

A Mixture of Buffing Dust and Chrome Shavings as a Filler for Nitrile Rubbers

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ABSTRACT: The incorporation of biopolymers, such as chrome shavings and buffing dust, into rubber blends makes it possible to obtain biodecomposable collagen–elastomer materials with good utility properties. It is the presence of a biopolymer in multicomponent polymeric materials that facilitates enzymatic hydrolysis and results in biodecomposition through the loss of cohesiveness and polymer scattering. The undertaking of such original studies was justified by the benefits resulting from a new generation of polymeric materials and the need for a solution

to the problem of growing amounts of wastes by waste management in the tanning industry. In this study, the effect of a mixture of chrome shavings and buffing dust on the properties of nitrile rubbers was examined. The dust and shavings, in a 1:1 proportion, were mixed with 5 parts by weight of zinc oxide and, in this form, was added to the rubber blends. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 122: 2899–2906, 2011

Key words: biomaterials; biopolymers; crosslinking

INTRODUCTION

From the literature, it follows that chrome shavings or buffing dust have been used to fill elastomers,^{1–7} but a mixture of shavings and dust has not been used as a filler for butadiene–acrylonitrile rubber (NBR) or carboxylated butadiene–acrylonitrile rubber (XNBR).

A thorough review of the literature concerning the utilization of collagen wastes and their hydrolyzates as fillers of elastomers has been given in previous articles.^{1,8,9} This article completes and updates the literature on this subject matter.

Collagen wastes, after their modification and drying, were used as protein fillers of natural, nitrile, and butadiene–styrene rubbers. In polar rubbers, fillers recovered from wastes performed the function of vulcanization accelerators.¹⁰ Composites of this type were used in footwear industry to produce shoe soles. Such products were easy to dye and provided a comfortable feeling of coolness.¹¹

A composite containing 10–60 parts by weight of chrome-tanned collagen fibers per 100 parts by weight of natural or synthetic rubbers was patented. The blend has been used to produce tires for braking wooden wheels.

The increase in leather waste content in the composite resulted in a higher resistance to motion and, consequently, decreased the distance traveled by the wheels.¹²

Also patented was a composition of rubber material for the production of antislip soles for sports footwear; the vulcanizates obtained contained 20–30% collagen fibers.¹³

Various wastes, such as leather scraps, viscose fibers, blends of polyester and glass fibers, and blends of vinyl and carbon fibers in amounts of about 20 wt % were incorporated into a polymeric composite based on a phenol–formaldehyde matrix. These composites were examined to assess the effect of the incorporated fillers on their frictional properties in view of their potential use for sliding and frictional units of machinery.¹⁴

Leather wastes and vinyl–ester–carbon fiber blends appeared to be useful fillers for composites for frictional machine parts, whereas the wastes of viscose fibers and leather were found to be good fillers for composites for sliding elements (after they were saturated with silicone oil).

Also tested were poly(vinyl alcohol) (PVA) materials containing 5–15% collagen hydrolyzate (Kortan) to assess their ability to decompose in the natural environment. A 10% addition of collagen hydrolyzate to PVA resulted in increases in the tensile strength and Young's modulus of this polymer and a drop in its elongation. Moreover, the presence of the collagen hydrolyzate in the polymeric films brought about higher rates of their dissolution in water and the faster mineralization of PVA in soil after 60 days, as measured by the quantity of liberating CO₂.¹⁵ Also performed were tests to check the nutrient characteristics of films containing collagen

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hydrolyzate. Lettuce shoots covered with a film of PVA–collagen hydrolyzate showed regular growth, in contrast to uncovered shoots.

Tchmutin et al.¹⁶ tested the biodegradation of polymeric composites filled with collagen hydrolyzate obtained by the enzymatic hydrolysis of chrome-tanned shavings by means of dielectric measurements and sample weight losses. The higher the protein hydrolyzate content in the polyethylene matrix was, the shorter the biodegradation time was. Moreover, hydrolyzate concentrations over 20 vol % caused cavity biodegradation in the samples tested.¹⁶

Trials have been undertaken to obtain biodegradable composites containing collagen hydrolyzate recovered from leather wastes. As there was also the problem of the nondisposed nonprotein portion of these wastes, the collagen wastes were incorporated in an unchanged form into elastomers to obtain biodegradable materials under natural conditions.

