The properties of elastomers obtained with the use of carboxylated acrylonitrile-butadiene rubber and new crosslinking substances

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Abstract: In this work, new crosslinking substances containing zinc, sodium, magnesium and aluminum ions for carboxylated acrylonitrile-butadiene rubber (XNBR) were investigated. The crosslinking density of the vulcanizates obtained was studied by equilibrium swelling in solvents. Additionally, the results confirmed the presence of ionic clusters in metal-containing XNBR vulcanizates. It was proved that these crosslinks were generated due to interactions occurring between metal ions and functional groups of rubber, namely carboxyl groups. The appearance of these unconventional crosslinks was certified by various investigations, *i.e.* dynamic mechanical thermal analysis (DMTA), infrared studies or equilibrium swelling of vulcanizates in toluene under ammonia treatment.

Keywords: carboxylated acrylonitrile-butadiene rubber, metal-containing compounds, crosslinking, ionic clusters.

Właściwości elastomerów otrzymanych z karboksylowanego kauczuku butadienowo-akrylonitrylowego z użyciem nowych substancji sieciujących

Streszczenie: Badano nowe substancje zawierające jony cynku, sodu, magnezu lub glinu jako czynniki sieciujące do karboksylowanych kauczuków akrylonitrylowo-butadienowych (XNBR). Gęstość usieciowania otrzymanych wulkanizatów wyznaczano metodą pęcznienia równowagowego w rozpuszczalnikach. Stwierdzono występowanie klastrów jonowych w wulkanizatach XNBR zawierających jony metali. Wykazano, że węzły sieci tworzyły się dzięki oddziaływaniom występującym między jonami metalu i grupami funkcyjnymi kauczuku, czyli grupami karboksylowymi. Występowanie tych niekonwencjonalnych węzłów sieci potwierdziły wyniki dynamiczno-mechanicznej analizy termicznej (DMTA), spektrofotometrii w podczerwieni oraz badania pęcznienia równowagowego wulkanizatów w toluenie w obecności amoniaku.

Słowa kluczowe: karboksylowany kauczuk akrylonitrylowo-butadienowy, związki zawierające metale, sieciowanie, klastry jonowe.

Rubber polymers can be crosslinked conventionally, what led to arising of covalent C-C or sulfur bonds in elastomer matrix. Initially, it was put into practice with the use of organic peroxides or radiation [1—9]. However the most widely applied technology to cure rubber is sulfur together with suitable activators and accelerators of sulfur vulcanization [10—15]. Depending on the conditions of elastomers vulcanization with sulfur-containing crosslinking systems the reaction in a polymer results in formation of poly-, di- and monosulfidic bonds. There is unconventional crosslinking, consisting in partial or total neutralization of functional groups of rubber as well [16—23]. For that purpose one can utilize metal oxide or other chemical compound containing substituent groups capable of reacting with macromolecules [23—28]. The macromolecules coming into existence this way assumed the shape of salts [16, 19]; while the neutralization degree was high enough to obtain the vulcanizates containing ionic crosslinks [29, 30]. By a choice of the crosslinking agents and procedures it is possible to form in the elastomer different types of bonds, covalent or ionic, which, in turn, affects the properties of obtained materials and allows to meet better special application requirements [23, 31, 32]. Hence, one can say that the appropriate choice of the ingredients of polymer blends enables tailoring and achieving of a desirable combination of the properties of obtained materials [33].

Taking into consideration peculiar properties of elastomer networks with ionic crosslinks there has been much attention paid to preparing of such linkages and their features [29, 34—47].

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In polymer processing more and more interesting is safety of the usage of individual compounds. It is known that some substances applied in production of rubber are harmful. Therefore, it is necessary to substitute harmful chemicals by others safer but exhibiting similar or even better chemical activity [27, 48—50]. The weightiness of the matter emphasizes, *e.g.* the investigations concerning the usage of ethyl thiourea [51] or applying new materials of core-shell structure to crosslink rubbers [41, 42, 44, 52].

The objective of the present work is the presentation of new crosslinking substances for carboxylated acrylonitrile-butadiene rubber (XNBR) and their role in inducing specific interactions inside the elastomer network.

