

Barbara Wolska*¹, Władysław M. Rzymiski*²

Thiuram disulfides in curing of partially hydrogenated acrylonitrile-butadiene rubber

Curing of partially hydrogenated acrylonitrile-butadiene rubber (P-HNBR; bound acrylonitrile content: 34 wt %; hydrogenation degree: 94.5 or 96.0 mol. %; residual $[>C=C<]_{trans}$ double bond content: 0.67 or 0.49 mol/kg resp.) with tetramethyl- (TMTD, molecular weight $M = 240$ g/mol), tetraethyl- (TETD, $M = 296$ g/mol), tetraisobutyl- (TiBTD, $M = 408$ g/mol) or tetrabenzylthiuram (TBzTD, $M = 544$ g/mol) disulfide was studied. It has been found that, among thiuram disulfides (TDS) investigated, only TMTD used in the amount ≥ 0.10 mol/kg rubber (≥ 2.4 phr) showed accepted curing activity and reached curing degree in the absence of ZnO. Apart from curing, the heating of TDS with P-HNBR in the absence of ZnO, is accompanied by modification of rubber main chains with thiuram moieties bound with rubber in the amount of 20÷60 % of TDS incorporated, saturation to some extent of $>C=C<$ double bond and by degradation of main chains. The extent of chain degradation acts p to curing acts q reaches $p/q = 0.05 \div 0.09$. The added ZnO greatly improves the curing activity of all TDS used, but – at the same time – enhances the P-HNBR main chains dehydrogenation processes. The networks formed during curing with TDS in the presence of ZnO contain mono- (5 ÷ 55 %), di- (5 ÷ 60 %) and even polysulfide crosslinks, in the proportion depending on ZnO amount and kind of TDS used. The increase in curing temperature (>433 K) decreases the achieved curing degree and enhances the modification and dehydrogenation processes of the rubber chains as well, but exhibits small effect only on the chemical structure of the crosslinks formed.

Key words: hydrogenated acrylonitrile-butadiene rubber (HNBR), thiuram disulfides, curing activity

Disiarczki tiuramu w sieciowaniu częściowo uwodornionego kauczuku butadienowo-akrylonitrylowego

Zbadano sieciowanie częściowo uwodornionego kauczuku butadienowo-akrylonitrylowego (P-HNBR; zawartość związanego akrylonitrylu: 34 % mas.; stopień uwodornienia: 94,5 lub 96,0 % mol.; zawartość resztkowych wiązań podwójnych $[>C=C<]_{trans}$: 0,67 i 0,49 mol/kg kauczuku) za pomocą disiarczku tetrametylo- (TMTD), tetraetylo- (TETD), tetraizobutylo- (TiBTD) lub tetrabenzylotiuuramu (TBzTD). Stwierdzono, że w nieobecności ZnO jako aktywatora jedynie TMTD, użyty w ilości $> 0,10$ mol/kg kauczuku, jest substancją sieciującą badane elastomery. Towarzyszy temu nasycanie części wiązań podwójnych $>C=C<$ oraz degradacja makrocząsteczek kauczuku.

ZnO jako aktywator wyraźnie zwiększa efektywność działania zastosowanych disiarczków, jednakże zwiększenia zawartości ZnO w mieszaninie ponad wartość optymalną, zależną od rodzaju disiarczku, intensyfikuje procesy rewersji oraz reakcje modyfikacji łańcucha głównego elastomeru, w tym odwodornienie. Wzrost temperatury reakcji do 463 K zwiększa wprawdzie szybkość sieciowania, ale przy $T > 443$ K intensyfikuje procesy odwodornienia kauczuku i rewersji oraz zmniejsza osiągnięty stopień usieciowania. Z punktu widzenia osiąganego stopnia usieciowania oraz najmniejszej podatności na rewersję najlepsze wyniki uzyskano stosując disiarczki tetraizobutylo- lub tetrabenzylotiuuramu.

Słowa kluczowe: uwodorniony kauczuk butadienowo-akrylonitrylowy (HNBR), disiarczki tiuramu, aktywność sieciująca

1. Introduction

Network structure, reached curing rate and crosslinks density, and properties of cured rubbers are

strongly influenced by kind and amount of curing agent used [1-6]. Rubbers cured with peroxide contain $>C-C<$ crosslinks only and show good thermal and ageing resistance [7]. The use of conventional curing systems, containing sulfur, accelerators and activators, leads to networks comprising mono-, di- and polysulfide crosslinks $>C-S_{x \geq 2}-C<$ and to products of higher tensile strength and abrasion resistance, but lower dynamic and thermal resistance compared to rubbers cured with peroxide [1, 2]. Sulfur curing is often accompanied by reversion. Additionally, the conversion products of some accelerators,

* Technical University of Łódź, Institute of Polymer and Dye Technology, 90-924 Łódź, Stefanowskiego 12/16, Poland

¹ Present affiliation: Gates Polska Sp. z o. o, Jaworzyńska 210, 59-220 Legnica

² Corresponding author; e-mail: rzymiski@p.lodz.pl

e.g. nitrosoamines, are toxic. There are reasons to search for new substances and methods for the curing of elastomers, especially of low unsaturation, for example of partially hydrogenated acrylonitrile-butadiene rubber (P-HNBR).

