

Buffing dust as a filler of carboxylated butadiene-acrylonitrile rubber and butadiene-acrylonitrile rubber

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Abstract

Buffing dust from chrome tanned leather is one of the difficult tannery wastes to manage. It is also hazardous to both human health and the environment. The scientific literature rarely reports studies on dust management, especially on its utilization as a filler for elastomers. In this connection we have made an attempt to use this leather waste as a filler for rubbers such as XNBR and NBR. The addition of the buffing dust to rubber mixes brought improvement in mechanical properties, and increase in resistance to thermal ageing as well as in electric conductivity and crosslink density of vulcalizates.

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1. Introduction

According to the data presented at the 14th UNIDO conference, the tanning industry discards solid tanned wastes with a chemical composition comparable to that of tanned leather end product [1]. The quantitative compositions of solid wastes in relation to tanned leather (heavy cow hide–finished leather 3 kg/m²; goat and sheepskin–surface of finished leathers, about 0.75 m²) are listed in Table 1. From the presented data it follows that the world production of chrome tanned leather causes formation of 805,657 tons/year of solid tanned wastes [3,4].

As follows from the known methods of solid tanned waste utilization [1,5] currently it has approached to develop utilization methods that rely on the protein portion and chromium compounds recovery or the protein portion destruction (incineration, biogas) and only chromium compounds recovery. In both cases, the obtained results have not been fully satisfactory because detanning methods or chemical and enzymatic hydrolysis of chrome tanned wastes cause the formation of various forms of degraded collagen. Therefore, other methods of leather wastes utilization are looked for. One of the methods of the utilization of chrome tanned shavings was their use, beside aluminum oxide,

for the production of ceramic materials [6]. Shavings were incinerated at 800 °C (with energy recovery) the obtained ash was mixed with Al₂O₃ in various proportions: 2, 5, 10, 20, 30 parts by wt. of the ash per 100 parts by wt. of the ceramic body. The obtained ceramic materials characterized good usable properties. In turn, for the production of porous bricks were used waste shavings from fleshing and vegetable tanning [7]. Their contents in the clay were: 1, 3, 5 and 10% by wt. Density, thermal conductivity, and strength of the obtained bricks were decreasing with the increase in the content of added wastes. The most suitable level of the wastes was 5%.

Buffing dust used to prepare activated charcoal with a larger adsorption capacity than activated charcoal obtained from wood. Buffing dust [8] was dried at 95 °C. The temperature of furnace was increased to 310 °C to remove volatile organics. Next, it was impregnated with MgO then activated at temperatures: 600, 700, 800 and 900 °C for 2 h in a muffle furnace. After removing the ashes, the obtained activated charcoal (particle size 1.0, 0.5 and 0.3 mm) was used to examine the sorption kinetic of acid dye on buffing dust based activated charcoal at different experimental conditions. The adsorption of acid dye (at 30 °C, pH 3.5 and the dye concentration 125 mg/l) on the activated charcoal prepared from buffing dust (carbonization temperature 900 °C) increased from 5.94 mg/g to 6.25 mg/g and the adsorption coefficient increased from 0.012 to 0.026 min⁻¹, when the size of activated charcoal particles was decreased

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Table 1
 Chrome-tanned leather wastes formed in the leather industry [2]

	Heavy cow hides	Light cow hides	Goat and sheepskins	
Useless splits, leather shavings, wet blue trimmings	171 ^a	513 ^a	180 ^a	651,221 ^b
Dry leather wastes: leather dust, trimmings	27.7 ^a	83.2 ^a	151.3 ^a	154,436 ^b

^a In tons/million m² of tanned leather.

^b In tons/year.

from 1.00 mm to 0.3 mm but the time required to reach the equilibrium of adsorption decreased from 120 min to 20 min. This would mean that the decrease in particle size of activated charcoal prepared from buffing dust brought about an increase in the surface accessible for dye adsorption from solution. It was also observed that at pH 3.5, particle size of activated charcoal 0.3 mm (carbonization temperature 900 °C) and dye concentration 125 mg/l, the increase in adsorption temperature from 20 to 48 °C caused the increase in adsorption constant from 0.026 min⁻¹ to 0.083 min⁻¹. The adsorption capability decreased insignificantly. On the other hand, the rate of dye uptake from solution was decreasing with the increase in pH. At pH 2, temperature 30 °C (particle size of activated charcoal, carbonization temperature of leather dust and dye concentration were the same as above) the dye uptake was the highest, reaching almost 100% but rate constant was 0.05 min⁻¹. With the increase in the carbonization temperature of buffing dust from 600 to 900 °C, at 30 °C, pH 3.5 (dye concentration and particle size of activated charcoal were the same as above) the adsorption capability of activated carbon increased from 6.13 to 6.25 mg/g. The percentage dye removing power was 98.1% and 99.94% at the buffing dust activation temperature 600 °C and 900 °C, respectively. Conversion of buffing dust into activated charcoal is a rational idea of combating solid waste pollution caused by this mass as activated charcoal obtained from buffing dust generated in leather industry as a solid was able to remove 6.247 mg of dye per gram at a concentration of 125 mg/g at pH 3.5 and a temperature of 30 °C compared to the commercial activated carbon which has only 6.225 mg/g as adsorption capacity.

