Thermal properties and combustibility of elastomer–protein composites

Part II. Composites NBR–keratin

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Abstract This article presents the test results of thermal properties and flammability of crosslinked nitrile rubber in the presence of zinc oxide or nano-zinc oxide containing waste keratin, using the test results obtained by means of a derivatograph, DSC, and oxygen index. The influence of modified montmorillonite (NanoBent) on selected properties of investigated elastomer–protein composites has also been studied. The composites' thermal stability and flammability depend on the method of composite preparation and the quantity of added keratin. The addition of waste keratin reduces the flammability of NBR–keratin composites.

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

Introduction

Elastomers and materials made of them are commonly used in various spheres of life. Despite numerous ecological restrictions and considerable amounts of process and post-consumer wastes produced, often being difficult to manage, the world production and consumption of elastomers and related products have been systematically increasing since 2002 [1]. In this connection, studies concerning the effects of the composition of polymeric blends, mostly multicomponent products, on the properties of materials made of them

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are continually up to date and very important issue in both cognitive and practical terms. In recent years, one has observed a greatly increased interest in elastomeric materials with special properties, resistant to the action of both considerably lowered and elevated temperatures, flame-retardant, and characterized by appropriate mechanical strength. Of particular importance is a reduction in the flammability of polymeric materials because of serious health and live hazards posed by products emitted during fires as well as repeatedly huge material losses. Therefore, much attention has been paid to processes proceeding at elevated temperature and phenomena accompanying combustion, such as flame and glow propagation, heat emission, toxic substance formation, and smoke emission. Recently, a rapid development in the manufacturing field of new polymeric materials such as polymer nanocomposites has been observed [2–8]. The reduction achieved in the size of compound particles incorporated into a polymeric matrix from micrometers to nanometers enables us to obtain composites with better, often new properties [9, 10]. Commonly used nanofillers included laminar aluminosilicates modified with organic compounds. From a literature review, it follows that nanomaterials containing intercalated montmorillonite show better thermal and strength properties than those filled with conventional fillers. Nanometric dimensions are also shown by the macromolecules of keratin that, according to the scientific literature, can be used as filler of elastomers [11, 12]. Polymeric materials filled with keratin show good functional properties and after their exploitation period, they are bio-decomposed, which is of great importance from the ecological point of view.

This study presents the findings concerning the effect of keratin, derived from environmentally arduous waste from the tanning industry wastes, on the thermal properties and flammability of butadiene–acrylonitrile rubber (NBR)

crosslinked by means of dicumyl peroxide with zinc oxide or nano-zinc oxide as crosslinking activators. Elastomeric-protein materials containing a modified montmorillonite were also examined.

Experimental

Under investigation was a butadiene–acrilonitrile rubber, NBR, (Perbunan 2255VP from Lanxess Deutschland Gmbh, containing 22 % of combined acrilonitrile, average mass particle viscosity $M_v = 268.900$ g/mol, elements content: C = 82.93 %, H = 9.38 %, N = 5.59 %, S = 1.57 %, O = 0.53 %) crosslinked with the use of dicumyl peroxide, DCP (product of Merc-Schuhardt, 0.3 parts by wt.) in the presence of

– zinc oxide, ZnO (5 phr)—sample denoted with N, and
– nanometric zinc oxide, nZnO [13–15] (1 phr)—sample denoted with nN, as vulcanization activator and technical stearine (1 phr).

ZnO is a product from Huta Oława, first class, with surface area 5–7 m^2 g^{-1} and particle size of 0.1–0.9 μm, and na-nometric ZnO (nZnO)—from Nanostructured & Amorphous Materials Inc. (USA), with surface area 50 m^2 g^{-1} and particle size of 130–165 nm, and spherical morphology.

As a filler, we used keratin (K) recovered from Kalisz Tannery Plant (Poland) with average particle size of about 165 nm and the main elements' contents: N = 15.4 % and S = 2.26 % [16]. Keratin was incorporated into elastomer in a quantity of 5, 10, and 30 phr. The composites con-taining keratin were, respectively, designated with the following symbols: N5 K, N10 K (with ZnO), and nN5 K, nN10 K (with nZnO).