The results of published studies [1, 2] indicate, that tetramethylthiuram disulfide (TMTD) used to cure diene rubbers leads to network containing mono- and disulfide crosslinks, and the acrylonitrile-butadiene rubber (NBR) cured with this disulfide is characterized by enhanced thermal stability [8, 9]. Thus our work concerns the curing of partially hydrogenated acrylonitrile-butadiene rubber with thiuram disulfides of different chemical structure (TDS), offered recently by some companies. The studies cover the influence of amount and structure of TDS, the residual double $>C=C<$ bonds content in rubber, the presence of activator (ZnO) and the curing temperature ($423 \div 463$ K) as well on the P-HNBR curing, on the structure of the crosslinks formed and on selected properties of cured rubbers. The results of such investigations, excluding some our preliminary findings [10], were not still published.

2. Materials and methods

The technical P-HNBR (Therban C3446 and C3467 from Bayer AG/Lanxess AG, bound acrylonitrile content: 34 wt. %; hydrogenation degree: 94.5 or 96.0 mol. %; residual double bond $[>C=C<]_{trans}$ content: 0.49 or 0.67 mol/kg rubber resp.), and tetramethyl- (TMTD), tetraethyl- (TETD), tetraisobutyl- (TiBTd) or tetrabenzyl-

thiuram disulfide (TBzTD) from Vanderbilt Co. were used. The rubber mixes were prepared using two-roll mill and sheets of 1 mm thickness were moulded in press and heated for given time t determined from vulcanometric measurements $M = f(t)$ at selected temperature ($423 \div 463$ K), according to standard procedures. The crosslinks density and the structure of the crosslinks formed were analysed on the basis of determined Mooney-Rivlin elasticity constants $2C_1$ [11, 12] and the equilibrium swelling data in toluene (Q_v^{TOL}) or methyl ethyl ketone (Q_v^{MEK}) before and after action of thiol-amine reagents [13, 14]. Flory-Rehner equation and Huggins interaction parameter μ for cured rubber-solvent [15] were used to calculate crosslinks density. Bio-Rad spectrophotometer and press molded elastomer foils of < 0.05 mm thickness were used for IR studies. Other properties of cured rubber were determined using published and standard methods adopted and proved for such investigations in our Institute and in previous studies [15, 16].

3. Results and discussion

3.1. Effect of TDS kind on P-HNBR curing in absence of ZnO

At the first we investigated the curing of P-HNBR ($[>C=C<] = 0.49$ or 0.67 mol/kg) with TMTD, TETD, TiBTd or TBzTD in the absence of activator (ZnO). From vulcanometric data $M_t = f(t)$ (not shown here) it follows that among all TDS used only TMTD exhibited accepted

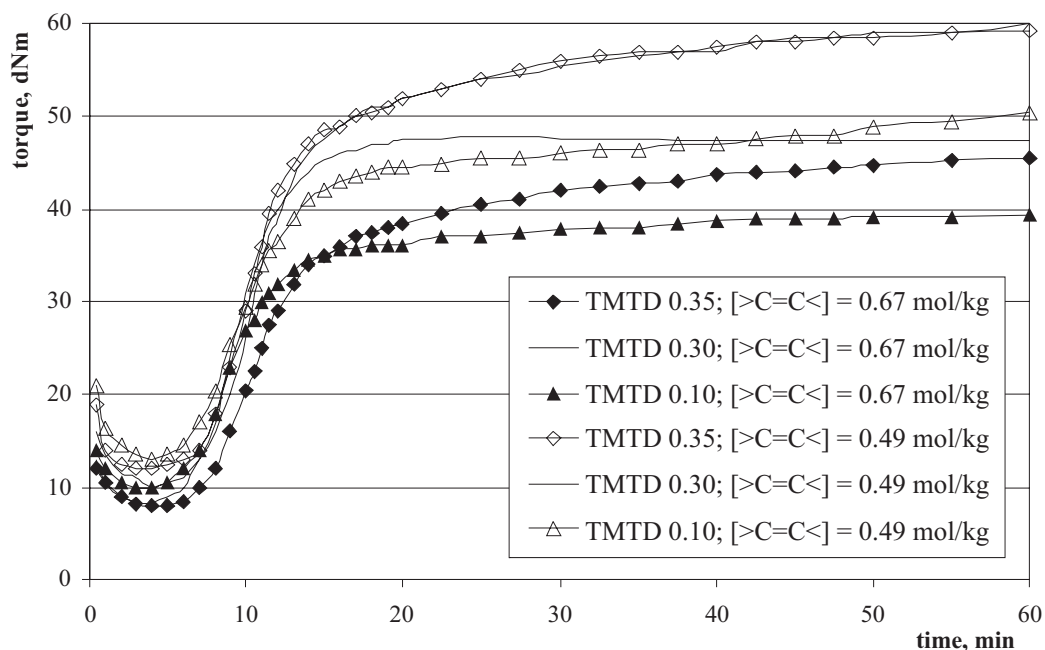


Fig. 1. Vulcanometric curves for P-HNBR ($[>C=C<] = 0.49$ or 0.67 mol/kg rubber) heated at $T = 433$ K with TMTD (0.10 - 0.35 mol/kg rubber) in the absence of ZnO

Rys. 1. Krzywe wulkametryczne sieciowania P-HNBR ($[>C=C<] = 0,49$ lub $0,67$ mol/kg kauczuku) za pomocą TMTD (0,10 - 0,35 mol/kg kauczuku) w $T = 433$ K w nieobecności ZnO

curing activity and curing degree after heating at 433 K for time shorter than 20 min. Note, that TBzTD in the absence of ZnO showed no curing activity in unsaturated acrylonitrile-butadiene rubber as well [16].

