

SILICA OBTAINED VIA PYROLYSIS OF „GREEN” TIRES AS AN ACTIVE FILLER IN NATURAL RUBBER BASED COMPOSITES

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Abstract

There's a tendency towards a massive implementation of the so called "green" tires. The reinforcing filler in them constitutes mainly of SiO_2 . It provides lower rolling resistance and therefore lower fuel consumption compared with a carbon black. The object of the study is a new material containing silica and carbon black with nano-sized particles (SiO_2D), produced by the recycling of scrapped „green” tires via pyrolysis, as a filler in rubber composites based on natural rubber. The curing characteristics, as well as the mechanical and dynamic properties of compounds, which contain SiO_2D , conventional SiO_2 and zinc soaps, have been studied. It has been established that the mechanical and dynamic properties of the vulcanizates filled with SiO_2D are lower, but similar to those filled with conventional SiO_2 . The zinc soaps containing mixtures have a lower viscosity and their vulcanizates have a lower aging resistance.

Key words: waste tires, pyrolysis, solid residue, silica, zinc soaps

INTRODUCTION

Using reinforcing fillers has been of major importance for the production of natural rubber based compounds. The requirements that modern tyres have to meet are: high strain-stress properties and good dry and wet grip, low rolling resistance, hence less fuel consumption and last but not least longer exploitation time. Tires possessing those desired properties were produced yet in 1992 by Michelin. The company was the first to use high dispersion silica as a filler combining it with various organosilanes. That triggered the production of the so called "green tires" whose rolling resistance is about 20% higher than that of the carbon black filled tire treads. The former have better wet grip with no compromises concerning their tread wear [1-4].

It is known that silica (SiO_2) having hydroxyl groups on its surface is used as a filler in the tread for "green tires". Organosilanes like bis(3-triethoxysilylpropyl) disulfide or bis(3-triethoxysilylpropyl) tetradisulfide are implemented for improving the dynamic properties of those 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 dispersion of this filler in the rubber matrix. The technological mixing regime has a great importance for running the above-mentioned reactions. Reactions between the second functional group of silane and the rubber molecules occur during vulcanization provoking chemical "polymer-filler" bonds. The interactions described reduce the rolling and abrasion resistance of the tyres and enhance their adhesion on wet roads [5-7].

There are different ways of managing the tires waste such as tire retreading, mechanical grinding, rubber reclaim, combustion, pyrolysis etc. Pyrolysis is not a new method for recycling and utilization of waste tires. 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. The product thus obtained could be used as active filler for manufacturing various rubber items [1].

All said above allows the assumption that pyrolysis-cum-water vapor of SiO_2 -filled vulcanizates will lead to preserving the hydroxyl groups over the surface of the SiO_2D obtained via pyrolysis. It is also possible to regenerate the hydroxyl groups that have reacted with the ethoxy groups of TESPD or TESPT silanes. The hydroxyl groups located on the surface of SiO_2D particles will hinder their temperature caused agglomeration. Hence, the particles will have their initial size and the chemical nature of their surface will not change.

In previous studies a solid product SiO_2D has been obtained as a result of subjecting the tread of “green” tires (Michelin Energy 195/65R 15) to pyrolysis-cum-water vapor. It has been found by

IR-FTIR and EDXRF spectroscopy that the product contains 65% of SiO_2 , 30% of carbon, 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. Composites comprising ZnO as well as such comprising zinc salts of long-chain fatty acids have been investigated. Differences have been established neither in the mechanical properties (Modulus 300, tensile strength, abrasion, etc.) nor in the dynamic properties (heat build-up, $\tan \delta$, etc.) of the vulcanizates filled with SiO_2D and of those filled with conventional SiO_2 and carbon black at a 2: 1 ratio. 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 [5].

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. [8, 9].

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. Furthermore, ZnO is in many vulcanization systems a precursor to zinc-derived accelerators. [10]. There are other investigations supposing that Zn^{2+} -ions form these active complexes with accelerators, which are more reactive than the free accelerator. [11].

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 vulcanization. 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 [12] too. 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. [13]. 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. [8, 12].

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. [11].

The purpose of the work presented is to investigate the influence of silica containing solid residue, obtained via pyrolysis-cum-water vapour of waste “green” tires tread (SiO_2D) as an active filler on the properties of natural rubber based composites in the presence of various kinds of zinc soaps and absence of the conventional zinc oxide.

EXPERIMENTAL

1. Materials

The investigations were performed using the following materials:

Natural rubber SVR 10 was used as a polymer matrix. SiO_2D – a solid product obtained by pyrolysis-cum-water vapor of the tread of waste “green” tires (Michelin Energy 195/65 R 15) was used as an active filler in rubber mixtures. The product contains 65% of SiO_2 , 30% of carbon, 3% of ZnO, and 2% of other components. 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, bis(triethoxysilylpropyl)tetrasulfide (TESPT, Si 69), N-tert-butyl-2-benzothiazolesulfenamide (TBBS) and sulfur were also of commercial grades.

