Comparison of the Effects of Collagen and Modified Collagen Fillers on the Properties of XNBR Rubber

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ABSTRACT: The aim of this study was to compare the effects of 5 to 30 parts by weight of unmodified and modified collagen on the properties of XNBR rubber vulcanized with a cross-linking system. This study is a part of experimental series concerning polymeric materials that are biodegradable due to their filling with a waste protein such as collagen. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1984–1991, 2009

Key words: biodegradable; biopolymers; elastomers; fillers

INTRODUCTION

The problem of the utilization of chrome-tanned leathers continues to be a live research issue.[1,2] The present review concerns recent studies on the utilization of tanned leather wastes as additives to polymeric materials. Leather wastes have been used as fillers of isoprene, nitrile, and natural rubbers as well as PVC. The relevant literature is not voluminous, and it concerns mainly polymers filled with leather powder or shavings of chrome-tanned leathers. There are also examples of using hydrolyzates of leather wastes to prepare biodegradable materials.[3,4–6,7]

Babanas et al.[8,9] suggest also the possibility of using collagen as filler for PCV plasticized with octyl phthalate. Authors have observed that the increase in the leather powder content (10–60 parts by weight of collagen per 100 parts by weight of PCV) is accompanied by the increase in the density and hardness of the composites and deterioration in their mechanical properties. To improve the dispersion of leather powder, it was treated with EVA copolymer, which increased the tensile strength of PVC-collagen composite by 30%. Leather dust together with silica was used as a filler of PVC.[10] This additive decreased the density of the composite by 30–40%, but increased its maximal elongation.

Chrome-tanned leather shavings were used as filler of nitrile rubber[11] and natural rubber.[12] Before incorporation into the rubber mix, the shavings were neutralized with sodium carbonate (Na_2CO_3), ammonia (NH_3), and sodium hydroxide (NaOH). The addition of sodium carbonate and ammonia neutralized chrome shavings to nitrile rubber brought improved dispersion in elastomeric matrix and mechanical properties, whereas sodium hydroxide neutralized shavings exhibited poor properties. Swelling of the vulcanizates in water and 1% NaOH was found to increase with leather loading, whereas in methyl ethyl ketone (MEK) a reversed trend was observed.

Ravichandran and Natchimuthu used chrome shavings after neutralization with 1% urea solution or ammonia solution (NH_3) or sodium bicarbonate solution ($NaHCO_3$) as fillers of natural rubber (RSS Grade).[13] On the basis of the SEM micrographs, the authors have found that the modified chrome shavings were better dispersed in the elastomer medium and better interacted with the polymer matrix. Vulcanizates containing neutralized shavings had greater cross-link density and higher tensile strength.

Collagen hydrolyzate (Hykol E), obtained by enzymatic hydrolysis of chrome tanned shavings[14] (after separation of chromium (III) salts) was used to prepare biodegradable materials consisting of polyvinyl alcohol (PVA)-glycerin-collagen hydrolizate.[3] The biodegradation process was tested by the determination of the quantity of emitted CO_2 according to the procedure ASTM D5209-92.[15] It has been found that the addition of protein hydrolyzate and glycerin to polyvinyl alcohol (PVA) considerably accelerates the

degradation of PVA as the yield of measured CO_2 increases to 94%.

In further tests, the compositions of the obtained thermoplastic PVA-Hykol-glycerin films were optimized.[4] It was observed that the increase in the addition of collagen hydrolyzate is accompanied by increased water absorption by the obtained films, whereas the addition of glycerin adversely affects the water absorption capability.[5] A pure PVA film has a limited biodegradability at low temperature (5°C). The biodegradation rate at this temperature increases after the addition of collagen hydrolyzate. The obtained films can be used as biomaterials.

Lešinsky et al.[6] also tested the effect of collagen hydrolyzate on the biological degradation of PVA, using soil and water tests. They observed a positive influence of collagen hydrolyzate on the degradation, but simultaneously a low biodegradability of PVA under the conditions used.