Table 1. Effect of TMTD amount on increase in vulcanometric torque ΔM_{25} , volume equilibrium swelling in toluene Q_v^{TOL} and $2C_1$ elasticity constants of P-HNBR after curing at $T = 433$ K for $t = 25$ min in the absence of ZnO
Tabela 1. Wpływ ilości TMTD na przyrost momentu wulkametrycznego ΔM_{25} , objętościowe pęcznienie równowagowe w toluenie Q_v^{TOL} i stałe elastyczności $2C_1$ P-HNBR usieciowanego w $T = 433$ K, w ciągu 25 min, w nieobecności ZnO

Rubber	Therban C3449; [>C=C<] = 0.49 mol/kg			Therban C3467; [>C=C<] = 0.67 mol/kg		
	ΔM_{25} dNm	Q_v^{TOL} ml/ml	$2C_1$ MPa	ΔM_{25} dNm	Q_v^{TOL} ml/ml	$2C_1$ MPa
0.10	27.0	5.03	-	32.3	3.46	0.05
0.20	36.9	4.25	-	40.7	3.92	0.72
0.30	39.5	2.99	0.30	43.7	3.22	1.01
0.40	32.0	3.31	0.28	41.4	3.77	0.67
0.50	31.1	3.01	0.14	39.4	5.34	0.65

The vulcanometric data for P-HNBR/TMTD system indicated that the achieved curing degree after heating for 25 min ΔM_{25} , higher as expected in more unsaturated rubber, depends on the TMTD amount used and reached a maximum for 0.3 mol TMTD/kg rubber,

Fig. 1. The equilibrium swelling degree Q_v^{TOL} and Mooney-Rivlin elasticity constants $2C_1$ confirmed these observations, Tab. 1. It differs from the peroxide curing of P-HNBR and other rubbers, in that the crosslinks density increases linearly with peroxide amount used for curing [7, 16].

On the basis of sol-gel analysis and Charlesby-Pinner equation [17] the extent of degradation processes of rubber chains during curing with TMTD was determined. The gel concentrations $[TMTD]_g = 0.084$ and $[TMTD]_g = 0.020$ mol TMTD/kg rubber for rubber of lower and higher unsaturation used were obtained from extrapolation of linear relation $\log[S] = f(\log[TMTD])$ to $S = 1$. S denotes the sol fraction, i.e. the fraction extracted by methyl ethyl ketone from cured rubber, purified formerly with boiling methanol. Farther, the extrapolation of linear relations $S + S^{1/2} = f([TMTD]_g/[TMTD])$ to $[TMTD]_g/[TMTD] = 0$ gave rather unexpected high ratio of the degradation p to crosslinking acts q , i.e. $p/q = 0.052$ or $p/q = 0.093$ for P-HNBR containing 0.49 or 0.67 mol >C=C</kg rubber resp., Fig. 2. It differs $p/q = 0$ obtained for peroxide curing of these rubbers [15].

The curing of P-HNBR with TMTD is accompanied by decrease in relative absorption intensity of IR band at 970 cm^{-1} (>C=C<)_{trans} comparing to 1424 cm^{-1} (-CH₂-) (Fig. 3) and by bonding of TMTD decomposition and conversion products, probably as dimethylthio- and dimethyldithiocarbamide groups, to double bonds of the rubber. It follows from the determined content of sulfur ($1 \div 2$ wt.%) combined with cured rubber. From the

