

EVALUATING THE EFFECT OF ZINC RESINATE UPON THE PROPERTIES OF NATURAL RUBBER VULCANIZATES

N. Todorova, I. Radulov, N. Dishovsky

University of Chemical Technology and Metallurgy
8 Kliment Ohridsky, 1756 Sofia, Bulgaria
E-mail: ntodor@mail.bg

Received 27 July 2012
Accepted 12 September 2012

ABSTRACT

The influence of zinc resinate on the vulcanization of natural rubber is studied in presence of accelerators with different chemical structure. The aim of present investigation is to study the activation action of resinate on the vulcanization process. The vulcanization characteristics, physico-mechanical parameters of the vulcanizates as well as their resistance to the thermal aging are studied. The possibility to replace zinc oxide with zinc resinate as an activator is investigated. This is necessary concerning the tenfold lower zinc content in resinate as well as its good technological compatibility with the rubber matrix. The ecological importance of zinc resinate used is discussed as well.

Keywords: vulcanization, activators, zinc resinate, natural rubber.

INTRODUCTION

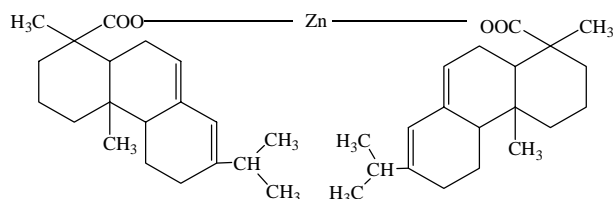
The latest developments in the synthesis of polymers and ingredients as well as the constantly increasing requirements for environment protection have always been taken into account when developing rubber technologies. The most common example in the case is treadwear of pneumatic tires which exploitation leads to evolvement of environmentally harmful zinc oxide. According to some data about 300,000 tons of zinc oxide is used in the European Union, three fourth of which is spent on the production of tires and rubber items [1]. An EU-supported project, entitled ECOZINC, was set up for reducing maximally zinc oxide usage in the production of rubber compounds [2]. As a result, many scientists and companies joined their efforts in the search of a substituent of ZnO [3-8]. The new routes to solving the problem involve zinc-containing organic compounds: first of all zinc stearate [9,13], zinc-m-glycerolate and zinc-2-ethylhexanoate, the latter being more effective of the former two [10]. S. Borros et al. have experimented on

replacing zinc oxide with alkali and earth alkali oxides, layered double hydroxides, etc. [11]. Those compounds were synthesized according to [12]. Thiodiglycol metal complexes have been also used for the purpose [14], namely in NR and SBR rubber based blends.

Some of the theoretic claims evoked our idea to study the effect that zinc resinate produces upon the properties of natural rubber based blends containing various vulcanization accelerators and evaluate its capacities as a vulcanization agent.

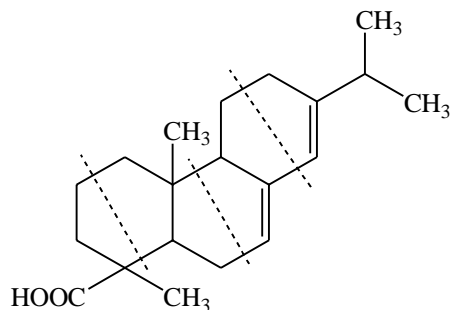
The theoretical claims are the following:

1/ The resinate is a zinc salt of the resin acids which are monocarboxylic resin acids of isocyclic structure - chiefly abietic, levo-piramic and dextro-piramic acids. Its formula is:



2/ The compounds of isocyclic structure are considered as dimmers (terpenes), trimers and isoprene polymers (polyterpenes) while their oxygen derivatives - as terpenoids. Natural rubber is the most important terpenoid in the case.

3/ The following interpretation of abietic acid formula reveals why it and the other resin acids could also be regarded as isoprenoids [15,16].



Thus the acid is similar to natural rubber wherein the dominating component is 1,4-*cis*-polyisoprene.

As seen, on one hand, zinc content in the resin ate is much lower than that in ZnO, while, on the other hand, it could be expected to have good technological compatibility with natural rubber due to the similarity in their chemical nature and to the good dispersion in the elastomer matrix.