Keratin was also incorporated into polymeric blends in the form of a mixture with ZnO prepared by careful rub-bing of both components in a mortar. Composites con-taining the rubbed keratin–ZnO mixture are designated as N5 Kr, N10 Kr, and N30 Kr, respectively.

In addition, montmorillonite NanoBent ZS-1 (ZS) [7], made in Poland, modified with an ammonium salt con-taining OH groups, with an average particle size of 20–60 μm and layer displacement of 3.8–3.9 nm, was incorporated into N5 K blend in a quantity of 5 phr (sample designated as N5 KZS).

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 optimal vulcanization time τ_{90}, determined according to the stan-dard: PN-ISO 3417:1994.

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

Swelling measurements of vulcanizates in water (Q_{H_2O}) lasting for 48 h were carried out in the same way as in the case of swelling in toluene. In addition, water content in the swollen vulcanizates (Z_{H_2O}) was determined.

The mechanical properties of the 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 deter-mine tensile strength and elongation at break before (TS_{b1} and E_{b1}) and after thermal-oxidative aging (TS_{b2} and E_{b2}).

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

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

The measurements of broad-angle X-ray scattering angle (WAXS) in nanocomposites were carried out at room temperature by means of a Philips X-ray apparatus at the Lodz CMMS (Polish Academy of Sciences). Diffraction patterns were recorded within the angle range of $2\Theta = 1$–7°; measurement step 0.05°; measurement time 25 s; radiation Cu Kα ($\lambda = 0.15418$ nm); operation in the transmission mode.

The thermal analysis was preformed as under:

– air atmosphere—90 mg samples were heated in a derivatograph furnace (MOM Budapest) at a heating rate of 7.9 °C min^{-1} within the temperature range from 20 to 800 °C using Al_2O_3 as a reference substance. Thermal curves' sensitivities were as follows: TG = 100, DTA = 1/5, and DTG = 1/20.
– inert atmosphere—by means of differential scanning calorimetry [17] (DSC-204 Netzsh), using portions of about 5 mg at a heating rate of 10 °C min^{-1} within temperature ranges from 20 to −100 and −100 to 500 °C.

The flammability of vulcanizates was determined by the method of oxygen index using an in-house designed apparatus [18]. The flammability was also assessed on the basis of sample combustion time under air, or the time after which the sample was extinguished. The sample's 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

The composition of elastomeric blends exerts a small influence on the duration of their vulcanization time (τ_{90}) at $T = 160$ °C; nevertheless, under the influence of zinc

oxide with nanometric dimensions, the crosslinking of NBR proceeds at slightly slower rate (Table 1). Regardless of the type of zinc oxide used, because of the influence of keratin, the degree of elastomer crosslinking (α_c) increases as well as the swelling of vulcanizate in a hydrophilic solvent such as water (Table 1: Q_{H_2O}, Z_{H_2O}). The increased water absorption of NBR vulcanizates filled with keratin indicates their increased susceptibility to bio-decomposition resulting from facilitated transport of enzymes (Table 1). The elastomer–protein composites show proper mechanical properties; although the increased keratin content causes their deterioration, it exerts no significant effect on the resistance of the materials to thermo-oxidative aging determined by coefficient S (Table 1). A clear improvement in the mechanical properties of the polymeric composites investigated occurs under the influence of the modified montmorillonite incorporated, N5 KZS (Table 1). The results of our study show that the presence of keratin does not impede the intercalation of the nanofiller ZS used by NBR as shown by the weakly marked, single peak in the X-ray curves of N5 KZS and NZS (vulcanizate N containing 5 phr of ZS) (Fig. 1).

The results of derivatographic analysis under air show that the keratin used contains 4.4 % of adsorbed water and is protein resistant to the action of heat at elevated temperature. The indices of its thermal stability, as temperatures of sample 5 and 50 % mass loss, are $T_5 = 210$ °C; and $T_{50} = 410$ °C [16].