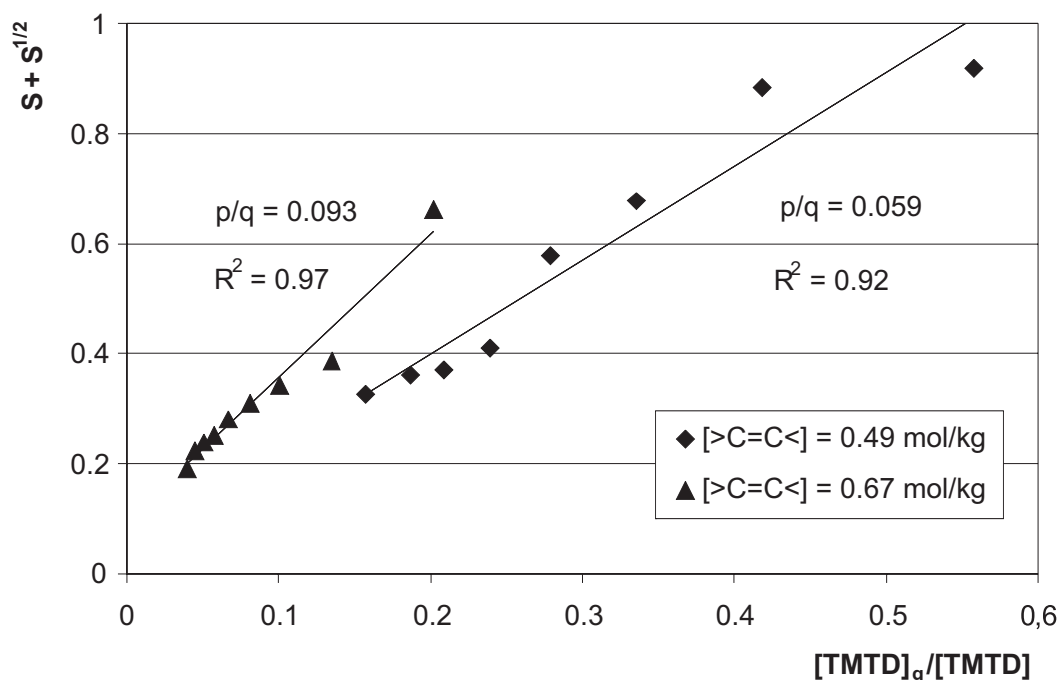


Fig. 2. Content of sol fraction S in cured P-HNBR as function of reduced $[TMTD]_g/[TMTD]$ concentration in rubber; coordinate system according to Charlesby and Pinner [17]

Rys. 2. Zawartość frakcji żolowej S w usieciowanym P-HNBR w funkcji zredukowanego stężenia $[TMTD]_g/[TMTD]$ w kauczuku; układ współrzędnych według Charlesby'ego - Pinnera [17]

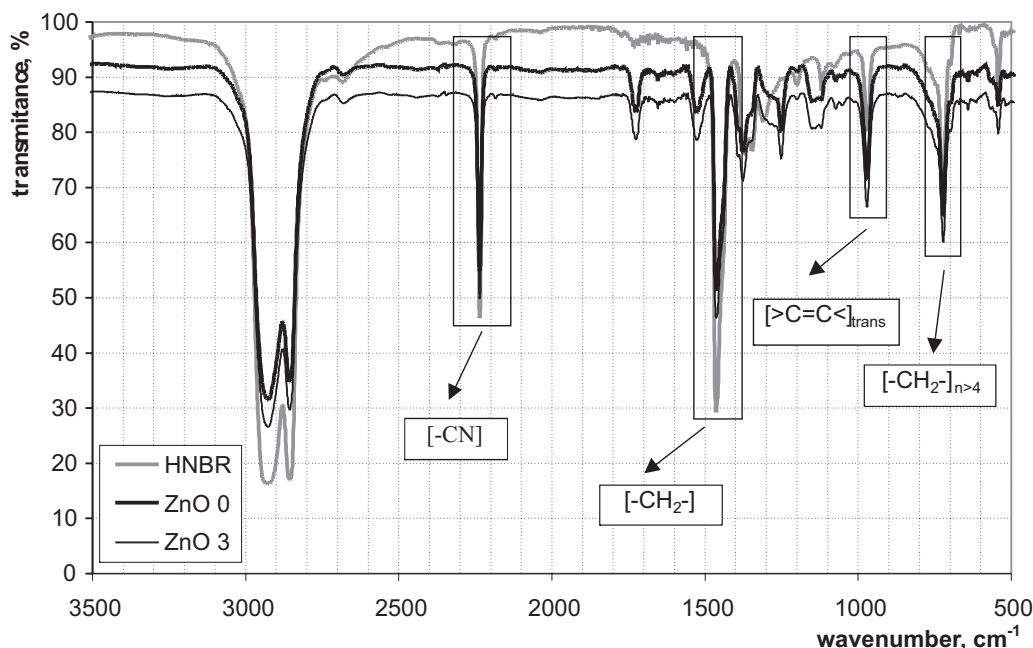


Fig. 3. FT-IR spectra of P-HNBR ($[>C=C<] = 0,67$ mol/kg) before (HNBR) and after heating at $T = 433$ for $t = 25$ min with TMTD (0.20 mol/kg rubber) in absence (ZnO 0) or in the presence of 3 phr ZnO (ZnO 3)

Rys. 3. Widma FT-IR przed (HNBR) i po ogrzewaniu P-HNBR ($[>C=C<] = 0,67$ mol/kg) w $T = 433$ K w ciągu 25 min z TMTD (0,20 mol/kg kauczuku) w nieobecności (ZnO 0) lub w obecności 3 cz. wag. ZnO (ZnO 3)

bound sulfur content and the amount of substances extracted by hot methanol from cured rubber it follows that 20 ÷ 60 % of TMTD incorporated became combined with P-HNBR, probably as pendant groups. According to [1, 2, 6] the bonding of TDS moieties with rubber is one of steps leading to cure of the diene rubbers with these disulfides.