Kolomaznik et al.[16] have performed enzymatic hydrolysis of chrome leather shavings and used the obtained collagen hydrolyzate, after dechroming, to cross-link epoxy resins (DGEBA) with molecular weights from 348 to 480 Da.[7] The obtained materials were assessed by the differential scanning calorimetry (DSC). The reaction was carried out at 205–220°C, i.e., at a temperature lower by about 30–40°C than that of thermal degradation of collagen hydrolyzate. The reaction leads to biodegradable polymers that might facilitate recycling of plastic parts in products of the automotive and/or aeronautics industry provided with protective films on this basis.

In this article, we compared the effects of various amounts of unmodified and modified collagen on the properties of XNBR rubber vulcanized with a cross-linking system selected on the basis of previous tests, including zinc oxide and sulfur with an accelerating agent.[17] These studies are a part of experimental series concerning polymeric materials that are biodegradable due to their filling with a waste protein such as collagen.

EXPERIMENTAL METHODS

The objects of the study were waste untanned collagen, chrome-tanned collagen, chrome-tanned and greasy collagen, contained in leather powder, chrome-tanned shavings, and buffing dust of chrome-tanned cow hides. Chromium (III) content given as Cr_2O_3 was 4.25–4.48%, PN-EN ISO 4684 : 2006 (U).

Shavings and buffing dust were subjected to multistage disintegration and sieved through a 0.2-mm mesh. In this manner powders were obtained.

The powders were characterized using elementary and thermal analysis, Fourier transform infrared

(FTIR) spectroscopy (BIO-RAD 175C) with a microscope attachment; scanning electron microscopy (SEM), the size of particles was measured by the technique of dynamic light diffusion DLS (Zetasizer Nano S90) and isoelectric point (IEP) was assessed by electro-kinetic measurements (Zetasizer 2000).

The waste collagen was used as a filler of carboxylated butadiene-acrylonitrile rubber XNBR (Krynac X7.50, 7% carboxyl; 27,5% acrylonitrile; Bayer AG).

Rubber mixes were prepared by using a laboratory mixing mill as already published.[18]

The kinetics of rubber mixes vulcanization was determined at a temperature about 423 K according to the standard PN-ISO 3417 : 1994. Based on rheometric curves the following were calculated: optimal time of vulcanization (τ_{90}), the increase in the torque moment (ΔL), and activity of filler (a_f) using Wolff's equation[19]:

$$\frac{\Delta L}{\Delta L_0} - 1 = a_f \cdot \frac{m_f}{m_p}$$

where ΔL, increase in the torque of mix with protein; ΔL_0, increase in the torque of mix without protein; a_f, activity of filler; m_f, phr of filler; and m_p, phr of polymer.

Vulcanization of the mixes was carried out at a temperature of 423 K, in time assessing on the based rheometric curves.

The equilibrium swelling in toluene, toluene and ammonia vapors was determined at a temperature of 298 ± 1 K for 48 h according to the standard PN-ISO 1817:2001/ap1:2002. The cross-link density was assigned using Flory–Rhener's equation.[20]

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

$$A = (\Delta\nu_{NH3}/\nu^T) \cdot 100\%$$

where:

$$\Delta\nu_{NH3} = \nu^T - \nu^{T+NH3}$$

$\Delta\nu_{NH3}$, concentration of the ion lattice points decomposing under the influence of ammonia (mol/cm^3); ν^T, ν^{T+NH3} - cross-link densities of vulcanizates assigned accordingly in toluene and toluene with ammonia vapors.

The content of mono-, di- and polysulfide bonds in the vulcanizates under investigation was determined by two thiol-amine analysis.[21] To calculate Q_w after the treatment with thiol-amine solutions, with the unknown value of m_o, we used the formula (the result is burdened with a small error):

$$m_s^* = m_s[1 - (m_m/m_c)]$$

where m_s^*, mass of a sample after swelling and drying, corrected about part of mineral substances; m_s, mass of a sample after swelling and drying; m_m, mass of mineral substances (contained in mix); m_c, mass of all components of mix.

Knowing the lattice density ν, it was possible to calculate the concentration of lattice nodes N in the cross-linked sample swollen in toluene after the treatment with thiol-amine solution:

$$N = 2\,\nu/f = \nu/2 = 1/(2^*Mc)$$

$$M_c = d_k/\nu$$

where N, concentration of lattice nodes after the treatment with thiol-amine solution [mol/g]; ν, lattice density [mol/cm³]; f, functionality of lattice; d_k, density of rubber [g/cm³]; M_c, numerical average molecular weight of chains between lattice nodes [g/mol].

