

Thermal properties and combustibility of elastomer–protein composites

Part I. Composites SBR—keratin

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Abstract The article describes the measurements results of the influence of waste keratin on the properties of cross-linked styrene-butadiene rubber especially taking its thermal properties and flammability into consideration. The bio-polymer used was thoroughly examined by means of derivatography, elementary analysis, FTIR spectroscopy, Zetasizer nano S90, and Zetasizer 2000. It has been found that the presence of protein facilitates the cross-linking of the elastomer investigated and the elastomeric-protein materials are characterized by good thermal and mechanical properties as well as a considerably increased resistance to thermooxidative aging. Under the influence of keratin, the flammability of the composites obtained is decreased.

Keywords Thermal analysis · Thermal stability · Combustibility · Elastomers · Keratin · Protein · Elastomer–protein composites

Introduction

Most polymeric materials are characterized by a high flammability depending on both the type of polymer and the remaining components of the blend. In order to reduce the flammability of polymers and polymeric materials, there

used various additives known as flame-retardant compounds. A flame-retardant agent should be compatible with the polymer in question, its thermal decomposition temperature should be similar to that of the macromolecular compound and its presence should exert no adverse effect on the polymer functional properties [1–5]. Currently used flame-retardant compounds contain elements such as: Cl, Br, P, B, Sb, Mo, and N. They should be environmentally friendly and capable of effectively reducing the emission of fume and toxic or chemical aggressive volatile products during the combustion of polymeric materials [6–8]. In recent years, a considerable attention has been paid to polymeric nanocomposites because they show a higher thermal stability, a lower flammability, and smaller fire hazard compared to conventional polymeric blends [9]. Polymeric composites containing fillers of nanometric dimensions are made from both thermoplastic and thermosetting polymers. The function of fillers is most frequently fulfilled by various types of laminar silicates, inorganic compounds, and fullerenes or nanotubes [10, 11]. Although the preparation of primary particles of nanometric dimensions presents no major difficulties, it is of significant importance to select appropriate chemical compounds to prevent their aggregation and agglomeration. The aggregates of microscopic dimensions are not completely decomposed during mixing filler with a polymer even in the field of high shearing stresses [12, 13]. Rong et al. [14] have prevented the formation of silica particle aggregates in a polymeric matrix by grafting various monomers on 7 nm silica particles.

From the review of literature, it follows that keratin can be used as a filler of polymeric blends [15–18]. Keratin is a protein resistant to the action of many chemical agents and physical factors. The thermal decomposition of most protein, including keratin, ranges from 50 to about 200 °C. The heating of keratin results in structural changes at a

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temperature of about 130 °C (in an aqueous medium), while at higher temperatures, e.g., 200 °C, amino acids are decomposed. Popescu and Wortmann [19] examined the behavior of keratin at a high temperature. The explanation of the high thermal stability of keratin lies in the structure of its macromolecule. DSC measurements have shown that the denaturation of dry keratin proceeds within the temperature range of 230–240 °C. If keratin contains water, its denaturation temperature is decreased. Based on kinetic investigation and chemical analysis, it has been found that in the alpha-helices of keratin-containing water, at first the S–S bonds of cystine are split, while in the alpha-helices of dry keratin, a controlled pyrolysis process takes place.

From the patent specification [15], it follows that the incorporation of keratin as a filler into rubber blends used to make winter tire treads beneficially influences the tire adherence under various conditions on roads. Keratin was incorporated to styrene-butadiene rubber (SBR) in the form of a mixture with carbon black in amounts from 1 to 20 parts by weight. The results obtained were compared with those of vulcanizates containing only carbon black as filler and there was found an improvement in breaking on an ice-covered road surface.

Loreth [16] has published a patent specification concerning the use of coconut-keratin fiber mixtures a component of winter tire treads. The mixture consisted of cellulose fibers (cotton or coconut) and keratin (wool or fur) in a proportion from 1:5 to 5:1. It was incorporated to SBR in a quantity from 2 to 25 parts by weight. The use of this solution resulted in an improvement in winter tire traction by over 12% compared to that of tire tread with a conventional composition.

