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## THE EVALUATION OF BIS(4METHYLPHENYLSULFONYLDITHIOCARBIMATO)ZINCATE (II) (ZNIBU) ACTIVITY IN THE VULCANIZATION OF NBR COMPOUNDS AND ITS EFFECT ON THEIR MECHANICAL PROPERTIES

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**Abstract.** The effect of accelerator type on the vulcanization process and mechanical properties of nitrile rubber (NBR) compounds was investigated. Three commercial accelerators were selected, *N-N-t*-butyl-2-benzothiazole sulfenamide (TBBS), tetramethylthiuram disulfide (TMTD) and bis(dimethyldithiocarbamate)zinc (II) (ZDMC) and compared with the compound bis(4methylphenylsulfonyldithiocarbamate)zincate (II) (ZNIBU). Surprisingly, it was found that the optimum vulcanization time for ZNIBU showed better results than for TBBS.

**Keywords:** dithiocarbamates, zinc complexes, vulcanization, mechanical properties, nitrile rubber.

### 1. Introduction

Metal dithiocarbamates have been synthesized and characterized in the recent years [1-5]. Special interest in the study of metal dithiocarbamates arose from the striking structural features presented by this class of compounds and also due to their diversified applications, in particular in rubber vulcanization. Among metal dithiocarbamates used in the rubber industry, zinc dithiocarbamates are the most widely employed as they are considered ultra-accelerators due to the fast curing rates they impart to rubber compounds [6, 7].

Zinc dithiocarbamates are suitable accelerators for most rubbers, especially the diene-type ones. However, these compounds are highly polar and tend to bloom when mixed to non-polar rubbers like natural rubber (NR) [7]. In earlier studies bis(4methylphenylsulfonyl-

dithiocarbamate)zincate (II) (ZNIBU), a zinc salt dithiocarbamate, was evaluated as accelerator for NR compounds and it was found that in the presence of this compound vulcanization proceeds at slower rates when compared with any of the commercial accelerators investigated [7, 8].

This work reports the vulcanization of NBR using ZNIBU and compares its activity with the commercial accelerators: bis(dimethyldithiocarbamate)zinc(II) (ZDMC), *N-N-t*-butyl-2-benzothiazole sulfenamide (TBBS) and tetramethylthiuram disulfide (TMTD). Nitrile rubber (NBR), due to its high polarity, has excellent oil resistance and degrades at very high temperatures. It is widely used in products like oil seals, water pump seals, blow out preventors, fuel lines, hoses, and fuel pump diaphragms, because of its high oil, solvent, and fuel resistance and low gas permeability [9]. Thus it is expected that ZNIBU will present activity as accelerator for NBR higher than it did for natural rubber. The interest in the research on dithiocarbamate-metal-complexes lies on the similarities these compounds show when compared with the dithiocarbamate complexes, mainly as far as the presence of the  $Zn(S_2C=NR)_2$  moiety in the former structures is concerned. The zinc(II)-bis(dithiocarbamate) complexes are, necessarily anionic species. So, the improvement and/or modulation of the vulcanization activity is an interesting possibility, which can be accomplished either by modifying the solubility of the complexes salts with the use of different cations or different R groups on the dithiocarbamate structures, or by using active counter ions [10].

## 2. Experimental

### 2.1. Methods and Materials

The solvents were purchased from Merck and used without further purification. The chemicals sulfonamide, zinc acetate dihydrate, and tetrabutylammonium bromide were purchased from Aldrich. Carbon disulfide and potassium hydroxide were provided by Vetec. The compound  $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2\text{K}_2\cdot 2\text{H}_2\text{O}$  was prepared in dimethylformamide from 4-toluenesulfonamide,  $\text{CS}_2$  and KOH, as described elsewhere [10].

Nitrile rubber N615B (33 % bond acrylonitrile), Mooney viscosity [ML (1 + 4) 373 K] of 56 and 25 % total solids, was supplied by NITRIFLEX S.A. Industria e Comercio, Rio de Janeiro, Brazil.