Table 1 Influence of keratin on properties of NBR composites and nanocomposites

Sample	$\tau_{90}/$ min	α_C	Q_{H_2O}	$Z_{H_2O}/$ %	$TS_b/$ MPa	$E_b/$ %	S
N	25	0.136	0.014	1.37	7.68	979	0.81
N5 K	35	0.147	0.033	2.15	3.43	728	1.07
N5 Kr	25	0.155	0.034	2.41	3.95	812	0.80
N5 KZS	20	0.140	0.033	2.20	4.53	806	1.03
N10 K	35	0.149	0.048	3.56	2.90	691	1.01
N10 Kr	25	0.146	0.047	3.56	2.35	691	1.23
N30 Kr	35	0.154	0.110	6.69	2.36	667	0.82
nN	30	0.128	0.011	0.93	5.59	895	0.89
nN5 K	35	0.163	0.035	2.59	1.90	350	1.14
nN10 K	30	0.171	0.048	3.69	2.30	714	0.75

N, NBR crosslinked in the presence of ZnO; NxK, vulcanizate N containing x phr of keratin (x = 5, 10); NxKr, vulcanizate containing x phr of rubbed keratin (x = 5, 10, 30); N5 KZS, vulcanizate N5 K containing 5 phr of NanoBent ZS; nN, NBR crosslinked in the presence of nZnO; nNxK, vulcanizate nN containing x phr of keratin (x = 5, 10); τ_{90}, optimal time of vulcanization; α_C, crosslinking degree; Q_{H_2O}, swelling of composites and nanocomposites in water; Z_{H_2O}, water contents after 48-h swelling of composites and nanocomposites in water; TS_b, tensile strength at break; E_b, elongation at break; S, aging coefficient
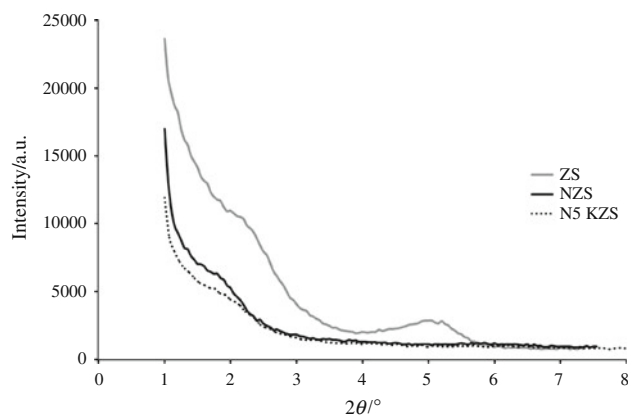

Fig. 1 XRD curves of NanoBent ZS, nanocomposites NZS (vulcanizate N containing 5 phr of ZS), and N5 KZS

Under neutral gas, the evaporation of water uncombined with keratin becomes visible in the high endothermic peak in the DSC curve at $T = 112$ °C (Fig. 2). Successive endothermic processes at $T = 259$ and $T = 306$ °C are connected with the thermal decomposition of the protein. The DSC curve shows no symptom connected with the glass transition of keratin. From the literature, it follows that the glass transition temperature (T_g) of this biopolymer is affected by both the water contained in it and the content of α and β keratin [16, 19]. In this connection, T_g is at $\Delta T = 30–130$ °C, i.e., within the range of temperature, at which water evaporates (Fig. 2). Considering the considerable thermal effect caused by the evaporation of water physically combined with the polymer (change in enthalpy $\Delta H = 166$ J g^{-1}), the glass transition process resulting from its thermal capacity, shown by the changes in the position of thermal curve base line, is "masked".