From [1, 2, 6, 10] it follows that the networks of diene rubbers cured with TMTD contain first of all the $>C-C<$, $>C-S-C<$ and $>C-S_2-C<$ crosslinks. Our results showed that in P-HNBR cured with TMTD in the absence of ZnO over 70 % crosslinks are di- and polysulfide.

3.2. Effect of ZnO on P-HNBR curing with TDS

Curing of rubber with TDS alone, i.e. without activators, is applied rather seldom. So we investigated the effect of ZnO as activator on the P-HNBR curing ($[>C=C<] = 0.67$ mol/kg) with these disulfides. The values of scorch time t_{02} , higher increase in vulcanometric torque ΔM , wide plateau and shorter curing time indicated great influence of ZnO on P-HNBR curing with TDS. The achieved curing degree depends both on the TDS used and its ratio to ZnO, reaching the highest value at molar ratio: ZnO/TMTD = 0.028; ZnO/TETD = 0.018 and ZnO/TBzTD = 0.018, Fig. 4. Higher ZnO amount intensifies the reversion, especially during prolonged heating time. Bound sulfur content and the amount of substances extracted with boiling methanol from cured

rubbers indicate the bonding of TDS moieties with P-HNBR chains. Its value (25 ÷ 40 % of TDS incorporated), lower than during heating without ZnO, i.e. even ~0.15 (TETD and TiBTD), ~0.23 (TMTD) or ~0.28 (TBzTD) of its initial concentration, depends on kind of TDS used, but does not depend on the ZnO content in the system.

Table 2. Changes in relative intensity of IR absorption bands of P-HNBR (Therban C3467) cured at 433 K for 25 min with 0.30 mol TMTD/kg rubber in the presence of ZnO

Tabela 2. Zmiany względnej intensywności pasm pochłaniania w IR P-HNBR (Therban C3467) sieciowanego za pomocą TMTD (0,30 mol/kg kauczuku) w $T = 433$ K w ciągu 25 min, w obecności ZnO

ZnO, phr	P-HNBR	1.5	3.0	4.5	6.0
Relative intensity of IR absorption bands					
$[>C=C<]/[-CN]$ ~ 970/2235	0.337	0.481	0.535	0.572	0.649
$[-CH_2-]_{n \geq 4}/[-CN]$ ~ 720/2235*	0.674	0.666	0.719	0.692	0.728

P-HNBR: uncured rubber (kauczuk nieusieciowany)

* $[-CH_2-]_{n \geq 4}/[-CN] \sim 720/2235$; a. v. (średnia) = 0.698 ($\pm 0,028$) in all samples studied (dla wszystkich próbek)

New absorption bands at $1500 \div 1550$ cm^{-1} (probably $-S-SC-N<$ groups), at ~ 1200 and ~ 1300 cm^{-1} (probably $>C-N<$ bands in aliphatic amines) and an increase in relative absorption intensity of band at 970 cm^{-1} ($>C=C<$)_{trans} comparing to band at 1424 cm^{-1} ($-CH_2-$),

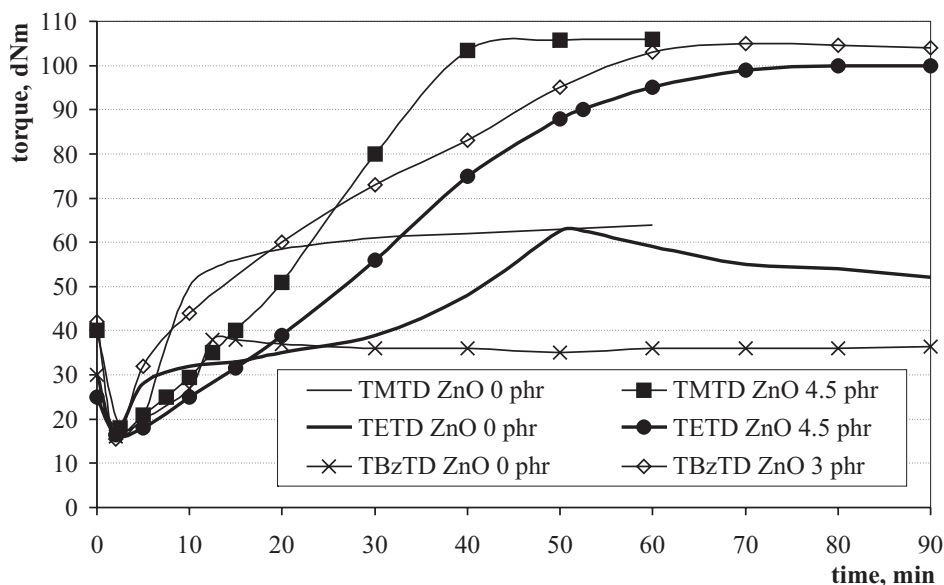


Fig. 4. Effect of TDS kind (0.20 mol/kg rubber) on P-HNBR ($[>C=C<] = 0.67$ mol/kg) curing at $T = 433$ K without (ZnO 0 phr) or in the presence of ZnO (3 or 4.5 phr)