### 2.2. Synthesis of ZNIBU

The synthesis was performed according to the scheme in zinc(II) acetate dehydrate and tetrabutylammonium bromide were added to a solution of potassium 4-methylphenylsulfonyldithiocarbamate dehydrate in methanol and water. The mixture was stirred at room temperature for 1 h and the yellowish solid product was filtered, washed with distilled water, ethanol and diethyl ether and dried under reduced pressure, yielding  $(\text{Bu}_4\text{N})_2[\text{Zn}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]$ . The details of the reaction are described elsewhere [10].

### 2.3. Vulcanization

Nitrile rubber was compounded following the formulation, according to ASTM D 3187: nitrile rubber, NBR (100 weight parts), accelerator ( $0.8$  or  $1.2\cdot 10^{-3}$  mol/100 g of rubber), stearic acid (1.0 phr), zinc oxide (3.0 phr), sulfur (1.5 phr). According to Hamed and Rattanasom [11], for solid rubbers, the sulphur/accelerator ratio will determine the type of sulfide crosslinks produced, either mono-, di- or polysulfide ones. Thus, as the ZNIBU molar mass is much higher than that of the other accelerators, in order to compare the activities, the accelerators were added (in mol) as shown in Table 1.

All the additives used in the formulation were of grades commonly used in the industry. The mixture was carried out in a roll mill with 1:1.25 friction rate, at room

temperature. Rheometric parameters were determined in an oscillating disk rheometer, from Tecnologia Industrial, at 423 K and  $1^\circ$  arc, according to ASTM D 2084. The mixes were vulcanized and molded into sheets in a hydraulic press operating at 423 K and 3.0 MPa. From the sheets, specimens for stress strength (DIN 53504) and tear resistance (ASTM D 624) tests were cut. The hardness of the vulcanized compositions was determined using a Shore A durometer.

## 3. Results and Discussion

The efficiency of ZNIBU as accelerator for nitrile rubber vulcanization was investigated by rheometry. Table 2 shows the data from rheometric curves obtained for ZNIBU and the commercial accelerators, TBBS, TMTD, and ZDMC. The selection of the three last compounds was done taking into account that they pertain to different classes of accelerators and therefore they will impart different characteristics of cure rate, safety scorch, number and type of the crosslinks formed [11].

From data in Table 2 it can be seen that by increasing the amount of accelerator optimum vulcanization time ( $t_{90}$ ) undergoes a reduction in all cases. The lowest values were given by ZDMC and the highest by TBBS. The compounds accelerated with ZNIBU presented  $t_{90}$  values which were close to the values for TMTD. The scorch time,  $ts_1$ , is the time available for processing before crosslinks are appreciably formed. At higher concentration of accelerator, this parameter decreased for TMTD and ZDMC, increased for TBBS and remained unchanged for ZNIBU. Minimum torque, which is related to the viscosity of the compound before vulcanization does not change significantly and the three accelerators presented values of the same magnitude. The difference between maximum and minimum torques is related to the degree of cure and was found to be the highest for ZNIBU and TMTD, suggesting that these two compounds were the most efficient accelerators for the NBR compounds in this study. This behavior can also be observed in the rheometric curves recorded during vulcanization of the compounds in the presence of 0.0008 and 0.0012 moles of accelerator, as shown in Figures 1 and 2, respectively. However, as seen in Fig. 2, for higher amounts of accelerator, the TMTD curve, once the maximum value of torque is reached, starts to decrease, which means that degradation is occurring. This behavior is not observed when any of the other accelerators is used.

Table 3 shows the results of mechanical tests. It is possible to note that the compositions with ZNIBU show higher values of 300% modulus and stress resistance than any of the other compositions with the commercial accelerators. However, as for elongation, the composition with ZNIBU gave the lowest values. Results for tear strength of ZNIBU compositions were comparable to the other ones. In all cases the results of hardness were of the same magnitude.