EXPERIMENTAL

Chrome leather shavings and buffing dust were subjected to multistage disintegration to prepare a powder that was then sieved through a 0.2-mm mesh.

The content of chromium(III) as Cr₂O₃ ranged from 4.25 to 4.48% according to the standard PN-EN ISO 4684:2006 (U).

The powder obtained was tested by means of elementary and thermal analyses, Fourier transform infrared spectroscopy (Bio-Rad 175C, Institute of Polymer and Dye Technology, Łódź, Poland) with a microscope attachment, and scanning electron microscopy.

The size of the particles was measured by dynamic light diffusion (Zetasizer Nano S90, Institute of Polymer and Dye Technology, Łódź, Poland), and their isoelectric point was assessed by electrokinetic measurements (Zetasizer 2000).¹

The dust and shavings, in a 1:1 proportion, were mixed with 5 parts by weight of zinc oxide and, in this form, were used as a filler for XNBR (Krynac X7.50, 7% carboxyl and 27.5% acrylonitrile, Bayer AG, Institute of Polymer and Dye Technology, Łódź, Poland) and NBR (Europrene N 3960, 39% acrylonitrile, Polimeri Europa SPA, Institute of Polymer and Dye Technology, Łódź, Poland).

The rubber mixes were prepared with a laboratory mixing mill, as previously reported.¹⁷

The kinetics of the rubber mixes' vulcanization were determined at a temperature of 423 K according to the standard PN-ISO 3417:1994. On the basis of the rheometric curves, the following parameters were calculated with Wolff's equation: the optimal time of vulcanization (τ_{90}), increase in the torque (ΔL), and activity of the filler (a_f).¹⁸

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

where ΔL is the increase in the torque of the mix with protein (dNm), ΔL_0 is the increase in the torque of the mix without protein (dNm), m_f is the parts per hundred resin of the filler, and m_p is the parts per hundred resin of the polymer.

Vulcanization of the mixes was carried out at a temperature of 423 K to determine their τ_{90} values.

The equilibrium swelling in toluene and toluene with 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 crosslink density was assigned with Flory–Rehner's equation.¹⁹ The percentage content (A) of the ion lattice points decomposing under the influence of ammonia were calculated as follows:

$$A = (\Delta v_{\text{NH}_3} / v^T) \times 100\% \quad (2)$$

where

$$\Delta v_{\text{NH}_3} = v^T - v^{T+\text{NH}_3} \quad (3)$$

where Δv_{NH_3} is the concentration of the ion lattice points decomposing under the influence of ammonia (mol/cm³) and v^T and $v^{T+\text{NH}_3}$ are the crosslink densities of the vulcanizates assigned accordingly in toluene and toluene with ammonia vapors (mol/cm³).

The contents of monosulfide, disulfide, and polysulfide bonds in the vulcanizates under investigation were determined by two thiol–amine analyses.²⁰

To calculate Q_w (equilibrium swelling [mg/mg]) after the treatment with thiol–amine solutions with the unknown value of m_o (mass of the sample before swelling), we used the following formula (the results were burdened with a small error):

$$m_s^* = m_s [1 - (m_f / m_c)] \quad (4)$$

where m_s^* is the mass of the sample after swelling and drying, corrected for the amount of mineral substances; m_s is the mass of the sample after swelling and drying; m_m is the mass of the mineral substances (contained in the mix); and m_c is the mass of all of the components of the mix.

Knowing the lattice density (v mol/cm³), we were able to calculate the concentration of lattice nodes (N) in the crosslinked sample swollen in toluene after the treatment with the thiol–amine solution:

$$N = 2v/f = v/2 = 1/(2M_c) \quad (5)$$

$$M_c = d_r / v \quad (6)$$

where N is the concentration of lattice nodes after the treatment with the thiol–amine solution (mol/g), f is the functionality of the lattice, d_r is the density of

rubber (g/cm^3), M_c is the numerical-average molecular weight of the chains between the lattice nodes (g/mol).