Chrome tanned leather shavings [9] were used as adsorbents of anionic (SDBS), cationic (DTB) and nonionic (X-100, TX-100) surfactants. Anionic surfactants were the best adsorbed by the waste material over the range of pH from 4.0 to 8.0. The adsorbing power of SDBS increased with temperature, which indicated a chemical character of the adsorption. On the other hand, the adsorbing power of cationic and nonionic surfactants was limited. These facts suggest that amino groups and Cr(III) combined with collagen are adsorption sites in the leather wastes. Another utilization method of chrome tanned leather wastes was their used for the production of yeast [10]. First, a hydrolysate was obtained from the wastes [11]. Then solutions with various contents of glucose, sulfates and hydrolysate were prepared. In these media, yeast was developed. The highest content of Cr³⁺ per 1g of dried yeast was obtained for the solution containing 7 g/L of glucose, 5 g/L of (NH₄)₂SO₄, and 145 mg/L of hydrolysate, obtaining at the same time a high content of biomass: 1.53 g/100 mL.

It is also possible to use waste leather particles as a filler of polymer. Andreopoulos and Tarantili [12] have incorporated leather wastes into PVC with dioctyl phthalate as plasticizer. The addition of the leather wastes caused that density and hardness of the composites increased, whereas their tensile properties were considerably deteriorated with the incorporation of leather. In order to improve mechanical properties, the granulated leather was modified with vinyl acetate to form an adhesive layer on the granules surface, which considerably improved the tensile strength of composites by 30%.

Leather dust with silica was used as a filler of PVC [13]. This additive decreased the density of the composite by 30–40%, but increased its melting point and maximal elongation.

Chrome tanned leather wastes in the form of shavings [14] were used as filler of nitrile rubber. Prior to incorporation into the rubber mix, the shavings were neutralized with Na₂CO₃, NH₃ and NaOH. The addition of sodium bicarbonate and ammonia neutralized chrome shavings to nitrile rubber brought improved vulcanization characteristics 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 MEK a reversed trend was observed.

Modified chrome shavings were also utilized as a filler of natural rubber [15]. It has been found that they do not disperse well in polymer due to their acidic character and the vulcanizates have worse properties. Therefore, prior to incorporation into the rubber mix, the shavings were neutralized with urea, ammonia and sodium bicarbonate. Then, the composite polymers containing neutralized leather wastes became useful for the production of structural materials, motor-car accessories, shoe soles, flooring materials with antistatic properties and good air permeability.

At the Institute of Polymers and Dye Technology [16,17] studies on utilization of solid chrome tanned leather wastes were carried out. Shavings of chrome tanned leather have been utilized to fill rubbers such as: IR, XNBR, NBR. The obtained biodegradable vulcanizates show good usable properties.

The aim of the present study is utilization of equally noxious solid tanned waste-buffing dust by using it as filler of carboxylated butadiene-acrylonitrile rubber-XNBR (Krynac X7.50) and butadiene-acrylonitrile rubber-NBR (Nipol N 41).

Buffing dust has not been used as an individual filler of polymers so far. It is a waste that is formed after buffing process of fat liquoring leather. Therefore this form of dust should facilitate its dispersion in elastomeric media.

In connection with the aim of the study, it was decided to determine the addition sequence of components: buffing dust, zinc oxide, Limanol PEV as well as to assess the effect of buffing dust on the properties of mixes and vulcanizates of XNBR (Krynac X7.50) and NBR (Nipol N 41). The range of researches included:

- (1) Preparation and characteristic of buffing dust: determination of Cr(III) and (IV) contents, determination of particle size.
- (2) Setting the procedure of component addition to elastomeric mixes.
- (3) Testing the influence of buffing dust on properties of mixes and vulcanizates.

