The effect of modified biopolymers and poly(vinyl alcohol) on carboxylated acrylonitrile-butadiene rubber properties*)

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Abstract: The aim of the research was to determine the impact of modified biopolymers such as: enzyme hydrolyzate of collagen, enzyme hydrolyzate of keratin and poly(vinyl alcohol) PVAL (or PVA) on the properties of carboxylated acrylonitrile-butadiene rubber (XNBR) vulcanizates. Biopolymers were obtained from industrial waste leather in the form of collagen from chrome tanned leather shavings and keratin from cattle hair. The rheometric, mechanical properties, cross-linking density, Fourier Transform Infrared spectra (FT-IR) and Ultraviolet-Visible spectra (UV-Vis) were examined. Thermo-oxidative aging and biodecomposition processes were also performed. The introduction of natural bioadditives and PVAL influenced the improvement of cross-linking density of the obtained XNBR composites — probably by creating a common spatial network with the elastomeric matrix. Increased hardness, resistance to thermal aging and susceptibility to the action of microorganisms in soil were observed.

Keywords: waste, biopolymer, hydrolyate of keratin/collagen, elastomer, composite.

Wpływ modyfikowanych biopolimerów i poli(alkoholu winylowego) na właściwości karboksylowanego kauczuku akrylonitrylo-butadienowego

Streszczenie: Zbadano wpływ zmodyfikowanych biopolimerów, takich jak: enzymatyczny hydrolizat kolagenu, enzymatyczny hydrolizat keratyny oraz poli(alkohol winylowy) (PVAL, używany też skrót PVA) na właściwości wulkanizatów karboksylowanego kauczuku akrylonitrylo-butadienowego (XNBR). Biopolimery pozyskiwano z odpadów przemysłu skórzanego. Określono właściwości reometryczne, mechaniczne i gęstość usieciowania wulkanizatów oraz ich budowę chemiczną. Zbadano także procesy starzenia termooksydacyjnego oraz biorozkład. Wprowadzenie do mieszanki kauczukowej naturalnych biododatków oraz PVAL wpłynęło na poprawę gęstości usieciowania uzyskanych kompozytów XNBR, prawdopodobnie w wyniku tworzenia wspólnej sieci przestrzennej z matrycą elastomerową. Otrzymane wulkanizaty XNBR charakteryzowały się zwiększeniem twardości, odporności na starzenie termiczne oraz podatności na działanie mikroorganizmów występujących w glebie.

Słowa kluczowe: odpady, biopolimer, hydrolizat keratyny/kolagenu, elastomer, kompozyt.

For many years, the technology of plastics was based on the material's strength and its resistance to a variety of physical, chemical or biological factors. New trends in organic polymeric materials demand materials that are functional for a limited time, after which biological decomposition follows under natural conditions. This leads to an increased interest in modern technologies to produce environmentally-friendly polymers. Currently, there is a dynamic increase in the production of biodegradable polymers. For this reason, waste biopolymers such as: hair keratin, feather keratin and chrome tanned leather shavings and leather dust extraction have begun to enjoy considerable interest in recent years. Collagen is the major component of tannery waste; it is biodegradable and bioresorbable. Keratin occurs to a slightly lesser degree as waste but is a valuable mineral source of nitrogen and sulfur. Here, at the Institute of Polymer and Dye Technology, we have conducted research on preparing biodecomposable elastomer composites using waste biopolymers (collagen, keratin) and their modifications, such as hydrolyzates, for a long time [1—3].

An interesting topic for many scientists is the use of poly(vinyl alcohol) (PVAL) and biopolymers as additives for films and composites. Thus, for example, the use of PVAL and collagen in biomedical applications. Scientists [4] prepared a Hybrid Polymer Network (HPN) of chito-