EXPERIMENTAL PART

Materials

The materials used in this study are characterized in Table 1. The rubber blends containing XNBR and various crosslinking agents were prepared. The composition of these blends specifying amounts of the components given in weight parts per hundred parts of rubber is listed in Table 2. The amount of BZC in blends B1-B4 and STR in blends ST5-ST13 was selected so as to provide the equivalent amount of zinc that would be contained in the 4, 5 and 10 phr of AAZn, respectively. The metal ethoxides [NaOEt, $Mg(OEt)_2$, $Al(OEt)_3$] were used in amounts sufficient to neutralize carboxyl groups of rubber taking into account the valence of metal.

Preparation of vulcanizates

Compounds were mixed at the temperature of about 35 °C using a laboratory two-roll mill with a cylinder diameter of 200 mm and a length of 450 mm. The rolls were refrigerated by circulating cold water through them during blending. The friction between the cylinders was 1:1. First, a raw rubber was masticated for 4 minutes and then ingredients were added. The equality of mixing was maintained by adjusting the gap between rolls, time of blending and uniform cutting operation.

T a b l e 2. Formulations of the rubber blends

Symbol of blend	Content of components in XNBR blend, phr					
	AAZn	BZC	STR	NaOEt	$Mg(OEt)_2$	$Al(OEt)_3$
A2.5	2.5					
A4	4.0					
A5	5.0					
A7.5	7.5					
A10	10.0					
A15	15.0					
A20	20.0					
B1		1.7				
B2		2.1				
B3		3.1				
B4		4.2				
ST5		1.7	5.3			
ST7		1.7	6.7			
ST10		1.7	10.0			
ST13		1.7	13.3			
S1				6.0		
S2					5.0	
S3						4.8

Rubber sheets were produced with the thickness of about 6—8 mm and stored at the temperature of 2—6 °C for 48 h and later molded in an electrically heated hydraulic press at 160 °C to form the vulcanizates no more than 1 mm thick. The proper curing time (until the samples developed a 90 % increase in torque) was established using a rheometer with oscillating disc according to ASTMD 2084-81 standard.

Methods of testing

The crosslinking density of the vulcanizates (ν) was determined from equilibrium swelling of the vulcanizates immersed in toluene. The crosslinking density defined as the number of moles of network bonds per volume unit of rubber was calculated from widely used Flory-Rehner equation [53]. Treatment with ammonia con-

T a b l e 1. Characteristics of the materials used

Materials	Properties	Source
carboxylated acrylonitrile-butadiene rubber (XNBR, trade name Krynac 7.5X)	6.4 wt % of carboxylic groups; 26.3 wt % of acrylonitrile mers; density of 0.99 g/cm^3	Lanxess
zinc acetylacetonate (AAZn)	Purity 99.99 %, melting temperature T_m = 136 °C	Sigma-Aldrich Chemical
sodium ethoxide (NaOEt)	Purity 96 %	Sigma-Aldrich Chemical
magnesium ethoxide [$Mg(OEt)_2$]	Purity 98 %	Sigma-Aldrich Chemical
aluminum ethoxide [$Al(OEt)_3$]	Purity 97 %, T_m = 157—160 °C	Sigma-Aldrich Chemical
zinc carbonate basic (BZC)	Purity grade — purum p.a.	Fluka
zinc 2-ethyl-hexanoate (STR, trade name Structol ZEH)	Purity grade — pure	Schill&Seilacher

sisted of swelling the vulcanized samples in toluene under ammonia saturated vapor in desiccator at the room temperature for a period of 48 h (ν_A) to recognize whether the crosslinked polymers contain non-covalent crosslinks [54, 55]. The concentration of the specific links was estimated from the difference between ν and ν_A. According to [56] and own observations, NH_3 contributes to the disintegration of the links formed at the filler-rubber interfaces. The equilibrium swelling data were interpreted using the value of μ being a parameter of the polymer-solvent interaction which was determined on the basis of our previous work [44]. It amounted to: $\mu = 0.4132 + 0.4341V_r$ for XNBR-toluene and $\mu = 0.4833 + 0.3274V_r$ for XNBR-toluene+NH_3 (where V_r means the volume fraction of rubber in swollen vulcanizate).

The tensile testing was performed using a universal testing machine (Zwick, model 1435) operating at a constant crosshead speed of 500 mm/min at the room temperature. At least five samples were tested for each vulcanizate. The evaluation of the total modulus in stress-strain experiments were adequately modelled by Mooney-Rivlin approximation [57]:

$$\sigma^* = \frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + 2C_2\lambda^{-1} = \nu RT + 2C_2\lambda^{-1} \tag{1}$$

where: σ^* — the reduced stress, σ — the applied stress, λ — an extension ratio of the sample, C_1, C_2 — the Mooney-Rivlin constants [58].