2. Experimental methods

- Buffing dust was subjected to multistage disintegration to prepare a powder that was then sieved through a 0.2 mm mesh; chromium(III) content given as Cr_2O_3 –3.0%, PN-EN ISO 4684:2006 (U).
- Determination of chromium(III) and (VI) given as Cr_2O_3 in vulcanizates carried out according to the standards PN-74/P-22110 and PN-EN ISO 20344:2005, respectively.
- The obtained powder was characterized using a spectroscope FTIR (BIO-RAD 175C) with a microscope attachment; the size of its particles was measured by the technique of dynamic light diffusion DLS (Zetasizer nano S90) and its isoelectric point was assessed by electro-kinetic measurements (Zetasizer 2000).
- Then the buffing dust was used as a filler of carboxylated butadiene-acrylonitrile rubber-XNBR (Krynac X7.50) and butadiene-acrylonitrile rubber-NBR (Nipol N 41):
 - The kinetics of rubber mixes vulcanization was determined at a temperature about 433 K according to the standard PN-ISO 3417:1994. Based on rheometric curves, were calculated: τ_{90} –optimal time of vulcanization, ΔL –the increase in the torque moment and a_f –activity of filler [17];
 - Vulcanization of the mixes was carried out in the same manner as in publication [17];
 - 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 817:2001/ap1:2002; The crosslink density was assigned using Flory–Rheener equations [18];
 - The mechanical properties were measured with Zwick apparatus 1442, 1435 PN-ISO 37:1998;
 - 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 100 h. The coefficient of ageing was determined from the following relationship (1):

$$S = \frac{[\text{TS}_{b1} \times E_{b1}]}{[\text{TS}_{b2} \times E_{b2}]} \quad (1)$$

where S is the aging coefficient, TS_{b1} is the tensile strength after thermal aging, E_{b1} is the elongation at break after thermal aging, TS_{b2} is the tensile strength before thermal

aging and E_{b2} is elongation at break before thermal aging.

- Determination of the Shore A hardness of vulcanizates according to the standard PN-80/C-04238;
- Determination of the Schob elasticity of vulcanizates according to the standard PN-C-04255:1997;
- Determination of shock absorbing capacity by Schob's impact method in elastomer according to the standard PN-54/C-04268;
- Electrical conductivity according to the standard PN-85C-04259/01;
- Scanning Electron Microscopy, using SEM (IWC PAN in Warsaw);
- Microbiological experiments carried out according to standard PN-EN ISO 846 (biological material, methods, interpretation of the results), microbiological culture mediums [19]:
 - the low-value nutrient medium consisted of: NaNO_3 2.0 g, KH_2PO_4 0.7 g, K_2HPO_4 0.3 g, KCl 0.5 g, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.01 g, agar 20 g, water 1000 mL, pH 6.0–6.5;
 - the nutrient medium of full value had the same composition as above plus 30 g of glucose;
 - the solution of the salt had the same composition as above without the glucose and agar.

3. Discussion and results

3.1. Analysis of the SEM micrograph and FTIR spectrum of the buffing dust

The structure of buffing dust consists of clearly isolated collagen fibers (Fig. 1). This seems to be due to the presence of fatliquors that surround the fibers causing their separation. The presence of fatliquors in the buffing dust is indicated by the bands in FTIR spectrum at wave numbers 2900 cm^{-1} and 1755 cm^{-1} , being characteristic of fatty substances (Fig. 2).

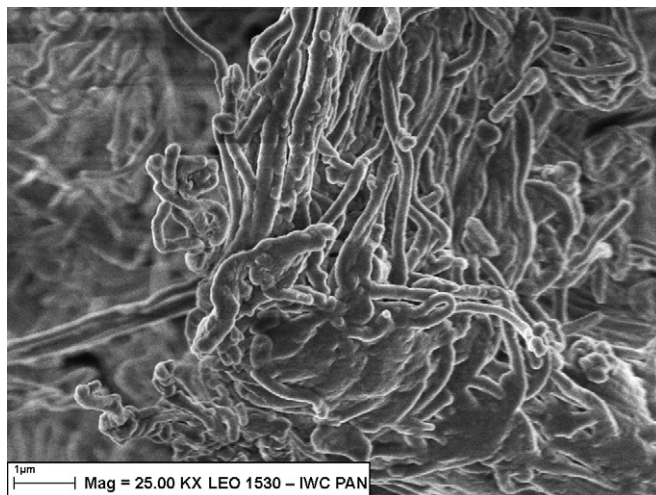


Fig. 1. The SEM micrograph of the buffing dust.