Table 1

Amounts of accelerator added  
in NBR compounding

Accelerator	Molecular mass	Mass (g) in $0.8\cdot 10^{-3}$ mol	Mass (g) in $1.2\cdot 10^{-3}$ mol
ZNIBU	1013	0.81	1.22
TMTD	240	0.19	0.29
ZDMC	306	0.24	0.36
TBBS	238	0.19	0.29

Table 2  
Rheometric parameters for NBR mixes compounded with TBBS, TMTD, ZDMC, or ZNIBU as the accelerator

Accelerator	Accelerator amount, $10^{-3}$ mol/100g of rubber	MI, dN·m	Mh, dN·m	Mh-MI, dN·m	ts <sub>1</sub> , min	t <sub>90</sub> , min	CRI, s <sup>-1</sup>
TBBS	0.8	3.1	15.4	12.3	12.6	49.2	2.7
	1.2	3.1	16.5	13.4	13.8	41.9	3.6
TMTD	0.8	3.1	20.3	17.2	6.0	13.2	13.8
	1.2	2.8	22.5	19.7	5.4	10.2	20.8
ZDMC	0.8	3.3	19.6	16.3	3.0	7.2	23.8
	1.2	3.4	17.3	13.9	2.4	4.8	41.6
ZNIBU	0.8	3.7	23.6	19.9	3.0	15.0	8.8
	1.2	3.6	21.8	18.2	3.0	13.8	9.3

Note: MI – minimum torque; Mh – maximum torque; ts<sub>1</sub> – scorch time; t<sub>90</sub> – optimum vulcanization time; CRI – cure rate index; TBBS – *N-t*-butyl-2-benzothiazole sulfenamide; TMTD – tetramethylthiuram disulfide; ZDMC – bis(dimethyldithiocarbamate)zinc(II); ZNIBU – bis(4-methylphenylsulfonyldithiocarbimato)zincate(II)

Table 3  
Mechanical properties of NBR compositions

Property	Accelerator amount, $10^{-3}$ mol/100g of rubber	Accelerator			
		TBBS	TMTD	ZDMC	ZNIBU
300% Modulus, MPa	0.8	0.9 ± 0.1	1.4 ± 0.1	1.2 ± 0.1	2.2 ± 0.1
	1.2	1.1 ± 0.0	1.5 ± 0.1	1.5 ± 0.1	1.8 ± 0.2
Tensile strength, MPa	0.8	2.2 ± 0.4	3.2 ± 0.4	2.3 ± 0.1	3.6 ± 0.4
	1.2	2.2 ± 0.3	3.0 ± 0.3	2.3 ± 0.2	3.2 ± 0.2
Elongation at break, %	0.8	850 ± 92	593 ± 39	610 ± 27	465 ± 44
	1.2	694 ± 69	551 ± 22	462 ± 41	518 ± 10
Tear strength, KN/m	0.8	15.1 ± 0.2	16.5 ± 0.7	14.4 ± 0.4	14.0 ± 1.9
	1.2	13.5 ± 0.3	14.5 ± 0.3	19.6 ± 0.2	15.5 ± 1.6
Hardness, Shore A	0.8	41 ± 0.4	42 ± 0.4	42 ± 0.5	41 ± 0.4
	1.2	42 ± 1.0	41 ± 0.5	40 ± 1.0	38 ± 0.4

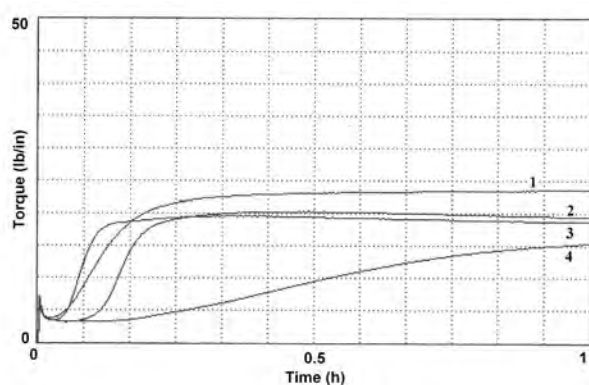


Fig. 1. Rheometric curves for NBR compounded with 0.0008 mol of different accelerators: ZNIBU (1); TMTD (2); ZDMC (3) and TBBS (4)

