

## Research Article

# Innovative Application of Biopolymer Keratin as a Filler of Synthetic Acrylonitrile-Butadiene Rubber NBR

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The current investigations show the influence of keratin, recovered from the tanning industry, on the thermal and mechanical properties of vulcanizates with synthetic rubber acrylonitrile-butadiene rubber NBR. The addition of waste protein to NBR vulcanizates influences the improvement of resistance at high temperatures and mechanical properties like tensile strength and hardness. The introduction of keratin to the mixes of rubber previously blended with zinc oxide (ZnO) before vulcanization process leads to an increase in the cross-linking density of vulcanizates. The polymer materials received including addition of proteins will undergo biodecomposition in natural conditions. After soil test, vulcanizates with keratin especially keratin with ZnO showed much more changes on the surface area than vulcanizates without protein. In that aerobic environment, microorganisms, bacteria, and fungus digested better polymer materials containing natural additives.

## 1. Introduction

The present research is a continuation of our studies [1] concerning the utilization of waste keratin, originating from cow hide unhairing, so far used up to a small extent. The point is to incorporate keratin into NBR rubber as a filler. The utilization of wastes from the tanning industry has been long of interest to many research centers, including the Technical University of Lodz. Hence, our research strategy consists of two issues:

- (1) reduction in environmental pollution by the tanning industry,
- (2) recovery of biopolymers to use them in the preparation of biodegradable materials.

From the literature review given in previous papers [2–4], it follows that the addition of keratin to polymer blends can exert a beneficial effect on their properties. For example, the incorporation of keratin to isoprene rubber increases tensile strength, and these polymer materials have better ageing properties.

Aluigi et al. [5] have obtained nanofibers from a blend of sheep wool keratin and polyethylene oxide (PEO). The

obtained polymer blends were characterized by the scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). The measurements of the fiber diameters show that the production of keratin/PEO nanofibers is more strongly influenced by the applied voltage than the pure PEO nanofibers. The spectroscopy and thermal analysis of keratin containing polymer materials show that the electrospinning process makes the natural keratin sulfur accumulation difficult, consequently resulting in the formation of lesser amount of complex protein conformations.

Goncharova et al. have incorporated protein hydrolyzates into cis-1,4-polyisoprene rubber [6–8]. They have described the modification of isoprene rubber with the wool keratin hydrolyzate dispersed in anionic surfactants such as lecithin. As a result, the degree of protein dispersion in the isoprene matrix was increased, and consequently the tensile strength and abrasion resistance of the obtained elastomeric blends were increased, and their viscosity was decreased.

Acrylonitrile rubbers are elastomers of special applications. They consist of butadiene and acrylonitrile copolymers whose percentage proportion determines their resistance to oil and freeze. Used in applied hydraulics and pneumatics,

nitrile vulcanizates show high elasticity and tensile strength, oil resistance and a low permanent compressive strain. Owing to these properties, both XNBR and NBR are of interest to many researchers.

From the studies of Subrahmanian and Ganapathy [9] and Park [10], it follows that it is the “donor” sulfur system that determines acceptable strength properties, elasticity, and resistance to ageing of NBR and ethylene-propylene-diene (EPDM) vulcanizates designed for seals. Samples of the vulcanizates under investigation were incubated for 24–96 h at 70–100°C, and then the structure of these polymer blends was observed by means of SEM. Based on testing mechanical properties and hardness as well as SEM analysis of the polymer blends with and without sulfur, the authors have found that the sulfur present in the system is responsible for their resistance to ageing.

Thermal stability, behavior during swelling in motor oil, and dielectric properties of NBR blends with PVC/PVAc [poly (vinyl chloride)/poly (vinyl acetate)] copolymer have been examined by Botros et al. [12]. Based on viscosity measurements and SEM of these blends, a good compatibility of the components has been found regardless of the quantity of rubber or PVC/PVAc.

The great number of publications in the literature [13–17] relating the good mechanical proprieties of nitrile rubber (NBR) induced us to occupy in ours investigations just this rubber.

The common use of nitrile rubbers as well as the proecological aspect prompted us to carry out studies on nitrile blends containing a biopolymer such as waste keratin. The aim of the present study is to obtain polymer blends with good performance properties and capable of biodegradation after their working life.