4/ The chemical structure above gives a clue of the significant mobility of Zn²⁺ which is of great importance for its application as a vulcanization agent.

5/ The resin ate contains about 7.5 % of Zn while its concentration in the oxide is ten times higher – about 80 % [17].

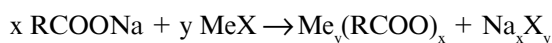
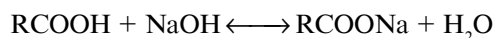
The present work reports on the investigations on the effect that zinc resin ate has upon the main characteristics (vulcanization, physicomechanical and physicochemical) of natural rubber based compounds and vulcanizates in the presence of various accelerators. The aim of investigations carried out is to evaluate the capacities of zinc resin ate as a vulcanization agent.

EXPERIMENTAL

Preparation and characteristics of zinc resin ate (Zn(R)₂)

Zn(R)₂ was prepared according to the classical technology for precipitated sicatives [18,19]. The initially

prepared water soluble salts of the respective organic acid (rosin soaps) were subjected to an exchange reaction with the water soluble salts of the sicative metal (Zn in the case). The reaction proceeded as follows:



where X is the anion of the respective acid.

The exchange reaction was carried out using the aqueous solution of the respective soap and a 10-20% solution of the sicative metal salt. The sicative sediment formed was washed with water and dried. The sicative sediments are of high purity and their metal content is considered to be close to the theoretical one [20].

The obtained Zn(R)₂ was characterized by IR spectroscopy. Fig. 1 presents the compared spectra of the initial colophony and Zn(R)₂.

As seen two new peaks at 1576 cm⁻¹ and 1407 cm⁻¹, assigned to the asymmetric and symmetric vibration of the carboxyl ion, respectively, appear in the spectrum of Zn(R)₂ which are not present in the colophony spectrum. Meanwhile the peak characteristic of the carboxyl group at 1697 cm⁻¹ disappears in the spectrum of Zn(R)₂.

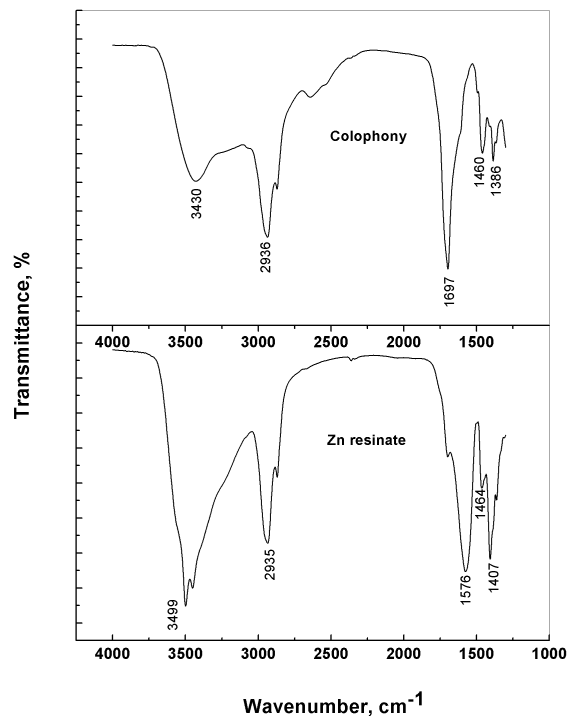


Fig. 1. IR spectra of the colophony and Zn(R)₂

The change in the peak at 3430 cm^{-1} corresponding to the vibrations of the carboxyl group vibrations is also visible.

Preparation of the rubber compounds and their compositions

Two types of NR based compounds were used to study the capacities of $\text{Zn}(\text{R})_2$ as a vulcanization agent. Tetramethylthiuram disulfide (TMTD) was used as an accelerator to prepare the first type of blends and mercaptobenzothiazole (MBT) for the second one (Tables 1 and 2).

The rubber compounds were prepared on an open two-roll laboratory mill (Length/Diameter L/D 320 mm x 160 mm and friction 1,27). The speed of the slow roll was 25 min^{-1} .

Table 1. Compositions of the blends based on NR(SMR10) using MBT accelerator.