The percentage content of poly-, di-, and monosulfide bonds was determined from the formulas.

$$[C - S_x - C] = [1/(2^*Mc)_{toluene} - 1/(2^*Mc)]_I/1/(2^*Mc)_{toluene}]^*100\%$$

$$[C - S_2 - C] = [1/(2^*Mc)]_I - 1/(2^*Mc)]_{II}/1/(2^*Mc)_{toluene}]^*100\%$$

$$[C - C + C - S - C] = [1/(2^*Mc)]_{II}/1/(2^*Mc)_{toluene}]^*100\%$$

where $1/(2^*Mc)_{toluene}$, concentration of lattice nodes after the treatment with toluene [mol/g]; $1/(2^*Mc)]_I$, concentration of lattice nodes after first analysis [mol/g]; $1/(2^*Mc)]_{II}$, concentration of lattice nodes after second analysis [mol/g].

The mechanical properties were measured with Zwick apparatus 1442, 1435 PN-ISO 37:1998; Shore A hardness of vulcanizates was determined according to the standard PN-80/C-04238. Resistance to thermal ageing was determined according to the standard PN-88/C-04207. The principles of determination rely on exposing a sample to the action of circulating air at a temperature of 343 K for 72 h. The coefficient of ageing was determined from the following relationship[22]:

$$S = [TS_b' \cdot E_b']/[\,TS_b \cdot E_b]$$

where S, aging coefficient; TS_b', tensile strength after thermal aging [MPa]; E_b', elongation at break after thermal aging [%]; TS_b, tensile strength before thermal aging [MPa]; E_b, elongation at break before thermal aging [%].

The effect of buffing dust and chrome-tanned leather shavings on the biodecomposition capability of the XNBR vulcanizates was tested by incubation samples in active universal soil (humidity 80%), at T = 303 K for 30 days. After this time was estimated surface of samples and tested mechanical properties.

DISCUSSION OF TEST RESULTS

Characteristic of chrome-tanned leather shavings and buffing dust

The chemical constitution of collagen contained in chrome-tanned shavings differs from that of collagen contained in the buffing dust because it is derived from various phases of the production cycle. The shavings originate from tanned leather, whereas the dust from tanned, greased, and colored leather. The differences can be seen by comparing the FTIR spectra of shavings and dust (Fig. 1).The spectrum of dust shows maxima within the region 2800–3000 cm⁻¹ and at a wave number of 1800 cm⁻¹ indicating the presence of fatty substances that are absent in the spectrum of shavings. Moreover, in both spectra one can observe a broad spectrum at 3200–3500 cm⁻¹ corresponding to valency vibration of ─OH groups in side chains and terminal groups. A band of deformation vibration of first and second order amide (─NH) appears at 1665 cm⁻¹. The band with a low intensity at 1410 cm⁻¹ corresponds to valency vibration of ─COO⁻ groups. The band of valency and deformation vibration of C═O group appears at a wave number of 1245 cm⁻¹, whereas those of C─O are seen at 1095 and 1345 cm⁻¹. The presence of Cr─O bonds is indicated by the bands at 510–590 cm⁻¹.

The influence of oiling agents is seen in the structure of the buffing dust. Comparing the SEM images of shavings [Fig. 2(a)] and dust [Fig. 2(b)] one can see a clear isolation of collagen fibers in the dust brought about by the incorporated oiling substances that separate the fibers by enclosing them.

The performed elementary analysis allowed the determination of elements that appear in shavings and dust. From the obtained data (Table I) it follows that the powders have similar contents of Cr (III), but they considerably differ in the content of nitrogen derived from the protein substance, collagen.

The results of thermal analysis determine the thermal stability of shavings and dust (Table I). Losses of shavings and dust at a temperature of 423 K (the vulcanization temperature) do not exceed 5%, which indicates the possibility of their use in the vulcanization processes as fillers of rubber mixes.