The percentage contents of the polysulfide, disulfide, and monosulfide bonds were determined from the following formulas:

$$[C - S_x - C] = [1/(2M_c)_{\text{toluene}} - 1/(2M_c)_I] / [1/(2M_c)_{\text{toluene}}] \times 100\% \quad (7)$$

$$[C - S_2 - C] = [1/(2M_c)_I - 1/(2M_c)_{II}] / [1/(2M_c)_{\text{toluene}}] \times 100\% \quad (8)$$

$$[C - C + C - S - C] = [1/(2M_c)_{II} / 1/(2M_c)_{\text{toluene}}] \times 100\% \quad (9)$$

where $1/(2M_c)_{\text{toluene}}$ is the concentration of lattice nodes after the treatment with toluene (mol/g), $1/(2M_c)_I$ is the concentration of lattice nodes after the treatment with the first thiol-amine solution (mol/g), and $1/(2M_c)_{II}$ is the concentration of lattice nodes after the treatment with the second thiol-amine solution (mol/g).

The mechanical properties were measured with a Zwick apparatus 1442, 1435 according to PN-ISO 37:1998, Institute of Polymer and Dye Technology, Łódź, Poland.

The resistance to thermal aging was determined according to the standard PN-88/C-04207.

The principles of determination rely on the exposure of a sample to the action of circulating air at a temperature of 343 K for 72 h. The coefficient of aging (S) was determined from the following relationship:

$$S = [TS'_b E'_b] / [TS_b E_b] \quad (10)$$

where TS'_b is the tensile strength after thermal aging (MPa), E'_b is the elongation at break after thermal aging (%), TS_b is the tensile strength before thermal aging (MPa), and E_b is the elongation at break before thermal aging (%).

The hysteresis properties were measured with a Zwick apparatus 1442, 1435 according to PN-ISO 37:1998, but the Mullins' effect (R_H ; %) was calculated according to the following equation:

$$R_H = [(W_1 - W_5) / W_1] \times 100\% \quad (11)$$

where W_1 is the energy in the first cycle (kJ/m^2) and W_5 is the energy in the fifth cycle (kJ/m^2).

To determine the carboxyl group ($-\text{COOH}$) content of the selected vulcanizates, the unfilled and filled XNBR vulcanizates were extracted with acetone. The determination of the $-\text{COOH}$ content was performed in the mixture of tetrahydrofuran and toluene (the titrant was ethanol).

TABLE I
Effect of the Shavings-Dust Mixture on the Mechanical Properties of the NBR Vulcanizates

Properties	Sample				
	N	N5S-B	N10S-B	N20S-B	N30S-B
Properties	0	5	10	20	30
S_{100} (MPa)	1.04	1.56	2.00	2.46	3.18
S_{300} (MPa)	1.75	2.73	3.15	3.71	4.48
TS_b (MPa)	3.79	4.16	4.36	5.65	6.55
E_b (%)	596	487	516	668	656
Hardness (Shore A)	69	60	62	66	70

Other components of the mixes (phr): NBR, 100; S, 2.5; MBTS (dibenzothiazyl disulfide), 1.5; ZnO, 5; stearic acid, 2. TS_b , tensile strength; E_b , elongation at break.

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

DISCUSSION OF THE TEST RESULTS

Effect of the shavings-dust mixture on the properties of NBR

The incorporation of chrome shavings or buffing dust into NBR improved the mechanical properties, and the filled vulcanizates showed resistance to accelerated aging.¹ Thus, the assessment of the effects of these fillers on the NBR properties seemed to be of great interest. Moreover, the use of a shavings-dust mixture as a filler of NBR is an original idea that has yet been unpublished in the literature.

The prepared rubber blends contained different contents of the filler: 0, 5, 10, 20, and 30 parts by weight of the filler mixture per 100 parts by weight of NBR (Table I).

As the content of the shavings-dust mixture was increased, the value of TS_b also increased, and in each case, it was higher than that of the reference vulcanizate.