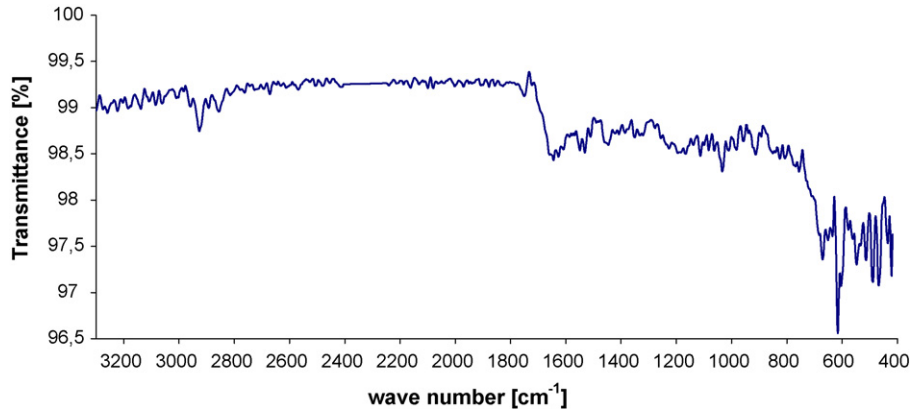


Fig. 2. FTIR spectrum of the buffing dust.

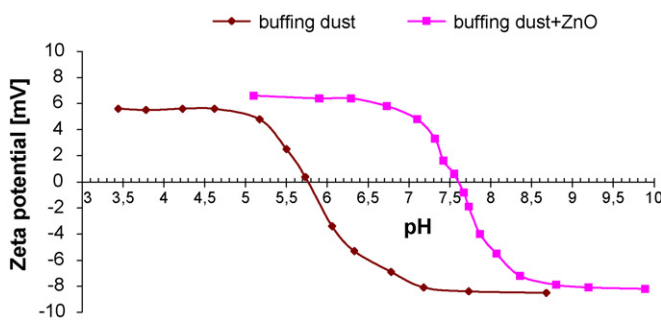


Fig. 3. The Zeta potential of water dispersions of the buffing dust and the dust mixed with ZnO in function pH (concentration 0,1 g/l).

3.2. Determination of the zeta potential

The measurements of zeta potential of the buffing dust indicate an acidic character of its surface, as confirmed by the value of *pI* 5.8 (Fig. 3). Blending the buffing dust with ZnO caused shifting the isoelectric point towards more basic pH values, which indicates a change in the chemical character of the buffing dust surface to more alkaline. It proves that after addition ZnO the state of the dust surface undergo the change. In blurred layer appeared more positive charges and therefore had to introduce more negative ions from outside and the isoelectric point shifted towards a higher pH value. The more basic *pI* of the filler convinces its better dispersion in polymer and the vulcanizate gains better properties. Thus, prior to the addition of buffing dust to the rubber mix, it should be mixed with zinc oxide to facilitate the

incorporation into the mix and to improve the filler dispersion in the elastomeric matrix.

3.3. Measurement of particles size of chrome-tanned buffing dust

The measurement of buffing dust particle size in aqueous dispersion (0.025 mg/l), after treatment with ultrasounds (1 h) shows that it ranges from 295 to 526 nm, while the highest percentage content - 29% is shown by particles with a size 417 nm (Fig. 4). The size of ZnO (Fig. 5) ranges from 185 to 372 nm, the highest percentage content - 24% is shown by particles with a size 262.3 nm. So, the addition of ZnO to the dust was expected to change the size of its particles. Indeed, after blending the dust with ZnO, its particle size was decreased from 262 to 331 nm, which was also accompanied by a considerable improvement in the system polydispersion (Fig. 6). Particles with a size 295 nm constituted the highest content amounting to 50%. Thus, it is most beneficial to add dust with ZnO to rubber mixes, since this composition should improve the dispersion of dust in the mix.

3.4. The composition of rubber mixes

During the studies were carried out XNBR and NBR mixes with 5 and 10 parts by wt. of the buffing dust incorporated in different ways to the mixes with Limanol PEV as a dispersing agent. Based on rheometric measurements of the obtained mixes and mechanical tests of their vulcanizates, it has been found that the best properties are shown by mixes and vulcanizates con-

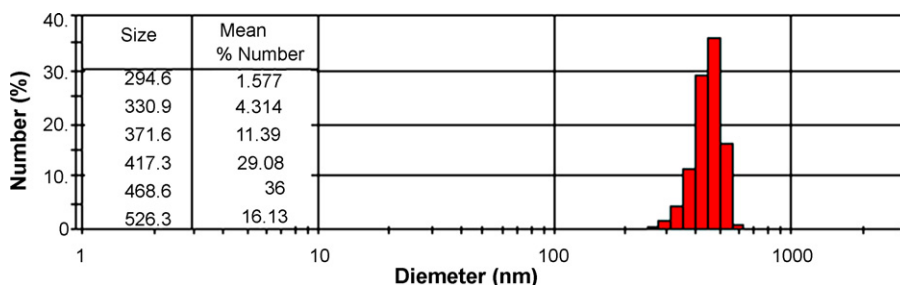


Fig. 4. Distribution of particles size of the buffing dust.