For three chosen samples the crosslinking density was evaluated using Mooney-Rivlin approximation [57].

Stress relaxation was monitored at the room temperature at 200 or 300 % of strain for a half an hour (using a universal testing machine Zwick, model 1435). To attain the required strain an initial rate of 100 mm/min was applied. The rate of relaxation (n) was given by existing empirical relationship [59]:

$$\sigma = Kt^{-n} \tag{2}$$

where: K — constant, t — time.

The Mullins effect was studied at 200 % of elongation and the crosshead displacement rate of 500 mm/min using a universal testing machine. The work corresponding to the first sample stretching ($W1$) was measured.

The test-piece used for tensile, Mooney-Rivlin and stress relaxation tests were cut into the dumbbell shape (4 mm wide and a central neck 12 mm long) with a razor blade.

Dynamic mechanical thermal analyses (DMTA) were carried out with an analyzer MK3 Rheometric at the fixed frequency of 5 Hz and the heating rate of 2 deg/min. The experiments were performed on the samples placed in the chamber cooled with nitrogen under conditions of tension. The stress was applied parallel to the orientation direction of the samples.

Infrared analysis was performed on BIO RAD FTS 175C spectrometer applying total internal reflection method (ATR) using a ZnSe crystal. All the spectra were obtained at the resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Crosslinking density

The results of crosslinking density determination for prepared vulcanizates are presented in Table 3. It was stated that zinc acetylacetonate (AAZn) was an efficient crosslinking substance for carboxylated acrylonitrile-butadiene rubber. From the data follows that crosslinking density of vulcanizates (ν) increased at first with the increase in the AAZn content in the rubber blend and then successively decreased. Presumably, when the concentration of zinc acetylacetonate used to prepare rubber blends heightened its solubility in polymer matrix grew slower. Such a simple statement was in agreement with outcomes of calculations of crosslinking efficiency, determined as the ratio of crosslinking density to the molar content of crosslinking substance.

T a b l e 3. The parameters of elastomer's structure of XNBR vulcanizates

Symbol of sample	$\nu \cdot 10^5$ mol/cm^3	$\frac{\Delta\nu_A}{\nu}$ 100 %	$\nu_{MR} \cdot 10^5$ mol/cm^3	crosslinking efficiency
A2.5	1.32	34.1		0.139
A4	1.43	30.8		0.086
A5	1.75	26.8		0.092
A7.5	1.88	25.5	0.33	0.066
A10	1.76	43.7		0.046
A15	1.42	47.2		0.025
A20	1.56	51.9		0.020
S1	3.08	95.4		0.070
S2	4.18	93.1		0.094
S3	3.62	57.7		0.082
B1	1.19	76.5		0.079
B2	1.74	76.4		0.092
B3	1.92	72.9	0.08	0.067
B4	2.44	84.8		0.064
ST5	0.83	61.4		0.046
ST7	1.26	67.5		0.057
ST10	1.91	74.9	0.14	0.062
ST13	2.20	70.4		0.054

ν, ν_{MR} — crosslinking density estimated from equilibrium swelling in toluene or Mooney-Rivlin analysis, respectively; $\Delta\nu_A$ — decrease of crosslinking density under the influence of ammonia.

Apart from that, the employment of AAZn to crosslink XNBR led to the formation of non-conventional interactions. Swelling of vulcanizates in toluene upon ammonia vapor allowed one to confirm the presence of crosslinks in the elastomer network which do not have any covalent character. These specific interactions were destroyed to some extent under ammonia treatment what led to decrease of crosslinking density (Table 3.) This corresponded to remarks in numerous papers [41, 42, 44, 56, 60].

Another group of compounds used with success as new XNBR crosslinking agents were metal ethoxides. The application of alkoxides of univalent or divalent metals yielded a great percentage of specific crosslinks in obtained vulcanizates (Table 3). As mentioned before these interactions were unstable in basic medium. Taking into account crosslinking efficiency, one could suppose that three alkoxides added to rubber blends revealed similar solubility in the polymer matrix. But the amount of ionic linkages was the smallest in the case of vulcanizate containing aluminum ethoxide (Table 3).