The presence of keratin improves the mechanical properties of composites [17], which probably results from the formation of a common spatial network between keratin and elastomer. Similar interactions were observed when keratin was incorporated into carboxylated butadiene-acrylonitrile rubber [18]. The incorporation of five parts by weight of keratin with ZnO into elastomer matrix increased the density of cross-linking, improved mechanical properties, resistance to thermal aging and many other properties of elastomeric materials containing this biopolymer. Elastomer–protein compositions show also very significant properties from the ecological point of view as they have an increased susceptibility to biodecomposition after their working life.

The aim of this study was to assess the effect of waste keratin as filler of the compositions of butadiene-styrene, on their properties, especially thermal stability and flammability. Zinc oxide and nanozinc oxide were used as vulcanization activators of the cross-linking of elastomer–protein compositions.

Experimental

The object of this study was keratin (K) recovered from the influents of tanning industry (Kalisz Tannery Plant) derived from liming and depilation of cow hides with hair structure preserved. Keratin was released from tannery wastes followed by drying, disintegration, and powdered, while the powder obtained was sieved through a screen with a mesh diameter of 0.1 mm.

Biopolymer was characterized by

- FTIR spectroscopy by spectrophotometr Bio-Rad FTIR 175C, with a microscope attachment SPLIT,
- elementary analysis: sulfur and nitrogen determined in Molecular and Macromolecular Center of Research PAN in Lodz,
- measurement particle of size, by the technique of dynamic light scattering using Zetasizer nano S90,
- measurement of potential Zeta by Zetasizer 2000.

Under investigation, there was also styrene-butadiene rubber (Ker 1500, containing 23.5% of styrene mers, product of Synthos S.A.) cross-linked with the use of elementary sulfur (1.5 parts by weight) with a vulcanization accelerator *N*-cyclohexyl-2-bezoylsulfenamide, Tioheksam CBS (2 parts by wt.) in the presence of

- zinc oxide, ZnO (five parts by wt.)—vulcanizate denoted with SBR,
- nanometric zinc oxide, nZnO (one part by wt.)—vulcanizate denoted with nSBR,

as vulcanization activator and stearic acid (one part by wt.).

ZnO is a product from Huta Oława, first class, surface area 5–7 m²/g and particle size 0.1–0.9 μm and nanometric ZnO (nZnO)—from Nanostructured & Amorphous Materials Inc. (USA) surface area 50 m²/g and particle size 130–165 nm, spherical morphology.

Keratin, K, used as a filler, was incorporated into elastomer in a quantity of 5 and 10 parts by weight per 100 parts by weight of rubber. The composites containing keratin were designated with the following symbols: SBR5K, SBR10K (with ZnO), and nSBR5K, nSBR10K (with nZnO), respectively.

Rubber mixtures prepared with the use of a laboratory rolling mill at room temperature were vulcanized in an electrically heated press shelves at 160 °C for vulcanization time. Vulcanization time τ_{90} and increase of torque ΔL :

$$\Delta L = L_H - L_L$$

where L_L is the minimum of torque and L_H is the maximum of torque were determined according to the standard PN-ISO 3417:1994.

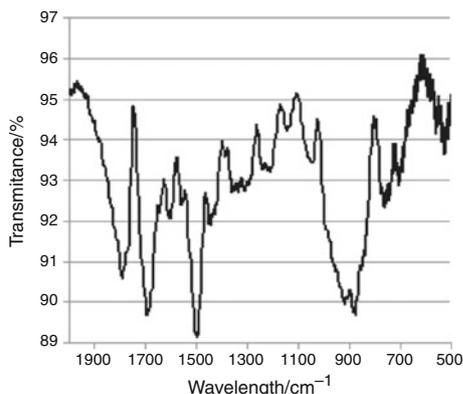


Fig. 1 FTIR spectrum of keratin

The cross-linking degree of composites, $\alpha_c = 1/Q_w$, was determined according to equilibrium swelling Q_w in toluene (PN-ISO 817:2001/ap1:2002).

The mechanical properties of tested composites were tested according to 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 thermooxidative aging (TS_{b2} and E_{b2}).