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san (CS) with PVAL using radiation degraded chitosan. Thanks to the introduction of chitosan, the hydrophilicity of the materials was increased while the crystallinity of the HPN structure decreased. In addition to that, researchers did not observe any negative toxic effects of HPN on the cell viability of human fibroblasts. Scientists [5] prepared porous polymeric membranes based on collagen and hydroxyapatite (HA). Modern hybrid composites of collagen hydrolyzate, poly(vinyl alcohol) and hydroxyapatite (CH)-PVAL/HA were tested by means of thermal and structural analysis using common techniques: Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). Based on both SEM images and hemolysis analyses, the obtained nanocomposites were found to have good quality and hemocompatibility. Lešinský D. *et al*. [6] developed a new material, a water-soluble blend of PVAL and collagen hydrolyzate (PVAL/CH). The study focused on the biodegradation of three different variants of mixtures containing collagen. The degradation process was carried out in an aqueous environment and in compost. On the basis of these tests, degradation rates were determined for both test systems and carbon conversion rates were calculated by drawing up a carbon balance out of the aquatic test. The analysis of the results showed a positive influence on the degradation of collagen, as well as a low biological degradability of PVAL. Hybrid blends of PVAL and CH, a valuable waste from the leather industry, have been formed by extrusion blow molding into films that are degradable in the environment [7]. The extruded PVAL films contained from 5 to 15 wt % of collagen hydrolyzate. The propensity of these films to degradation in the environment was examined. It was found that the films of PVAL/CH show a high tendency to degrade, which may contribute to the development of possible applications of these materials, *e.g.* in agriculture.

A common issue in the literature is the determination of the degradation process and thermal properties of mixtures of collagen hydrolyzate (CH) and poly(vinyl alcohol) (PVAL) [8]. Through catalysis with acetic acid, NH_2 groups in collagen are blocked and PVAL is protected from acid catalysis products. To facilitate the removal of PVAL/CH compounds from the mold during the extrusion of the film, talc should be use instead of silica. Then, films containing up to 30 wt % of collagen can be obtained, which in consequence will be more easily biodegradable. Another study focused on the effect of CH and glycerol on the properties of water-soluble PVAL films and blends [9]. Strong interactions between the various components of the compounds and their influence on the properties of the obtained films were observed. Langmaier F. and his team [10] demonstrated that the enzymatically hydrolyzed collagen from chrome tanned leather has a certain resemblance to polyamides with a high content of nitrate amides. The average molecular weight of the polymers is comparable to that of the polyamides. Thanks to their properties, the hydrolyzates were used for cross-linking epoxy resins. Their addition had positive effects on stiffness, flexibility, resistance to moisture and chemically derived resins. Based on a preliminary study, it was found that the addition of hydrolyzed proteins increases the degree of biodecomposition of oxides.

Films, composites containing keratin and PVAL are less common than materials containing collagen. More porous and biocompatible keratin hydrogels were obtained using Electron Beam Irradiation (EBI) [11]. The radiation dose and the concentration of keratin solutions were changed, while additives such as poly(vinyl alcohol) and poly(ethylene imine) were introduced. The latter compound had a positive impact on the films since they increased the rate of film gelation. Keratin from chicken feathers is a commonly used adhesive. It is used as a means of a bonding factor — a polymer matrix with cotton material, polyester. Keratin from chicken feathers is a significantly better adhesive than PVAL material because of its high susceptibility to biodegradation [12]. Keratin better bonds polyester/cotton than PVAL, which leads to a material with higher mechanical strength but less resistant to abrasion. The Chemical Oxygen Demand (COD) decreases much more in the case of keratin than PVAL. Keratin is much cheaper and biodegradable. Therefore, it can replace PVAL.

The mechanical and thermal properties of chitosan materials containing keratin hydrolyzates under the action of ultraviolet radiation were studied [13]. The keratin hydrolyzate was included in an amount of 5 to 30 wt % in chitosan films. The materials were subsequently irradiated with radiation light of an appropriate wavelength (254 nm), and then the surface free energy was determined. The resulting films were examined in terms of breaking strength, elongation at break and Young's modulus. On the basis of these results it was found that the mechanical properties of chitosan/keratin films depend on UV radiation. However, the properties of these films are better than those of films containing only chitosan or only keratin. Chitosan is more susceptible to photo-oxidation than keratin. Researchers [14] have used small particles of sheep keratin in order to be mixed with a solution of poly(L-lactide) (PLLA) in 1,4-dioxane to obtain paraffin microspheres. The results confirmed the hypothesis that keratin can provide scaffolding that improves the interactions between osteoblasts and PLLA polymeric material.