NBR crosslinked with dicumyl peroxide under the influence of heating undergoes thermal crosslinking processes at two temperatures: $\Delta T_1 = 180–270$ °C and
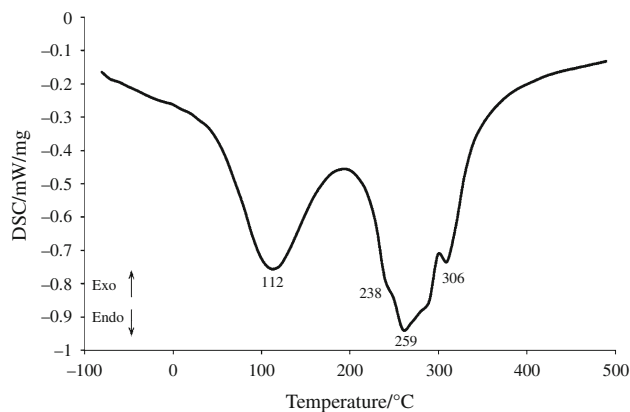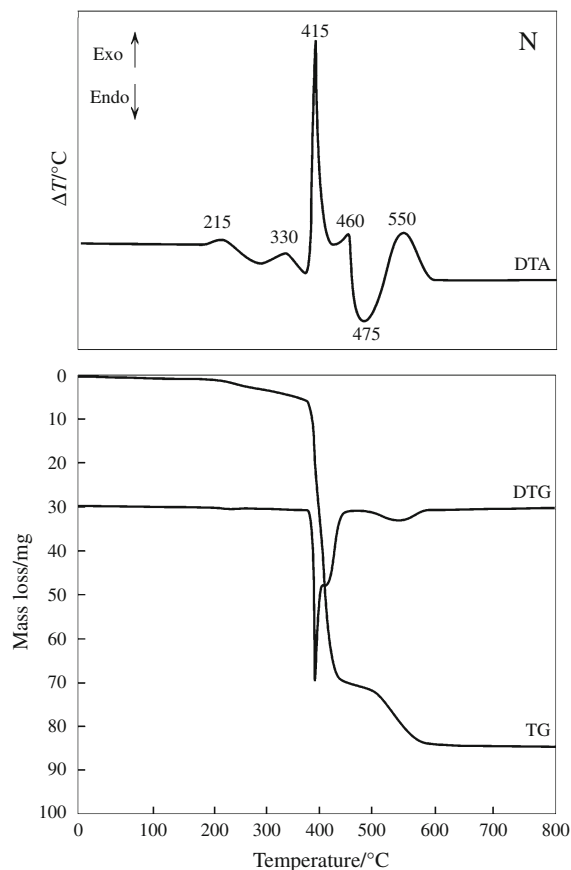

Fig. 2 DSC curve of keratin

Fig. 3 DTA, TG, and DTG curves of N

Fig. 4 DTA, TG, and DTG curves of nN

$\Delta T_2 = 300$–370 °C (Fig. 3). The thermal crosslinking within the lower temperature range proceeds due to the decomposition of hydroxyl groups contained in the elastomer and formed in it during heating. At $\Delta T_2 =$ 300–370 °C crosslinking proceeds as a result of crosspolymerization of butadiene mers contained in the macromolecules of the elastomer, which is accompanied by chain fragmentation and formation of small quantities of volatile products of their thermal decomposition (Fig. 3) [20]. At $T \sim 400$ °C, an intensive thermal decomposition of the elastomer begins, while the resultant residue combusts as shown by the exothermic peak recorded in the DTA curve at $T = 545$ °C. The use of nZnO in the vulcanization of elastomer does not change the character of its thermal transitions, but it increases the maximum rate temperature of its first stage of thermal crosslinking (Fig. 4). The increase in the temperature of the first thermal crosslinking stage of NBR also occurs under the influence of keratin incorporated into the elastomeric blend (Fig. 5). It indicates that both nZnO and keratin impede the formation of hydroperoxides, decomposition of which initiating the first thermal crosslinking stage of NBR occurs at a higher temperature.
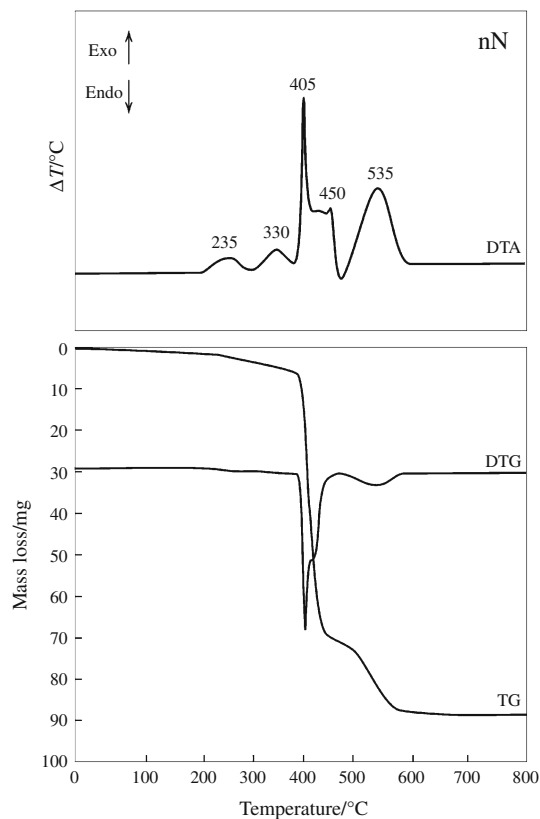
The comparative analysis of the test results listed in Table 2 leads to a conclusion that the thermal stability of the crosslinked NBR, determined with index T_5, decreases under the influence of keratin. On the other hand, the presence of keratin does not change the elastomer thermal stability determined with index T_{50}. It should be, however, underlined that under the influence of the biopolymer used, regardless of the type of zinc oxide, the thermal decomposition rate of the elastomer–protein composite (dm/dt) obtained is considerably reduced, and the resultant residue after this process (P_w) is increased (Table 2). It is very important from the point of view of reduction in the flammability of the composites investigated, as the change in both the parameters mentioned indicates that lower quantity of volatile and flammable thermal decomposition products passes to flame.