Rys. 4. Wpływ rodzaju TDS (0,20 mol/kg kauczuku) na sieciowanie P-HNBR ($[>C=C<] = 0,67$ mol/kg) w $T = 433$ K bez (ZnO 0 phr) lub w obecności ZnO (ZnO 3 lub ZnO 4,5 phr)

were found in IR spectra of cured P-HNBR, Fig. 3, Tab. 2. The analysis of results obtained lead to conclusion that, contrary to the saturation of $>C=C<$ bonds observed during rubber heating with TDS alone (without ZnO), the P-HNBR curing with TDS-ZnO system is accompanied not only by bonding of TDS moieties but includes

the dehydrogenation of rubber chains too and indicates more complex reactions in the rubber-TDS-ZnO system comparing to system without ZnO. The networks of P-HNBR cured with TDS-ZnO system contain great amount of mono- (30 ÷ 55 %), but even polysulfide (45 ÷ 69 %) crosslinks, Tab. 3.

Table 3. The influence of curing temperature T on selected properties of P-HNBR cured for optimum time with TDS in the presence of 3 phr ZnO; $[TDS] = 0.20$ mol/kg rubber

Tabela 3. Wpływ temperatury procesu T na wybrane właściwości P-HNBR usieciowanego w optymalnym czasie za pomocą TDS w obecności 3 cz. wag. ZnO; $[TDS] = 0,20$ mol/kg kauczuku

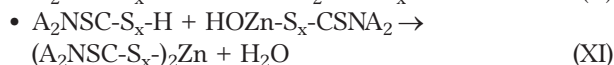
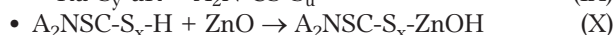
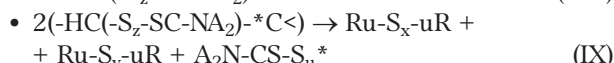
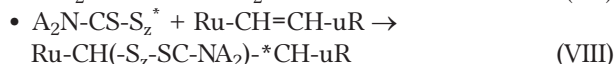
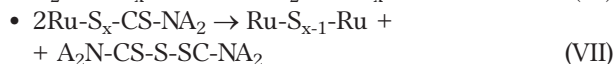
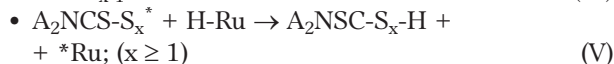
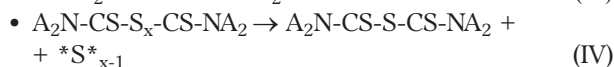
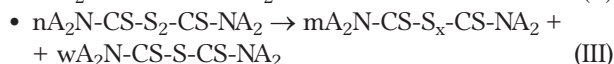
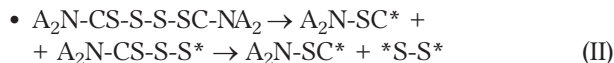
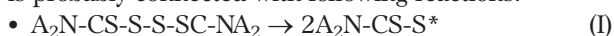
TDS	T, K	$S_{comb.}$	Q_V^{MEK}	ΔM_{max}	Crosslinks structure, %		
		wt.%	ml/ml	dNm	C-S-C	C-S ₂ -C	C-S _x -C
TMTD	433	1.02	9.44	77.1	40	13	47
	443	0.93	9.94	79.4	32	19	49
	453	0.93	12.5	76.4	30	16	54
	463	0.88	12.56	53.6	31	16	53
TETD	433	0.84	9.18	96.9	8	42	50
	443	0.85	11.09	69.9	14	47	39
	453	0.76	12.23	61.0	10	55	35
	463	0.76	14.21	56.0	10	60	30
TBzTD	433	0.87	5.16	91.3	20	38	41
	443	0.79	6.09	69.3	8	42	50
	453	0.78	6.33	60.0	7	43	50
	463	0.80	6.58	56.0	13	43	44
TiBTD	433	0.93	8.86	67.2	43	57	No
	443	0.83	8.88	67.2	50	50	No
	453	0.88	9.93	52.9	56	50	No
	463	0.72	9.99	49.8	48	52	No

3.3. Effect of temperature on P-HNBR curing with TDS

An increase in the process temperature improves the curing rate. We found, as expected, that during P-HNBR curing ($[>C=C<] = 0.67 \text{ mol/kg rubber}$) with TDS-ZnO system the increase in temperature speeds up the curing rate and lowers the scorch time t_{02} . However, the observed increase in vulcanometric torque ΔM , thus the reached curing degree, and the content of combined sulfur decrease with the curing temperature. At the same time the reversion processes become more and more intensive, especially during heating at $T > 433 \text{ K}$ for prolonged time, Fig. 5 and 6, Tab. 3. The increases in curing temperature had no important effect on the crosslinks structure being formed, Tab. 3. Note, that in P-HNBR cured with TiBTD-ZnO system no polysulfide crosslinks were present.

The increase of curing temperature enhances the dehydrogenation processes. It follows from the decrease in relative intensity of absorption bands $[>C=C<]/[-CN]$ from $\sim 0,34$ in the case of uncured P-HNBR to ~ 0.60 after its curing with TMTD-ZnO system at $T = 463 \text{ K}$.

