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Influence of silica yielded from the pyrolysis-cum-water vapour of waste “green” tires on the properties of epoxidized natural rubber based composites in the presence of different kinds of zinc soaps

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Abstract

Recently there is a tendency towards the use of renewable materials with non-petroleum origin in automobile tire production. Carbon black as a filler in rubber mixtures for automobile tires production recently being often replaced with silica. Decomposition of waste tires is one of the biggest world ecological problems nowadays. The object of the study is a material containing silica and carbon black with nano-sized particles (SiO2D), produced by the recycling of scrapped „green” tires via pyrolysis, as a filler in rubber composites based on epoxidized natural rubber. The possibility this material to be used again as filler in epoxydized natural rubber based composites has been studied. The curing characteristics, as well as the mechanical and dynamic properties of SiO2D filled compositions in the presence of various additives (zinc soaps), that influence on the properties listed above, have been studied. The presence of zinc soaps leads to lower viscosity of composites and influences the cross-linking, which in itself leads to changes of mechanical and dynamic properties of vulcanizates. The results of the study about mechanical and dynamic properties of vulcanizates show that the studied filler is not active enough in comparison to commercial grades silica and its reinforcing effect is significantly lower.

Keywords: *waste tires, pyrolysis, solid residue, silica, epoxydized natural rubber, vulcanization activators, zinc soaps*

1. Introduction

The rubber blends, intended for production of heavy automobile tires, are based mainly on a natural rubber. In answer of global problem with petroleum depletion, there is a tendency towards the replacement of petroleum materials with other synthetic or natural materials with non-petroleum origin. Increasingly it is preferred carbon black, obtained from petroleum raw materials, to be replaced with inorganic reinforcing fillers, such as silicon dioxide (silica). There are some technological problems which affect the compatibility between standard natural rubber and silica. The non-polar character of natural rubber and strong decrease of its viscosity with the increasing of temperature during the mixing as well as the polar character of silica particles hinder filler distribution in the rubber matrix [1-7]. One of the steps to deciding this problem is the replacement of standard natural rubber with epoxidized natural rubber (ENR). In result of epoxidation, there is a increase of rubber polarity. ENR is reinforced well by silica even in the absence of couple agents (organosilanes) [8]. By the other hand, organosilanes like bis(3-triethoxysilylpropyl)disulfide or bis(3-triethoxysilylpropyl)tetradisulfide are implemented for improving the dynamic properties of silica reinforced natural rubber based vulcanizates. During the mixing the absorbed moisture in the filler promotes the hydrolysis of silanes ethoxy groups. That leads to interactions with hydroxyl groups of SiO_2 and to a better distribution of this filler in the rubber matrix. This interactions described reduce the rolling and abrasion resistance of the tires and enhance their adhesion on wet roads [9-11]. In relation with all said above there is a tendency towards a massive implementation of so called “green” tires, which use high dispersion silica as an active filler in combination with various organosilanes. “Green” tires are characterized with about 20% lower rolling resistance and better wet grip without compromising with their abrasion [12-14].

Pyrolysis is one of the most perspective methods for recycling and utilization of waste tires, including waste “green” tires. The solid yield, obtained via pyrolysis of waste “green” tires, comprises mainly silica and could be reused as active filler in other rubber vulcanizates. Under normal conditions the pyrolysis of vulcanizates filled with silica having hydroxyl groups on its surface might lead to undesired calcification parted by agglomeration of the filler particles. Assumedly in the course of pyrolysis-cum-water vapor of SiO_2-reinforced vulcanizates the hydroxyl groups on the filler surface may be preserved and those that have reacted with silanol ones might be recover. Moreover, the chemical nature of SiO_2 surface as well as its particles size will remain the same [15]. In previous studies a solid product SiO_2D has been obtained via pyrolysis-cum-water vapor of model vulcanizates with the same compound like those of “green” tires tread. It has been found by IR-FTIR and EDXRF spectroscopy that the product contains 65% of SiO2, 30% of carbon black, 3% of ZnO, and 2% of other components. The mechanical and dynamic properties and SEM micrographs of the vulcanizates of model sSBR/BR-based blends having a different SiO_2D filler content have been compared to those of vulcanizates filled with conventional SiO_2 and carbon black at a 2:1 ratio. Differences have been established neither in the mechanical properties (Modulus 300, tensile strength, abrasion, etc.) nor in the dynamic properties (heat build-up, tan δ, etc.) of the vulcanizates filled with SiO_2D and of those filled with conventional SiO_2 and carbon black at a 2 : 1 ratio. It has been established that the mechanical and dynamic properties of the vulcanizates filled with SiO_2D are slightly lower, but similar to those filled with conventional SiO_2. The size of SiO_2D particles has been found to be the same as that of conventional SiO_2. Their distribution in the rubber matrix also does not differ [15].