The zeta potential measurement of chrome shavings and buffing dust qualified a chemical character
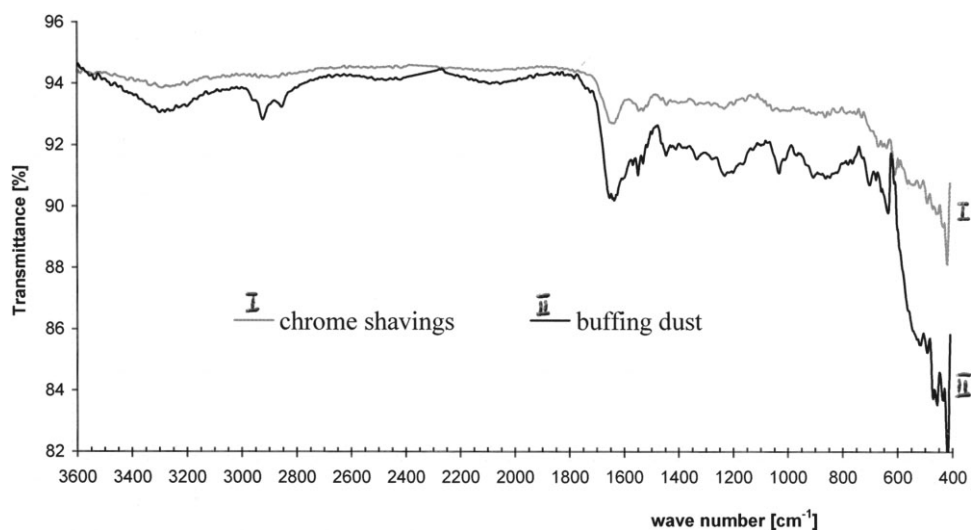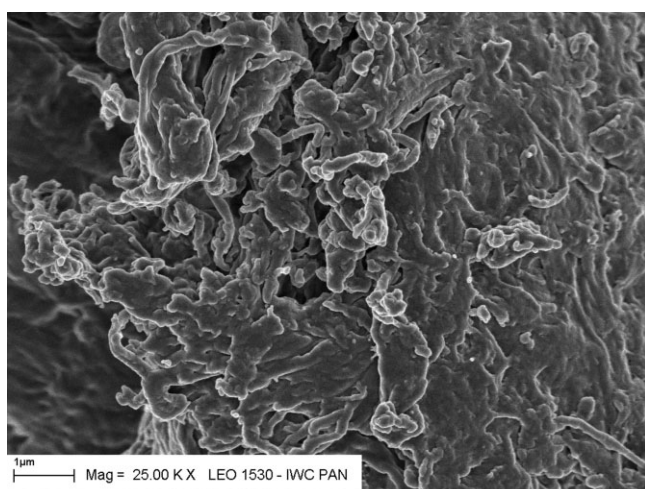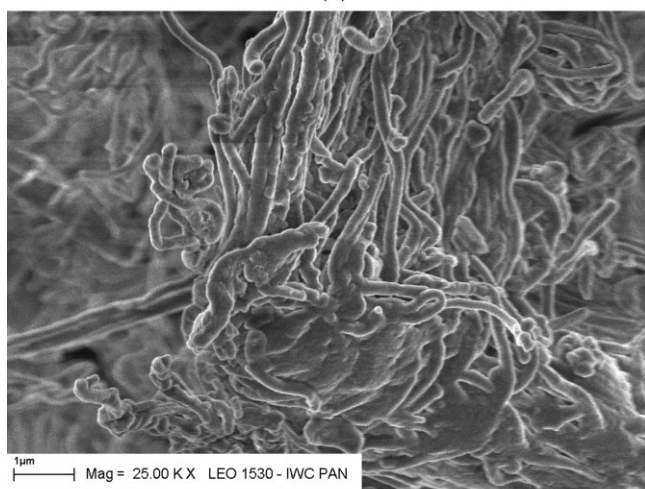
Figure 1 IR spectrums of chrome shavings and buffing dust.