The increase in the filler mixture content was accompanied by an increased elongation at break. In addition to the increased values of TS_b and E_b , the values of the moduli at elongations of 100 and 300% were increased when the rubber was filled with the shavings-dust mixture.

The NBR vulcanizates containing from 5 to 20 parts by weight of the filler mixture showed a lower hardness than that of the reference sample. Only the vulcanizate containing the highest content of the filler mixture showed a hardness similar to that of the reference sample.

TABLE II
Crosslink Density and Lattice Nodes of NBR with the Shavings–Dust Mixture

Experiment	Sample			
	N	N5S-B	N20S-B	N30S-B
v^T (10^4 mol/cm ³)	1.0	0.9	1.2	1.3
C–C, C–S–C (%)	35.7	27.8	12.9	10.1
C–S ₂ –C (%)	49.9	8.5	18.3	8.8
C–S _x –C (%)	14.4	63.6	68.8	81.1

C–C, carbon lattice nodes; C–S–C, monosulfide lattice nodes; C–S₂–C, disulfide lattice nodes; C–S_x–C, polysulfide lattice nodes.

The changes in tensile strength could be explained by means of the crosslinking density and the lattice structure of the NBR vulcanizates (Table II). In the case of the vulcanizate containing 5 parts by weight of the filler mixture, the crosslinking density was comparable to that of the standard, and hence, this vulcanizate had a tensile strength similar to that of the standard. The remaining vulcanizates showed higher crosslinking densities than that of the standard; this resulted in their higher tensile strength.

The increased crosslinking density brought about by the presence of the shavings–dust mixture indicated its participation in the formation of the lattice. The changes in the rubber structure after the incorporation of the shavings–dust mixture were observed in the IR spectra (Fig. 1). The intensity of the bands at 1450 and 760 cm^{−1} was changed; this indicated the participation of methylene groups and *cis*-1,4-mers in the crosslinking process. As a matter of fact, in the structure of the rubber containing collagen in the form of leather shavings and dust, there was less carbon, monosulfide, and sulfide bonds and more polysulfide nodes responsible for the improvement in the strength properties.

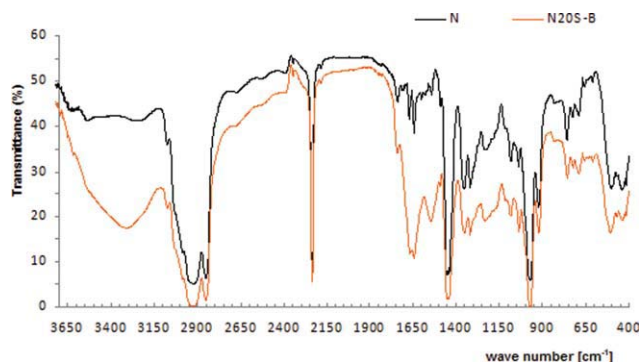


Figure 1 IR spectra of the NBR vulcanizates: unfilled vulcanizates (N) and vulcanizates filled with the shavings–dust mixture (N20S-B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Hysteresis Properties of the NBR Vulcanizates

Sample	ΔW (kJ/m ²)	R_H (%)
N	2.35	59.0
N5S-B	8.66	76.6
N20S-B	13.60	78.2
N30S-B	14.81	81.7

The occurrence of rubber–filler interactions was confirmed by R_H , which was higher in the filled vulcanizates than in the standard.

The hysteresis properties of the NBR vulcanizates are listed in Table III. The incorporation of the shavings–dust mixture into the NBR vulcanizate structure brought about an increase in the hysteresis loss (ΔW). With increasing filler mixture content, the value of ΔW increased; that is, the vulcanizate rigidity increased, and the propagation of stresses deteriorated.