The accelerated sulfur vulcanization of rubber is a complicated chemical process. The detailed reaction scheme of vulcanization process is still not well studied, although the practical application of rubber vulcanizates has been known for more than 150 years [16, 17]. The high activity of zinc oxide can be explained on the basis of the chemistry of complex formation. A preceding reaction with stearic acid forms the rubber hydrocarbon-soluble zinc stearate and liberates water before the onset of cross-linking [18]. There are other investigations supposing that Zn^{2+}-ions form these active complexes with accelerators, which are more reactive than the free accelerator [19]. It seems that the complex, formed from accelerator, sulfur, two-valent zinc from the zinc oxide and fatty acid, represents the actual accelerating agent, whose activity controls the formation of sulfur cross-links in the time of cure process. Action, similar to that of the fatty acids, is performed also by their zinc salts - so called zinc soaps. The zinc soaps of a short aliphatic chain (C6-C8) display an activating action in the absence of zinc oxide too [20]. The replacement of zinc oxide by zinc soaps in the rubber compound, results in decrease of the content of zinc ions, defined as eco-toxic [21]. The zinc salts of the organic acids with a longer aliphatic chain (C16-C18) have a less expressed activating action, but adding them to rubber compounds in which zinc oxide and thiazole accelerator are present, leads to an improvement of compounds, plasticity as well as of the tensile strength and the elasticity of their vulcanizates. [16, 20]. Various soaps of the organic acids have been investigated in natural rubber compounds in order to demonstrate the dependency of their properties on their structure. The influence of the chain length, branching and aryl group content on the cross-link density and reversion resistance has been studied. Investigated rubber compound is intended for production of tires. It has been found out that in some of the cases, the reversion resistance during vulcanization is considerably improved [19].

The purpose of this study is to investigate the influence of solid residue, obtained via pyrolysis-cum-water vapour of “green” tire treads, containing mainly silica, as active filler on the properties of epoxidized natural rubber based composites, comprising various kinds of zinc soaps, in the presence and absence of zinc oxide and stearic acid.

2. Materials and methods

2.1. Materials

The investigations were performed using the following materials:

Epoxidized natural rubber (Epoxyprene-25), purchased from San-Thap International Co.,Ltd, was used as a polymer matrix. Epoxyprene-25 is a cis 1,4 – polyisoprene, which comprises 25±2% epoxide groups randomly dispersed along the polymer backbone. SiO_2D – a solid residue, obtained via cum-water vapor pyrolysis of ENR based model vulcanizate, comprising 70 phr SiO_2

(Ultrasil 7000 GR). The ash content of the solid residue is about 95,4%, 89% from which are presented of silica (SiO_2), 5.5% of zinc oxide and the rest – from other compounds such as: Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, TiO_2, CuO, etc. The zinc resinate is purchased from Chemos GmbH, Germany. Plastikol is a trade product, comprising a mixture of different fatty acid zinc salts. It is manufactured by the "Industrial Chemistry" Ltd company in Bulgaria. The acids in Plastikol are mainly unsaturated – about 50% oleic and 15% linoleic one. Plastikol incorporates also saturated fatty acids – about 30% stearic and 5% palmitic acid. The zinc content is about 8%. The other ingredients such as zinc stearate, zinc oxide, stearic acid, bis(triethoxysilylpropyl)disulfide (TESPD, Si 266), N-tert-butyl-2-benzothiazolesulfenamide (TBBS) and sulfur were also of commercial grades.

2.2. Methods

The vulcanization characteristics of the rubber compounds were determined at 160°C on a Moving Die Rheometer Monsanto (MDR 2000 Alpha Technologies) according to ISO 3417:2008. The mechanical properties of the studied composites were determined according to ISO 37:2011. The Shore A hardness of the studied composites was determined according to ISO 7619-1:2010, while the abrasion - according to ISO 4649:2010. Complex dynamic modulus and heat build-up of studied vulcanizates were determined on a Goodrich flexometer at a 850 min^{-1} deformation rate. The dependences of the mechanical loss angle tangent (tan δ) on the temperature of the studied composites were investigated using a Dynamic Mechanical Thermal Analyzer Mk III system (Rheometric Scientific). The data were obtained at a frequency of 5 Hz and strain amplitude of 64 µm in the temperature range from -50°C to 100°C using a heating rate of 3°C/min under single cantilever bending mode.

2.3. Preparation of rubber composites

The formulations of the compounds based on epoxydized natural rubber (Epoxyprene-25) are presented in a Table 1.

	Ctrl	**ZnSt**	**Pl**	**Ctrl'**	**ZnSt'**	**Pl'**
ENR, Epoxyprene-25	100	100	100	100	100	100
SiO_2D	70	70	70	70	70	70
ZnO	-	-	-	4	4	4
Stearic acid	-	-	-	1	1	1
Zinc stearate	-	5	-	-	5	-
Plastikol	-	-	5	-	-	5
TESPD, Si 266	5	5	5	5	5	5
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	2	2	2	2	2	2

***Table 1.** Compositions of the investigated rubber compounds /phr/.*

The rubber compounds were prepared at two stages according to the mixing schedule presented in Table 2. At the first stage the mixing was performed on a Brabender Plasti-Corder PLE651 fitted with a 300 cm^3 cam type mixer. The silane coupling agent (TESPD, Si 266) was mixed with the studied filler prior to their placing into the mixer camera. At the second stage zinc oxide, stearic acid (presented only in second series of rubber mixtures), sulfur and the accelerator were added to the mixture compounds on an open two-roll laboratory mill L/D 320x160 and friction 1,27. The vulcanization process of the natural rubber based compounds was carried out in an electrically heated hydraulic press using a special homemade mold at temperature 160°C and under pressure 10 MPa.