(a)

(b)

Figure 2 (a) SEM micrographs of chrome shavings (magnification 25.00 KX). (b) SEM micrographs of buffing dust (magnification 25.00 KX).

of fillers surface (Table I). IEP value for shavings and dust was 6.5 and 5.8 what indicated on acidic character fillers surface. Blending the shavings or buffing dust with zinc oxide (IEP^{ZnO}, 8.6) caused shifting the isoelectric point toward more basic pH values, which indicates a change in the chemical character of the fillers surface to more alkaline. It proves that after addition ZnO the state of the dust surface undergo the change. The more alkaline character of the filler convinces its better dispersed in polymer and the vulcanizate gains better properties.[23] Thus, before the addition of shavings or dust to the rubber mix, it should be mixed with ZnO to facilitate the incorporation into the mix and to improve the filler dispersion in the elastomeric matrix.

An important value that characterizes fillers is the size of their particles. The size of shavings and dust particles was measured in an aqueous dispersion (0.025 mg/L), after their treatment with ultrasounds (1 h). The size of shavings particles ranges from 262 to 417 nm, among which particles measuring 331 nm constitute the highest content amounting to 31%. The size of dust particles is within a wider range: 295–526 nm, whereas the fraction with the highest numerical content (36%) has a size of 469 nm. When shavings or dust are blended with the same quantity of ZnO, their particle sizes are changed. The size of shavings or dust particles blended with ZnO is decreased. The highest content 40 and 50% is shown by particles with a size of 208 and 295 nm for shavings and dust, respectively. Probably ZnO particles separate shavings or dust particles in water solution. It makes difficult connection in aggregates thus size of shavings or dust particles blended with ZnO is decreased.

<div align="center">

TABLE I
Characteristic of Chrome Shavings and Buffing Dust

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Researches	Chrome shavings		Buffing dust	
Wave number [cm^{-1}]				
3200–3500	v, —OH groups in side chains and terminal groups		v, —OH groups in side chains and terminal groups	
2800–3000	–		v, —CH$_2$, —CH$_3$ groups inside chains and terminal groups	
1665	δ, first- and second-order amide		δ, first- and second-order amide	
1410	v, —COO$^-$ groups		v, —COO$^-$ groups	
1245	δ, v, —C=O groups		δ, v, —C=O groups	
1095 i 1345	δ, v, —C—O groups		δ, v, —C—O groups	
510–590	v, Cr—O bonds		v, Cr—O bonds	
Content of elements [%]				
Cr	4.25		4.48	
N	11.50		7.82	
Dry matter	84.69		89.49	
Ash	11.67		6.82	
Isoelectric point [mV]	Shavings	Shavings + ZnO	Dust	Dust + ZnO
IEP	6.5	7.8	5.8	7.6
Size of particles [nm]	269–417	185–262	295–526	252–331
Size of fraction with the highest numerical content [nm]	331	208	469	295
Number fraction [%]	36	40	36	50

v, valency vibration; δ, deformation vibration

Influence of 5 to 30 phr buffing dust on the properties of XNBR mixes and vulcanizates

The effect of 5, 10, 20, or 30 parts by weight of buffing dust directly blended with ZnO on the properties of mixes and vulcanizates of XNBR rubber cross-linked hybrid-wise (ZnO + S + MBTS) was assessed.

From the vulcametric measurements it follows that the increase in the content of dust is accompanied by an increase in the minimal torque moment L_{min} and consequently the viscosity of the mix is decreased (Table II). The presence of dust has brought about an increase in the cross-linking degree of the mix, as indicated by the higher increment of torque moment, ΔL, of the filled mix as compared to that of the standard. However, with the increase in the filler content the value of ΔL is slightly decreased. The highest activity is shown by the dust added in a quantity of five parts by weight as indicated by the value of the rheometric coefficient of activity. From the determinations of swelling in toluene it follows that the increase in the filler content results in a clearly increased cross-linking density of the vulcanizates. Despite this fact, the values of tensile strength, TS_b and elongation at break, E_b, decrease as confirmed by the strength tests. The highest tensile strength is shown by the vulcanizate containing five parts by weight of the buffing dust. This results from the very good orientation of rubber

macromolecules due to the applied stress. In the presence of higher quantities of the filler, the orientation of rubber macromolecules is most likely to be considerably limited, which brings about a decrease in the crystallization capability or its complete deficiency. Therefore, the tensile strength decreases. As the dust content in the rubber increases, one can observe an increase in the rubber hardness confirmed by the increased moduli at elongations of 100, 200 and 300% and decreased elongation at break indicating a drop in elasticity and increased hardness of the vulcanizates.