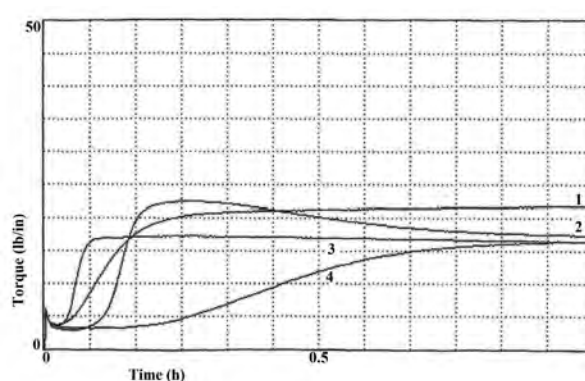


Fig. 2. Rheometric curves for NBR compounded with 0.0012 mol of different accelerators: ZNIBU (1); TMTD (2); ZDMC (3) and TBBS (4)

## 4. Conclusions

Mechanical properties of NBR compounds formulated with ZNIBU were similar to those obtained with commercial accelerators. Nevertheless the values of 300% modulus and tensile strength given by the new accelerator were higher than those found for NBR compounds vulcanized in the presence of three of the most used commercial accelerators: TBBS, TMTD, and ZDMC.

The results obtained for optimum vulcanization time with ZNIBU used as accelerators are close to the values found for TMTD and better than those obtained with TBBS. The values of  $t_{90}$  in the presence of ZDMC were much lower than those for the compositions with other accelerators. These results were already expected since ZDMC is considered an ultra accelerator.

From the results obtained it can be concluded that ZNIBU is an example of a novel class of accelerator for rubber vulcanization. Other analogous compounds are being prepared to extend the studies on their vulcanization activities.

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## References

[1] Ono D., Bragdon J. and Jaeger D.: *Physicochem. & Eng. Aspects*, 2007, **308**, 141.

[2] Nicola C., Ngoune J. et al.: *Inorg. Chimica Acta*, 2007, **360**, 2935.

[3] Shaheen F., Badshah A., Gielen M. et al.: *J. Organometallic Chem.*, 2007, **692**, 3019.

[4] Yin H., Zhai J., Sun Y. and Wang D.: *Polyhedron*, 2008, **27**, 663.

[5] Travnicek Z., Pastorek R. and Slovak V.: *ibid*, 411.

[6] Ondrusova D., Jona E. and Simon P.: *J. Thermal Anal. & Calorimetry*, 2002, **67**, 147.

[7] Hofmann W.: *Rubber Technology Handbook*. Hanser, New York 1989.

[8] Mariano R., Oliveira M., Rubinger M. and Visconte L.: *Eur. Polym. J.*, 2007, **43**, 4706.

[9] Shiny P. and Rani J.: *J. Elastom. & Plastics*, 2006, **38**, 199.

[10] Perpetuo G. et al.: *Polyhedron*, 2003, **22**, 3355.

[11] Hamed G. and Rattanasom N.: *Rub. Chem. Techn.*, 2002, **75**, 323.

### ОЦІНКА АКТИВНОСТІ БІС(4-МЕТИЛФЕНІЛСУЛЬФОНІЛДИТІОКАРБІ- МАТО)ЦИНКАТУ (II) В ПРОЦЕСІ ВУЛКАНІЗАЦІЇ І ЙОГО ВПЛИВ НА МЕХАНІЧНІ ВЛАСТИВОСТІ КОМПОНЕНТІВ НК

*Анотація.* Вивчено вплив природи прискорювача вулканізації на перебіг процесу і механічні властивості нітрилових каучуків (НК). Проведено порівняння N, N-трет-бутил-2-бензотіазолсульфенаміду, дисульфиду тетраметилтиураму та біс(диметилдитіокарбамато)цинкату (II) з біс(4-метилфенілсульфонілдитіокарбамато)цинкатою (II). Встановлено, що оптимальний час вулканізації досягається на досліджуваному прискорювачі.

*Ключові слова:* дитіокарбімати, комплекс цинку, вулканізація, механічні властивості, нітриловий каучук.