The new substances used to crosslink XNBR were BZC and STR as well (Table 3). The increasing concentration of these compounds contributed to ν upturn. Measurements of vulcanizates' equilibrium swelling in toluene and toluene under ammonia vapors certified that both BZC and STR took part in creating specific crosslinks in elastomer matrix. These interactions were destroyed by ammonia vapors. In the case of samples containing BZC the higher amount of curing substance the higher concentration of ionic crosslinks with the exception of B3 sample. Whereas in elastomers enriched with STR higher amounts of non-covalent crosslinks destroyed by ammonia occurred at 10 and 13.3 phr of STR. The crosslinking efficiency analysis suggested that application of BZC led to prepare vulcanizates in which the ratio of crosslinking density to the amount of curing substance was almost the same for B3 and B4 materials. The additional amount of STR into materials decreased the crosslinking efficiency (as compared with crosslinking efficiency of B1 sample, equal to 0.079).

It should be pointed out that there is very good evidence that ionic clusters are formed using proposed XNBR crosslinking substances have very low crosslinking efficiencies and much lower apparent crosslinking densities observed. These serve as a reinforcing filler or quasi crosslinks.

IR measurements

The IR spectra of XNBR vulcanizates, containing 15 phr of AAZn and vulcanizate crosslinked only using dicumyl peroxide (this spectrum was added as a reference), are shown in Fig. 1. As mentioned above, there are nitrile (-CN) and carboxylic (-COOH) groups in the structure of XNBR. At the curing temperature a reaction between AAZn and the polymer chains took place involving formation of the metallic carboxylate. Special attention was paid to the spectral region of the carboxyl and cyano groups to establish the existence of differences between the sample containing AAZn and sample crosslinked using dicumyl peroxide. In XNBR crosslinked with dicumyl peroxide the carboxylic acid group existed predominantly as hydrogen-bonded acid dimer and has a characteristic infrared carbonyl stretching vibration located at 1697 cm^{-1}. The carbonyl stretching vibrations band of the monomeric carboxylic acid group was converted to band at 1641 cm^{-1}, characteristic for the ester. It revealed that using AAZn as the curing substance led to decrease of the band corresponding to acid dimer and broadened the acid salt band (Fig. 1). These ionic salts occurred as multiplets or their associations forming a separated microphase inside the vulcanizate structure, confirming the presence of ionic bonds in the crosslinked material. In the case where crosslinking AAZn was used the disappearance of carboxylic groups was almost complete (the signal at 1697 cm^{-1}) and no sharp band was observed in the spectrum. Additionally, a new broad peak (in fact, there was observed the splitting of the band) corresponding to dimers' carboxyl groups appeared at the wavenumber 1589—1611 cm^{-1}. Moreover, the shoulder that appeared at 1418 cm^{-1} was also related to the formation of the salt. Regarding to the band associated with stretching vibration in the cyano groups at 2237 cm^{-1} both spectra showed slight differences in intensity what indicated small activity of these groups during crosslinking reaction regardless of whether AAZn was used. Apart from this the signal connected with deformation vibrations of -COH groups was not found. Therefore, according to our previous works [44] and other studies on that matter [31], the presence of ionic interactions in XNBR vulcanizates between zinc ions of AAZn and carboxyl groups of polymer was proved.

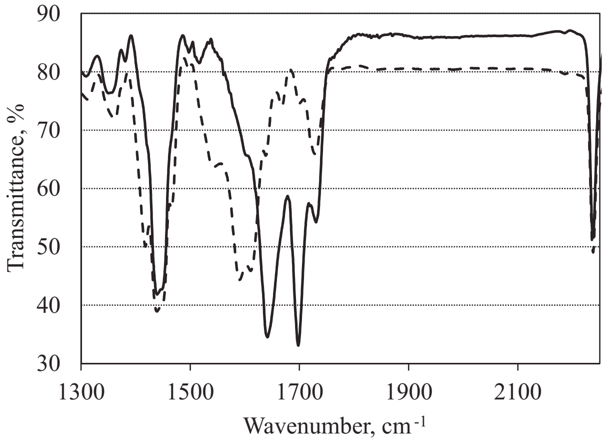

Fig. 1. IR spectrum of XNBR vulcanized with AAZn (dotted line) or dicumyl peroxide (solid line)