Influence of 5 to 30 phr chrome shavings on the properties of XNBR mixes and vulcanizates

The effect of the chrome-tanned shavings content in XNBR rubber differs from that of buffing dust, which has been already observed at the stage of vulcanization kinetics. The increase in shavings content is accompanied by the increment in the minimal torque moment L_{min} and consequently in the mix viscosity, but the value of this increment is considerably higher than that in the case of the buffing dust (Table III). The incorporation of shavings into the rubber mix resulted in an increased degree of its cross-linking as indicated by the higher value of the increment in the torque moment ΔL of the filled mix in relation to that of the standard. However, together

TABLE II
Properties of XNBR Mixes and Vulcanizates with 0, 5, 10, 20, 30 phr Buffing Dust

Component	Component content [phr]				
XNBR rubber	100	100	100	100	100
ZnO + buffing dust	5 + 0	5 + 5	5 + 10	5 + 20	5 + 30
		Rheometric properties			
L_{min} [dNm]	9	11	11.40	12.60	16
ΔL [dNm]	51.3	74.5	72.8	71.7	70.4
a_f	–	9	4.2	2	1.2
		Crosslink density			
v_t [10^4 mol/cm^3]	2,100	2,358	3,210	4,621	5,110
		Mechanical properties			
S_{100} [MPa]	1.98	3.24	5.04	6.74	9.58
S_{200} [MPa]	2.87	5.46	6.73	8.66	13.42
S_{300} [MPa]	4.25	8.10	8.50	10.12	15.12
TS_b [MPa]	15.70	22.32	19.89	17.71	16.15
E_b [%]	492.30	486.93	452.11	399.82	358.50
Hardness [°Sh A]	70.6	75.2	76.2	81.4	87.0

Another components of mixes: S (2.5), MBTS (1.5), and stearic acid (2).

with the increase in the filler content one can observe a clear drop in the cross-linking degree of the mix. The highest value of coefficient a_f was obtained when the shavings content was five parts by weight, which indicates that this filler shows its highest activity when it appears in that quantity in the rubber mix.

The cross-linking density of vulcanizates increases slightly with the increase in the shavings content, whereas their strength decreases (with 30 parts by weight of the shavings content the strength is below that of the standard). The vulcanizate containing five parts by weight of shavings shows the highest strength (15.87 MPa), similar to that of the standard. As the shavings content increases, there is a observed decrease in the values of moduli at elongations of 100, 200, and 300%, which indicates decreased vulcanizate rigidity and increased elonga-

tion at break or elasticity. The incorporation of 5–30 parts by weight of shavings exerts only a slight influence on the vulcanizate hardness.

Comparison of the effects of untanned collagen, chrome-tanned collagen and chrome-tanned and greasy collagen on the properties of XNBR rubber

As indicated by the above tests, the best properties of XNBR rubber were obtained by the incorporation of five parts by weight of the chrome-tanned and oiled collagen (buffing dust) or the chrome-tanned collagen (shavings). Comparing the effect of five parts by weight of the collagen contained in the buffing dust or shavings, one should also take into account the values obtained for the untanned collagen, which would emphasize the sense of incorporating the tanned collagen into rubber mixes. From

TABLE III
Properties of XNBR Mixes and Vulcanizates with 0, 5, 10, 20, and 30 phr Shavings

Component	Component content [phr]				
XNBR rubber	100	100	100	100	100
ZnO + chrome shavings	5 + 0	5 + 5	5 + 10	5 + 20	5 + 30
		Rheometric properties			
L_{min} [dNm]	9	14.5	16.40	18.60	25.70
ΔL [dNm]	51.3	89.2	85.26	72.2	69.10
a_f	–	14.8	2.7	2	1.2
		Crosslink density			
v_t [10^4 mol/cm^3]	2,100	2,279	2,312	2,679	2,861
		Mechanical properties			
S_{100} [MPa]	1.98	2.44	2.24	1.67	1.49
S_{200} [MPa]	2.87	3.65	3.10	2.27	2.05
S_{300} [MPa]	4.25	5.56	4.02	3.14	2.69
TS_b [MPa]	15.70	15.87	9.36	8.90	8.40
E_b [%]	492.30	448.10	502.25	522.80	535.07
Hardness [°ShA]	70.6	79.0	79.2	81.1	82.4

Another components of mixes: S (2.5), MBTS (1.5), and stearic acid (2).