The thermooxidative aging resistance was investigated according to the standard PN-88/C-04207. The aging coefficient, S , was determined from the following relationship:

$$S = \frac{TS_{b1} \cdot E_{b1}}{TS_{b2} \cdot E_{b2}}$$

Fig. 2 The size of keratin particles

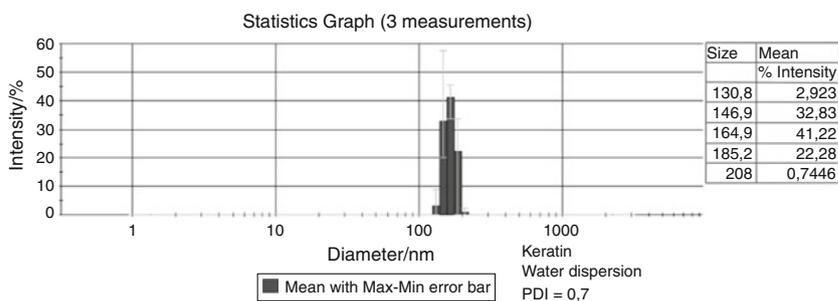
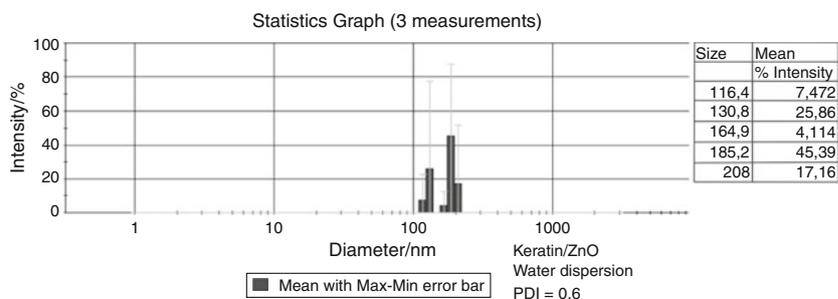


Fig. 3 The size of keratin particles mixed with ZnO



The thermal analysis was performed under air atmosphere. 90 mg samples were heated in a Paulik, Paulik, Erdey derivatograph furnace at a heating rate of 7.9 °C/min within the temperature from 20 to 800 °C using Al₂O₃ as a reference substance. Thermal curves sensitivities were as follows: TG = 100, DTA = 1/5, and DTG = 1/20.

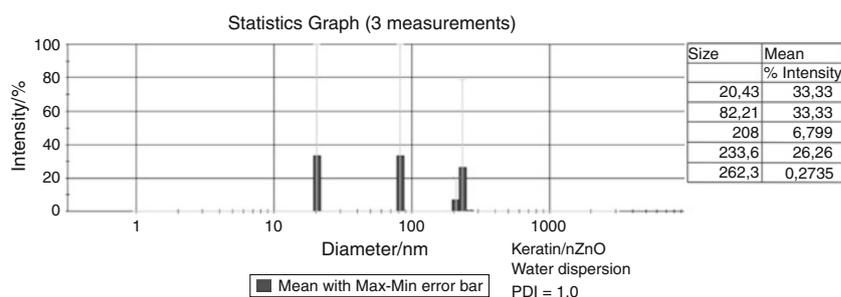
The flammability of vulcanizates was determined by the method of oxygen index using an apparatus of our own construction [20]. The flammability was also assessed on the basis of sample combustion time under air or time, after which the sample was extinguished. The sample shape and dimensions, its arrangement, and flame treatment time were the same as in the case of the oxygen index method (PN-ISO 4589-2).

Results and discussion

Waste keratin, K, was examined by means of elementary analysis, particle size, thermal analysis, Zeta potential, and IR spectroscopy.

The presented absorption maxima confirm the presence of characteristic bands derived from peptide bonds of cattle hair keratin (Fig. 1). The typical bands characteristic of proteins, showing maxima derived from the vibration of primary, secondary, and tertiary amides within the range of wavelength 1698–1250 cm⁻¹. The bands of S–S and C–S bonds indicate the presence of cysteine and cystine in the protein investigated within the range of 1030–810 and 536–776 cm⁻¹ (Fig. 1).

Fig. 4 The size of keratin particles mixed with nZnO



Ninety-six percent of the keratin particles tested have a size ranging from 146 to 185 nm (Fig. 2). After mixing with zinc oxide, nearly 100% of Keratin/ZnO particles had dimensions from 116 to 208 nm (Fig. 3). The mixing of keratin with nanometric zinc oxide, Keratin/nZnO (Fig. 4), resulted in a fraction with dimensions from 20 to 82 nm (66% of particles) and the remaining portion of particles showed dimensions from 208 to 262 nm (33%). The decrease in keratin particle dimensions as a result of mixing with nZnO should improve the dispersion of components in the elastomeric matrix and consequently also the properties of the material obtained.