Composition	K-0	K-1	K-2	K-3
NR(SMR10)	100,0	100,0	100,0	100,0
ZnO	5,0	-	-	-
$\text{Zn}(\text{R})_2$	-	5,0	10,0	15,0
St	1,5	1,5	1,5	1,5
MBT	1,0	1,0	1,0	1,0
S	2,0	2,0	2,0	2,0

Table 2. Compositions of the blends based on NR(SMR10) using TMTD accelerator.

Composition	T-0	T-1	T-2	T-3
NR (SMR10)	100,0	100,0	100,0	100,0
ZnO	5,0	-	-	-
$\text{Zn}(\text{R})_2$	-	5,0	10,0	15,0
St	1,5	1,5	1,5	1,5
TMTD	1,0	1,0	1,0	1,0
S	2,0	2,0	2,0	2,0

Characteristics of the prepared rubber compounds and the vulcanizates obtained

The following vulcanization characteristics were determined: M_L - minimum torque, which is the measure of the effective viscosity of the rubber compounds studied; M_H - maximum torque as a measure of the vulcanizate stiffness; $\Delta M = M_N - M_L$ - a parameter of the vulcanizate crosslink density; t_s - induction period of vulcanization and t_{90} - the optimum vulcanization time. The above vulcanization characteristics were determined from the vulcanization isotherms taken on a Monsanto oscillating disc vulcameter at 160°C according to ISO 3417:2002. The vulcanization was carried out on a hydraulic press with electric heating at 160°C and 100 Pa.

The following parameters of the vulcanizates were determined:

- Modulus at 100 % and 300 % elongation (M_{100} and M_{300}) according to ISO 37:2002;
- tensile strength (σ) according to ISO 37:2002;
- relative elongation (ϵ_{rel}) according to ISO 37:2002;
- residual elongation (ϵ_{res}) according to ISO 2285:1996
- Shore hardness (Sh) according to ISO 7619:2001;
- thermal aging resistance (72h at 70°C) according to ISO 188:2002;

The parameters of the vulcanizates crosslinking were determined by the equilibrium swelling rate according to the method described in [21].

RESULTS AND DISCUSSION

Vulcanization characteristics of the studied rubber compounds

The vulcanization isotherms of the studied elastomer blends are presented in figures 2 and 3. Tables 3 and 4 summarize their vulcanization characteristics.

As the figures show, regardless of the accelerator, the vulcanization process in the presence of $\text{Zn}(\text{R})_2$ differs significantly from the one carried out in the presence of ZnO. The amount of $\text{Zn}(\text{R})_2$ is also an important factor. When the accelerator is MBT the vulcanization characteristics of the compounds differ slightly. No differences in the induction period have been observed while in the case of using TMTD the compounds do differ in their t_s .

The comparative of the data analysis reveals many differences in the main vulcanization characteristics of

Table 3. Vulcanization characteristics of the rubber compounds with MBT as an accelerator.

Compound code	K-0	K-1	K-2	K-3
M_L , Nm	2,3	0,8	0,8	1,3
M_H , Nm	63,3	29,2	39,0	44,3
$\Delta M=(M_H-M_L)$	74,9	30,0	38,2	43,0
t_s , min.sec	1,10	1,34	2,50	3,10
t_{90} , min.sec	3,21	2,42	4,17	5,41

Table 4. Vulcanization characteristics of the rubber compounds with TMTD as an accelerator.

Compound code	T-0	T-1	T-2	T-3
M_L , Nm	1,7	1,5	1,2	0,7
M_H , Nm	104,8	59,5	63,4	58,1
$\Delta M=(M_H-M_L)$	103,1	58	62,2	57,4
t_s , min.sec	1,11	1,18	1,12	1,13
t_{90} , min.sec	1,45	1,44	1,43	1,49

the elastomer compounds prepared using the two types of accelerator.

The compounds prepared with MBT and comprising $Zn(R)_2$ at 5,0 and 10,0 phr have much lower minimum torque M_L than the etalon ones with ZnO.

A decrease of M_L with the increasing $Zn(R)_2$ amount has been also observed for the compounds prepared with TMTD accelerator.