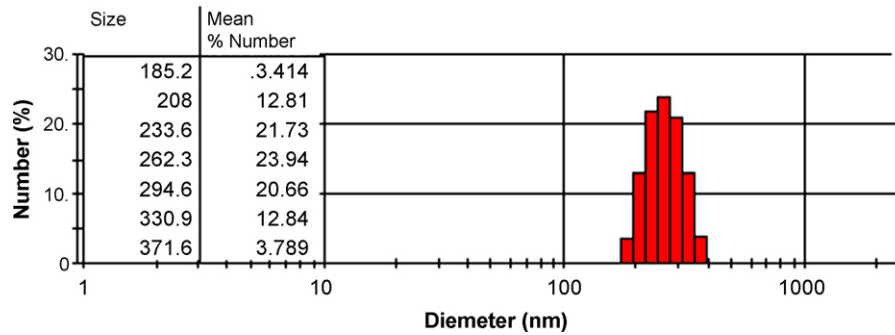


Fig. 5. Distribution of particles size of ZnO.

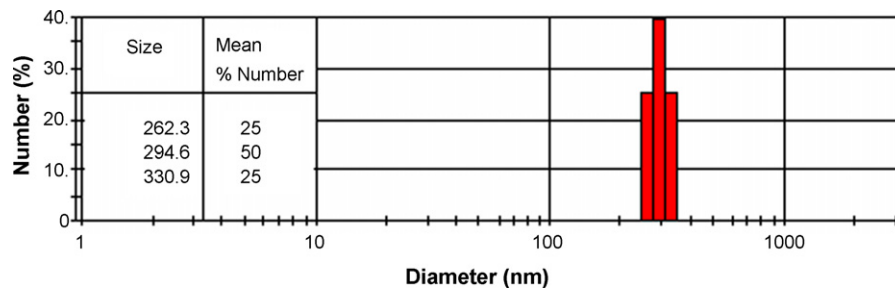


Fig. 6. Distribution of particles size of the buffing dust + ZnO.

Table 2
Consist of mixes and vulcanizates of the XNBR, NBR rubber

Composition	Parts by wt.			
XNBR rubber	100	100	–	–
NBR rubber	–	–	100	100
ZnO + dust	5 + 0	5 + 5	5 + 0	5 + 5

Sulfur 2,5; Stearic Acid 2; MBTS 1,5; Polnox N 1; Limanol PEV 2.

taining five parts by wt. of the buffing dust added after previous blending with five parts by wt. of ZnO. The compositions of the rubber mixes are listed in Table 2.

3.5. Rheometric properties of XNBR and NBR rubber mixes

From the rheometric parameters, it follows that the addition of buffing dust to the carboxylated butadiene-acrylonitrile rubber and butadiene-acrylonitrile rubber caused a decrease of their vulcanization time, τ_{90} (Table 3). This indicates that the filler interacts with the accelerator. The role of cross-linking activators is probably played by the active chemical groups on the dust surface such as $-NH_2$, $-OH$ and $-COOH$. The incorporation of the buffing dust into XNBR brought a decrease in the minimal

torque (L_{min}) by more than 50%, which indicates a decreased viscosity of the mix. On the other hand, in the case of NBR, the addition of the filler caused an increase in the L_{min} , or the viscosity of this mix. Moreover, the incorporation of buffing dust into both XNBR and NBR caused an increased in their torques ΔL (Table 3), which indicates an increase in the degree of cross-linking of the dust-containing mixes. The increase in ΔL of the mixes with buffing dust is connected with the activity of filler and its reinforcing action. The activity of the buffing dust is higher in XNBR, while that in NBR is lower almost by 50%. Nevertheless, the buffing dust can be considered to be an active filler of both elastomers: XNBR and NBR.

3.6. Crosslink density of XNBR and NBR vulcanizates

Based on the equilibrium swelling in toluene (Table 4) it was observed that the incorporation of buffing dust brought an increase in the crosslink density of vulcanizates, which is shown by their lower swelling Q_w^T in comparison with the standard vulcanizates. This is confirmed by the values of crosslink density calculated from the swelling in toluene [17] (Table 4). Moreover, the crosslink density of the XNBR vulcanizates with dust is considerably higher than that of NBR vulcanizates. The vulcanizates with dust show also a higher concentration of decomposing net-

Table 3
Rheometric properties of the XNBR, NBR rubber mixes out of and with the buffing dust

	L_{min} (dNm)	ΔL (dNm)	t_{90} (min)	a_f
XNBR out of dust	50.4	42.3	20	–
XNBR with dust	20	124.8	18	39
NBR out of dust	10.2	55.5	19	–
NBR with dust	18.5	104.2	16	17.5

Table 4

Equilibrium swelling in toluene Q_w^T , in toluene and ammonia vapors Q_w^{T/NH_3} and crosslink density ν_r , concentration of the ion lattice points decomposing under the influence of ammonia $\Delta\nu$ and percentage content of the ion lattice points decomposing under the influence of ammonia A