Mechanical performance of the vulcanizates

The mechanical properties of vulcanizates containing AAZn to cure XNBR were determined and results are collected in Table 4. It is believed that formation of labile (*e.g.* under NH$_3$ vapors) ionic crosslinks inside the elastomer network can improve the tensile properties of vulcanizates [61]. The effect of AAZn on these properties was investigated thoroughly. These results correlated well with the crosslinking density of the samples. The tensile strength (*TS*) increased rapidly with the increase of concentration of AAZn and showed the maximum at 7.5 phr of the crosslinking substance. On this basis it could be concluded that certain individuals, namely ionic crosslinks, participated in stress dissipation within studied vulcanizates. It was stated that there was an optimum of ionic crosslinks concentration (about 75 %) ensuring the maximum of *TS* of vulcanizates. A similar tendency was observed in the case of modulus at relative elongation of 100 and 300 % (*M*100 and *M*300, respectively). The *M*300 values were not close to *TS* of vulcanizates what can indicate the vulcanizates were not over-crosslinked. The elongation at break (*EB*) kept over 600 % for samples with a wide range of AAZn amount. To examine the properties of samples obtained with the use of suggested crosslinking substance the tension recovery process was also investigated. This dynamic property refers to the release of mechanical energy as heat from an applied cyclical deformation of the vulcanizate [10]. It was pointed out that the highest value of energy loss, during the first sample deformation, characterized vulcanizate containing 10 phr of AAZn. It could indicate that this elastomer had a great tendency to shock absorption.

Table 4. The mechanical properties of XNBR vulcanizates obtained with AAZn or metal ethoxides

Symbol of sample	*M*100 MPa	*M*300 MPa	*EB* %	*TS* MPa	*W*1 kJ/m^2
A2.5	0.79	0.93	1308	2.22	14.3
A4	0.90	1.08	1027	2.19	16.2
A5	1.15	1.45	832	3.31	18.4
A7.5	1.21	1.66	853	5.91	16.1
A10	1.15	1.64	618	3.34	20.2
A15	1.03	1.46	652	3.30	16.9
A20	0.90	1.28	689	3.60	12.2
S1	0.92	1.14	1096	3.56	12.2
S2	0.99	1.46	825	5.25	28.8
S3	0.82	1.04	1264	2.80	14.2

Actually, it appeared that $Mg(OEt)_2$ influenced advantageously *TS* and work necessary for the first sample stretching in comparison to other metal alcoxides used as XNBR crosslinking substances. This observation is specified in Table 4. Mechanical properties of elastomers containing BZC or STR were determined and results were compiled in Table 5. Moreover, it was evident that applying of BZC without adding STR to crosslink XNBR led to obtaining elastomer with higher values of *M*100, *M*300 and *TS* and lower values of *EB* (Table 5). But applying of STR caused a decrease in modulus at 100 % elongation, tensile strength and elongation at break in comparison to B samples with BZC. Besides, that vulcanizate had good shock absorption capacity what was recommended by the value of work necessary for the first sample stretching (*W*1).

Table 5. The mechanical properties of XNBR vulcanizates obtained with BZC and/or STR

Symbol of sample	*M*100 MPa	*M*300 MPa	*EB* %	*TS* MPa	*W*1 kJ/m^2
B1	1.10	1.40	868	8.12	15.1
B2	1.04	1.33	861	4.72	16.0
B3	1.15	1.63	796	8.11	20.1
B4	1.33	2.12	708	10.8	24.0
ST5	0.92	1.12	1002	3.20	14.3
ST7	0.83	1.08	1156	3.91	13.0
ST10	0.92	1.13	1190	4.72	13.6
ST13	0.89	1.08	1212	4.45	15.0