Stage 1, Brabender Plasti-Corder PLE651, Rotor speed 40 rpm, Temperature 140ºC			
Mixig order	Ingredients	Mixing time, min	Cumulative time, min
1	Epoxydized natural rubber (Epoxyprene-25)	2	2
2	Zinc stearate, Zinc resinate, Plastikol	2	4
3	SiO_2D and TESPD (Si 266)	5	9
Stage 2, Laboratory Two Roll Mills, Friction 1.27			
1	1st stage rubber batch	0	2
2	Zinc oxide and Stearic acid	2	2
3	Sulfur and TBBS	5	7

Table 2. *Mixing schedule of the investigated rubber compounds.*

3. Results and discussion

3.1. Curing properties

Table 3 shows the main vulcanization characteristics of studied rubber compounds in the absence of zinc oxide and stearic acid, determined via their cure curves (Figure 1) at 160 ^{o}C.

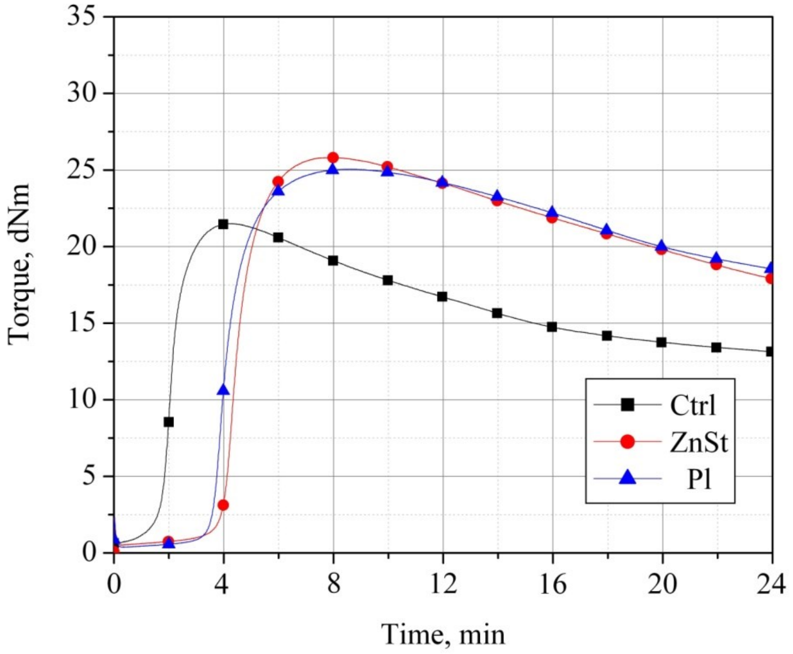

Figure 1. *Cure curves of the studied rubber compounds in the absence of ZnO and stearic acid, taken at 160°C.*

It is obvious from Figure 1, that for all investigated compounds there is a strongly expressed reversion in their cure curves after reaching the optimum curing time (T_{90}). The reversion is most apparent with the control compound (Ctrl) in the absence of vulcanization activators.

	Ctrl	ZnSt	Pl
Minimum torque, ML, dNm	0.62	0.50	0.36
Maximum torque, MH, dNm	21.51	25.83	25.05
ΔM=MH-ML, dNm	20.89	25.33	24.69
T_{s2}, min:s	1:37	3:55	3:34
T_{90}, min:s	2:51	5:40	5:29
V, %/min	81	56	51

Table 3. *Vulcanization characteristics of the studied rubber compounds in the absence of ZnO and stearic acid.*

From Table 3 it is seen, that the scorch time (T_{s2}) is shortest with the control mixture (Ctrl) and it prolongs in the presence of zinc soaps. That is typical for the substances, which have an activating effect under the vulcanization accelerators. In regard to the optimum curing time (T_{90}), the control mixture has the shorter T_{90} in comparison with those of the mixtures, comprising zinc soaps. Their optimum curing times are twice longer. The lower cure rates of the compounds, comprising zinc soaps, compared to those of the control mixture /Table 3/, confirm the fact, that the vulcanization activators lead to a delay of the cure rate, but contribute to a denser crosslink network and favorable changes of its structure.

It is considered that the difference between the maximum and minimum torque (ΔM) gives an indirect idea of crosslink network density. It is seen from Table 3 that the mixtures, containing zinc stearate (ZnSt) and plastikol (Pl), have the highest values of ΔM, compared to the value of ΔM of control mixture, which is apparently lower. That confirms completely the said above about activating additives. In addition it could be said, that the values of ΔM of the composites, comprising various zinc soaps, are commensurable.