The isoelectric point of keratin is at pH 4.1, while after mixing keratin with ZnO or nZnO, it was slightly shifted toward more acidic pH values (Table 1).

Keratin contains 2.26% of sulfur (Table 1) derived from cysteine and methionine amino acids. Sulfur not only can facilitate the cross-linking processes but also can increase the resistance of the elastomeric materials to accelerated thermal aging. The presence of 15% of nitrogen in keratin (Table 1)—an element belonging to the group of flame-retardant agents—should reduce the flammability of the elastomeric materials containing this biopolymer. Both the high nitrogen content in the keratin of cattle hair and the high values of keratin thermal stability (Table 1) should

contribute to a reduction in the flammability of the keratin-containing vulcanizates.

The results of thermal analysis under air have shown that the waste keratin, K, used contains 4.4% of physical combined water (Table 1) and therefore its weight loss begins at a temperature of 50 °C (Fig. 5). The thermal decomposition of keratin takes place at $T = 210$ °C and proceeds in two stages as shown by two exothermic processes recorded in DTA curve at $T = 310$ °C and $T = 510$ °C, respectively (Fig. 5). From the literature review [9], it follows that the first stage is connected with the protein denaturation. The second stage, beginning at $T = 360$ °C results in a total destruction of protein. The residue after keratin thermal decomposition amounts to 10.5%. The results of the derivatographic analysis of keratin indicate that it is a protein resistant to the action of

Table 1 Characteristic of keratin

Research	Keratin
Content of mineral/%	$S = 2.26$ $N = 15.00$
Content of physical combined water/%	4.4
Thermal resistance/°C	
T_5	220
T_{50}	510
P_{800}	63
Isoelectric point IEP	
Keratin	pH = 4.1
Keratin/ZnO	pH = 3.4
Keratin/nZnO	pH = 3.4

T_5 temperature of 5% mass loss, T_{50} temperature of 50% mass loss, P_{800} residue after heating up to 800 °C

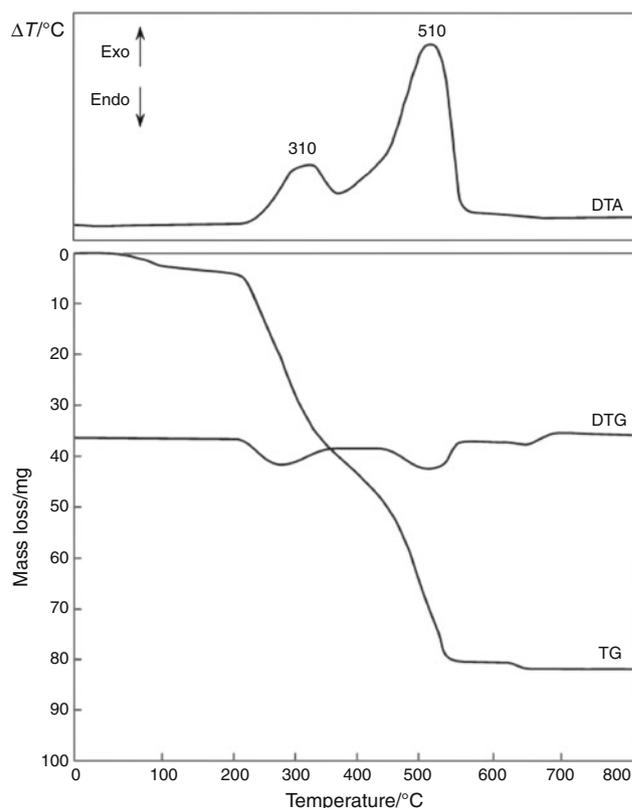


Fig. 5 Thermal curves (DTA, TG, and DTG) of keratine

elevated temperature. The indices of its thermal stability amount to $T_5 = 210\text{ }^\circ\text{C}$ and $T_{50} = 410\text{ }^\circ\text{C}$ (Table 1).

The analysis of FTIR spectra of SBR and nSBR vulcanizates showed changes in the intensity of the absorption maxima resulting from the incorporation of keratin into the structure of the elastomer tested (Fig. 6). The changes in band intensities at wavelength 1545 cm^{-1} (vibration from butadiene mers with addition 1.2), 970 cm^{-1} ($\text{C}=\text{C}_{\text{trans}}$), and 700 cm^{-1} (vibration from styrene ring) indicate the formation of a common network between keratin and elastomer as shown by our earlier examinations [18].