	Q_w^T (mg/mg)	Q_w^{T/NH_3} (mg/mg)	$\nu_r 10^4$ (mol/cm ³)	$\Delta\nu 10^4$ (mol/cm ³)	A (%)
XNBR out of dust	1.41	1.42	2.69	1.03	38
XNBR with dust	1.08	1.23	4.79	2.47	51
NBR out of dust	2.89	3.05	0.83	0.61	74
NBR with dust	2.57	2.87	1.07	0.81	76

work nodes under the influence of ammonia, which indicates a higher number of ionic nodes being formed. The addition of dust to XNBR brought an increase in the number of ionic nodes by 13%, while in the case of NBR it is only by 2% in comparison with the vulcanizates out of dust.

According to A. Eisenberg, B. Hird, R.B. Moore [20] ZnO forms with carboxyl groups of XNBR rubber multiplets (a) and clusters of ionic aggregates (b) (Fig. 7). We supposed that ZnO forms with carboxyl groups of buffing dust multiples and clusters of ionic aggregates too. Moreover it is supposed that zinc ions of zinc carboxylate salts are co-coordinated by amine groups of buffing dust (c) (Fig. 7).

However, the presence of covalent bonds is not excluded. The presence of –COOH groups in XNBR probably makes it possible to form additional polymer-collagen (from buffing dust) links (Fig. 8).

The chemical interaction between the filler and XNBR elastomer is confirmed by SEM micrographs (Fig. 9). At a magnification 1.00 kx, the surfaces of vulcanizates without and with the buffing dust do not differ and show a similar topography. When the magnification is five times higher (5.00 kx) the filler agglomerates are visible on the surface of dust-containing vulcanizate. As follows from the pictures taken at a magnification 25.00 kx, the dust is clearly combined with the elastomeric matrix.

3.7. Mechanical properties of XNBR and NBR vulcanizates

The mentioned above newly formed chemical bonds during the cross-linking of dust-containing XNBR vulcanizates seem to be responsible for the considerable improvement in the mechanical properties of these vulcanizates: increased tensile strength and decreased maximal elongation in compare to the standard (Table 5). The improvement in strength parameters of dust-containing NBR vulcanizates is rather small.

Determination quality of chromium(VI) performed according to the norm PN-EN ISO 20344:2005 (V) 6.11 –content

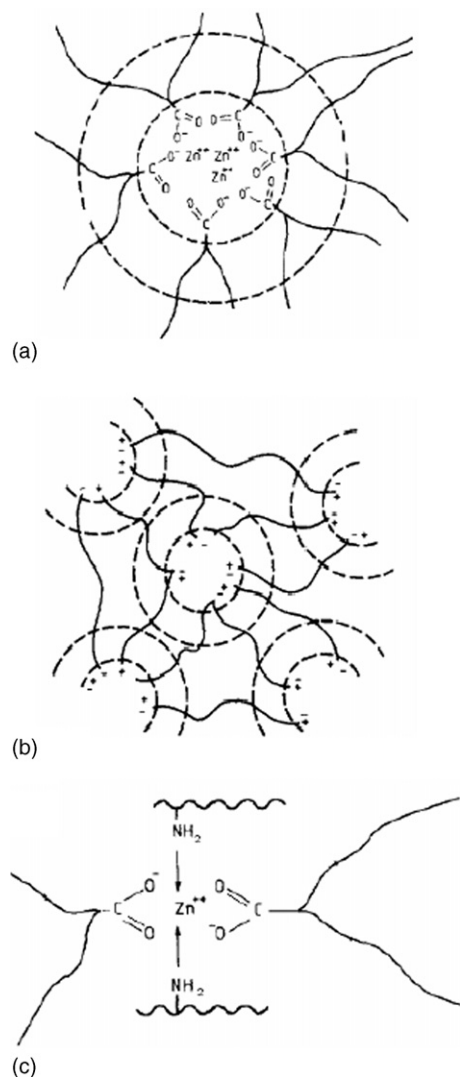


Fig. 7. Schematic of interactions: XNBR rubber-ZnO-buffing dust. (a): Interaction carboxyl groups from buffing dust and XNBR rubber with zinc ions (multiplet). (b): Clustered multiplets. (c): Co-ordination of amine groups (from buffing dust) with zinc ion of carboxylic acid salts.