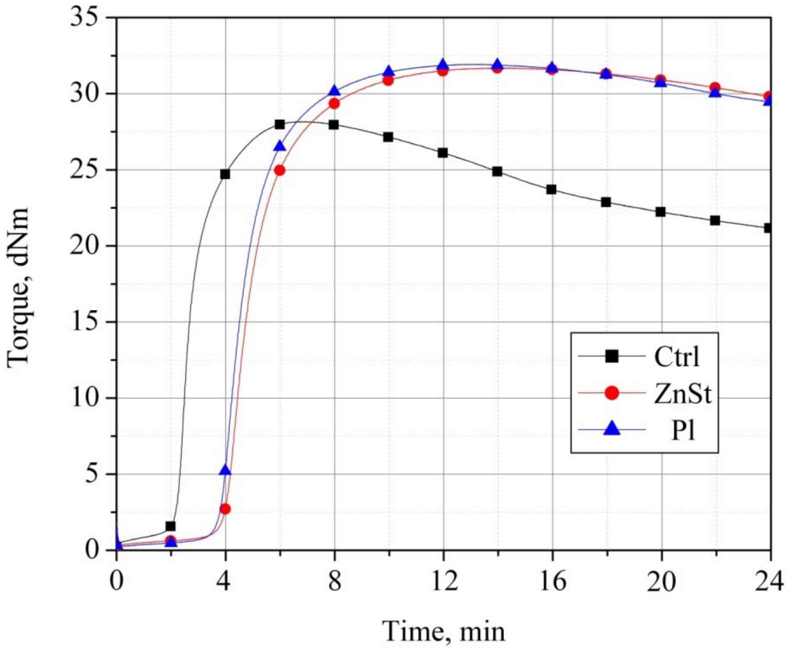

Figure 2. *Cure curves of the studied rubber compounds in the presence of ZnO and stearic acid, taken at 160°C.*

Table 4 shows the main vulcanization characteristics of studied rubber compounds in the presence of zinc oxide and stearic acid, determined via their cure curves /Figure 2/ at 160 ^{o}C. It is seen from cure curves, that the mixture, containing only ZnO (Ctrl’), has a strongly expressed reversion after reaching the optimum curing time (T_{90}), while with the mixtures, comprising combination of zinc oxide and zinc soap (ZnSt’ and Pl’), the reversion in the longer curing times than T_{90} is insignificant.

	Ctrl’	ZnSt’	Pl’
Minimum torque, ML, dNm	0.52	0.36	0.26
Maximum torque, MH, dNm	28.17	31.71	31.93
ΔM=MH-ML, dNm	27.65	31.35	31.67
T_{s2}, min:s	2:11	3:57	3:46
T_{90}, min:s	4:15	7:26	6:57
V, %/min	48	29	31

Table 4. *Vulcanization characteristics of the studied rubber compounds in the presence of ZnO and stearic acid.*

As Table 4 shows, the presence of zinc oxide in all studied compounds leads to prolongation of the optimum curing times (T_{90}) in comparison with T_{90} of the compounds from the first series. In addition, it can be said that the optimum curing times are longest with the mixtures, containing combination of zinc oxide and zinc soaps (ZnSt’ and Pl’). In full compliance with all said above, the compounds ZnSt’ and Pl’ has the shortest cure rates. According to Table 4, the presence of zinc oxide in all studied compounds from the second series leads to an overall increase of the maximum torque values (MH), respectively ΔM values. That is most strongly expressed with the mixture, containing a combination of zinc oxide and zinc soap (ZnSt’ and Pl’). Obviously the combined effect of zinc oxide and zinc soaps significantly increases the density of the formed crosslink network. Probably this combined effect leads to the forming of a more stable crosslink network, characterized with less polysulfide bonds. The last suggestion could be a reason for the reversion resistance of the mixtures, comprising a combination of zinc oxide and zinc soaps, in the longer curing times.

3.2. Mechanical properties

The mechanical properties of rubber mixtures vulcanizates, cured in optimum curing time (T_{90}) /Table 5/ and fourfold longer curing time ($4xT_{90}$) /Table 6/ were studied with the intent to be seen how their values are influenced by the reversion of the cure curves for each of the investigated mixtures.

	Ctrl	ZnSt	Pl	Ctrl’	ZnSt’	Pl’
Modulus 100, M_{100}, MPa	2.6	4.6	3.6	3.7	4.4	3.8
Modulus 300, M_{300}, MPa	7.5	10	8.4	9.7	7.7	8.1
Tensile strength, σ, MPa	9.3	10.2	8.4	11.1	10.6	8.8
Elongation at break, ε_1, %	375	300	300	345	310	335
Residual elongation, ε_2, %	20	15	15	20	15	15
Shore A hardness	70	74	72	72	75	74
Abrasion, mm^3	303	219	250	261	225	243

Table 4. *Mechanical properties of the vulcanizates from studied rubber compounds, cured in optimum curing time (T_{90}).*

It may be noted, that there are no considerable differences in the mechanical properties of the studied vulcanizates, cured in T_{90} independently of the presence or absence of zinc soaps. By the other hand, the presence of zinc oxide leads to a slight increase of the tensile strengths (σ) of the rubber mixtures vulcanizates from the second series, compared to those of the rubber mixtures vulcanizates from the first series, which do not contain zinc oxide. Both in two series, the vulcanizates from the mixtures, comprising zinc soaps, have a better abrasion resistance than those of the control mixtures vulcanizates.

	Ctrl	ZnSt	Pl	Ctrl’	ZnSt’	Pl’
Modulus 100, M_{100}, MPa	2.7	3.7	2.8	3.6	4.4	4.0
Modulus 300, M_{300}, MPa	6.9	-	6.3	8.7	-	-
Tensile strength, σ, MPa	7.1	8.0	6.3	8.9	8.6	7.4
Elongation at break, ε_1, %	310	280	300	320	255	260
Residual elongation, ε_2, %	10	10	10	20	10	10
Shore A hardness	70	73	70	72	75	74

Table 5. *Mechanical properties of the vulcanizates of the studied rubber compounds, cured in 4x optimum curing time ($4xT_{90}$).*

Nevertheless, it cannot be seen the tendency toward improving of the abrasion resistance in the presence of combination of zinc oxide and zinc soaps.