Thus, the objective of this work was to study the effect of modified biopolymers such as the enzymatic hydrolyzate of collagen, enzymatic hydrolyzate of keratin and PVAL on the properties of XNBR rubber. The properties have been assessed by determining rheometric, mechanical and thermal properties, density of crosslinking, FT-IR analysis, color change and Soil Test. Why exactly do we use XNBR rubber in this research? It is due to the presence of carboxylic groups that, on the basis of previous studies [1—3, 15, 16], show high affinity for polar groups like: -NH_3^+, -COO^-, that are present in modified biopolymers. Carboxylated acrylonitrile-butadiene rubber is an elastomer with free acid groups. It can be used in a solid form or as a latex. The construction of the main chain structure, the content and placement of the carboxylic groups affect the properties of its compounds. The introduction of macromolecules susceptible to create ionic bonds results in a change of the properties of the elastomer such as increasing the tensile strength, abrasion and dynamic resistance to oils, as well as increasing the glass transition temperature and hydrophilicity and reducing the susceptibility to crystallization.

EXPERIMENTAL PART

Materials

— Keratin and collagen were recovered from the effluents of the tanning industry (Kalisz Tannery Plant) (Fig. 1). They are derived from the liming and unhairing process of cow hides with preservation of hair structure.

— Carboxylated acrylonitrile-butadiene rubber XNBR Krynac X7.50 from Bayer AG, (containing 6.7 % of carboxylated group and 27 % of acrylonitrile structural units, Mooney viscosity: ML (1+4) 100 °C 47±5 MU).

— Poly(vinyl alcohol) PVAL [the molecular weight 72000, pH (4 % H_2O) = 5—8, degree of hydrolyzis is 85—89 %] produced by POCH S.A. Gliwice, Poland.

— The rubber cross-linking agent is sulfur S_8 with a density of 2.07 g/cm^3, obtained from Tarnobrzeg (Poland), and the activating agent of the cross-linking process is ZnO from Huta Oława (Poland), with a specific surface area of 5—7 m^2/g and particle size 0.1—0.9 µm.

— NaOH, H_2SO_4, toluene, ammonia — POCH S.A., Gliwice (Poland).

— Novo Unhairing Enzyme NUE 12 MP, Novozymes A/S Rething Tomorrow Company, Bagsvaered (Denmark).

Preparation of keratin and collagen

After being obtained from tannery wastes, keratin and collagen were dried, shredded and powdered. The obtained powder was sieved through a screen with a mesh diameter of 0.1 mm. Then, the obtained keratin and collagen were subjected to two-step enzymatic hydrolyzis with yields of 88 % and 82 %, respectively. The parameters of the two-step enzymatic hydrolyzis were:

1st step: 0.25 M NaOH, temp. 85 °C, reaction time 2.5 h, neutralization to pH = 9 — 1 M H_2SO_4,

2nd step: application of proteolytic enzyme — Novo Unhairing Enzyme NUE 12 MP, temp. 50 °C, time 3 h, dry at temp. 50 °C, (Fig. 2).

Preparation of composites

In the next step, the obtained enzymatic hydrolyzates were incorporated as fillers into carboxylated acrylonitri-

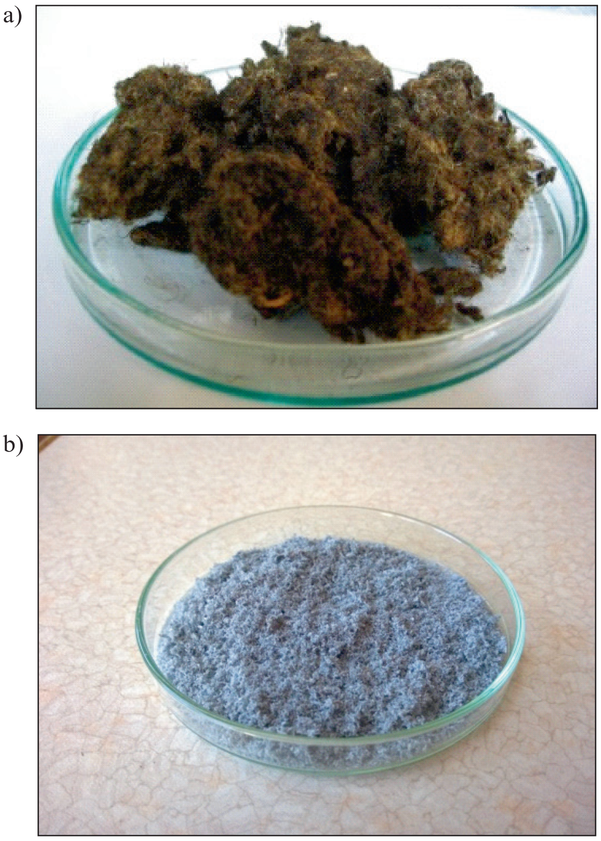

Fig. 1. Pictures of tannery waste: a) keratin (cattle hair), b) collagen (chrome shavings)

