubber butadiene–acrylonitrile vulcanizates, was assigned according to the standard PN-83/C-04215.
- Concentration of the ion lattice points decomposing under the influence of ammonia (mol/cm^3) to the vulcanizates M1, M2, M3, M4:

$$\Delta V_{\text{NH}_3} = \nu_e^T - \nu_e^{T/\text{NH}_3} \quad (8)$$

Percentage content of the ion lattice points decomposing under the influence of ammonia A (%):

$$A = \left(\frac{\Delta V_{\text{NH}_3}}{\nu_e^T} \right) \times 100\% \quad (9)$$

where ΔV_{NH_3} is the concentration of the ion lattice points decomposing under the influence of ammonia (mol/cm^3).

- The tensile strength of vulcanizates was tested according to standard PN-82C/04205 with a Zwick apparatus, model 1435, obtained tensile strengths T_s (MPa) and elongation at break ε_b (%).

3. Discussion and results

3.1. Determination of the zeta potential

Zeta potential depends of the nature of particle and the surrounding medium. It describes the behavior of particles in the dispersing medium and thus electrostatic properties and the stability of dispersion. At the isoelectric point, the particles easily connect in the larger groups showing the minimum of electrophoretic mobility, it shows the greatest tendency of particles to aggregation. Additionally, this point characterizes the minimum of solution viscosity. Therefore, determine the zeta potential of the chrome-tanned leather powder and its mixture with ZnO in an aqueous dispersion. Based on the obtained results, the dependence of zeta potential on pH was plotted and the resultant graph is shown in Fig. 1. It is seen that the isoelectric point of the chrome-tanned leather powder falls at pH about 6.5. After mixing the waste protein with ZnO, the isoelectric point shifted towards a higher pH value of 7.8. It proves that after addition ZnO the state of protein surface undergo the change. In blurred layer appeared more positive charges and therefore, had to intro-

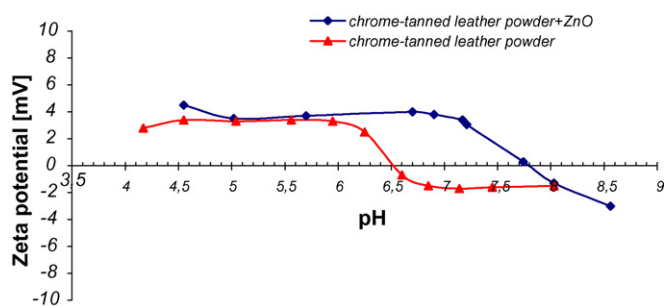


Fig. 1. The zeta potential of water dispersions of the leather tanning powder and the powder mixed with ZnO in function pH (concentration 0.1 g/l).

duce more negative ions from outside and the isoelectric point shifted towards a higher pH value.

3.2. Measurement of particles size of chrome-tanned leather powder

The size of filler particles and the way it is incorporated into the mixes has got a huge influence on the dispersion in the elastomer matrix. In turn, the dispersion decides about the quality of the obtained mixes and properties of the resultant vulcanizates. When the sizes of particles are in range from 0.01 to 1 μm ; then such filler is an active filler and perform reinforcing functions. Before, preparation of mixes with the chrome-tanned leather powder, carried out measurement of particles size: chromium-collagen powder, chromium-collagen powder mixed with ZnO and chromium-collagen powder mixed with ZnO and Limanol PEV. The results of measurements of particle size in an aqueous dispersion are shown in Fig. 2, as a function number particles (%) from their diameter (nm). Size of chromium leather powder particles are in the wide range from 82.21 to 233.6 nm and polydispersity index (PDI) of this solution carry out 0.845. Addition of ZnO to the chrome-tanned leather powder causes change in the distribution of chromium-collagen particle size which are in the narrow range from 130.8 to 164.9 nm, PDI is near to one what indicates a homogenous system. In the same way the addition of ZnO and Limanol PEV to the protein powder extends the range of this particle size but the PDI is lower and system is less homogenous than collagen with ZnO. Thus, it is most beneficial to add chrome-tanned leather powder mixed with ZnO to rubber mixes, since this composition should provide the best dispersion of chromium-collagen in the mix and Limanol PEV should be added separately.