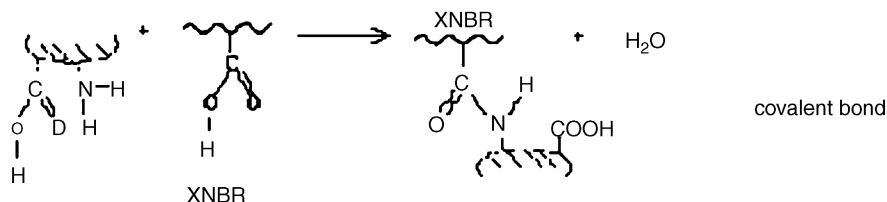
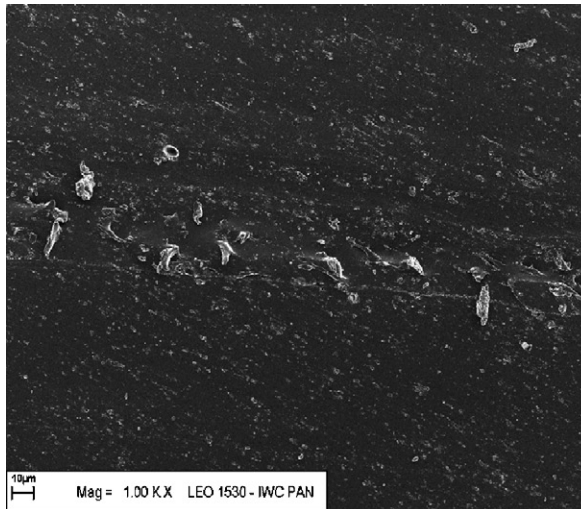
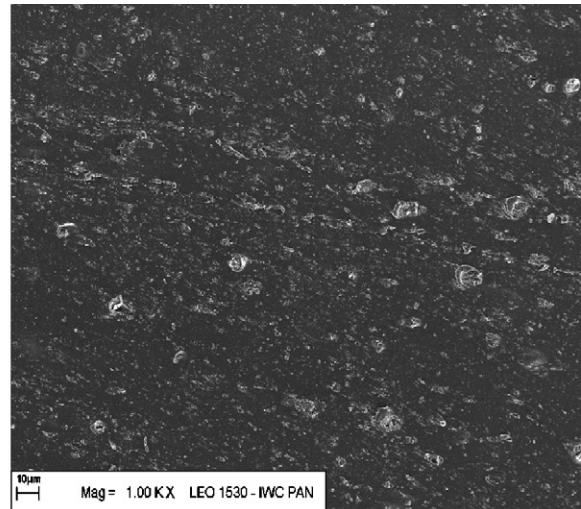


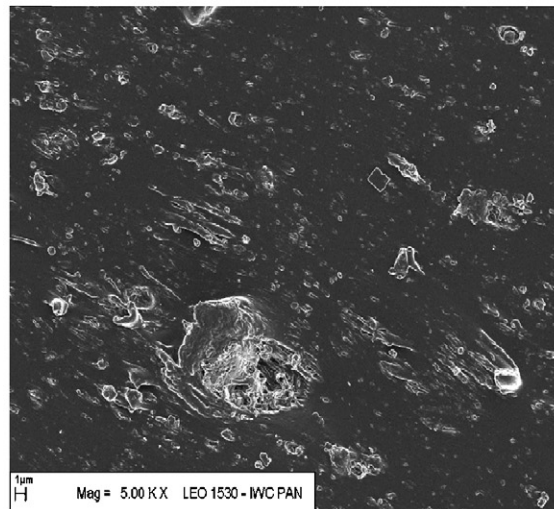
Fig. 8. Schematic of potential interaction: XNBR rubber-buffing dust.



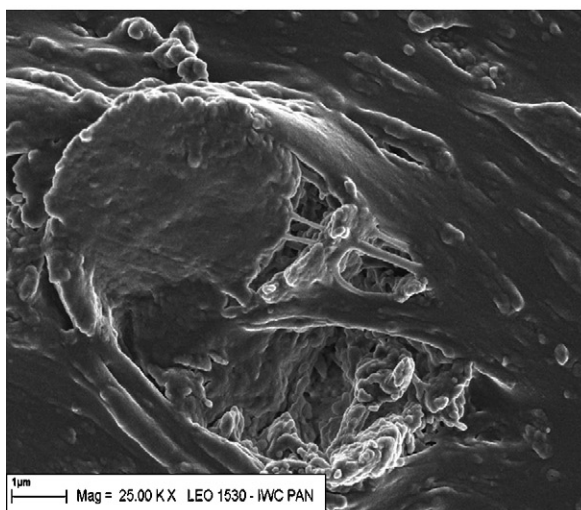
XNBR vulcanizate out of the buffing dust (1.00 kx)