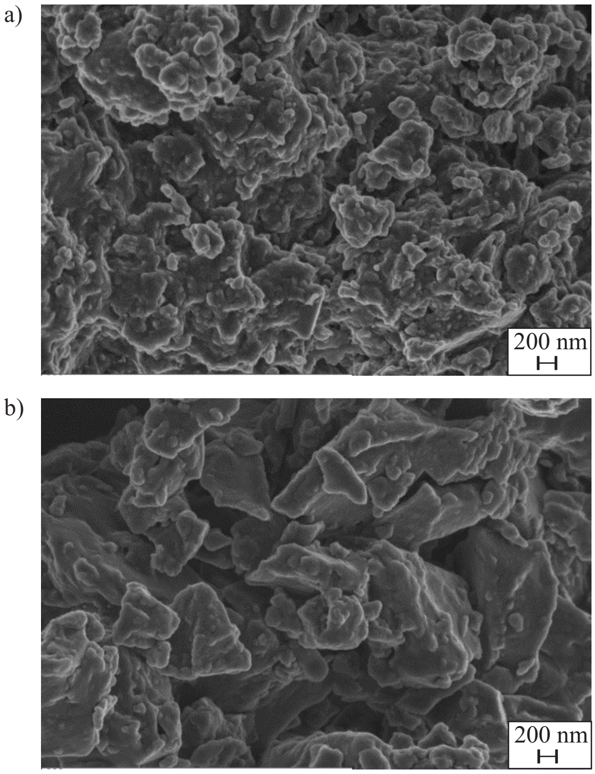

Fig. 2. SEM pictures of enzymatic hydrolyzates: a) keratin, b) collagen; magnification 50000×

le-butadiene rubber XNBR. The content of rubber compounds are listed in Table 1. All compounds were mixed with PVAL with a particle size ≤ 0.25 mm, obtained through the use of a vibrating sifter, AS 200 CONTROL production of RETSCH GmbH. The protein hydrolyzate was added to the compounds with zinc oxide as an activating agent. The rubber compounds were prepared by means of a mixing mill at a roll temperature of 30 °C and friction of 1.15. The vulcanization of the mixtures was carried out in a vulcanization mold at 150 °C for the time τ_{90} according to the standard PN-ISO 3417:1994 (vulcameter with an oscillating rotor WG-02). The vulcanization of the rubber compounds was carried out in steel moulds placed between electrically heated press shelves at the temperature of 150 °C for τ_{90}.

Table 1. Content of rubber compounds

Compounds, phr	X	XP	XPHK	XPHC	XPHKC
Poly(vinyl alcohol) (P)	-	10	10	10	10
Keratin hydrolyzate (HK)	-	-	10	-	-
Collagen hydrolyzate (HC)	-	-	-	10	-
Mix of hydrolyzates (HKC)	-	-	-	-	20

The other components: XNBR — 100 phr, ZnO (zinc oxide) — 5 phr, S (sulfur) — 2.5 phr, technical stearin — 2 phr, MBTS (dibenzothiazyl disulphide) — 1.5 phr.

Methods of testing

— Analysis by infrared spectroscopy was conducted using a Bio-Rad 175 C type spectrometer with FT-IR analysis using the total internal reflection method.

— The determination of the degree of cross-linking from equilibrium swelling was determined in: toluene, toluene with ammonia vapors and in water, in accordance to the standard PN-ISO 817:2001/Ap1:2002.

The spatial network density of XNBR vulcanizates set in toluene and toluene with vapors of ammonia were calculated using the Flory-Rehner formula:

$$\nu^{r}_{e} = -[\ln(1 - \nu_{r}) + \nu_{r} + \mu\nu^{r2}]/[\nu_{o}(\nu^{r1/3} - 2\nu_{r}/f)] \qquad (1)$$

where: ν'_{e} — the concentration of effective chains in a solvent (toluene or toluene and ammonia) [mol/cm^3], ν_r — the volume of rubber in swollen gel, network capability is 4, ν_o — molar volume of the solvent [mol/cm^3].