3.3. The influence of chrome-tanned collagen on mechanical properties of mixes and vulcanizates XNBR

The compositions and rheometric, mechanical properties of the obtained mixes and vulcanizates of carboxylated butadiene-acrylonitrile rubber are listed in Table 1. From the rheometric parameters it follows that the addition of chrome-tanned collagen in a quantity of 5 parts by wt. mixed with 5 parts by wt. zinc oxide to the carboxylated butadiene-acrylonitrile rubber clearly increases the increment of torque, ΔL , that characterizes the degree of vulcanizate cross-linking. In the case of

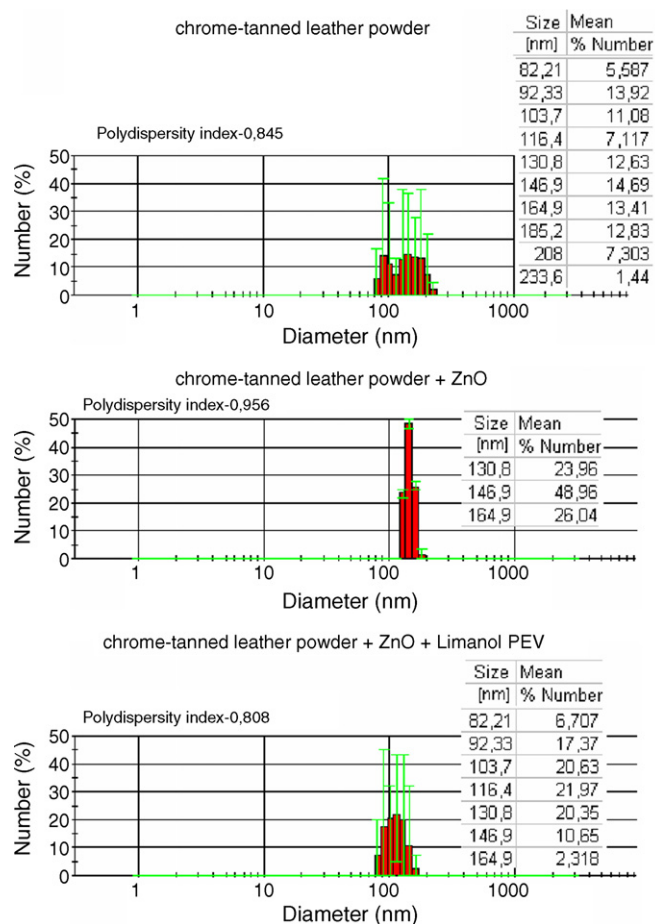


Fig. 2. Distribution of particle size.

filled mixes, the value of torque increment is connected with the reinforcing action of the filler. Based on the increments of torque, ΔL , of M1 and M2 mixes, calculated the filler activity. The obtained value of activity was 15.03 being considerably higher than one. Thus, it may be assumed that the chrome-tanned collagen, added in a quantity of 5 parts by wt. to the mix of XNBR rubber and Limanol PEV, is an active filler. From the results that are given in Table 1 it follows that the addition of collagen to the carboxylated butadiene-acrylonitrile rubber clearly influences on the improvement the mechanical properties of XNBR vulcanizates. Vulcanizates XNBR containing 5 parts by wt. of chrome-tanned collagen, show considerably higher tensile strength than the vulcanizates XNBR without protein. One can assume that in the presence of filler particles there is a good orientation of rubber macromolecules due to the applied stress, which results in increased crystallization capabilities. Therefore, the tensile strength and the elongation at break are increased. The topics of oxidation of chromium(III) salts to the chromium(VI) salts were analysed by ourselves. Vulcanizate of carboxylated butadiene-acrylonitrile rubber includes 0.11% chromium(III) given as Cr_2O_3 (measurement according to the norm PN-74/P-22110) [11]. Determination quality of chromium(VI) performed according to the norm PN-EN ISO 20344:2005 (V) 6.11 – content chromium(VI) – 0.00 mg/kg did not show presence of chromium(VI) salts. From the thermogravimetry experiments

Table 1
Consist and properties of mixes and vulcanizates of the XNBR, NBR rubber

Number of rubber mixes	M1	M2	M3	M4
Component (parts by wt.)				
Carboxylated butadiene–acrylonitrile rubber (XNBR)	100	100	–	–
Butadiene–acrylonitrile rubber (NBR)	–	–	100	100
Zinc oxide + collagen	5 + 0	5 + 5	5 + 0	5 + 5
Sulfur 2,5; stearine acid 2; MBTS 1,5; polnox N1; Limanol PEV 2 (rheometric properties)				
ΔL (dN m) the increase in the torque moment	42.3	74.1	55.5	66.3
τ_{09} (min) optimal vulcanization time	20	13	19	18
a_f filler activity	–	15.03	–	3.89
Modulus (Mechanical properties)				
M_{100} (MPa)	1.41 ± 0.06	1.77 ± 0.08	0.91 ± 0.05	1.14 ± 0.06
M_{200} (MPa)	2.18 ± 0.04	2.56 ± 0.09	1.40 ± 0.07	1.60 ± 0.09
M_{300} (MPa)	3.78 ± 0.27	3.64 ± 0.18	1.90 ± 0.00	2.03 ± 0.00
Tensile strength: T_s (MPa)	8.51 ± 1.68	13.18 ± 1.65	2.11 ± 0.35	2.25 ± 0.07
Elongation at break: ε_b (%)	385.32 ± 26.43	489.72 ± 26.92	312.95 ± 51.91	267.15 ± 43.50

[12] results that in vulcanization temperature 150 °C only 6% of vulcanizate decayed.