It could be assumed that in both cases the higher $Zn(R)_2$ amount acts as a softener; i.e. it decreases the viscosity of the non-vulcanized rubber compound. That could be explained by the fact that the organic part of

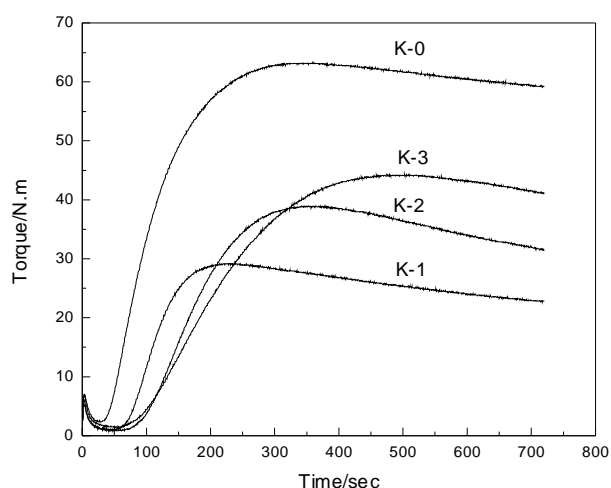


Fig. 2. Vulcanization isotherms of the rubber compounds with MBT as an accelerator.

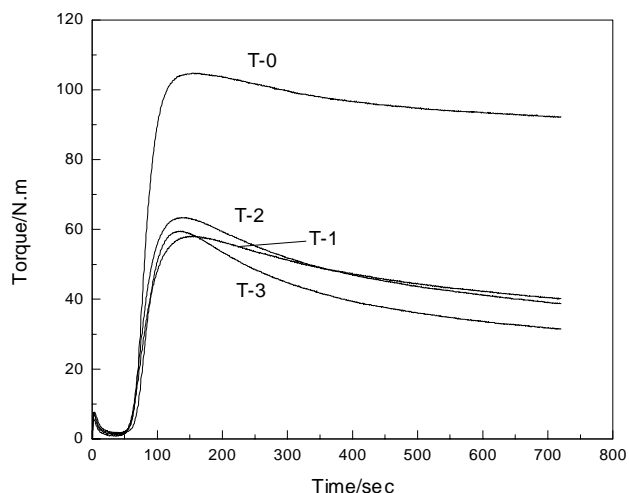


Fig. 3. Vulcanization isotherms of the rubber compounds with TMTD as an accelerator.

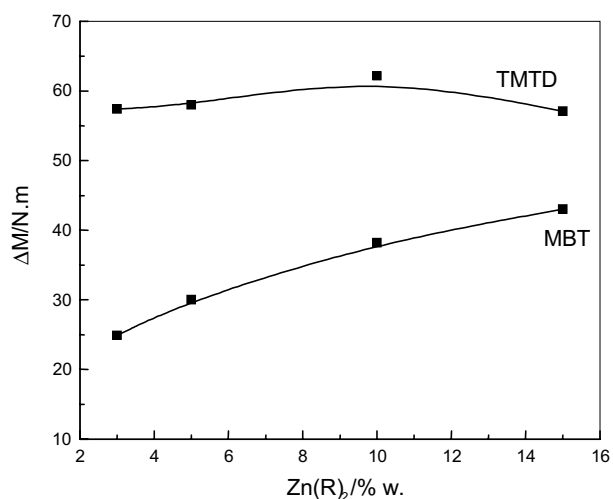


Fig. 4. Dependence of ΔM on $Zn(R)_2$ amount.

Zn(R)₂ is rather voluminous and expands the distance between the rubber macromolecules weakening the macromolecular interactions. A similar effect has been observed in the case of zinc stearate [13].

The maximum torque M_H which is a measure of the vulcanizates stiffness for both types of compounds comprising Zn(R)₂ is lower than that of the etalon compound with ZnO. The increase of Zn(R)₂ amount in the compounds prepared with MBT leads to M_H rise to 43 N m.

As mentioned above, ΔM = (M_H-M_L) is a very important parameter. Its values similar to the ones for M_H are much lower for both types of compounds comprising Zn(R)₂. That suggests much looser vulcanization crosslinking.

Fig. 4 plots the dependence of ΔM on Zn(R)₂ amount for both types of compounds. As shown the curves have different pattern and location. That allows the assumption that the two types of accelerators produce different crosslinking under the same other conditions, i.e. they influence the effectiveness of Zn(R)₂.