The Huggins parameter as a linear function of the degree of cross-linking ν_r, effects of rubber-solvent, $\mu = \mu_o + \beta\nu_r$ μ_o — directional factor straight line describing the relationship $\mu = f(\nu_r)$, for rubber: $\mu_0 = 0.487$, $\beta = 0.228$ for toluene and $\mu_0 = 0.483$, $\beta = 0.320$ for toluene and ammonia. And then there is the concentration of network nodes disintegrating under the influence of the ammonia vapors $\Delta\nu_{NH3}$ in the vulcanizates ($\Delta\nu_{NH3} = \nu_e^T - \nu_e^{T/NH3}$, where: $\nu_e^{T/NH3}$ — cross-link density calculated on the basis of equilibrium swelling in toluene and ammonia vapor [mol/cm^3]) and the percentage of network nodes disintegrating under the influence of ammonia vapors A_1 [$A_1 = (\Delta\nu_{NH3}/\nu_e^T) \cdot 100$ %].

— Mechanical properties: tensile strength (TS_b, MPa) and elongation at break (E_{b1}, %) were determined according to the standard PN-ISO 37:1998 using the tensile testing machine Zwick 1442, 1435.

— The resistance to thermal aging was investigated according to the standard PN-88/C-04207. The principle of determination consists in exposing an unstressed sample to the action of circulating air at a temperature of 70 °C for 168 h. Tensile strength and elongation at break of vulcanizates were measured before and after the aging procedure. The aging coefficient S was determined from the following relationship:

$$S = [TS_{b1} \cdot E_{b1}]/[TS_{b2} \cdot E_{b2}] \qquad (2)$$

where: TS_{b1} and E_{b1} — tensile strength and elongation at break after thermal aging, TS_{b2} and E_{b2} — tensile strength and elongation at break before thermal aging, respectively.

— The changes in color have been assessed using a CM-3600d KONICA MINOLTA spectrophotometer. The change of color was examined after thermo-oxidative aging process and Soil Test. The studies were visualized using the $\Delta E \cdot$ ab parameter and reflectometric spectra.

— Determination of the hardness by Shore's method — according to PN-80/C-04238. The hardness of rubber was measured with the use of an electronic hardness tester, type A from producer Zwick/Roell, pressure 12.5 N.

— SEM pictures were made to identify structural changes in the obtained composites using scanning electron microscopy SEM, Baldek SCD095 (Sputter Coated) LEO 1530.

— Biodecomposition of rubber, performed in soil (Soil Tests) — samples; paddle-shaped with dimensions 7.5 cm to 1.25 cm, and sampling of 0.4 cm; were placed in an active 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, December 2002.

RESULTS AND DISCUSSION

The use of waste as fillers for elastomers in order to improve and reinforce the properties of composites is extremely cost effective and constitutes a relevant solution. Large deposits of valuable protein, amino acids, mineral compounds contained in the keratin and collagen waste from leather industry can have an influence not only on improving the properties of the obtained materials but also, after the end of their service life, help the obtained composites become more easily assimilated into the natural environment. We expected the protein hydrolyzates and PVAL incorporation into the elastomer matrix to improve the properties of the obtained composites. Such improvements were observed in many of our earlier works [1—3, 15, 16].

T a b l e 2. The influence of waste protein hydrolyzates and PVAL on the rheometric properties of XNBR compounds

Rheometric property	X	XP	XPHK	XPHC	XPHKC
L_{min}, dNm	8	9	13	13	13
ΔL, dNm	60	114	113	101	105
$\tau_{0.2}$, min	2.0	2.1	1.0	1.4	1.3
τ_{90}, min	20	22	20	21	21

L_{min} — minimal torque moment, ΔL — the increase of torque moment, $\tau_{0.2}$ — scorch time, τ_{90} — time of vulcanization.

The effect of hydrolyzates and mixture of hydrolyzates on crosslinking kinetics of XNBR elastomer compounds is shown in Table 2. Unfortunately, the incorporation of the keratin and collagen hydrolyzates with PVAL into the structure of XNBR resulted in an increase in viscosity of the blends shown by the growth of minimum torques of XNBR compounds with the exception of sample X — a much lower increment of torque than others. But on the other hand, the presence of multifunctional fillers like protein hydrolyzates resulted in a clear shortening of the scorch time ($\tau_{0.2}$) — by almost half without negatively altering the optimal vulcanization time (τ_{90}), which is beneficial for the technological process. Figures 3 and 4 show the effect of natural fillers — enzymatic hydrolyzate of keratin and collagen — on the cross-linking density of the obtained protein-elastomeric materials.