## 2. Materials and Methods

The characteristic of object—keratin—was separated from tannery wastes originating from the liming and unhairing of cow hides with retaining the hair structure [1]. The keratin was separated from tannery effluent and then dried, disintegrated, and powdered followed by sieving through a sieve with a 0.1 mm mesh diameter.

The leather unhairing is a result of degradation of keratin in the hair follicles. During the tanning process, the rest of the cattle hair shaft contains keratin that is slightly hydrolyzed. After the tanning process, the molecular mass of the obtained keratin is 82857 Da, and the elemental analysis of sulfur and nitrogen percentage shall be 5% and 13%. On the basis of the literature data [18] the contents of sulphur and nitrogen in cattle hair are between 6% and 17%.

The obtained keratin was tested by FTIR spectroscopy, particle size, zeta potential, and molecular weight [1]. The particle size of the obtained keratin is 469 nm; if keratin is blended with zinc oxide (ZnO), the particle size decreases to 331 nm. Therefore, the blending of keratin with zinc oxide makes its incorporation easier into the elastomer matrix. FTIR analysis showed that powdered keratin is a typical protein spectrum with amide I, II, and III bonds (1658, 1534,

TABLE 1: The compositions of the mixes under investigation.

Content	Symbol		
	Standard	Sample I	Sample II
ZnO [phr]	5	5	—
Keratin [phr]	—	5	—
Keratin + ZnO [phr]	—	—	5 + 5

Other ingredients.

Acrylonitrile-butadiene rubber NBR (Nipol N41)—100 phr, sulfur—2,5 phr, dibenzothiazyl disulfide (MBTS)—1 phr, Polnox N—1 phr, Stearin—2 phr, ethylene glycol—2 phr, and phr—part by hundred rubber.

and 1232 cm<sup>-1</sup>). For potential zeta, isoelectric point carries out about pH = 4,6; after keratin blended with zinc oxide, we observe the shift—pH = 4,4. At this point, we observed the improvement of particles dispersal. The molecular weight of keratin is 82800 Da.

In this research, recovered keratin is used as a filler of acrylonitrile-butadiene rubber NBR-Nipol N41, Nippon Zeon Co (21% acrylonitrile's mers), Mooney viscosity ML (1 + 4) 100°C 45 ± 5.

Rubber mixtures prepared with the use of a laboratory rolling mill at room temperature were vulcanized in an electrically heated press shelves at 150°C for time  $\tau_{90}$ , determined according to the standard PN-ISO 3417:1994 (vulcameter with an oscillating rotor WG-02). The compositions of rubber mixes, to which keratin was added directly (sample I) or after blending with zinc oxide (sample II) to NBR, are given in Table 1.

The cross-linking density was determined from equilibrium swelling in the following solvents: toluene, toluene ammonia vapor, and in water (in accordance with the standard PN-ISO 817:2001/apl:2002). Four samples with different shapes were cut out from each vulcanizate, weighed, immersed in solvent, and stored in a thermostatic chamber at 25°C for 48 h. The samples were then reweighed and dried to a constant weight at 50°C. The density of rubber was measured according to the standard PN-ISO 2781+AC1:1996, and the density of lattice was found using Flory and Rehner's equation [19]. The assessment of the percentage of the content of carbon bonds as well as mono-, di- and polysulfide bridges in vulcanizates was done by the use of thiol-amine chemical analysis [20].

The activity of filler ( $a_f$ ) was counted on the basis of the paper [21].

The mechanical properties of tested composites were tested according to the standard PN ISO 37:1998 by means of Zwick tensile testing machine model 1435. Dumbbells with a measurement section width of 4 mm were used to determine tensile strength and elongation at break before ( $TS_{b1}$  and  $E_{b1}$ ) and after thermal-oxidative ageing ( $TS_{b2}$  and  $E_{b2}$ ). The thermal-oxidative ageing resistance was investigated according to the standard PN-88/C-04207. The ageing coefficient,  $S$ , was determined from the following relationship:

$$S = \frac{TS_{b1} \cdot E_{b1}}{TS_{b2} \cdot E_{b2}}. \quad (1)$$

The measurement of electric conduction was made according to the Polish standard PN-85C-04259/01. The determination of hardness by Shore's method was carried out according to PN-80C-04238. The hardness of rubber was measured with the use of electronically hardness tester, type A of firm Zwick/Roell, and pressure 12,5 N. The determination of elasticity was carried out according to Schob's method (PN-C-04255:1997). The determination of absorbing capacity was performed by the percussive method in Schobe's elastometer according to the standard PN-54/C-04268. FTIR spectroscopy (BIO RAD FTS 175C) of vulcanizates was performed by the transmission method. Samples in the form of thin films were prepared by pressing under a pressure of 150 MPa. The thermal analysis was performed under air atmosphere. 90 mg samples were heated in a derivatograph furnace (MOM Budapest) at a heating rate of 7.9°C/min within temperature from 20 to 800°C using  $\text{Al}_2\text{O}_3$  as a reference substance. Thermal curves sensitivities were as follows: TG = 100, DTA = 1/5, and DTG = 1/20.