The next parameter deserving interest is the Scorch time t_s standing for the induction period of the vulcanization process. For the compounds prepared with MBT it increases from 1,34 to 3,10 min.sec with the increasing Zn(R)₂ amount compared to 1,10 min.sec for the etalon with ZnO. The compounds with TMTD have the same t_s as the etalon sample with ZnO.

We consider the optimum vulcanization time - t₉₀ as the most important parameter.

Noteworthy is how it changes for the two types of rubber compounds. The compounds with TMTD have almost the same t₉₀ as the etalon sample with ZnO.

The case of the compounds with MBT is different. With the increasing Zn(R)₂ amount to 5,0; 10,0 and 15,0 phr t₉₀ increases from 2,42 to 4,17 and 5,41 min.sec., while the etalon sample with ZnO has t₉₀=3,21 min.sec.

Determining the crosslinks parameters

The determined parameters – molecular weight of the segment between two crosslinks - M_C and number of the intermolecular crosslinks – n give additional information on the vulcanizates crosslinks density.

The values of those parameters for the two types of compounds prepared with MBT or TMTD accelerator are presented Tables 5 and 6.

Tables 5 and 6 show the highest M_C to be in the case of the rubber compound comprising Zn(R)₂ at 5,0

Table 5. Network parameters of vulcanizates prepared with MBT accelerator.

Compound code \ Parameters	K-0	K-1	K-2	K-3
M _C	6500	21300	11400	13900
n	60	20	35	30

Table 6. Network parameters of vulcanizates prepared with TMTD accelerator.

Compound code \ Parameters	T-0	T-1	T-2	T-3
M _C	4500	13900	7700	7500
n	90	30	52	53

phr. As seen, the increase in its amount leads to lower M_C values. The best result achieved is for the compound comprising Zn(R)₂ at 10,0 phr which have M_C = 11400 and n=35 compared to M_C = 6500 and n=60 for the etalon sample with ZnO.

Table 6 presents analogous results for the compounds prepared with TMTD accelerator. The compounds comprising Zn(R)₂ at 10,0 and 15,0 phr have close M_C values - M_C = 7700 and M_C = 7500, respectively. The number of crosslinks is n=52 and n=53, while for the etalon sample with ZnO it is n=90.

The summary of the data in the two tables reveals that M_C values for the segments between two crosslinks for the rubber compounds comprising Zn(R)₂ activator are about 1,7 times higher than that for the etalon sample with ZnO (in the best case). Meanwhile the number of crosslinks – n in the compounds studied is about 60 % of the one in the etalon sample with ZnO. Those facts allow the main conclusion that Zn(R)₂ as an agent yields vulcanizates of looser crosslinking, if compared to that of the vulcanizates with ZnO. The fact is confirmed by the measured M_H values. Hence, the resin is less effective as a vulcanization agent. However, the experiments run with compounds comprising

neither ZnO, nor Zn(R)₂ have shown that Zn(R)₂ does act as a vulcanization agent. Those compounds had M_C = 27000 (samples prepared with MBT accelerator) and M_C = 18700 (samples prepared with TMTD accelerator) while the values for the compounds comprising Zn(R)₂ at 5 phr are M_C = 21300 and M_C = 13900, respectively (Tables 5-6).

Determination of physicomechanical parameters and the resistance to thermal aging

The experimental results presented in the previous paragraphs evidence that the usage of Zn(R)₂ as an activator results into a looser vulcanization structure. When using Zn(R)₂ as an activator the physicomechanical parameters of the compounds prepared with MBT accelerator are expectedly poorer than those of the vulcanizates with ZnO activator (Table 7).

The said above concerns especially M₁₀₀ and M₃₀₀. The change in tensile strength is more interesting. The vulcanizates of the etalon compounds comprising ZnO at 5,0 phr have σ = 14,7 MPa, while those with Zn(R)₂ at 5,0; 10,0 and 15,0 phr have σ = 9,7 MPa; σ = 11,0 MPa and σ = 14,1 MPa, respectively. Hence, the compounds comprising Zn(R)₂ at 15,0 phr have almost the same tensile strength as the vulcanizates with ZnO at 5,0 phr.