From the data given in Table 2, it follows that the lowest minimal torque, L_L , i.e., the lowest viscosity is shown by the composites containing no filler—SBR and nSBR. The value of torque increment, ΔL , connected with the yield of the cross-linking of composites is considerably higher in the case of composites containing keratin and ZnO, SBR5K, and SBR10K. These blends are also characterized by a shortened optimal vulcanization time, τ_{09} , which is a beneficial factor from the economic point of view. The test results also indicate the beneficial influence of keratin on the yield of the cross-linking of SBR blends containing nZnO, nSBR5K, and nSBR10K. Thus, the addition of keratin improves the strength parameters of the vulcanizates obtained (Table 2). In addition, the size of filler particles also testifies to it.

Regardless of the type of zinc oxide, the addition of keratin clearly increases the degree of the cross-linking, α_c , of SBR (Table 2). Under the influence of ZnO with the increase in α_c the content of sol, Z , in the swollen sample is decreased, which indicates that the components are better combined with the elastomeric matrix in the case of vulcanizates containing keratin, SBR5K and SBR10K, compared with the vulcanizates without keratin, SBR (Table 2).

Considering the mechanical properties of elastomeric materials, the incorporation of nanometric zinc oxide, nZnO, exerts a disadvantageous influence on them because it decreases their tensile strength, TS_b (Table 2). On the other hand, the use of zinc oxide, ZnO, in a quantity of 10 parts by weight of keratin clearly increases TS_b , which may result from the formation of a common network between the polymeric matrix and protein. The elongation at break, E_b , of the vulcanizates filled with keratin decreases, which seems to be due to the increase in the cross-linking degree of the elastomer (Table 2).

As already mentioned, keratin, thanks to the presence of some amino acids (cysteine, methionine), is characterized by antioxidative properties and therefore there is observed a considerable improvement in the resistance of keratin-containing SBR to accelerated thermooxidative aging as indicated by the increase in the aging coefficient,

Fig. 6 FTIR spectrum of nSBR vulcanizates

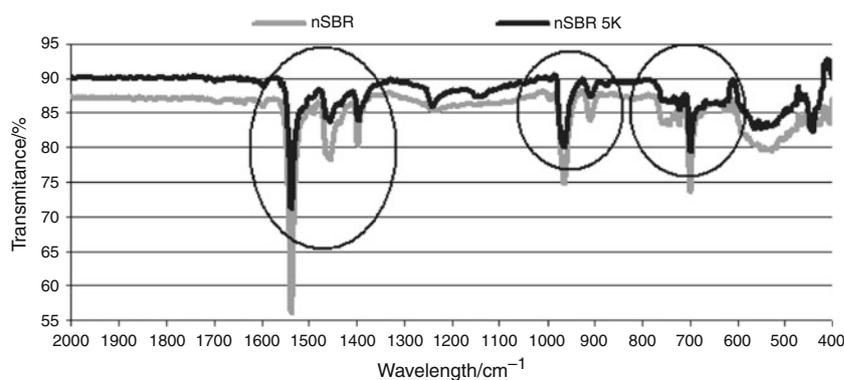


Table 2 Effect of keratin on rubber compounds parameters

Sample	L_L/dNm	$\Delta L/\text{dNm}$	τ_{09}/min	α_c	$Z/\%$	TS_b/MPa	$E_b/\%$	S	$Z_{\text{H}_2\text{O}}/\%$
SBR	17	91	20	0.22	9.3	2.37	364	0.72	1.83
SBR5K	19	143	10	0.32	8.0	2.36	141	0.96	1.98
SBR10K	21	141	10	0.33	6.9	2.58	134	0.98	2.92
nSBR	16	121	10	0.27	9.1	2.11	203	1.14	1.50
nSBR5K	18	124	10	0.34	17.7	1.52	156	1.41	2.67
nSBR10K	20	127	10	0.34	19.9	1.44	145	1.41	3.11

SBR sulfur vulcanizate with ZnO, SBR5K/SBR10K SBR vulcanizate containing 5/10 parts by weight of keratin, nSBR sulfur vulcanizate with nZnO, nSBR5K/nSBR10K nSBR vulcanizate containing 5/10 parts by weight of keratin, L_L minimum of torque, ΔL increase of torque, τ_{09} vulcanization time, α_c cross-linking degree, Z content of sol, TS_b tensile strength at break, E_b elongation at break, S aging coefficient, $Z_{\text{H}_2\text{O}}$ content of water sorption

S (Table 2) [18, 23]. This is probably due to the sulfur links that during aging can be converted into groups of antioxidative character such as thiol groups or sulfonic acid radicals. A particular increase in the resistance to thermo-oxidative aging was shown by the elastomer–protein composites cross-linked in the presence of nZnO.