2. Measurements

The mechanical properties of the composites studied were determined according to ISO 37:2011. The Shore A hardness of the composites studied were determined according to ISO 7619-1:2010, while the abrasion - according to ISO 4649:2010. Accelerated heat aging of the vulcanizates studied was tested according to ISO 188:2011. The coefficients of aging in terms of tensile strength (K_σ) and relative elongation at break (K_ε) were calculated by the help of the following equations:

$$K_\sigma = \frac{\sigma_2 - \sigma_1}{\sigma_1} \cdot 100, \%$$

Where: σ_1 – the tensile strength before aging;

σ_2 – the tensile strength after aging.

$$K_\varepsilon = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} \cdot 100, \%$$

Where: ε_1 – the elongation at break before aging;

ε_2 – the elongation at break after aging.

3. Preparation of rubber composites

The formulations of the compounds based on natural rubber – SVR 10 are presented in Table 1.

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

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Natural Rubber, NR-SVR 10	100	100	100	100	100
SiO ₂ D	70	70	90	70	70
Zinc stearate	-	5	5	-	-
Zink resinate	-	-	-	5	-
Plastikol	-	-	-	-	5
TESPD, Si 266	5	5	5	5	5
TBBS	1.5	1.5	1.5	1.5	1.5
Sulfur	2	2	2	2	2

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 cm³ cam type mixer. The silane coupling agent (TESPD, Si 266) was mixed with the filler studied prior to their placing into the mixer camera. At the second stage sulfur and the accelerator were added to the mixture compounded on an open two-roll laboratory mill L/D 320x160 and friction 1.27.

Table 2. Mixing schedule of the investigated rubber compounds.

Stage 1, Brabender Plasti-Corder PLE651, Rotor speed 40 rpm, Temperature 140°C			
Mixig order	Ingredients	Mixing time, min	Cumulative time, min
1	Natural rubber (SVR 10)	2	2
2	Zinc stearate, Zinc resinate, Plastikol	2	4
3	SiO ₂ D and TESPD (Si 266)	5	9
Stage 2, Laboratory Two Roll Mills, Friction 1.27			
1	1st stage rubber batch	2	2
2	Sulfur and TBBS	5	7

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.

RESULTS AND DISCUSSION

1. Curing characteristics of SiO₂D-reinforced rubber compounds

The vulcanization isotherms, recorded on a Monsanto (MDR 2000) rheometer at 160°C are presented in Fig. 1.

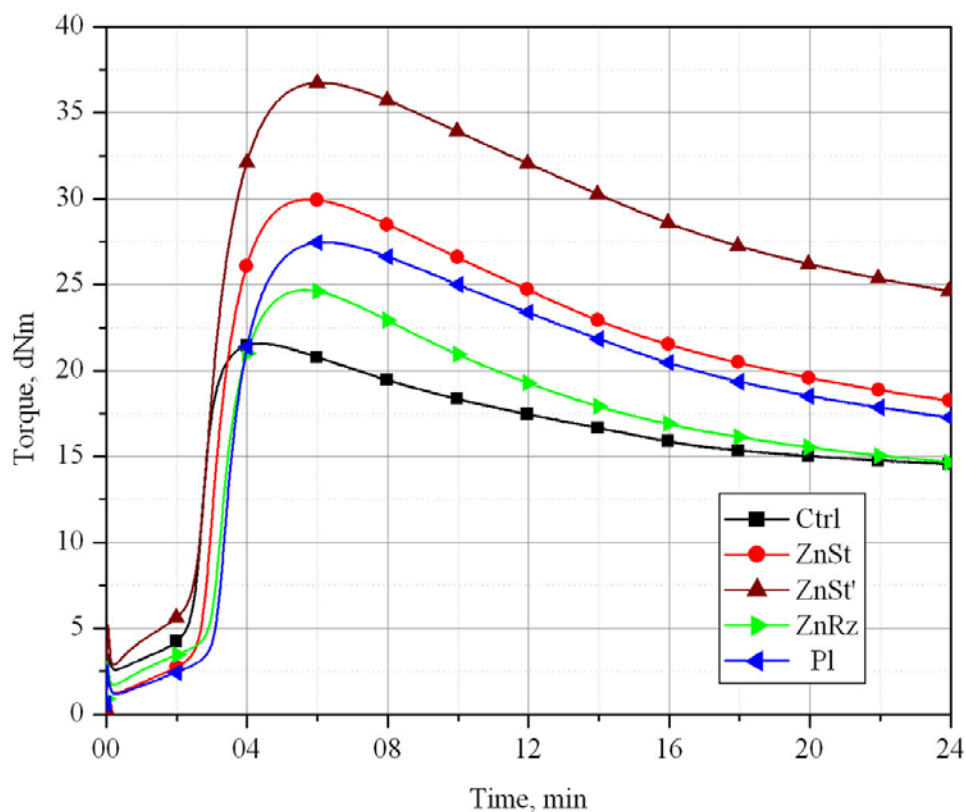


Figure 1. Vulcanization isotherms of the rubber compounds studied, recorded at 160°C.