The curing mechanism of diene rubbers with TDS remains not clear in details and is still investigated. One of the steps leading to curing is symmetrical and asymmetrical decomposition of disulfide $A_2N-CS-S-S-SC-NA_2$ to radicals: A_2N-SC^* , $A_2N-CS-S^*$, $A_2NCS-S-S^*$ and $*S-S^*$, and their further reactions with rubber RuH [1, 2, 6]. Thus, the formation of crosslinks of different structure ($>C-S_{x \geq 1}-C<$) in the systems studied is probably connected with following reactions:



Further conversion (VIII, IX) of the radicals formed (I-II, IV, V) and their reactions with rubber chains (V-VII) lead to sulfide crosslinks of different chemical structure. If ZnO is present in the system the hydroxyzinc dithiocarbamate and zinc dithiocarbamate is formed (X, XI), which takes a part in the curing reactions. All these reactions, their extent and yield, depend on the TDS kind and amount used, the presence and amount of ZnO and the TDS/ZnO ratio in the system, and on curing temperature as well.

4. Conclusions

Tetramethyl-, tetraethyl-, tetraisobutyl- and tetra-benzylthiuram disulfides (TDS) can be used as curing agents for the partially hydrogenated acrylonitrile-butadiene

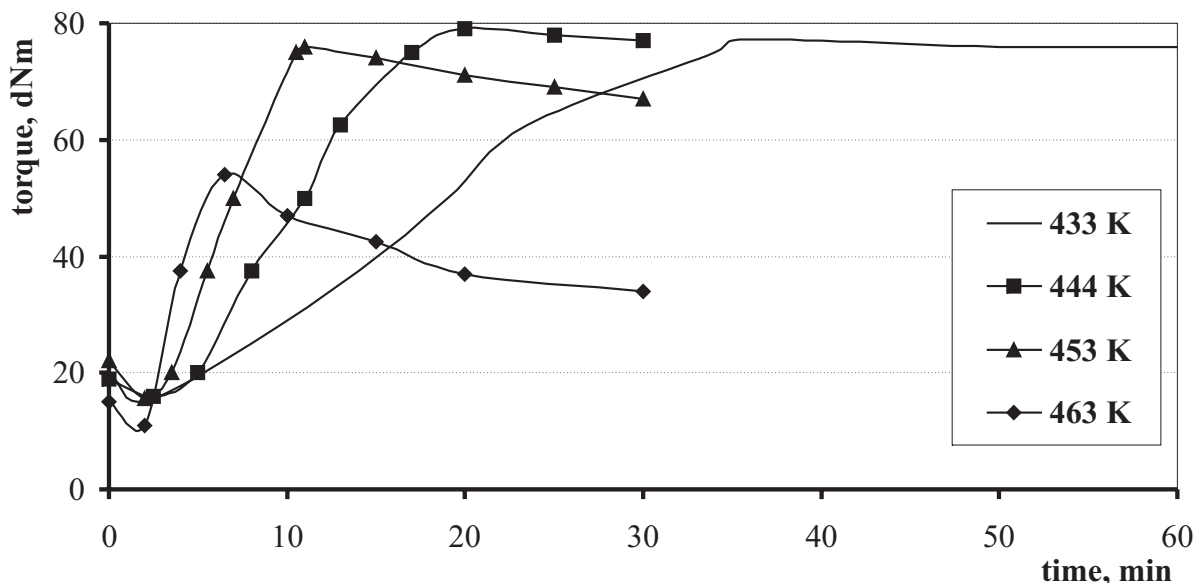


Fig. 5. The influence of temperature on the P-HNBR ($[>C=C<] = 0.67 \text{ mol/kg}$) curing with $0.20 \text{ mol TMTD/kg rubber}$ in the presence of ZnO (3 phr)

Rys. 5. Wpływ temperatury na sieciowanie P-HNBR ($[>C=C<] = 0,67 \text{ mol/kg kauczuku}$) za pomocą $0,20 \text{ mola TMTD/kg kauczuku}$ w obecności 3 cz. wag. ZnO