The relative elongation does not change considerably for all vulcanizates, neither do the residual elongation and Shore hardness.

Table 7. Physicomechanical parameters of vulcanizates prepared with MBT accelerator prior to their thermal aging.

Compound code	K-0	K-1	K-2	K-3
M ₁₀₀ , MPa	1,0	0,5	0,5	0,5
M ₃₀₀ , MPa	2,3	0,9	0,9	1,0
σ, MPa	14,7	9,7	11,0	14,1
ε _{rel.} , %	640	640	690	650
ε _{res.} , %	15	10	15	10
Sh	41	39	40	43

Table 8. Physicomechanical parameters of vulcanizates prepared with TMTD accelerator prior to their thermal aging.

Compound code	T-0	T-1	T-2	T-3
M ₁₀₀ , MPa	1,5	0,6	0,8	0,9
M ₃₀₀ , MPa	6,1	1,3	1,9	2,3
σ, MPa	27,6	20,4	21,1	21,8
ε _{rel.} , %	580	880	760	830
ε _{res.} , %	15	15	15	15
Sh	51	41	43	44

Much better are the results obtained when TMTD is used as accelerator (Table 8), although the parameters of the compounds comprising Zn(R)₂ are worse than those of the etalon compounds comprising ZnO.

With the increase in Zn(R)₂ up to 15,0 phr σ does not change considerably and its values are close to the one of the etalon compound.

The relative elongation of the vulcanizates comprising Zn(R)₂ is higher than that of the etalon compound. The Shore hardness is about 10 units lower.

As a whole the results prove that the vulcanizates comprising Zn(R)₂ activator have capacities for practical applications, especially when the materials should meet specific requirements.

Therefore the data on the accelerated thermal aging of the vulcanizates at 70°C for 72 h presented in Tables 9 and 10 are of particular interest.

Table 9. Aging coefficients of vulcanizates prepared with MBT accelerator.

Compound code	K-0	K-1	K-2	K-3
C _{tensile strenght}	7	9	15	17
C _{relative elongation}	12	17	19	17

Table 10. Aging coefficients of vulcanizates prepared with TMTD accelerator.

Compound code Coefficient	T-0	T-1	T-2	T-3
C _{tensile strength}	-15	-12	-10	-15
C _{relative elongation}	-25	-30	-32	-35

It is worth noting that according to the results presented the aging coefficients of the vulcanizates prepared with MBT accelerator are positive. That shows the values of the respective parameters to be higher than those prior to the aging. It is known that when the accelerators used belong to the class of thiazoles the bonds formed are predominantly polysulfide ones [22]. During the thermal aging those bonds break and the active sulfur thus evolved crosslinks additionally the vulcanizates. That improves their physicochemical parameters. Such an effect has not been observed for the vulcanizates prepared with thiuram. The values of the aging coefficients are negative. That shows that the values of the respective parameters decrease after the aging. Very significant differences in the aging coefficients for the vulcanized comprising ZnO and Zn(R)₂ have not been observed, although those comprising Zn(R)₂ are less resistant to aging. Further studies are needed to clarify the effect of the vulcanization crosslinking upon the thermal aging resistance.

CONCLUSIONS

The determined characteristics of vulcanizates comprising zinc resinate (at 5,0; 10,0 and 15,0 phr) have been compared to those of vulcanizates of analogous composition comprising zinc oxide at 5,0 phr. The zinc concentration in the latter is ten times higher than that in the resinate (80 % against 7,5 %).

It has been established that using zinc resinate instead of zinc oxide at equivalent amounts leads to a decrease of minimum and maximum torque values and to a prolongation of the induction period and optimum vulcanization time. When the accelerator used is mercaptobenzothiazole, the effects are more pronounced than those in the cases of implementing tetramethylthiuram disulfide.

As far as the physicochemical parameters are concerned, it has been found that for the vulcanizates comprising zinc resinate, they are slightly lower than those for the vulcanizates with zinc oxide. At higher amounts of zinc resinate the said differences get smaller.

It has been found the crosslinking of the vulcanizates comprising zinc resinate to be looser (less dense) than that of the vulcanizates comprising zinc oxide and the number of crosslinks to be about 60% of those in the compounds with zinc oxide.