The elastomer–protein composites obtained show an increased water sorption, especially in the case of nanocomposites nSBR5K and nSBR10K (Table 2). The water adsorbed facilitates the transport of enzymes, which accelerates the biodecomposition of these composites in the environment after their exploitation.

Under the influence of heating, the butadiene-styrene rubber vulcanized with sulfur, SBR, is thermally cross-linked within two temperature ranges: $\Delta T_1 = 220\text{--}290\text{ }^\circ\text{C}$ and $\Delta T_2 = 300\text{--}355\text{ }^\circ\text{C}$ (Fig. 7). The cross-linking in the lower temperature range proceeds due to the decomposition of hydroperoxide groups contained in the elastomer and formed in it during heating [21, 22]. At ΔT_2 , cross-linking takes place due to the cross-polymerization of butadiene units contained in the elastomer macromolecules, which is accompanied by the fragmentation of chains and formation of low quantities of volatile products of their thermal decomposition (Fig. 7). At $T \sim 360\text{ }^\circ\text{C}$, an intensive

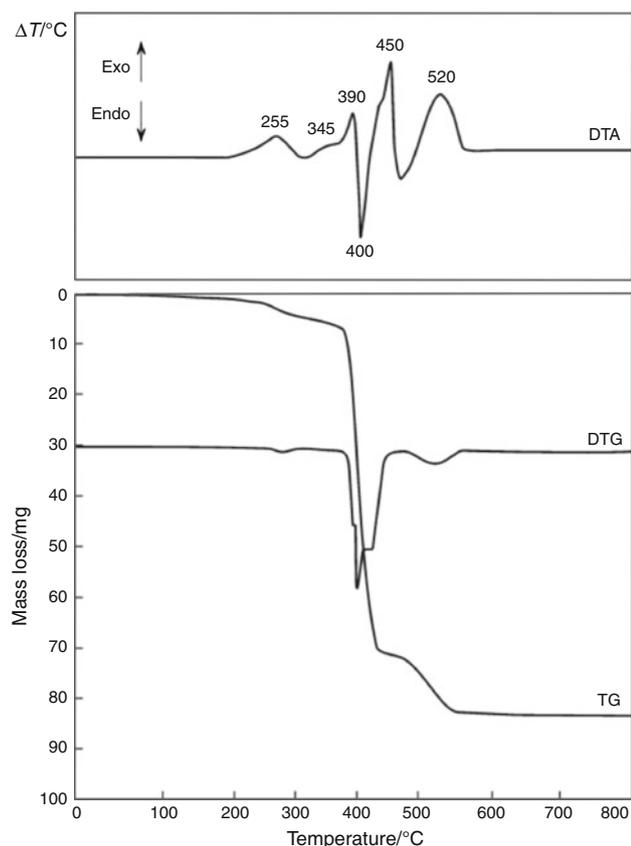


Fig. 7 Thermal curves (DTA, TG, and DTG) of SBR

thermal decomposition of elastomer begins, while the residue after this process is combusted as shown by the exothermic peak recorded in DTA curve at $T = 520\text{ }^\circ\text{C}$. The use of nZnO in the vulcanization of elastomer, nSBR sample, facilitate the processes of its thermal exothermic decomposition (Fig. 8), which is accompanied by a rapid increase in these processes and a decrease in the residue, P_w , after their finishing (Table 3). The vulcanizates containing waste keratin, regardless of the type of zinc oxide, undergo endothermic decomposition under air (Figs. 9, 10).