The well-known Mooney-Rivlin equation was used to evaluate the elastomeric network by plotting the reduced stress (σ^*) versus the reciprocal of the extension ratio ($1/\lambda$). Characteristics of such relationships for the investigated materials are presented in Fig. 2. The placement of the curves obtained for the samples elongated with differentiated rate (crosshead speed equal to 1000 mm/min and 25 mm/min) suggested that non-covalent crosslinks were formed in polymer network. The decrease of σ^* with increasing strain in the small strain range was noted. At large strains, the upturn in the reduced stress came from limited extensibility of network chains [62]. The diagram discussed in this section indicated: at higher extension rates the minimum modulus occurred at lower extensions in comparison to lower deformation rate. It is also worth noting that curves related to vulcanizates deformed at the crosshead speed equal to 1000 mm/min were lying above these characterizing samples strained at 25 mm/min. No distinction was revealed in the orientation of σ^* versus $1/\lambda$ curves in the case of the vulcanizates composed only of carbon-carbon bonds [44]. Greater values of σ^* during their deformation at higher rate arise from the fact that specific crosslinks had considerable rigidity. On the other hand the labile character of these crosslinks manifested itself when samples were more slowly deformed. Then, the limited extensibility of macromolecules appeared at lower deformations. It could be said that specific crosslinks obtained using new crosslinking agents acted as active fillers [44]. Moreover, this unstable character was reflected in the physical relaxation measurements at the room temperature of chosen vulcanizates.

The change in normalized stress (σ_t/σ_0) with time, shown in Fig. 3, indicated the time dependent stress decay until it reached equilibrium. If stress relaxation occurs, a part of the energy stored in the material is dissipated and a part of deformed polymer chains cannot retract. The stress relaxation behavior is mainly attributed to the breakage of filler-elastomer and filler-filler interactions [63]. But this mechanism can be controlled by the opportunity for destruction of specific interactions and their reconstruction in other locations in the elastomer network.

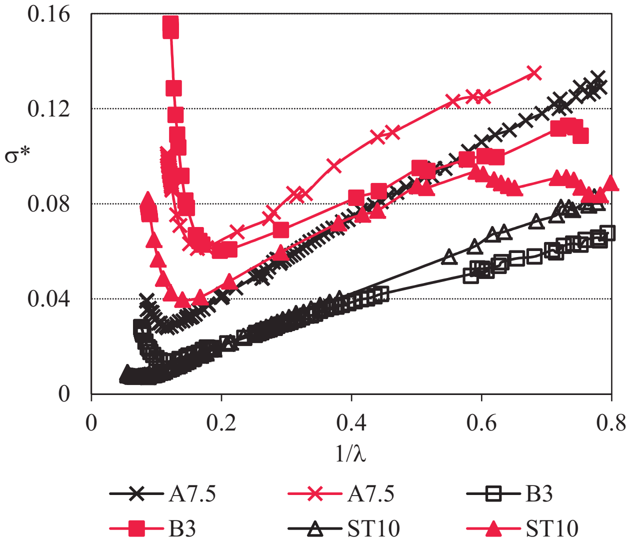

Fig. 2. The effect of inverse extension ratio (1/λ) on reduced stress (σ*) of XNBR vulcanizates deformed at different rates, crosshead speed equal to 25 mm/min (black curves) and 1000 mm/min (red curves), respectively

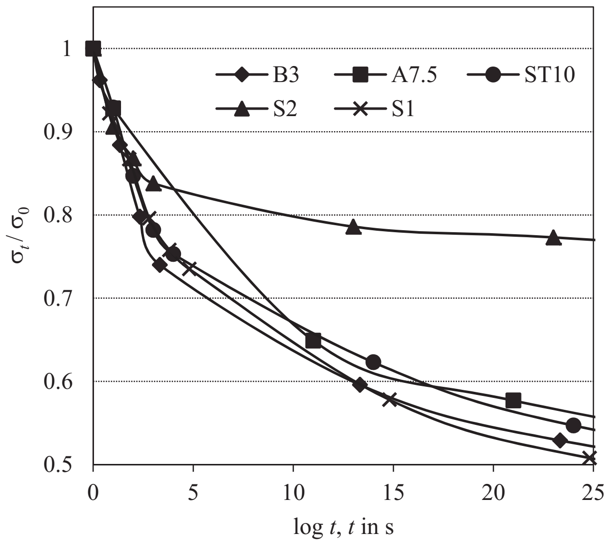

Fig. 3. The effect of time (*t*) on normalized stress (σ_t/σ^*) of XNBR vulcanizates at strain of 200 or 300 % at the room temperature

The substances containing zinc, magnesium, sodium and aluminum ions used to crosslink XNBR took part in creating unconventional crosslinks with rubber functional groups. These crosslinks were susceptible to stress dissipation during deformation (to the smallest extent this applies to S2 sample what is the manifestation of high crosslinking density of this vulcanizate, equal to 4.18 · 10^{-5} mole/cm^3).