Zinc resinate has turned to be a less effective vulcanization agent than zinc oxide but when there are special requirements regarding preparation of nontoxic and environmentally friendly rubber compounds it comes as an appropriate solution.

REFERENCES

1. A. Schröter, Tire Technology International, 2005.
2. A.V.Chapman, Safe rubber chemicals: Reduction of zinc levels in rubber compounds, TARRC/MRPRA, 1997; A.V. Chapman, Reducing zinc in rubber compounds, in: 2005, Proc. Int. Rubber Conference IRC '05, Maastricht, The Netherlands, June 6 – 9, 2005.
3. G. Heideman, R. N. Data, J. Noordermeer, B. van Baarle, Activators in Accelerated Sulfur Vulcanization, Rubber Chem. Technol., **77**, 3, 2004, 512-541.
4. G. Heideman, J. Noordermeer, R. N. Data, B. van Baarle, Modified Clays as Activator in Sulphur Vulcanisation: A Novel Approach to Reduce Zinc Oxide Levels in Rubber Compounds, Kautsch. Gummi Kunstst., **12**, 2003.
5. H. Irving, R. J. P. Williams, The stability of transition-metal complexes, J. Chem. Soc., 1953, 3192.
6. F. K. Lautenschlaeger, K. Edwards, Model Compound Vulcanization - Part V. The Effect of Chemical Additives and Fillers, Rubber Chem. Technol., **53**, 1, 27, 1980, 27-47.
7. V. Duchacek, A. Kuta, P. Pribil, J. Appl. Polym. Sci., **47**, 1993, 743.
8. P. Versloot, J. G. Haasnoot, J. Reedijk, M. van Duin, and J. Put, Sulfur Vulcanization of Simple Model Olefins Part III: Vulcanization of 2,3-Dimethyl-2-Butene in the Presence of Different Metal Complexes, Rubber Chem. Technol., **67**, 2, 1994, 263-279.

9. G. Heideman, J. Noordermeer, R. N. Data, B. van Baarle, Various Ways to Reduce Zinc Oxide Levels in S-SBR Rubber Compounds, *Kautsh. Gummi Kunstst.*, **95**, 2005, 1388.
10. A. Wei., *Rubber Industry of China*, **48**, 1, 2001.
11. Berta Vega Sanchez, *New Insights in Vulcanization Chemistry using Microwaves as heating Source*, Doctoral Thesis, Institute Quimic de Saria, Barcelona, Spain, 2010, 143.
12. W. T. Reichle, Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite), *Solid State Ionics*, **22**, 1, 1986, 135-141.
13. N. Tipova, *Disertatzija*, 2006 (in Bulgarian).
14. S. Taghvali-Ganjali, *Tire Thechnology International, Annual Review*, 2008, 32-34.
15. A.N. Nesmianov, N.A. Nesmianov, *Nachala organicheskoj chimii*, *Chimija*, Moskwa, 1974, 595 (in Russian).
16. J. Roberts, M. Kaserio, *Osnovi organicheskoj chimii*, T.2, Moskwa, 1978, 553, (in Russian).
17. *Chimicheskii entziklopedicheski slovar*, Moskwa, 1983, (in Russian).
18. V. S. Kiselev, *Olifa i laki*, 3 izd., Moskwa-Leningrad, 1940, (in Russian).
19. A.Ja. Drinberg, *Technologija plenkoobrazujustich veshtestv*, 2 izd., Leningrad, 1955 (in Russian).
20. M.F. Sorokin, L.G. Shod, Z.A. Kochkova, *Chimija i tehnologija plenkoobrazujustich veshtestv*, *Chimija*, Moskwa, 1981, (in Russian).
21. P. Nikolinski, *Technologija na kautshuka*, *Technika*, Sofia, 1962, 677, (in Bulgarian).
22. M. H. S. Gradwell, W. J. McGill, Sulfur vulcanization of polyisoprene accelerated by benzothiazole derivatives. II. Reaction of 2-mercaptobenzothiazole and its zinc salt with sulfur and ZnO in polyisoprene, *J. Appl. Polym. Sci.*, **58**, 1995, 2193-2200.