The surface of the composites obtained was tested with the use of scanning electron microscopy SEM, of firm LEO 1530. Testing the rubber biodegradation in soil (soil tests), samples were placed in an active compost universal soil (10 cm) and incubated at a temperature of 30°C and 80% RH. After 30 days of incubation, the appearance of samples was evaluated using microscopy. Tests were carried out according to the standard PN-En ISO 846.

### 3. Results and Discussion

**3.1. Analysis of Cross-Linking Density.** The cross-linking densities of the following three vulcanizates were tested: unfilled vulcanizate (standard), vulcanizate filled with keratin (sample I), and vulcanizate filled with keratin previously blended with zinc oxide (sample II) in toluene or in toluene under ammonia vapors. The results obtained are given in Table 2.

Based on the difference in the cross-linking densities, one can determine the interaction between rubber and filler.

A higher cross-linking density is achieved by vulcanizates containing keratin incorporated separately as well as that after direct blending with ZnO. The results of cross-linking density in toluene ( $\nu_T$ ) and in toluene and ammonia vapor ( $\nu_{T/\text{NH}_3}$ ) show a lot of ionic bonds in polymer matrix decomposing under the influence of ammonia (A1). Keratin blended with zinc oxide introduction to rubber vulcanizates structure cause the clear growth of number ionic bonds cracking under the influence of ammonia fumes (A1). The considerably less ionic bonds decompose under the influence of steams of ammonia if we introduce keratin and zinc oxide separately to vulcanizates (Table 2).

Equilibrium swelling in water ( $Q_w$ ) (Table 2) increases in the case of protein-elastomer vulcanizates. This results from the capability of hydrophilic protein to absorb water. The values of equilibrium swelling in water are low due to the chemical structure of NBR.

From the analysis of carbon bonds and mono-, di-, and polysulfide bonds ( $\text{C-S-C}$ ,  $\text{C-S}_2\text{-C}$ ,  $\text{C-S}_x\text{-C}$ ) (Table 2), it follows that the content of mono- and disulfide bonds in the

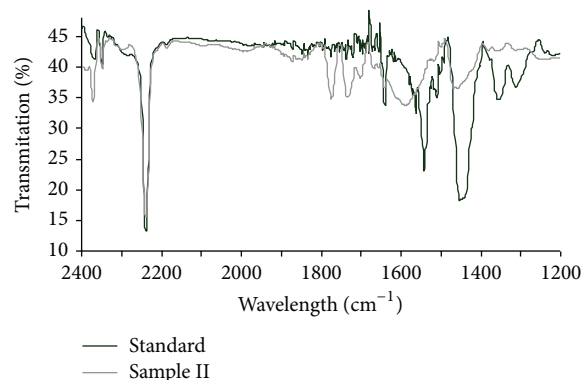


FIGURE 1: FTIR spectra of the NBR rubber vulcanizates without (standard) and with keratin blended with ZnO (sample II).

sample II—containing vulcanizate—is clearly the lowest as compared with those of the remaining vulcanizates, since this vulcanizate contains more ionic bonds than covalent bonds. The highest percentage content of these bonds is shown by the vulcanizate containing keratin (sample I); it also shows the lowest concentration of ionic lattice nodes. Short carbon bonds and mono- and disulfide bonds are stable, and to disrupt them, one should use a considerably higher energy than in the case of polysulfide bonds.

Based on this series of tests, one can conclude that keratin clearly increases the cross-linking density of the polymer materials. The presence of ionic bonds in the protein-elastomer structure does not exclude the existence of covalent bonds.

**3.2. FTIR Analysis.** The analysis of FTIR spectra of NBR vulcanizates consists in observing the changes in bands resulting from the incorporation of keratin into the structure of the elastomers under investigation. FTIR spectra are shown in Figure 1. For the nitrile elastomers, we can observe a characteristic band at 2240  $\text{cm}^{-1}$  originating from nitrile groups in NBR. This peak is much shorter for sample II than in standard, which testifies the existence of certain interaction between rubber and filler.