Additional information can also be deduced from the analysis of variation of glass transition temperature (T_g) of polymer component after adding sodium, zinc, magnesium and aluminum compounds. The extracted T_g values are listed in Table 6. At low temperatures all composites showed maxima at different temperatures. It appeared that only BZC and NaOEt led to the enlargement of T_g compared with other samples obtained by the use of new proposed curing agents. The tangent of delta (tan δ) versus temperature (T) curves for various elastomers containing metal ions are plotted in Fig. 4. The differences found were not only in the position of the maxima but also in the peak height. The incorporation of these agents did not lead to significant changes in the tan δ values for all samples discussed with the exception of the system consisting of XNBR and $Al(OEt)_3$. Materials containing ionic crosslinks are known to present two types of transitions — one at low temperature, following T_g and second one occurring at high temperatures resulting from the appearance of a hard phase due to ionic clusters or associates [42]. This second transition did not appear in the case of the vulcanizate cured with dicumyl peroxide containing only covalent carbon-carbon crosslinks, as it was described in our previous paper [41]. Applying of zinc 2-ethyl-hexanoate brought about the high-temperature transition due to more prominent non-covalent interactions which behaved as independent microphase inside the rubber matrix. Moreover, the maximum of the ionic transition was shifted to the higher temperatures and occurred at about 80 °C. It was believed that specific interactions between functional groups of rubber and zinc ions from STR occurred; it could be the evidence of ionic clusters presence. Such effect was not so evident in the case of other vulcanizates. Probably, the specific interac-

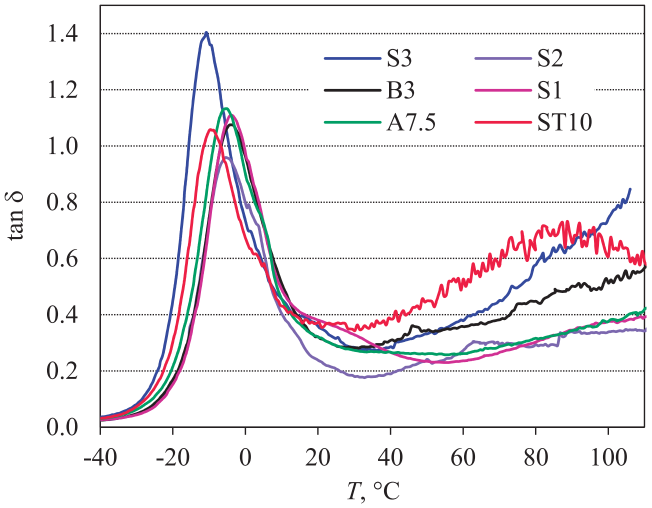

Fig. 4. The effect of temperature (*T*) on tan δ of XNBR vulcanizates

Table 6. The results of thermal analysis of selected XNBR vulcanizates

Property	Symbol of sample					
	A7.5	B3	ST10	S1	S2	S3
T_g, °C	-5.1	-3.6	-9.8	-3.8	-5.4	-10.7
tan δ at T_g	1.13	1.07	1.06	1.11	0.96	1.40
E'_{20}, MPa	6.72	6.43	4.56	6.68	8.76	2.88

T_g — glass transition temperature, tan δ at T_g — tangent delta related to T_g, E'_{20} — storage modulus of vulcanizates at 20 °C.

tions of carboxyl ligands of rubber and crosslinking substances were not intense and robust enough to cause conspicuous mobility restriction of polymer chains and formation of rubber areas manifesting their own phase transition as it was mentioned in the case of XNBR-STR structure. Table 6 shows the influence of new crosslinking compounds on the variation of elastic modulus (E') at 20 °C. The lowest value of the modulus at the room temperature (E'_{20}) was noticed for vulcanizate obtained using $Al(OEt)_3$ as the crosslinking substance.

CONCLUSIONS

Substances containing sodium, magnesium, zinc and aluminum ions were applied as new crosslinking agents for XNBR. Different studies, including equilibrium swelling measurements, infrared and DMTA analysis, reveal the formation of ionic crosslinks in XNBR vulcanizates. These clusters were generated thanks to interactions occurring between metal ions inserted into the polymer matrix *via* new proposed curing agents and carboxyl groups of rubber. These specific interactions were destroyed under ammonia treatment. The existence of ionic clusters exhibited good ability to slip along the polymer chain and reform, what influenced relaxation process at the room temperature.

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