For all vulcanizates, cured in fourfold longer curing time ($4xT_{90}$) /Table 5/, it is seen a significant decrease of their tensile strengths (about 30%). That is expected for the vulcanizates from mixtures, characterized with reversion in their cure curves, but is not expected for the others.

3.2. Dynamic properties

The decrease of the complex dynamic modulus with the increase of the dynamic deformation (Payne effect) is a measure of the filler distribution degree in the polymer matrix and corresponds with the heat build-up of the vulcanizates, due to the destruction of filler-filler bonding.

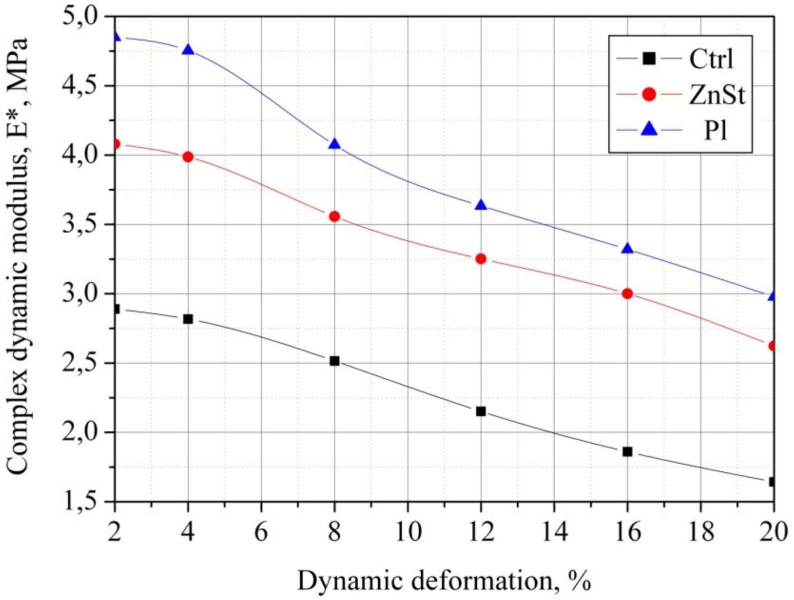

Figure 3. *The dependence of complex dynamic modulus (E*) on the dynamic deformation of the composites, studied in the absence of zinc oxide, cured in* T_{90}.

Figure 3 shows the dependence of complex dynamic modulus (E*) on the dynamic deformation of all composites, studied in the absence of zinc oxide and stearic acid, cured in optimum curing time (T_{90}). Vulcanizates of compounds, comprising zinc soaps, have a higher dynamic modulus with all sizes of the dynamic deformation, in comparison with the control mixture vulcanizate, in result of that the heat build-up of these vulcanizates are apparently lower than those of the control mixture vulcanizate. That is most pronounced with the larger dynamic deformations (12-20%) /Figure 4/.

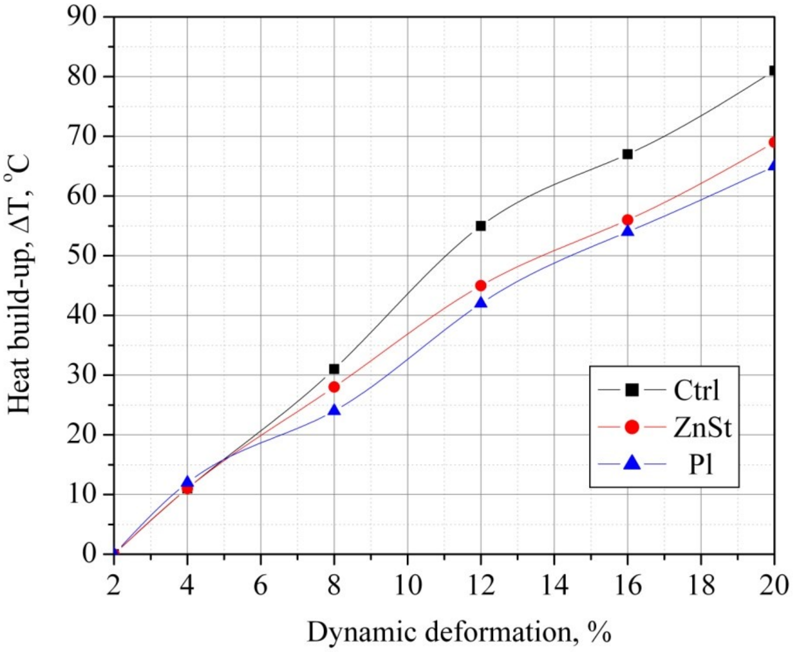

***Figure 4**. Heat build-up dependence on the dynamic deformation of the composites studied in the absence of zinc oxide, cured in T90.*

The dependence of complex dynamic modulus (E*) on the dynamic deformation of the composites, studied in the presence of zinc oxide, cured in optimum curing time (T_{90}) is shown in Figure 5.