The appearance of the bands 1774  $\text{cm}^{-1}$  and 1736  $\text{cm}^{-1}$  for sample II spectrum [22] and their absence in standard spectrum probably testify the influences between keratin and NBR rubber too. It could be maximum from  $\text{-C=O}$  protein group, whereas in powdered keratin spectrum appears only are bands at wavelength: 1724  $\text{cm}^{-1}$  [1].

The subsequent observed band originates from butadiene: 1639  $\text{cm}^{-1}$ . In the case of standard vulcanizate, the band at 1541  $\text{cm}^{-1}$  may indicate the appearance of zinc salts such as zinc stearates, while the shift of this band in the spectrum of the protein-containing vulcanizate (1601  $\text{cm}^{-1}$ ) may be explained by the formation of clusters between carboxyl and amino groups of protein (amide I band ( $\text{C=O}$ ): 1690–1630  $\text{cm}^{-1}$ ) and zinc cation [1]. Also near these wavelengths connected from amide groups, one can observe that it is possible to create ionic bonds between particles of protein and zinc oxide according to the mechanism in Figure 2(a).

TABLE 2: Cross-linking density determined by measurement of equilibrium module and equilibrium swelling.

Symbol	Parameters				Content of bonds [%]:	
	$\nu_T/\nu_{T/NH_3}$ [mol/dm <sup>3</sup> ] * 10 <sup>4</sup>	$\Delta\nu_{NH_3}$ [mol/dm <sup>3</sup> ] * 10 <sup>4</sup>	$A_1$ [%]	$Q_w$ for water [mg/mg]	C-C, C-S-C, C-S <sub>2</sub> -C	C-S <sub>x</sub> -C
Standard	0,70/0,45	0,26	37,14	0,055	9,30	90,70
Sample I	1,00/0,82	0,18	18,00	0,089	15,24	84,76
Sample II	1,08/0,44	0,64	59,26	0,092	2,98	97,02

$\nu_T$ —cross-linking density of vulcanizate calculated from the measurement of equilibrium swelling in toluene [mol/dm<sup>3</sup>]

$\nu_{T/NH_3}$ —cross-linking density of vulcanizate calculated from the measurement of equilibrium swelling in toluene and ammonia vapour [mol/dm<sup>3</sup>]

$\Delta\nu_{NH_3}$ —concentration of the ion lattice points decomposing under the influence of ammonia [mol/dm<sup>3</sup>]:

$$\Delta\nu_{NH_3} = \nu_T - \nu_{T/NH_3}$$

$A_1$ —percentage content of the ion lattice points decomposing under the influence of ammonia [%]:

$$A_1 = (\Delta\nu_{NH_3} / \nu_T) * 100\%$$

The parameters of rubber-elastomer interactions:

$\mu$ —Huggins' parameter (parameter of polymer-solvent interaction):

$$\mu = \mu_0 + \beta V_r$$

where

$V_r$ —volumetric content of elastomer in the sample under test

$\mu$ —the parameter of polymer-solvent interaction when  $V_r = 0$

$\mu_0$ —slope of the straight line describing the relationship:  $\mu = f(V_r)$

For NBR (Nipol N41) rubber: in toluene  $\mu_0 = 0.479$ ;  $\beta = 0.164$ ; in toluene and ammonia vapour

$$\mu_0 = 0.502; \beta = 0.282$$

$Q_w$ —equilibrium swelling in water [mg/mg]

C-C, C-S-C, C-S<sub>2</sub>-C; carbon, monosulfide and disulfide bonds [%]

C-S<sub>x</sub>-C; polysulfide bonds [%].