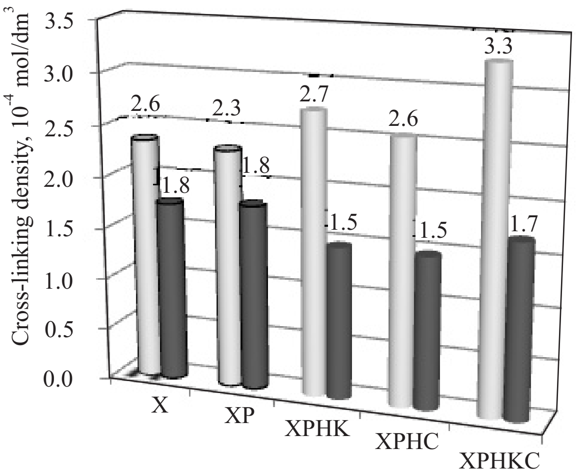

Fig. 3. The effect of hydrolyzates and PVAL on the cross-link density of XNBR vulcanizates: ■ ν^T — cross-linking of density in toluene, ■ $\nu^{T/NH3}$ — cross-linking of density in toluene and ammonia vapor

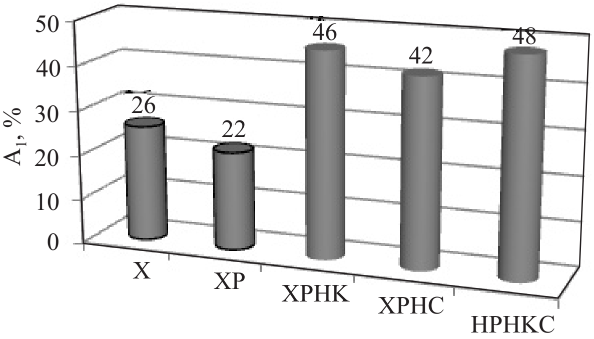

Fig. 4. The effect of waste hydrolyzates and PVAL on the percentage content of the ion lattice points decomposing under the influence of ammonia (A_1) of XNBR vulcanizates

Regardless of the type of filler used, the cross-linking density determined on the basis of equilibrium swelling in toluene (ν^T) is higher than for the unfilled composites XP or X (Fig. 3). In the case of the protein hydrolyzate the number of ionic nodes formed is higher than that found in unfilled XNBR vulcanizates (X and XP) (Fig. 4), as confirmed by the percentage content of the nodes of network decomposed under the influence of ammonia vapors (A_1). The introduction of PVAL into the elastomer structure (XP) resulted in a slightly lower number of ionic nodes compared to composite X. In general, the ionic node connections are created for keratin and collagen compound XPHKC. On the other hand, in the case of the unfilled elastomers, a considerably lower number of such nodes were formed. This may be due to the fact that the polymer has a strong affinity to the solvent, which increases the yield of rubber cross-linking *i.e.* the number of polymer-polymer bonds. The values of tensile strength are beneficial as they are similar to the value of standard TS_b (X or XP). Slightly higher values of TS_b were obtained in the case of the vulcanizates filled with the enzymatic hydrolyzate of keratin (XPHK) and enzymatic hydrolyzate of collagen (XPHC) (Table 3).

The values of elongation at break (E_b), for the investigated materials, are higher than the E_b value for XP, the

T a b l e 3. The effect of hydrolyzates products and PVAL on the mechanical properties of XNBR composites

Mechanical property	X	XP	XPHK	XPHC	XPHKC
TS_b, MPa	8.05 ± 0.01	7.83 ± 0.02	8.08 ± 0.06	8.09 ± 0.05	6.75 ± 0.04
E_b, %	365 ± 2	250 ± 4	278 ± 6	301 ± 3	258 ± 6
H, °Sh	58.2 ± 0.3	64.7 ± 0.7	69.1 ± 0.4	69.2 ± 0.3	67.4 ± 0.4

TS_b — tensile of the strength, E_b — elongation at the break, H — hardness.