Keratin contained in the peroxide vulcanizate of NBR does not change the character of the elastomer thermal transitions (Fig. 6; Table 3). A low content of protein (5 phr) decreases the glass transition temperature (T_g) of the rubber, and consequently, slightly increases its resistance to the action of low temperatures. Such a quantity of keratin also facilitates the crosslinking of the elastomer tested under nitrogen beginning at $T \sim 290$ °C (Table 3; Fig. 6).
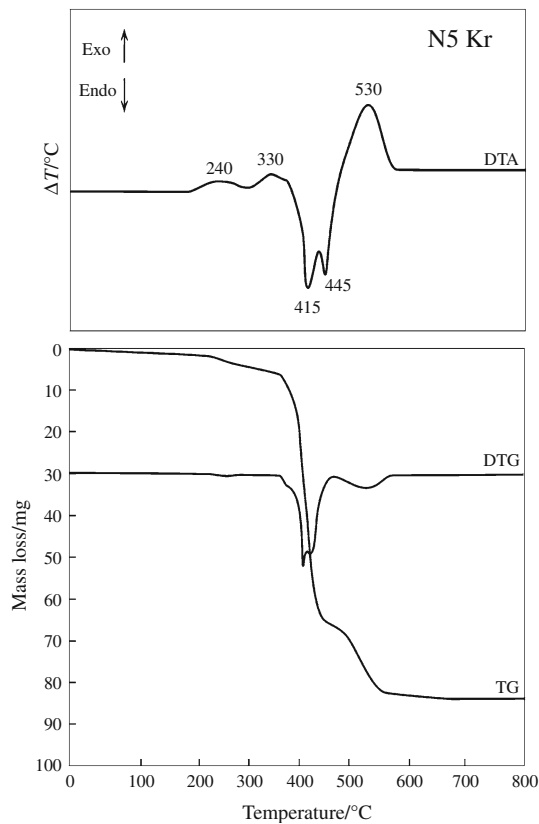
Fig. 5 DTA, TG and DTG curves of N 5Kr

Fig. 6 DSC curve of N5Kr

Table 3 Influence of keratin on thermal properties in neutral gas of NBR composites

Sample	$T_{g\ cool}$/°C	$T_{g\ heat}$/°C	T_{tc}/°C	ΔH_{tc}/J g^{-1}	T_D/°C
N	−54	−45	364	−645	470
N5 Kr	−60	−54	361	−695	461
N30 Kr	−53	−47	362	−622	462

T_g, glass transition temperature; T_{tc}, temperature of thermal crosslinking; ΔH_{tc}, change of thermal crosslinking enthalpy; T_D, temperature of destruction maximum rate

Table 2 Influence of keratin on thermal properties in air of NBR composites and nanocomposites