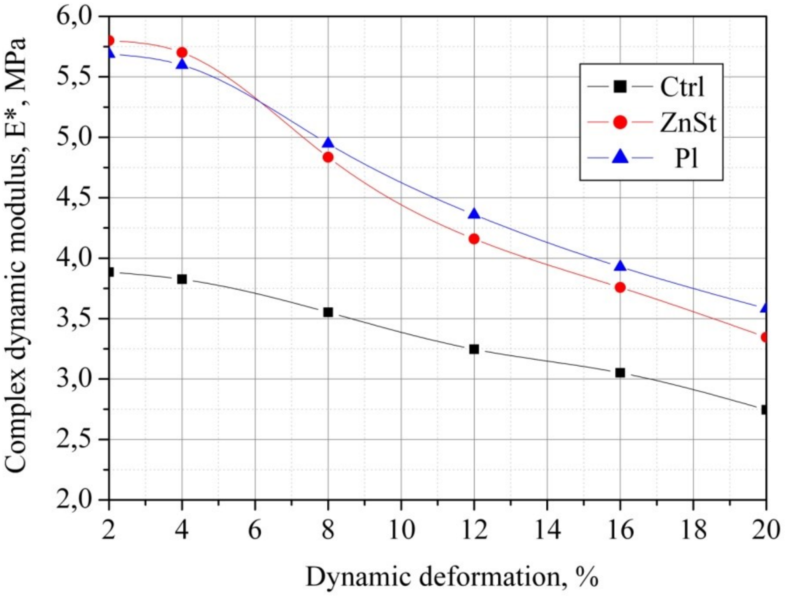

***Figure 5.** The dependence of complex dynamic modulus (E*) on the dynamic deformation of the composites, studied in the presence of zinc oxide, cured in T_{90}.*

It is obvious, that the presence of zinc oxide leads to a significant increase of the complex dynamic modulus with all sizes of the dynamic deformation of the investigated rubber mixtures vulcanizates from the second series, compared to the complex dynamic modulus of the vulcanizates from the first series (in the absence of zinc oxide).

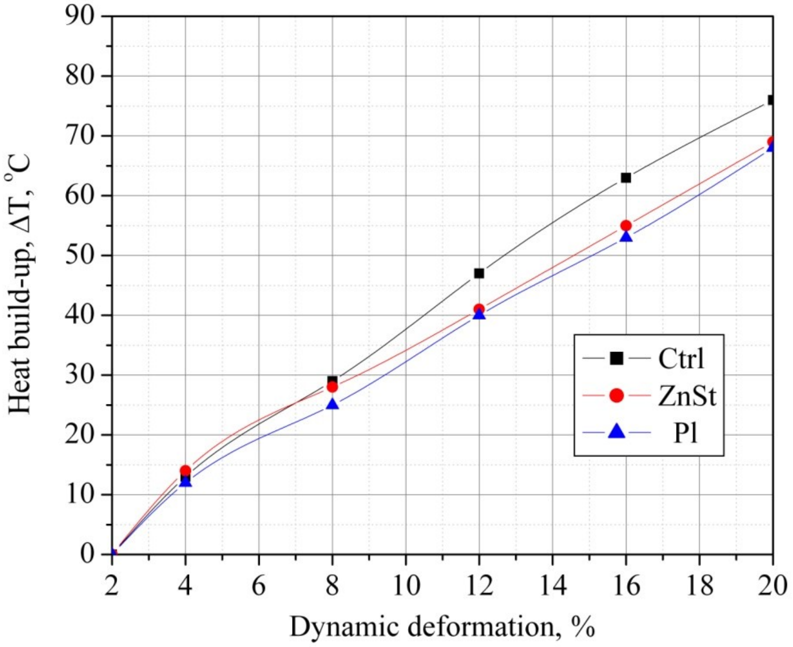

***Figure 6**. Heat build-up dependence on the dynamic deformation of the composites studied in the presence of zinc oxide, cured in T_{90}.*

In full compliance with that the heat build-up of vulcanizates, containing zinc oxide, is apparently lower. It is noteworthy, that the vulcanizates from the rubber compounds, comprising combination of zinc oxide and zinc soap, have a lower heat build-up than those, comprising only zinc oxide /Figure 6/.

As it is known, the mechanical loss angle tangent is a correlation between loss dynamic modulus (E") and storage dynamic modulus (E') – tan δ (tan δ = E"/E'). It gives an idea of the macromolecules mobility, as well as the phase transitions, which occur in the polymers.[22]

In Figure 7 and Figure 8 are presented the dependencies of the mechanical loss angle tangent (tan δ) on the temperature of rubber mixtures vulcanizates, studied in the absence of zinc oxide, cured in optimum curing time (T_{90}) and fourfold longer curing time ($4xT_{90}$). The temperature dependence of tan δ deserves interest since it is considered that tan δ at 60°C corresponds to the rolling resistance of the tires. It is seen from Figure 7 that tan δ at 60°C is apparently higher with the vulcanizate from the control mixture (Ctrl). The present of zinc soaps in the other rubber mixture vulcanizates from the first series leads to apparently lower values of tan δ at 60°C, respectively to lower rolling resistance, which is expected. It is known, that tan δ pick corresponds to the glass transition temperature (T_g) of the composites. In Figure 7 it is seen, that T_g of all investigated vulcanizates is about -15 ^oC.