3.4. The influence of chrome-tanned collagen on mechanical properties of mixes and vulcanizates NBR

The compositions and properties of the obtained rubber mixes and vulcanizates of NBR are listed in Table 1. The addition of chrome-tanned collagen in a quantity of 5 parts by wt. mixed with 5 parts by wt. zinc oxide to the butadiene-acrylonitrile rubber clearly increases the increment of torque too, ΔL , that characterizes the degree of vulcanizate cross-linking. In other words the protein caused the increase of cross-linking degree of vulcanizates. The effect of the chrome-tanned collagen is also seen in the considerably shortened time of vulcanization of M4 mix as compared with mix M3 that contains no protein. This indicates an interaction with the accelerator and consequently preventing the disruption of the cross-links being formed. The presence of –OH and –COOH groups of the protein is an activator of the cross-linking complex. The calculated value of filler activity of mix of NBR rubber was 3.89 and being lower than that found for the mix of XNBR rubber. The effect of collagen on the mechanical properties of NBR vulcanizates is rather slight; only an insignificant improvement in the tensile strength (T_s) of collagen-containing vulcanizates was obtained as compared to those without protein and their elongation at break was reduced.

3.5. Measure of the interaction between the filler and polymer-cross-linking density of XNBR and NBR vulcanizates

The difference of the cross-linking density in toluene and in toluene and ammonia vapors is measure of the interaction between the filler and polymer, because under the influence of ammonia vapors decompose the bonds of polymer–filler. On the basis of equilibrium swelling in toluene also in toluene and ammonia vapors of vulcanizates M1, M2, M3, M4; marked their density of cross-linking. The results of equilibrium swelling are

Table 2
The influence of collagen on equilibrium swelling and cross-linking density of the XNBR, NBR vulcanizates

Rubber	No. of mixes	Q_w^T	Q_w^{T/NH_3}	v_c^T	v_c^{T/NH_3}
XNBR	M1	1.647	1.526	2.617	1.890
	M2	1.505	1.504	3.178	1.956
NBR	M3	2.882	3.018	1.051	0.305
	M4	2.457	2.736	1.481	0.401

listed in Table 2. From the data it follows that there is an increase in the cross-linking density of leather powder-containing vulcanizates, which would indicate that collagen takes part in the cross-linking of XNBR and NBR vulcanizates. The highest cross-linking density is shown by vulcanizate M2, which is reflected in its best mechanical parameters. The values listed in Table 2 were used to calculate the concentration and percentage content of lattice nodes that decompose under the influence of ammonia vapors. The obtained results are listed in Table 3. The highest number of ionic lattice nodes was decomposed in the collagen-containing vulcanizates. This would mean that the addition of protein to vulcanizates increases the number of ionic nodes in the elastomer matrix. The highest number of lattice nodes, about 10.7%, was decomposed under the influence of ammonia vapors in the vulcanizates of XNBR rubber, most probably due to the presence of –COOH groups in XNBR, which make it possible to form additional polymer–collagen bonds.

Table 3
The influence of collagen on quantity of the ion lattice points decomposing under the influence of ammonia of the XNBR, NBR vulcanizates

Rubber	No. of mixes	ΔV_{NH_3} (mol/cm ³)	A (%)	ΔA (%)
XNBR	M1	0.726	27.7	10.7
	M2	1.222	38.4	
NBR	M3	0.746	70.1	2.8
	M4	1.080	72.9	

4. Conclusion

- The noxious wastes from the tanning industry such as chrome-tanned leather shavings can be used after multi-stage disintegration as active filler for rubber mixes.
- The leather powder mixed with zinc oxide is the best form of its addition to rubber mixes.
- The addition of leather powder decreases the vulcanization time of carboxylated XNBR and NBR rubber mixes.
- From the measurements of mechanical properties it follows that collagen added to the carboxylated butadiene–acrylonitrile rubber clearly increases its tensile strength and elongation at break.
- The studies on the effect of collagen on the properties of carboxylated butadiene–acrylonitrile rubber will be continued.

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