The incorporation of the shavings–dust mixture into NBR also resulted in a decreased friction force and its stabilization [Fig. 2(A)]. The total energy of a sample [Fig. 2(B)] containing the filler showed oscillations characteristic of a filler with a semireinforcing action.²¹

The effect of the shavings–dust mixture on the resistance to thermal aging of NBR is shown in Figure 3. The addition of collagen wastes to NBR

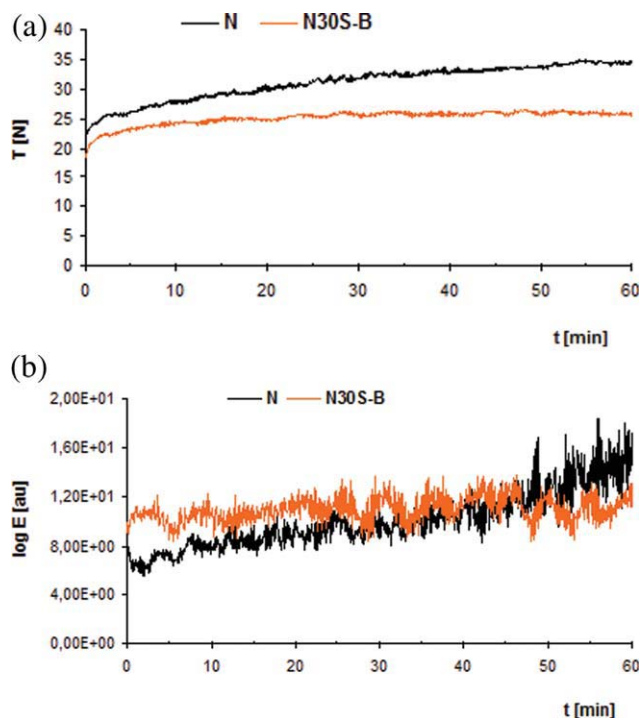


Figure 2 Changes in the (A) friction force (T) and (B) total energy (E) as a function of time (t) for the vulcanizates filled with the shavings–dust mixture. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

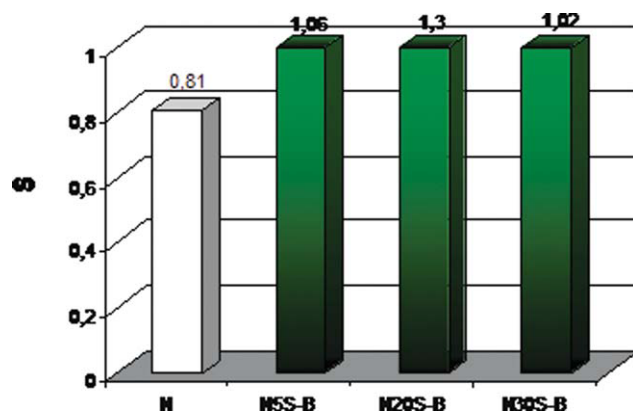


Figure 3 Effect of the shavings–dust mixture on the resistance to the accelerated thermooxidative aging of NBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

did not deteriorate its resistance to accelerated thermooxidative aging. The filled vulcanizates showed slightly higher values of S than the standard.

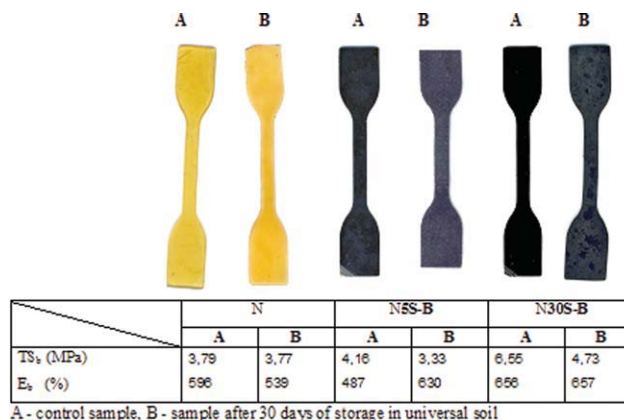
NBR materials containing the shavings–dust mixture

The biodecomposition of the NBR materials containing the shavings–dust filler was confirmed by the results of the strength tests after incubation in soil (Fig. 4). The drop in the sample strength after incubation in soil indicated the action of microorganisms on the structure of the collagen-containing NBR vulcanizates. With increasing filler mixture content in the NBR vulcanizate, its biodegradability clearly increased.