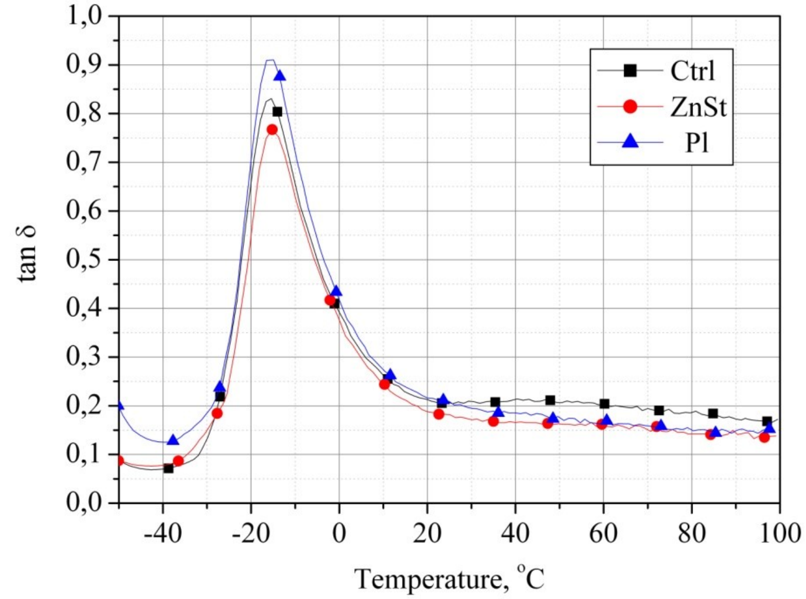

Figure 7. *The dependences of the mechanical loss angle tangent (tan δ) on the temperature of the composites in the absence of zinc oxide, cured in T_{90}.*

As Figure 8 shows, the longer curing time (4xT_{90}) leads to the most significant change on the dynamic properties of the vulcanizate from the mixture, comprising plastikol (Pl). That is expressed into the apparently higher tan δ at 60 °C of this vulcanizate in comparison with tan δ at 60 °C of the vulcanizate from this mixture, cured in optimum curing time (T_{90}).

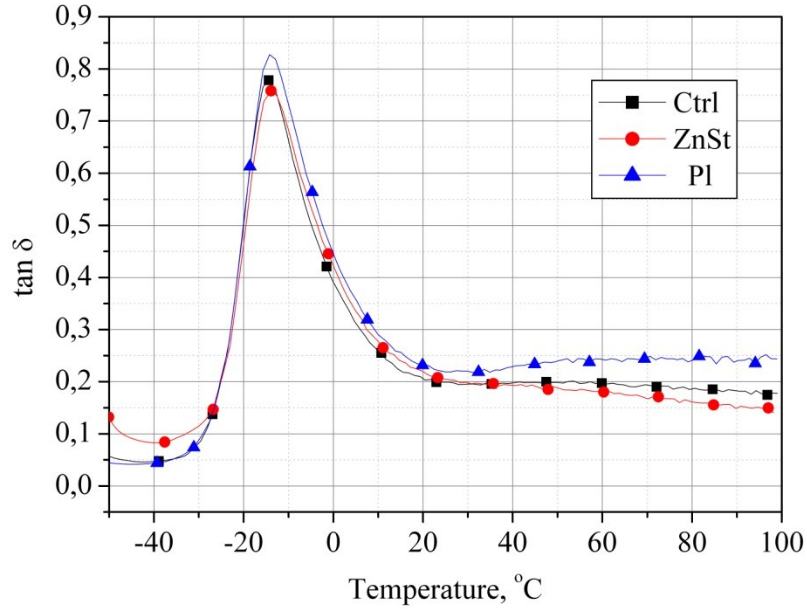

Figure 8. *The dependences of the mechanical loss angle tangent (tan δ) on the temperature of the composites in the absence of zinc oxide, cured in 4xT_{90}.*

In longer curing time (4xT_{90}) there is an insignificant change of tan δ at 60 °C of the vulcanizate from the mixture, comprising zinc stearate (ZnSt), compared to tan δ at 60 °C of the vulcanizate from the same mixture, cured in optimum curing time (T_{90}). It is apparent, that with the vulcanizates from control mixture (Ctrl), cured in optimum curing time (T_{90}) and fourfold optimum curing time (4xT_{90}), there is no change of tan δ at 60 °C /Figures 7 and 8/. Nevertheless, it is seen, that the vulcanizates from the mixture, containing zinc stearate (ZnSt) have the lowest tan δ at 60 °C, respectively the lowest rolling resistance.

In Figure 9 and Figure 10 are presented the dependencies of the mechanical loss angle tangent (tan δ) on the temperature of rubber mixture vulcanizates, studied in the presence of zinc oxide, cured in optimum curing time (T_{90}) and fourfold longer curing time (4xT_{90}).