TABLE IV
Comparison of the Effects of Untanned Collagen, Chrome-Tanned Collagen and Chrome-Tanned and Greasy Collagen on the Properties of XNBR Rubber Mixes and Vulcanizates

Component	Component content [phr]			
XNBR rubber	100	100	100	100
ZnO + buffing dust	5 + 0	5 + 5	–	–
ZnO + chrome shavings	–	–	5 + 5	–
ZnO + leather powder	–	–	–	5 + 5
Rheometric properties				
L_{min} [dNm]	9	11	14.5	13
ΔL [dNm]	51.3	74.5	89.2	77
a_f	–	9	14.8	10
Crosslink density				
v_t [10^4 mol/cm^3]	2,100	2,358	2,279	2,361
A [%]	40	50	48	43
C—C, C—S—C [%]	28.12	24.72	25.90	–
C—S$_2$—C, C—S$_x$—C [%]	71.88	75.28	74.10	–
Mechanical properties				
S_{100} [MPa]	1.98	3.24	2.44	2.39
S_{200} [MPa]	2.87	5.46	3.65	3.41
S_{300} [MPa]	4.25	8.10	5.56	5.13
TS$_b$ [MPa]	15.70	22.32	15.87	10.62
E_b [%]	492.30	486.93	448.1	414.37
S	0.83	0.83	0.88	1.39

Another components of mixes: S (2.5), MBTS (1.5), and stearic acid (2).

the data given in Table IV it follows that collagen in the form of leather powder or shavings caused increases the viscosity and cross-linking degree of the rubber mix. The vulcanizates containing these fillers have similar cross-linking densities, whereas the vulcanizate filled with the chrome-tanned shavings shows a better tensile strength, which is due to a higher number of the formed labile lattice nodes. The addition of collagen in the form of dust improves the vulcanizate strength by 42%. The presence of this filler brings about a slight increase in the viscosity of the mix in relation to that of the standard, and a considerable increase in its cross-linking degree. The improvement in the strength properties of the vulcanizate containing the buffing dust can be explained in terms of the highest number of labile lattice nodes and di- and polysulfide bonds. The reinforcing effect of the buffing dust can be connected with the capability of this filler to form its own structure as indicated by the high value of module S_{300} (8.10 MPa).

Comparing three different forms of collagen, their effects on the thermal ageing of XNBR rubber were assessed. The addition of dust in a quantity of five parts by weight does not influence the vulcanizate resistance to thermal ageing. An increased ageing coefficient S is observed in the vulcanizates filled with shavings as well as with powder. In the case of leather powder, the values of ageing coefficient are clearly higher. The improvement in the resistance to
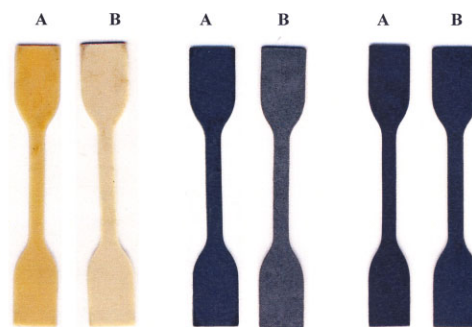
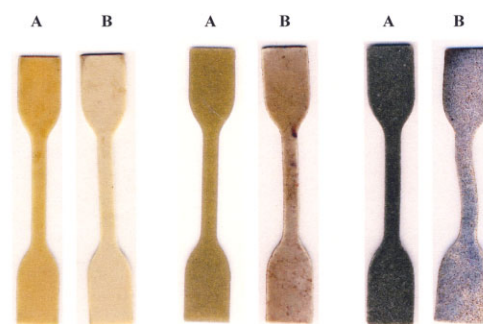|	XNBR rubber		Vulcanizate with **5** phr of buffing **dust**		Vulcanizate with **30** phr of buffing **dust**	
	A	**B**	**A**	**B**	**A**	**B**
TS$_b$[MPa]	15,70	12,87	22,32	16,60	16,15	9,30
E$_b$ [%]	492,30	503,69	486,93	558,95	358,50	498,32