Effect of the shavings–dust mixture on the properties of the XNBR mixes and vulcanizates

The presence of chrome shavings in the elastomeric matrix of XNBR did not improve the strength parameters but did increase the resistance to thermal aging. The incorporation of buffing dust into XNBR influenced the structure of the lattice and the strength of the vulcanizates.¹ Thus, we decided to combine the beneficial effects of both fillers and assess the effect of a shavings–dust mixture on the properties of XNBR.

The properties of the XNBR mixes and vulcanizates are listed in Table IV. An increase in the shavings–dust mixture content resulted in an increased viscosity of the rubber blend; this indicated an increased susceptibility of the filler to agglomeration with increasing filling extent of the blend. The presence of the filler also increased the degree of crosslinking in comparison to that of the standard. The mixture of equal parts of leather dust and shavings turned out to be an active filler of XNBR. The increase in the filling degree of the blend was



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

Figure 4 Effects of the 5- and 30-phr shavings–dust mixtures on the biodecomposition capabilities of the NBR vulcanizates in universal soil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

accompanied by a decreased mixture a_f , as confirmed by the decreasing values of the rheometric activity coefficients. The increasing filling degree of the blend resulted in an increase in the vulcanizate rigidity expressed by the modulus S_{100} (the strain at an elongation of 100%). This was accompanied by an increased modulus S_{300} (the strain at an elongation of 300%) and decreased elongation, which indicated an increase in the crosslinking density of the vulcanizate. As the degree of filling increased, the hardness of the blend also increased; this may have been an indirect measure of the drop in elasticity.²²

The highest strength of the filled vulcanizate was obtained with 5 parts by weight of the shavings–dust mixture, and it was slightly higher than that of the standard. With the increase in the filling degree, the strength of the vulcanizate decreased, despite its increased moduli and decreased elongation, that is,

TABLE IV
Effect of the Shavings–Dust Mixture on the Properties of the XNBR Mixes and Vulcanizates

Sample	XN	XN5S-B	XN10S-B	XN20S-B	XN30S-B
Shavings–dust (1:1) + ZnO	0 + 5	5 + 5	10 + 5	20 + 5	30 + 5
L_{\min} (dNm)	9.1	14.7	17.3	20.5	23.6
ΔL (dNm)	51.3	100.7	88.7	87.7	91.8
τ_{90} (min)	19	15	16	14	20
a_f	19	7	4	3	3
Hardness (Shore A)	65	77	80	83	84
S_{100} (MPa)	1.99	2.15	2.42	3.13	4.36
S_{300} (MPa)	4.25	5.23	5.43	6.53	8.17
TS _b (MPa)	15.70	16.39	13.14	11.24	10.61
E _b (%)	492	475	471	456	414

Other components of the mixes (phr): XNBR, 100; S, 2.5; MBTS, 1.5; stearic acid, 2. L_{\min} , minimal torque; TS_b, tensile strength; E_b, elongation at break.

TABLE V
Crosslink Density and Lattice Nodes of XNBR with the Shavings–Dust Mixture

Experiment	XN	XN5S-B	XN30S-B
v^T (10^4 mol/cm ³)	2.1	2.1	4.1
v_{NK} (%)	41	49	57
–COOH (%)	4.9		1.4
Content of nodes (%)		1.5	
C–C, C–S–C	28.1	28.4	38.5
C–S ₂ –C	15.1	13.9	51.9
C–S _x –C	56.8	57.7	9.6

v_{NK} , content of ionic nodes; –COOH, carboxylic groups; C–C, carbon lattice nodes; C–S–C, monosulfide lattice nodes; C–S₂–C, disulfide lattice nodes; C–S_x–C, polysulfide lattice nodes.

the density of crosslinking. The deterioration in the strength parameters of the vulcanizates with increasing filler mixture content may have resulted from the formation of close-crosslinked areas with a low elasticity that concentrated the stresses facilitating the expansion of microfractures; this led to a deterioration in the vulcanizate strength with increasing degree of filling.

When the content of the filler mixture was increased, the crosslinking density and the percentage fraction of ionic nodes in the spatial lattice structure of XNBR increased.