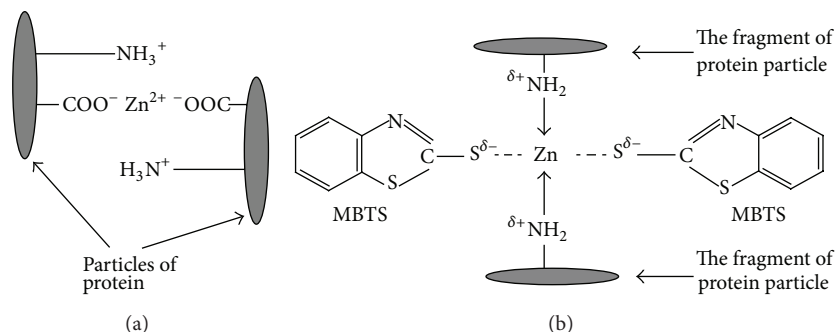


FIGURE 2: The schematic diagram shows (a) the probable coordination of ions of zinc with amine and protein carboxylic groups, (b) the possible complex connections between the fragment of protein particle (keratin), MBTS (dibenzothiazyl disulfide), and ZnO [11].

The changes in spectra indicate a probable formation of lattices between protein and the rubber mix components (MBTS, ZnO, sulfur, and stearin) and the rubber itself. Many aspects of the sulfur vulcanization mechanism have not been explained yet, but according to the literature data [22], numerous studies have been performed which indicate the formation of complexes between ZnO and mercaptobenzothiazole (MBT) during heating.

In the presented spectra at the wavelength 1527 cm<sup>-1</sup>, there appears a band that may originate from dimercaptobenzothiazole (MBTS)—its higher intensity is observed in the vulcanizate without keratin. Probably the activating agent such as MBTS facilitates the formation of a spatial lattice with the elastomer through complex formation with ZnO and amino groups of protein (Figure 2(b)). At the next wavelength 1454 cm<sup>-1</sup>, one can probably observe groups for which a shift is clearly seen in the protein-containing vulcanizate—1470 cm<sup>-1</sup> confirming the formation of complexes in the described schemes.

**3.3. Rheometric Properties.** The effects of keratin on the rheometric properties of NBR vulcanizates are listed in Table 3. From the data given in Table 3, it follows that the incorporation of keratin derived from cattle hair into NBR has brought about a slight decrease in the mix viscosity as the minimal torque  $L_L$  is decreased.

From the rheometric measurements, it follows that the increments of torque of all mixes are similar, but the highest value of  $\Delta L$  is reached by the mixes, in which keratin is blended with zinc oxide. ZnO not only plays here the part of activator of rubber cross-linking by the formation of stearate salts, but it also facilitates the incorporation of protein into the rubber mixes.

Additionally, the incorporation of protein into the NBR rubber mixes considerably shortened the vulcanization time, which may be of economic importance. The scorch time ( $t_{02}$ ) was also influenced by keratin addition because their value decreased. Already on basis of earlier investigations [1–4], we noticed that the introduction keratin or of hydrolyzate



TABLE 3: The influence of keratin on the rheometric properties of NBR mixes.

Parameters	Standard	Symbol Sample I	Sample II
$L_L$ —minimal of torque moment [dNm]	14,7	12,7	13,9
$\Delta L$ —the decrease of torque moment ( $\Delta L = L_{HR} - L_L$ [dNm])	67,0	69,4	70,8
$\tau_{0,9}$ —time of vulcanization [min]	15	9	7
$\tau_{0,2}$ —scorch time [min]	3,5	2,9	2,8
$a_f$ —filler activity [—]	—	0,72	1,13

$$(\Delta L / \Delta L_0) - 1 = a_f * (m_f / m_r)$$

where

$\Delta L$ —the increase of torque moment of mixes with protein

$\Delta L_0$ —the increase of torque moment of mixes without protein

$m_f$ —the weight parts of filler

$m_r$ —the weight parts of rubber.

TABLE 4: The influence of keratin on the mechanical properties of NBR vulcanizates.

Parameters	Standard	Symbol Sample I	Sample II
Tensile stress [MPa] at an elongation:			
100%	1,48 ± 0,03	1,08 ± 0,03	2,03 ± 0,01
200%	1,90 ± 0,04	1,50 ± 0,04	2,44 ± 0,01
300%	2,15 ± 0,00	1,91 ± 0,03	3,17 ± 0,02
TS—tensile strength [MPa]	2,23 ± 0,01	2,33 ± 0,01	2,90 ± 0,04
Eb—elongation at a break [%]	352 ± 2	382 ± 2	311 ± 3
S—the ageing coefficient [—]	0,65 ± 0,00	0,80 ± 0,04	0,90 ± 0,04
Shore's hardness A [IHRD]	46,8 ± 0,3	48,2 ± 0,2	48,1 ± 0,3
Shob's elasticity [%] (scale $H = 1$ )	28	24	26
Shock absorption—the number of pendulum leanout	8	5	6
$c_V$ —volume resistance [m * $\Omega$ ]	9,787 * 10 <sup>8</sup>	12,246 * 10 <sup>12</sup>	6,507 * 10 <sup>8</sup>
$c_S$ —surface resistance [m * $\Omega$ ]	8,572 * 10 <sup>10</sup>	5,790 * 10 <sup>10</sup>	5,511 * 10 <sup>10</sup>

to polymer materials causes its shortening of time of their vulcanization.