Sample	T_5/°C	T_{50}/°C	T_{Rmax}/°C	dm/dt/mm	P_w/%	T_S/°C	P_{800}/%
N	355	415	415	79	22	545	5
N5 K	305	415	395	51	24	525	6
N5 Kr	305	415	410	44.5	27	530	6
N5 KZS	335	420	415	47	29	525	8
N10 K	280	415	395	50	28	525	7
N10 Kr	285	415	410	42.5	29	535	8
N30 Kr	235	415	410	32	29	555	7
nN	325	410	405	58	20	535	1
nN5 K	285	415	405	44	24	550	2
nN10 K	330	420	415	41	25	550	6

T_5, temperature of composite 5 % mass loss; T_{50}, temperature of composite 50 % mass loss; T_{Rmax}, maximum temperature of composite thermal decomposition; dm/dt, maximum rate of composite thermal decomposition; P_w, residue after composite thermal decomposition; T_S, maximum combustion temperature of residue after composite thermal decomposition; P_{800}, residue after heating of composite up to 800 °C

Table 4 Flammability of NBR composites and nanocomposites containing keratin

Sample	t_S/s	OI
N	276	0.205
N5 K	324	0.235
N5 Kr	319	0.247
N5 KZS	323	0.238
N10 K	286	0.220
N10 Kr	295	0.228
N30 Kr	336	0.238
nN	205	0.181
nN5 K	310	0.193
nN10 K	305	0.197

t_S, time of burning in air; OI, oxygen index

The conclusions resulting from testing the thermal properties of the elastomer–protein composites investigated are confirmed by the measurements of their flammability. Regardless of the type of zinc oxide, under the influence of keratin contained in the peroxide vulcanizates of NBR, their flamma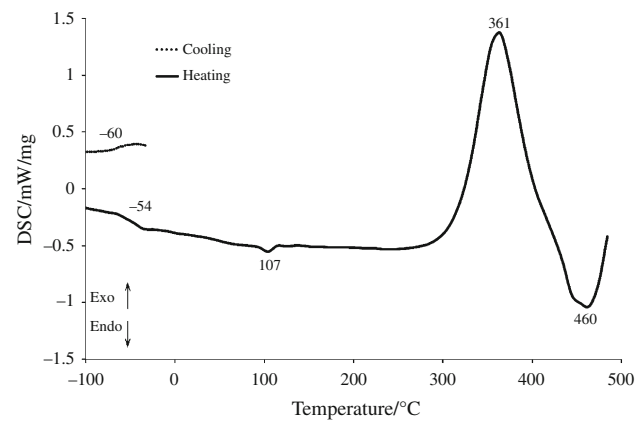bility has been decreased as shown by both the tests of combustion in air (t_s) and oxygen index (OI) (Table 4). The decreased flammability of NBR results, first of all, from a considerable reduction in its thermal decomposition rate (dm/dt) under the influence of keratin (Tables 2, 4) as well as the emission of nitrogen during vulcanizate destruction. Nitrogen as nonflammable gas considerably decreases the free-radical reactions of combustion in air and also reduces the diffusion of oxygen to the flame zone. In our opinion, the reduction in the flammability of the composites obtained is connected with nanometric size of keratin particles [21], but it can also

result from the chemical structure of peptide chains twisted in helixes that are combined by mono- and disulfide cystine bridges [22]. The method of incorporating the biopolymer into the elastomeric matrix (separately or in the form of a mixture with zinc oxide) does not exert any significant influence on the flammability of the composites obtained.

Conclusions

The composite thermal stability and flammability characteristics depend on the method of composite preparation and the quantity of added keratin.

The waste keratin used reduces the flammability of crosslinked nitrile rubber.

Regardless of the type of zinc oxide, the addition of waste keratin improves the crosslinking of NBR rubber by means of dicumyl peroxide.

The elastomer–protein composites show appropriate mechanical properties. However, a clear improvement in the composite strength parameters occurs under the influence of the modified montmorillonite incorporated.

The materials obtained are characterized by increased water absorption. The water content in swollen samples proportionally increases with the keratin content in the composites. This suggests an increased susceptibility of these materials to biodegradation in the environment after their exploitation period.