This confirmed the existence of rubber–filler interactions (Table V). After the filler mixture was incorporated, the intensity of the absorption band of carbonyl groups in –COOH at 1700 cm^{–1} decreased, and an absorption band occurred at 1530 cm^{–1} (characteristic of the carboxyl ion), which was accompanied by the broadening of the band at 3330 cm^{–1} (Fig. 5). The contribution of –COOH groups to the formation of bonds with the filler was confirmed by their decreasing content with increasing filling degree (Table V). Additionally, the intensity of the nitrile group band decreased; these groups probably

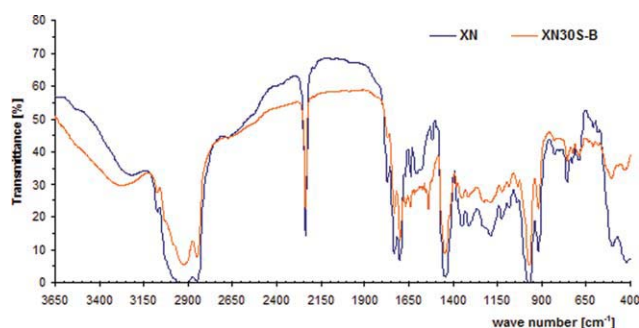


Figure 5 IR spectra of the XNBR vulcanizates: unfilled vulcanizates (XN) and vulcanizates filled with the shavings–dust mixture (XN30S-B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

participated in the formation of linkages of a physical character with the dust and/or shavings. A clear influence of the filler mixture on the structure of sulfide nodes was seen when its content was high (Table V). The vulcanizate containing 30 parts by weight of the filler mixture had a higher content of carbon, monosulfide, and disulfide nodes in relation to the unfilled vulcanizate.

XNBR materials containing the shavings–dust mixture

The effect of the shavings–dust mixture on the ability of the XNBR vulcanizates to decompose under the influence of microorganisms may be explained as follows (Fig. 6). With the presence of collagen derived from the shavings–dust mixture that filled the XNBR vulcanizate, the strength parameters deteriorated by 35%. Thus, the protein contained in the vulcanizate was a nutrient for soil microorganisms, hence the decrease in the strength and the increase in the elongation of the filled vulcanizates.

These vulcanizates were also changed visually; this also indicated their susceptibility to biodegradation. Both samples were discolored. The change in the color of the sample surface was observed in photos (Figs. 7–9). UV spectra of the changes in the sample surface color were taken and are given in Figures 7–9. From these spectra, it follows that the surface of the reference vulcanizate became slightly darker, whereas in the case of the vulcanizates containing the filler mixture, their surfaces were brightened, more with a lower the mixture content. Moreover, the surface of sample containing 5 parts by weight of the filler became rougher and more mat,



Sample	XN		XN5S-B		XN30S-B	
	A	B	A	B	A	B
TS ₂ (MPa)	15,70	14,87	16,39	10,15	10,61	6,92
E ₂ (%)	492	504	475	537	414	564

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

Figure 6 Effects of the 5- and 30-phr shavings–dust mixture on the biodecomposition capability of the XNBR vulcanizates in universal soil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

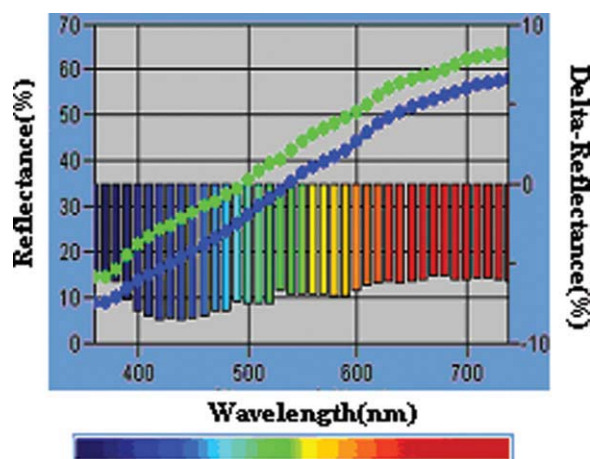


Figure 7 Color change in the unfilled XNBR vulcanizate (the green/top curve shows the vulcanizate before biodecomposition). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showing numerous pits. The materials containing 30 parts by weight of the filler mixture were also coarse and had pits.