The tests of thermal properties show that under the influence of keratin the thermal stability of vulcanizates

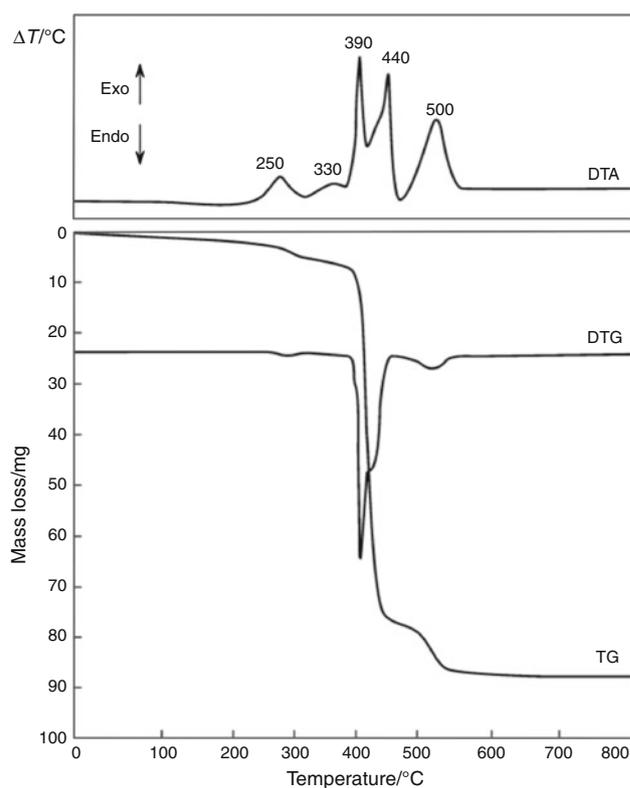


Fig. 8 Thermal curves (DTA, TG, and DTG) of nSBR

Table 3 Thermal properties of elastomer and its composites

Sample	$T_5/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$dm/dt/\text{mm}$	$P_w/\%$	$T_s/^\circ\text{C}$
SBR	300	405	56	21	520
SBR5K	255	400	53	21	505
SBR10K	250	400	49	22	500
nSBR	290	400	81	15	500
nSBR5K	235	395	47	17	505
nSBR10K	250	405	39	21	515

T_5 temperature of vulcanizate 5% mass loss, T_{50} temperature of vulcanizate 50% mass loss, dm/dt maximum rate of vulcanizate thermal decomposition, P_w residue after vulcanizate thermal decomposition, T_s maximum combustion temperature of residue after vulcanizate thermal decomposition