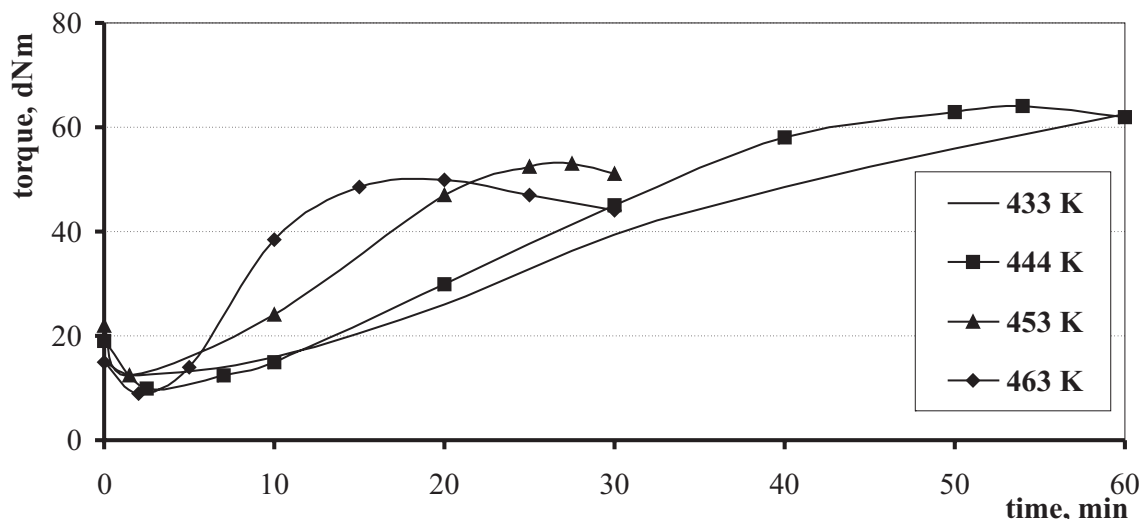


Fig. 6. The influence of temperature on P-HNBR ($[>C=C<] = 0.67$ mol/kg rubber) curing with 0.20 mol TiBTD/kg rubber in the presence of ZnO (3 phr)

Rys. 6. Wpływ temperatury na sieciowanie P-HNBR ($[>C=C<] = 0,67$ mol/kg kauczuku) za pomocą 0,20 mola TiBTD/kg kauczuku w obecności 3 cz. wag. ZnO

diene rubber consisting residual double $>C=C<$ bonds in the amount of >0.4 mol/kg rubber. Both the curing rate and degree are significantly influenced by the residual double bonds content in rubber, the structure and amount of TDS used and the presence of ZnO as curing activator as well. P-HNBR curing with TDS in the absence of ZnO is accompanied to some extent by the saturation of $>C=C<$ double bonds, scission of rubber chains and the bonding of disulfide decomposition and conversion products with the elastomer.

ZnO as activator improves significantly the curing activity of all TDS used. However, when the amount of ZnO used is greater than optimum one, the increase in reversion extent and in modification of rubber chains, especially in the dehydrogenation processes, occurs. The increase of curing temperature (up to $T = 463$ K) speeds up the curing rate, but at the same time, when $T > 443$ K, lowers the achieved crosslinks density and leads to intensification of reversion phenomena. In point of achieved curing degree and reversion stability best results can be obtained when tetraizobutyl- or tetrabenzylthiuram disulfides are used.

In the networks of P-HNBR cured with TDS without or in the presence of ZnO the mono-, di- and polysulfide crosslinks are present in the concentration and proportion depending on the amount and the structure of disulfide used, the presence of ZnO and the curing temperature as well.

References

1. Dogadkin B. A.: *Khimija elasmorov, Khimija, Moskva 1972, pp. 185 – 281.*
2. Coran A. Y.: "Vulcanization", Chap. 7 in: Mark J. E., Erman B., Eirich F. R. (editors): "Science and Technology of Rubber", Academic Press, New York 1994.

3. Rzymiski M. W.: *Polimery 2001, 46, 100-106.*
4. Rzymiski W. M.: *Intern. Polym. Sci. Technol. 2001, 28, T/78-T/84;*
5. Thörmer J., Mirza J., Szentivanyi Z., Obrecht W.: *Kautschuk Gummi Kunstst. 1988, 41, 1208; Rubber World 1989, 201, 25.*
6. Nieuwenhuizen P. J., Reedijk J., van Duin M., McGill W. J.: *Rubber Chem. Technol. 1997, 70, 368.*
7. Dlużeski P. R.: *Rubber Chem. Technol. 2001, 74, 451.*
8. Rybiński P., Janowska G., Kuberski S.: *Polimery 2003, 48, 183.*
9. Janowska G., Rzymiski W. M., Wolska B., Rybiński P., Ślusarska M.: *Prace Nauk. Inst. Technol. Org. Tworzyw Sztucz. Polit. Wrocl., Seria: Konferencje 2003(25), 536.*
10. Rzymiski W. M., Wolska B., Sobieniak A., Wojtczak E.: *Materiały Konf. Naukowo-Technicznej "Elastomery'2003 – Nauka dla Przemysłu", Pułtusk 12-13.06.2003, P18; Pr. Nauk. Inst. Technol. Org. Tworzyw Sztucz. Polit. Wrocl., Konferen. 2003(25), 460.*
11. Rivlin R. S.: *J. Appl. Phys. 1947, 18, 444.*
12. Mooney M.: *J. Appl. Phys. 1940, 11, 582.*
13. Campbell D. S., Saville B.: *Proc. Intern. Conf. Brighton 1967, 1; Rubber Chem. Technol. 1970, 43, 210.*
14. Kiroski D., Sims J., Packham D. E.: *Kautschuk Gummi Kunstst. 1997, 50, 716.*
15. Rzymiski W. M., Srogosz A.: *Elastomery 1996, 1(1), 11.*
16. Rzymiski W. M., Mikrut M., Magryta J., Wolska B.: *Polimery 2005, 50, 718.*
17. Charlesby A., Pinner S. H.: *Proc. Roy. Soc. London 1959, A249, 367.*

Thanks are due to the C. H. ERBSLÖH Poland for the tetraalkylthiuram disulfides granted for our investigations.