Table 4. Effect of hydrolyzed proteins and keratin/collagen hydrolyzate compounds on the thermo-oxidative aging process of XNBR vulcanizates

Property	X	XP	XPHK	XPHC	XPHKC
S [-]	0.60 ± 0.05	0.29 ±0.01	0.70 ± 0.05	0.68 ± 0.03	0.68 ± 0.04
Δ*E* · ab [-]	5.02 ± 0.10	4.99 ± 0.41	0.42 ± 0.03	2.01 ± 0.11	1.32 ± 0. 08
H,°Sh	60.00 ± 0.34	68.00 ± 0.27	74.50 ± 0.11	72.90 ± 0.09	77.20 ± 0.13

S — aging coefficient [-], Δ*E* · ab — the color coefficient [-], *H* — hardness [°Sh].

exception is X. Nevertheless, the obtained values indicate the possibilities of utilizing waste from the tanning industry in the form of modified, multifunctional fillers. The application of PVAL does not preferably influence the mechanical properties of elastomers with natural fillers. The value of determined Shore's hardness (Table 3) shows that the incorporation of waste hydrolyzates into the structure of the elastomer considerably increased this parameter in relation to that of the XP standard. This may be due to the processes that occur during protein hydrolysis, such as self-cross-linking of amino acids: cysteine and lysine formed in this reaction with dehydrated alanine to form lanthionine. Then, stable covalent crosswise bonds that decisively contribute to the increase in chemical resistance of the whole keratin and collagen structure are formed. The application of PVAL, thanks to its structure and characteristics, essentially affects the increase in hardness of the obtained XNBR materials. Subsequently, the enzymatic hydrolyzates of collagen and keratin can lead to a reduced motion of macromolecules in the elastomeric matrix, resulting in structure stiffening as confirmed by the changes occurring in the absorption bands of FT-IR spectra of the composites under investigation. The FT-IR analysis of the vulcanizates of carboxylated butadiene-acrylonitrile rubber (Fig. 5) shows the relationship between the elastomer and the incorporated modified protein.

The changes that took place in the structure of the elastomer after the introduction of the fillers provided a broad, high-intensity band at 1700 — 1500 cm^{-1} in terms of wave number, originating from the hydrolyzates. The band originates from valence asymmetric vibrations of the carbonyl groups C=O. Carboxyl groups, -COOH from XNBR in the spectrum of XNBR composite occur within the wave numbers 1761 — 1732 cm^{-1} and at 1265 cm^{-1}. Explicit changes as a result of the introduction of hydrolyzates observed in the spectra at 1196 — 900 cm^{-1} can indicate the formation of ionic bonds between rubber and hydrolyzate fragments, *i.e.* between –COO- and $–NH_3^+$ groups. At 605 — 632 cm^{-1}, the bands derived from covalent bonds and from butadiene groups (C=C) of cis conformation (C=C) can be observed. The incorporation of natural fillers into XNBR increased the resistance of this elastomer to thermal aging (Table 4), especially in the case of XPHK. The modified keratin and collagen contributed to these processes. The heating of proteins — their hydrolysis below 100 °C — lead to self-degradation to amino-acids such as cysteine, alanine. Table 4 shows the

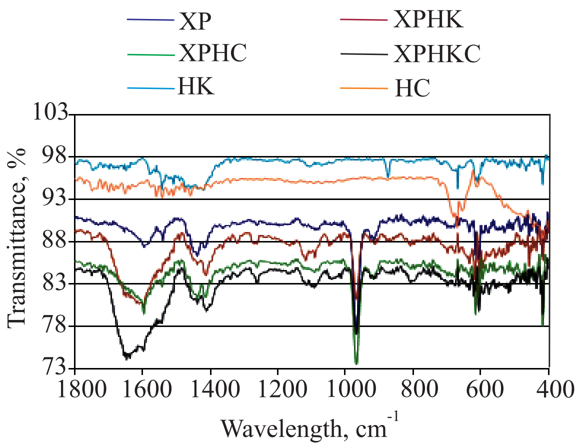

Fig. 5. FT-IR spectra of hydrolyzate — elastomer materials

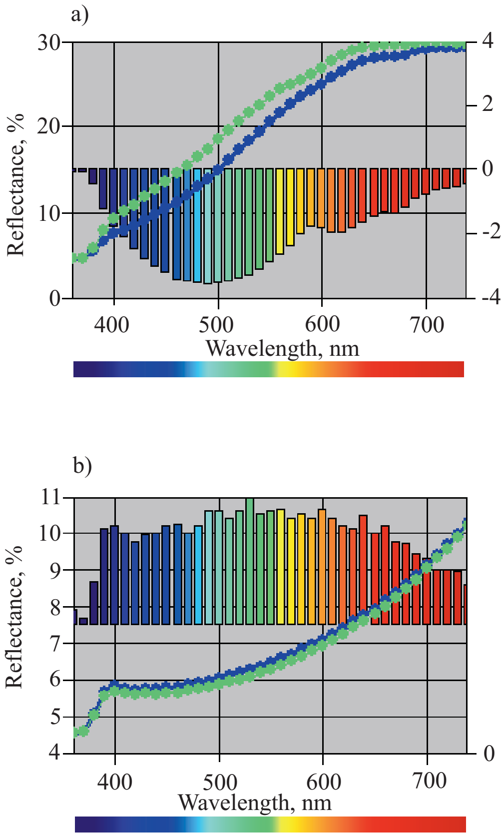

Fig. 6. The reflectometric spectra of the vulcanizates: a) standard (XP) before and after the aging process, b) sample with hydrolyzate of keratin (XPHK) before and after the aging process