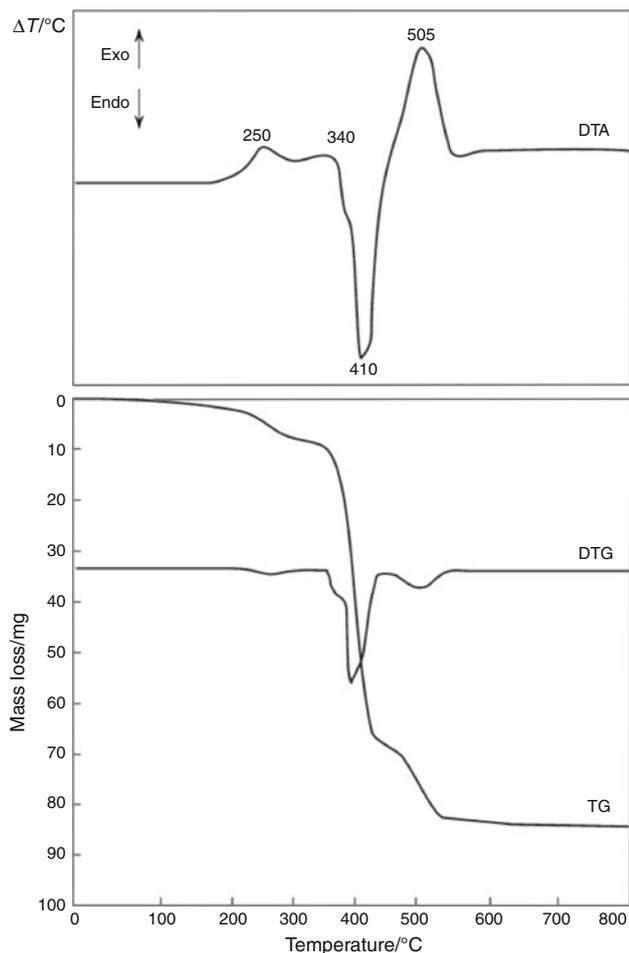


Fig. 9 Thermal curves (DTA, TG, and DTG) of SBR5K

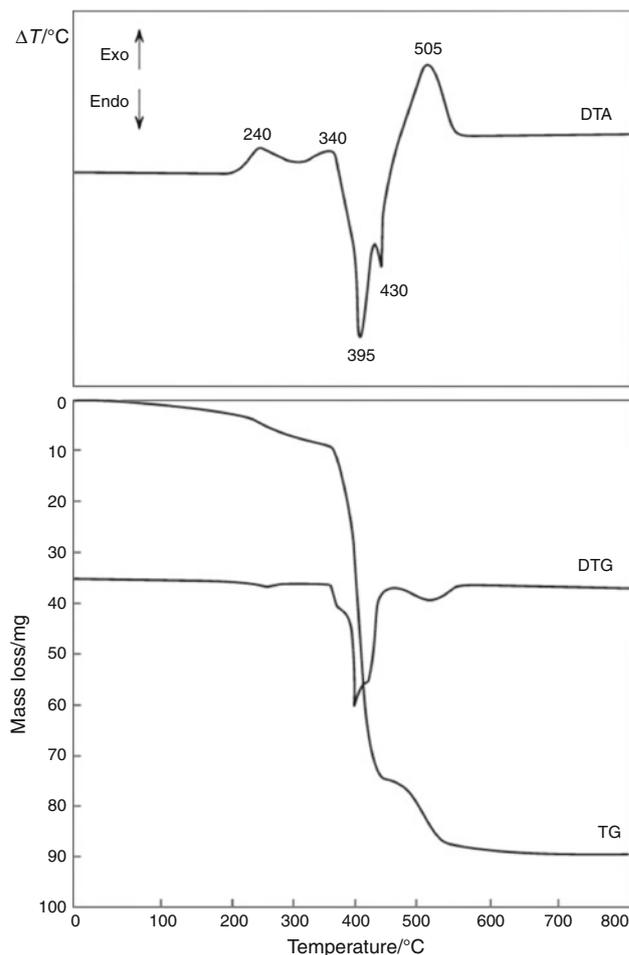


Fig. 10 Thermal curves (DTA, TG, and DTG) of nSBR5K

determined with the values of T_5 is decreased (Table 3). The presence of keratin does not exert any significant effect on the value of coefficient T_{50} but it brings about a considerable decrease in the thermal decomposition rate, dm/dt , of the elastomeric materials tested. This effect is particularly clear in the case of using nZnO in the cross-linking processes of elastomers, nSBR5K, and nSBR10K. The process of decreasing the destruction rate is accompanied by a greater residue after the thermal decomposition of vulcanizate, P_w (Table 3). Both thermal stability parameters, dm/dt and P_w , exert a significant influence on the decrease in vulcanizate flammability. They show that a lower quantity of volatile and flammable products of polymer destruction passes to flame as confirmed by the results of testing the flammability of the vulcanizates obtained. They also show that with the increase in the quantity of protein incorporated into SBR their oxygen index, OI, increases and their combustion time in air, t , is clearly prolonged (Table 4).

The decrease in the flammability of elastomeric materials containing keratin (Table 4) results also from nitrogen

and sulfur contained in it (Table 1). In this connection, during the combustion of the vulcanized filled with this protein, there are formed inflammable gases such as N_2 and SO_2 , which pass to flame and decrease the concentration of flammable gases. This leads to the reduction in the chain combustion reactions. The emission of inflammable destruction products impedes the diffusion of oxygen to the gaseous combustion zone and so to the flame.

Table 4 Combustibility of elastomer and its composites

Sample	t/s	OI
SBR	283	0.220
SBR5K	317	0.231
SBR10K	335	0.245
nSBR	226	0.216
nSBR5K	243	0.237
nSBR10K	345	0.252

t time of burning in air, OI oxygen index

Conclusions

Regardless of the type of zinc oxide used, the presence of keratin facilitates the cross-linking of SBR rubber by means of sulfur. The cross-linking of SBR in the presence of ZnO and waste keratin beneficially influences its mechanical properties. Under the influence of keratin, the resistance of the sulfur vulcanizates of SBR rubber to accelerated thermooxidative aging is increased.

Regardless of the type of zinc oxide, the waste keratin added decreases the rate of the thermooxidative decomposition of cross-linked SBR. The flammability of the sulfur vulcanizates of SBR rubber containing keratin is considerably lower than that of the unfilled vulcanizates.

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