CONCLUSIONS

The incorporation of a filler in the form of a leather shavings–dust mixture into NBR and XNBRs produced biodegradable collagen–elastomer materials with satisfactory performance properties.

The mixture used as a filler of NBR and XNBR was an active filler; this may indicate on a common structure of spatial lattices.

The equilibrium mixture of shavings and dust appeared to be a better filler for NBR than shavings

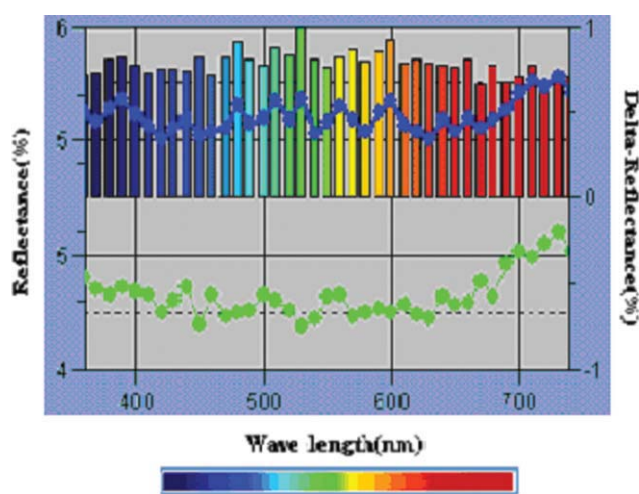


Figure 8 Color change in the XNBR vulcanizate filled with 5 phr of the shavings–dust mixture (the green/bottom curve shows the vulcanizate before biodecomposition). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

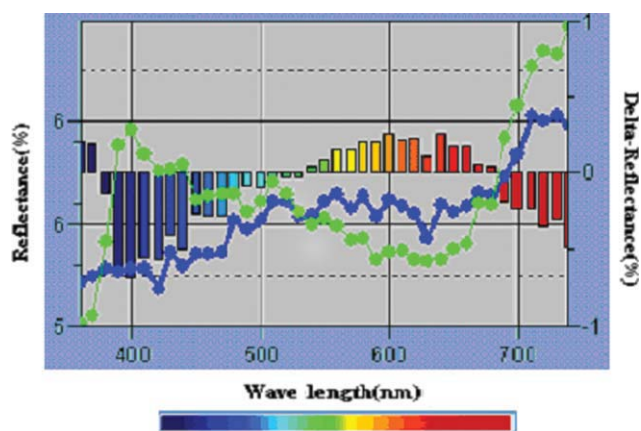


Figure 9 Color change in the XNBR vulcanizate filled with 30 phr of the shavings–dust mixture (the green curve, which starts at the bottom of the graph, shows the vulcanizate before biodecomposition). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

or dust used separately. The vulcanized filled with this mixture had higher strength values than that of the standard and a better resistance to accelerated thermal aging than that of vulcanizates filled only with shavings or dust.

The incorporation of the filler mixture into the rubber blend changed its viscosity slightly. This caused the length of vulcanization time to shorten, which is important from an economic point of view.

Practically, in the case of all of the collagen–elastomer materials obtained, their crosslinking density increased, probably because of the formation of filler–elastomer linkages. This was confirmed by the increased fraction of ionic nodes, decreased content of carboxyl groups, and the changed structure of sulfide nodes in the filled vulcanizate.

The NBR and XNBR polymeric materials containing the filler mixture could be biodegraded. The composition of the NBR vulcanizates containing the filler mixture is the subject of a patent application.

NOMENCLATURE

N	nitrile rubber blend with 0 phr filler
N20S-B	nitrile rubber blend with 20 phr shavings–dust mixture
M5S-B	I can't find this sign in text
XN5S-B	carboxylated nitrile rubber blend with 5 phr shavings–dust mixture

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