References

1. International Rubber Study Group, Rubber Industry Report, 2004;4:11.
2. Spasówka E, Rudnik E, Kijeński J. Biodegradable polymer nanocomposites. Polimery. 2006;9:617–26.
3. Janowska G, Mikołajczyk T, Boguń M. Effect of the type of nanoaddition on the thermal properties of polyacrylonitrile fibres. J Therm Anal Calorim. 2007;89:613–8.
4. Janowska G, Mikołajczyk T, Olejnik M. Thermal properties and flammability of fibres made from polyimidoamide nanocomposite. J Therm Anal Calorim. 2007;88:843–9.
5. Mikołajczyk T, Szparaga G, Janowska G. Influence of silver nano-additive amount on the supramolecular structure, porosity, and properties of polyacrylonitrile precursor fibres. Polym Adv Technol. 2009;20:1035–43.
6. Kucharska-Jastrząbek A, Janowska G. Effect of the network structure on the thermal properties and flammability of nitryle rubber nanocoposites. Przem Chem. 2010;89:1683–7.
7. Janowska G, Kucharska-Jastrząbek A, Rybiński P. Thermal stability, combustibility and fire hazard of butadiene-acrylonitrile rubber nanocomposites. J Therm Anal Calorim. 2011;103:1039–46.
8. Rybiński P, Janowska G, Jóźwiak M, Pająk A. Thermal properties and flammability of nanocomposites based on diene rubbers and naturally occurring and activated halloysite nanotubes. J Therm Anal Calorim. 2012;107:1243–9.
9. Langmaier F, Mládek M, Mokrej P, Kolomazník K. Biodegradable packing materials based on waste collagen hydrolysate cured with dialdehyde starch. J Therm Anal Calorim. 2008;93:547–52.
10. Li Y, Wang X, Wang J. Cation exchange, interlayer spacing, and thermal analysis of Na/Ca-montmorillonite modified with alkaline and alkaline earth metal ions. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-2109-1.
11. Przepiórkowska A, Chrońska K, Prochon M. Biodegradable elastomeric vulcanizates. Rubber Chem Technol. 2008;81:723–35.
12. Prochoń M, Przepiórkowska A, Zaborski Z. Keratin as a filler for carboxylated acrylonitrile-butadiene rubber XNBR. J Appl Polym Sci. 2007;106(6):3674–87.
13. Mohammadreza K, Shahin A, Saeedeh M, Alireza S, Younes CJ, Mehrzad M. Effect of ZnO nanoparticles on kinetics of thermal degradation and final properties of ethylene–propylene–diene rubber systems. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-2097-1.
14. Janowska G, Kucharska-Jastrząbek A. The effect of chlorosulphonated polyethylene on thermal properties and combustibility of butadiene-styrene rubber. J Thermal Anal Cal. 2010;101:1093–9.
15. Gaur MS, Pramod Kumar Singh, Suruchi, Chauhan RS. Structural and thermal properties of polysulfone-ZnO nanocomposites J Therm Anal Calorim. 2011.
16. Prochoń M, Janowska G, Przepiorkowska A, Kucharska-Jastrzabek A. Thermal properties and combustibility of elastomer–protein composites Part I. Composites SBR: keratin. J Therm Anal Calorim. 2012;109:1563–70.
17. Datta J, Balas A. DSC and thermal stability investigation of novel poly(ester–ether) glycols and poly(ester–ether)urethanes. J Therm Anal Cal. 2003;74:615–21.
18. Patent PRL 129411, 1987.
19. Popescu C, Wortmann FJ. Proceedings of the NATAS Annal Conference on Thermal Analysis and Applications, Germany, 2006.
20. Rybinski P, Janowska G. Influence of network structures of nitrile rubbers on their thermal properties. Polimery. 2009;54:275–82.
21. Prochoń M, Przepiórkowska A, Zaborski M. Elastomer-keratin composites. Kautsch Gummi Kunstst. 2006;10:520–5.
22. Feughelman MA, Lymand DJ, Willis BK. The parallel helices of the intermediate filaments of α-keratin. Int J Biol Macromol. 2002;30:95–6.