From previous studies [1], it follows that keratin recovered from cattle hair is an active filler of XNBR rubber. The presented rheometric measurements show that keratin is probably also an active filler of NBR rubber. The data listed in Table 3 show that the activity of filler increases if keratin prior to incorporation into the rubber mixes is blended with ZnO (sample II). The activity can show the building of common net of macromolecule. This seems to be due to polar groups, sulfur proteins that, in turn, can form crosswise bonds with the mix components as well as with the elastomer itself, thus affecting the material structure as confirmed by SEM.

**3.4. Mechanical Properties.** The effects of keratin on the mechanical properties of NBR vulcanizates are listed in Table 4. The value of elongation at a break (Eb) for samples I and II is higher than standard. The incorporation of keratin with ZnO caused an increase in all the parameters of tensile strength at elongations 100, 200, and 300%. The influence of keratin on mechanical properties is not large.

Considering tensile strength (TS) of standard (2,33 MPa) and the growth of tensile strength about 0,67 MPa for sample II (after the addition of keratin to composition), differences are really small. But the number of values is not large for all compositions. However, it suggested the improvement of mechanical properties for polymer materials after adding the keratin.

Vulcanizates containing 5 phr (parts per hundred rubber) of keratin show improved resistance to thermal ageing—the ageing coefficient is increasing, probably due to protein with groups of an antioxidizing character.

Based on the hardness, elasticity, and shock absorption tests (Table 4), it is clearly seen that the incorporated particles of the recovered filler stiffen the system of the polymer material under investigation. Vulcanizates filled with keratin are characterized by a lower elasticity and shock absorption.

Rubber vulcanizates belong to a group of insulating materials rather than conducting electric current (Table 4). However, both the surface and through electric resistances are decreased in the case of vulcanizates containing 5 phr of keratin blended directly with ZnO—sample II (as compared



FIGURE 3: Biodegradation: (a) standard (after and before soil test), (b) sample II with keratin (after and before soil test).

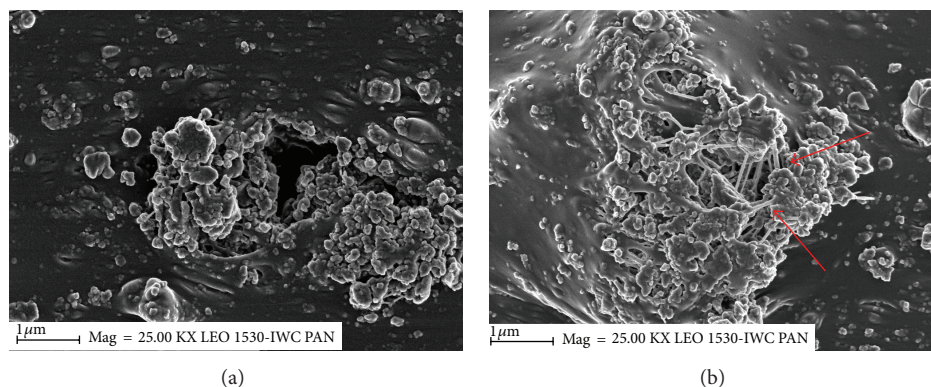


FIGURE 4: SEM images of (a) standard, (b) sample II (Mag—magnification  $\times 25000$ ). In (b), the arrows show the possible interactions between molecules of keratin and rubber or other elastomeric components of the mixture.

to those of unfilled vulcanizate). This seems to be due to the hydrophilic character of protein as indicated by the results of equilibrium swelling in water (Table 2).

**3.5. Thermal Analysis.** The thermal analysis for NBR materials shows the enlargement resistance on high temperatures effect in result introduction keratin to polymer matrix. The results of thermal analysis of NBR vulcanizates without (standard) and with keratin blended directly with ZnO (sample II) (5 + 5 phr) are listed in Table 5.