A - control sample, **B** - sample after 30 days of storage in universal soil

Figure 3 The effect of 5 and 30 phr buffing dust on the biodecomposition capability of the XNBR vulcanizates in universal soil. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermal ageing is likely to be due to the protein substance contained in the fillers. The highest content of nitrogen appears in the powder, less in the shavings and the least in the buffing dust. The presence of chromium (III) in the dust and shavings does not deteriorate the resistance to thermal ageing.

Biodecomposition of the collagen-elastomer composites containing 5 and 30 parts by weight of protein contained in the chrome-tanned shavings and buffing dust

The effects of the shavings and dust quantities on the capability of elastomer composites containing

	XNBR rubber		Vulcanizate with **5** phr of **shavings**		Vulcanizate with **30** phr of **shavings**	
	A	**B**	**A**	**B**	**A**	**B**
TS$_b$[MPa]	15,70	12,87	15,87	9,51	8,40	1,73
E$_b$ [%]	492,30	503,69	448,10	545,65	535,07	579,10

A - control sample, **B** - sample after 30 days of storage in universal soil

Figure 4 The effect of 5 and 30 phr shavings on the biodecomposition capability of the XNBR vulcanizates in universal soil. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

these fillers to degrade naturally were also examined. The results of testing the tensile strength of the composite samples before and after 30-day incubation in a universal soil are proof positive that the obtained composites of synthetic rubbers and protein fillers will be susceptible after their working life to the action of microorganisms. Figure 3 shows the effect of the dust quantity on the capability of the vulcanizates of XNBR rubber cross-linked hybridwise to biodecomposition.

The composite containing five parts by weight of the buffing dust is clearly discolored, has fine erosion pits. increased roughness and decreased brightness. On the surface of the composite containing 30 parts by weight of the buffing dust one can observe numerous gray spots indicating discoloration, pitting and increased roughness. Both samples show drops in strength and increase in elongation, which indicates the effects of soil microorganisms on the structure of collagen-containing composites. The strength of the composite containing five parts by weight of the buffing dust is decreased by 26%, whereas that of the composite with 30 parts by weight of dust by 42%.

The effect of shavings quantity on the capability of the vulcanizates of XNBR rubber also cross-linked hybridwise is illustrated in Figure 4. The surface changes resulted from the action of bacterial microflora on the vulcanizates filled with shavings are clearly visible. On the surface of the composite containing five parts by weight of shavings one can observe the discoloration of sample and the appearance of darker spots. The surface of the sample with 30 parts by weight of shavings has become almost white, rough, with numerous fine pits. Besides the visual evaluation of the samples, the strength of the shavings-containing composites after soil incubation was also tested. The vulcanizates with this filler has also shown lower strengths and higher elongations. The strength of the composites with 5 and 30 parts by weight of shavings has decreased by 40 and 79%, respectively.

CONCLUSIONS

Noxious chrome-tanned wastes such as shavings and buffing dust can be successfully used as fillers of elastomers that constitute biodegradable polymeric materials.

1. The buffing dust added in quantities of 5–30 parts by weight has turned out to be a reinforcing filler of XNBR rubber. The best properties of mixes and vulcanizates have been obtained using five parts by weight of this filler.
2. The chrome-tanned shavings incorporated in a quantity of five parts by weight into the mix of XNBR rubber have slightly improved their strength properties in relation to that of the standard. However, the increased content of this filler in the mix has brought about a decrease in the strength parameters of the vulcanizate.
3. Increased coefficients of thermal ageing have been obtained for the vulcanizates filled with shavings and untanned powder that contain considerable quantities of protein substance and play the role of anti-ageing agents, thermal stabilizers.
4. Collagen contained in the examined fillers constitutes a substrate for bacteria, hence the vulcanizate filled with the buffing dust or shavings are decomposed easier by soil microorganisms than those without these fillers.

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