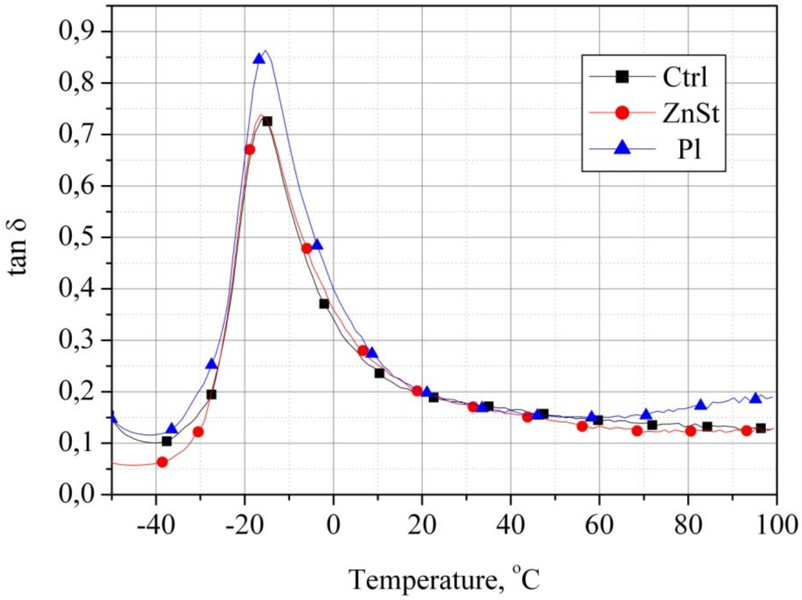

Figure 9. *The dependences of the mechanical loss angle tangent (tan δ) on the temperature of the composites in the presence of zinc oxide, cured in T_{90}.*

As Figure 9 shows, the values of tan δ at 60 °C are commensurable with the vulcanizates from all investigated compounds, containing zinc oxide, cured in optimum curing time (T_{90}). The presence of zinc oxide in all studied composites leads to a significant decrease of tan δ at 60 °C, respectively to a lower rolling resistance, compared to those of the composites, studied in the absence of zinc oxide, cured in the same vulcanization time (T_{90}). From Figure 10 it can be seen, that in fourfold longer curing time (4xT_{90}) tan δ at 60 °C are lower with the rubber mixture vulcanizate, comprising plastikol (Pl'), while in regard to the vulcanizates from mixtures, comprising only zinc oxide (Ctrl') and combination of zinc oxide and zinc stearate (ZnSt') the values of tan δ at 60 °C are higher. It may be noted, that the vulcanizates from all mixtures, comprising zinc oxide, cured in 4xT_{90} have apparently lower values of tan δ at 60 °C in comparison with the vulcanizates from the rubber mixtures, no containing zinc oxide, cured in the same curing time (4xT_{90}). That is most strongly pronounced with the vulcanizates, which contain plastikol in the presence and absence of zinc oxide.

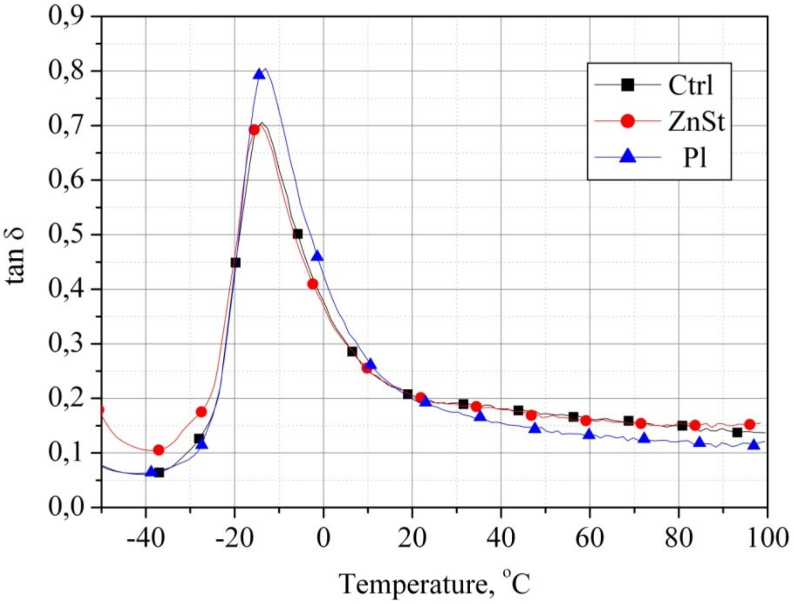

Figure 10. *The dependences of the mechanical loss angle tangent (tan δ) on the temperature of the composites in the presence zinc oxide, cured in 4xT$_{90}$.*

4. Conclusion

The possibility silica containing solid yield (SiO_2D), produced with the recycling of scrapped „green” tire treads via pyrolysis, to be used as active filler was examined. The influence of the filler on the properties of epoxidized natural rubber based composites, comprising various zinc soaps, in the presence and absence of zinc oxide was studied. The effect of separate use of zinc soaps as well as those of the combination with zinc oxide was also viewed. It was established that in full absence of vulcanization activators is available the significant reversion, which affect on the mechanical and dynamic properties of the studied vulcanizates. The separate present of zinc oxide, as well as the separate present of zinc soaps leads to apparently lower but still available reversion, hence to the improvement of density and structure of cross-link network of the vulcanizates. The combined effect of zinc oxide and zinc soaps leads to the greatest success in preventing of the reversion and it is almost absent. Studied filler does not provide the required reinforcing effect to be used for production of automobile tires. Nevertheless, this filler can be applied successfully in other rubber manufactures such as for irresponsible rubber composites.

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