Table 5. The effect of biocomponents on the surface and equilibrium swelling in water (Q_w) XNBR composites

	XP	XPHK	XPHC	XPHKC
Before Soil Test				
After Soil Test				
Q_w [-]	0.076 ± 0.002	0.389 ± 0.004	0.314 ± 0.003	0.642 ± 0.011

highest resistance to accelerated thermo-oxidative aging for hydrolyzate-filled composites. This is due to the fact that, after the hydrolysis process, more –SH groups of antioxidative character were formed, compared with the unfilled materials (X or XP). Hence, one may assume that, during the vulcanization processes, bonds of antioxidative character can be formed between the incorporated hydrolyzates and the remaining components of the rubber compound. The greatest protection of the color is shown by vulcanizates containing natural fillers and PVAL. The $\Delta E \cdot ab$ coefficient for those samples reached the lowest value of all the composites. The reflectometric spectrum of the reference sample (XP) and the sample containing the protein hydrolyzates (XPHK) are shown in Fig. 6. The overlap of the curves on reflectometric spectrum is considerably better in the case of the XPHK composite than XP, providing greater protection of the color of composites filled with hydrolyzates against UV-Vis radiation.

After the thirty-day incubation of samples in universal soil, vulcanizates containing natural biopolymers lose their color protection properties because the protein is degraded in soil during the biodecomposition process (by biotic factors in the environment) (Table 5). The most vulnerable polymers, under the action of soil microorganisms, were proven to be the composites that contain an enzymatic hydrolyzate of keratin (XPHK) and the mixture of hydrolyzates (XPHKC). Their surface was discolored, appearing blotchy and uneven. Due to the fact that the obtained hydrolyzates have a hydrophilic nature, therefore, its equilibrium swelling in water (Q_w) increases significantly compared with unfilled samples, leading to a much easier transport of enzymes accelerating the deterioration of the structure of these materials. Consequently, a faster biodecomposition of these materials in the environment can be expected.

CONCLUSIONS

The introduction of the enzymatic hydrolyzates of keratin, collagen and PVAL into the elastomeric matrix improves the rheological properties and cross-linking density of the obtained composites. The protein-elastomer composites are characterized by good rheological properties: the increased value of torque testifies to better cross-linking as confirmed by the cross-linking density, determined on the basis of equilibrium swelling in toluene and by a higher value of the hardness parameter.

The introduction of PVAL and bioadditives did not significantly affect the improvement of the tensile strength but positive effects are visible in the FT-IR spectra. New bands, band shifts or a partial appearance in FT-IR spectra seem to testify to the formation of interactions between the elastomer and the biopolymers. All vulcanizates subjected to the thermo-oxidative aging process, containing keratin, collagen, mix of hydrolyzates and PVAL filler, were characterized by a better resistance to the change of color in comparison to the unfilled material (XP). Water penetrates the composite structure through the hydration and swelling of biofillers, facilitating the transport of enzymes and faster biodecomposition of the composites after their exploitation life. This biodecomposition is additionally confirmed by the microbiological analysis showing a clear discoloration and irregularities in their surface and pinholes. All these changes point to the lack of a fungistatic effect and a great susceptibility of the vulcanizates filled with the enzymatic hydrolyzates of keratin (HK) and collagen (HC) to the action of soil microorganisms. The introduction of the HK or HC into the elastomeric rubber matrix has an effect on the creation of a common network of macromolecules along with the elastomer and other components of the mixture. Thanks to the accelerated degradation of the biopolymer itself in the biodecomposition process, the loss of cohesion of the polymer network and faster biodecomposition of the entire composite results as a consequence.

These materials can be applied as gaskets, mats *etc*., and other elements working in non-polar environments of solvents, oils, greases *etc*. However, after the service life of these materials, in a dumping ground as waste, they will be more susceptible to, and quickly undergo, biodecomposition in comparison to materials that do not include protein components.

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