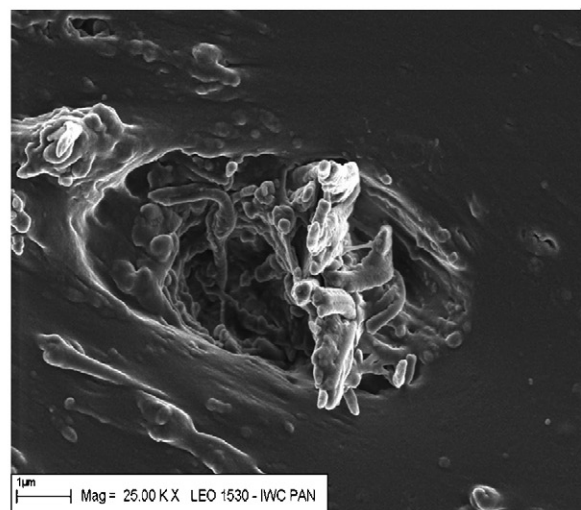
XNBR vulcanizate with the buffing dust (1.00 kx)



XNBR vulcanizate with the buffing dust (5.00 kx)



XNBR vulcanizate with the buffing dust (25.00 kx)



XNBR vulcanizate with the buffing dust (25.00 kx)

Fig. 9. The SEM micrographs of XNBR vulcanizates out of and with the buffing dust (the SEM micrographs at a magnification 25.00 kx present the area which is marked in the photo at a magnification 5.00 kx).

Table 5
Mechanical properties of XNBR and NBR vulcanizates out of and with the dust

	S_{100} (MPa)	S_{200} (MPa)	S_{300} (MPa)	TS_b (MPa)	E_b (%)	S
XNBR out of dust	1.41 ± 0.06	2.18 ± 0.04	3.78 ± 0.27	8.51 ± 1.68	385.32 ± 26.43	0.44
XNBR with dust	2.78 ± 0.07	5.0 ± 0.11	10.20 ± 12.78	14.88 ± 1.29	355.15 ± 28.71	0.96
NBR out of dust	0.91 ± 0.05	1.40 ± 0.07	1.90 ± 0.01	2.11 ± 0.35	312.95 ± 51.91	0.46
NBR with dust	1.29 ± 0.14	1.83 ± 0.22	2.28 ± 0.28	3.45 ± 0.39	458.62 ± 22.26	0.74

The stress at extension 100, 200, and 300, respectively: S_{100} (MPa), S_{200} (MPa), S_{300} (MPa); tensile strength: TS_b (MPa); elongation at break: E_b (%); aging coefficient: S .

Table 6
Mechanical properties of XNBR and NBR vulcanizates out of and with the buffing dust

	Shore A hardness ($^{\circ}$ Sh)	Schob elasticity (%)	Shock absorption	Electrical conductivity (S/cm)
XNBR out of dust	45	54	9	0.42×10^{-12}
XNBR with dust	58	21	6	0.19×10^{-11}
NBR out of dust	50	20	6	0.62×10^{-15}
NBR with dust	46	48	8	0.42×10^{-11}

chromium(VI)– 0.00 mg/kg did not show presence of chromium(VI) salts in obtained vulcanizates.

The ageing coefficients (S) calculated from the strength parameters (TS_b and E_b) before and after thermal ageing indicate that the increased resistance of both XNBR and NBR elastomers to thermal ageing is due to the presence of the buffing dust.

3.8. Other properties of XNBR and NBR vulcanizates

We examined the influence of buffing dust on other properties of XNBR and NBR vulcanizates (Table 6) namely: Shore hardness, Schob elasticity, shock absorption, electrical conductivity; from the obtained results it follows that the hardness of XNBR vulcanizates with buffing dust increased in comparison with the standard, which caused decrease in elasticity and shock absorbing capability of these vulcanizates. On the other hand, the NBR vulcanizates with buffing dust show a lower hardness but higher elasticity and shock absorption in relation to the standard.

From the measurements of equilibrium swelling in water it follows that the presence of buffing dust in the vulcanizates of both rubbers caused higher water absorption what was confirmed by the increase electrical conductivity of vulcanizates with the dust.

From the microbiological tests it follows that the vulcanizates with buffing dust, contrary to the standard, are a good nutrient medium for some micro-organisms such as Actinomycetales of the *Streptomyces* genus, bacteria of natural microflora and soil bacteria. This indicates that the obtained buffing dust-elastomer composites are biodegradable.

4. Conclusion

The buffing dust under investigation has turned out to be an active filler of both XNBR and NBR vulcanizates. Due to the presence of carboxyl groups in the XNBR vulcanizate, the protein filler interacts better with this elastomer as confirmed by

its higher cross-linking density, better strength properties, higher hardness as well as lower elasticity and shock absorption.

The study will be continued to find out what kind of bonds, if any, are formed between filler and rubber on the basis of model systems. The experimental work was sponsored by the Polish Committee of Research (KBN) No PBZ-KBN-N205 078 31/3750.

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