The range of beginning of term oxidizes degradation connected with processes of destruction and depolymerization for NBR vulcanizate with keratin. The 5% weight loss for standard is observed at temperature  $280^{\circ}\text{C}$ , but for sample II, just at  $330^{\circ}\text{C}$  (Table 5). Also we were observed 50% weight loss of standard at temperature  $430^{\circ}\text{C}$ , however, for sample II at temperature  $450^{\circ}\text{C}$ . The process of decomposition for standard follows in range of temperature  $480\text{--}560^{\circ}\text{C}$ , but for sample II, at  $500\text{--}650^{\circ}\text{C}$ . Above these temperatures follows burning of remains charred.

On the basis of the results of thermal investigations, it is possible to observe that for sample with keratin all the transformations they set are at higher temperatures than for standard. In result of introduction, the proteins to structure of elastomer the enlarged thermal resistance can probably effect of additional formation the intermolecular influences, growth of stiffness of studied arrangement, what it confirms the mechanical proprieties of vulcanizate with keratin.

**3.6. Biodegradation.** The susceptibility of samples (standard and sample II) on the soil microorganisms influences was examined, and the results were shown in Table 6 and Figure 3. On figure or in table the first vulcanizate plate was not working soil bacteria's, however, the second vulcanizate plate was serf working microflora.

After soil incubation, it observed that the introduction of keratin to NBR (sample II) caused considerable changes in the topography of studied surfaces. In Figure 4 numerous blisters and roughness appear, the surface went goes fogging and white stains appear. Surface change influenced also mechanical parameters like tensile strength (TS) and

TABLE 5: Thermal analyses of filled and unfilled vulcanizates of acrylonitrile-butadiene rubber NBR.

Symbol	Thermal analysis		
	Parameters		
	$T_5$ [°C]	$T_{50}$ [°C]	$P_{800}$ [%]
Standard	280	430	24
Sample II	330	450	26

$T_5$ —temperature at which the sample weight loss is 5% [°C]

$T_{50}$ —temperature at which the sample weight loss is 50% [°C]

$P_{800}$ —residue after the sample thermal decomposition in  $T = 800^\circ\text{C}$  [%].

TABLE 6: The influence of keratin on the mechanical properties of NBR vulcanizates after and before soil test.

Properties	Symbol			
	Standard		Sample II	
	After	Before soil test	After	Before soil test
TS—tensile strength [MPa]	2,23	2,20	<b>2,90</b>	<b>2,47</b>
Eb—elongation at a break [%]	352	320	<b>392</b>	<b>365</b>

elongation at a break (Eb). The mechanical properties of the standard did not undergo change (value of TS gets smaller only just 1,4%), but the value of tensile strength for sample II reduced about 15%. These investigations testify the increase of biodegradation ability of vulcanizates filled keratin.

**3.7. SEM Analysis.** The photographs of the vulcanizate filled with biopolymer taken by means of SEM are shown in Figure 4.

From the presented photographs, it follows that keratin forms a lattice with the elastomer and the remaining components of vulcanizate as seen in Figure 4(b). The agglomeration trends of the polymer materials in the presented vulcanizate are similar; the particles of keratin in the elastomer forms clusters with a complex structure, various shapes, and sizes.

## 4. Conclusions

Based on the performed tests, one can observe that the best properties are shown by the vulcanizates of NBR containing keratin blended directly with zinc oxide. The vulcanizate filled with 5 phr of keratin mixed with zinc oxide recovered from tannery wastes will show equally acceptable properties. The incorporation of keratin into NBR vulcanizates brings about an increase in their resistance to thermal ageing. Based on the cross-linking density, FTIR analysis, and SEM photographs, one can see a clear influence of protein on the formation of spatial lattice of elastomers between protein, zinc oxide, and the elastomer matrix. From the thermal analysis, it follows that the vulcanizate containing keratin blended with zinc oxide shows an increased resistance to heat; hence the materials made from it will be suitable for use at elevated temperatures, fulfilling the requirements of elastomers designed for special applications.

An elastomer material—sample II—has not only good usable properties; also thanks to the water absorption by protein, they will be more capable of biodegradation in the environment. About this testifying of vulcanizates pictures, show biodegradation of samples after 30 days incubation in universal soil. An additional benefit results from the utilization of tannery wastes and to some extent the reduction of environmental pollution. The addition of keratin to rubber influences the improvement of thermal stability and biodecomposition after these polymer materials serve life.

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