From the vulcanization isotherms we can see that there is no apparent influence of the zinc soaps upon the scorching time (T_{s2}). In all tested compounds, after reaching the maximum torque (MH), a reversion in the vulcanization isotherms is observed, which suggests a decreasing of the crosslink network density. This can therefore lead to deterioration of the mechanical properties of the vulcanizates in case of a longer curing time. In thick-walled products, such as car tires, the curing time is usually several times longer than the optimum curing time (T_{90}) of a 2 mm-thick sample.

Table 3 shows the vulcanization characteristics of the studied compounds, determined by the vulcanization isotherms.

Table 3. Vulcanization characteristics of the rubber compounds studied

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Minimum torque, ML, dNm	2.58	1.21	2.88	1.71	1.19
Maximum torque, MH, dNm	21.60	29.98	36.76	24.70	27.49
$\Delta M = MH - ML$, dNm	19.02	28.77	33.88	22.99	26.3
T_{s2} , min:s	2:10	2:20	1:28	2:17	2:43
T_{90} , min:s	3:15	4:10	4:13	4:15	4:31
V, %/min	29	21	22	21	19

From the table we can see that the minimum torque (ML) is not affected by the presence of zinc soaps, which slightly contradicts the statement that zinc soaps have a dispersible and plasticizing influence of the filled rubber compounds. The difference between the maximum and minimum torque (ΔM) is considered to give an indirect idea of crosslinks network density of the vulcanizates. ΔM for the control mixture (Ctrl) is 19 dNm. The presence of zinc salts soaps to the rising of this value, where the influence of zinc stearate and plastikol is more strongly pronounced, while with zinc stearate this influence is insignificant.

The optimum curing time (T_{90}) is longer for compounds in which zinc soaps are present. From the curing properties we can suggest that the ZnO present in the filler doesn't have an activating effect. The presence of zinc soaps has more of an activating effect, which leads to a slowing of the curing speed, but forms a denser crosslink network. During pyrolysis, carbon has probably covered the surface of ZnO, which blocks its effects as an activator. It can be suggested that for the same reason we do not observe a combined effect of ZnO and zinc soaps, leading to the forming of a stable crosslink, which is resistant to reversion when there is a longer curing time.

2. Mechanical properties of the vulcanizates studied

Table 4 presents the main mechanical properties of the vulcanizates of the rubber compounds studied prior to their accelerated heat aging in optimum curing time (T_{90}).

Table 4. Mechanical properties of the vulcanizates of the rubber compounds studied prior to their accelerated heat aging in optimum curing time (T_{90})

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Modulus 100, M_{100} , MPa	2.1	3.2	3.6	1.7	2.4
Modulus 300, M_{300} , MPa	10.4	14.4	14.0	8.7	10.7
Tensile strength, σ , MPa	16.9	20.5	17.7	16.7	18.0
Elongation at break, ϵ_1 , %	470	460	405	530	485
Residual elongation, ϵ_2 , %	25	30	30	30	30
Shore A hardness	72	75	80	72	73
Abrasion, mm^3	244	91	208	178	179

We can see that compounds containing zinc stearate have higher Modulus 100%, 300% and tensile strength, compared to the other compounds. Increasing the amount of filler in compounds containing zinc stearate does not lead to changes in Modulus 100 and 300% (M_{100} и M_{300}), but leads to an insignificant decrease of the tensile strength (σ).

Table 5 presents the main mechanical properties of the vulcanizates of the rubber compounds studied prior to their accelerated heat aging in 4x optimum curing time (T_{90}).

Table 5. Mechanical properties of the vulcanizates of the rubber compounds studied prior to their accelerated heat aging in 4x optimum curing time ($4 \times T_{90}$).

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Modulus 100, M_{100} , MPa	1.0	1.4	2.5	1.1	1.2
Modulus 300, M_{300} , MPa	4.7	6.8	9.9	4.6	5.5
Tensile strength, σ , MPa	7.9	12.0	11.9	9.5	10.1
Elongation at break, ε_1 , %	440	465	365	520	480
Residual elongation, ε_2 , %	20	25	20	10	25
Shore A hardness	70	70	78	67	70

From the table we can see that when there's a longer curing time, Modulus 100% и 300% (M_{100} and M_{300}) is decreased in all vulcanizates.

Figure 2 compares the tensile strengths of vulcanizates of the studied compounds, cured in the optimum curing time (T_{90}) and 4 times the optimum curing time ($4 \times T_{90}$).

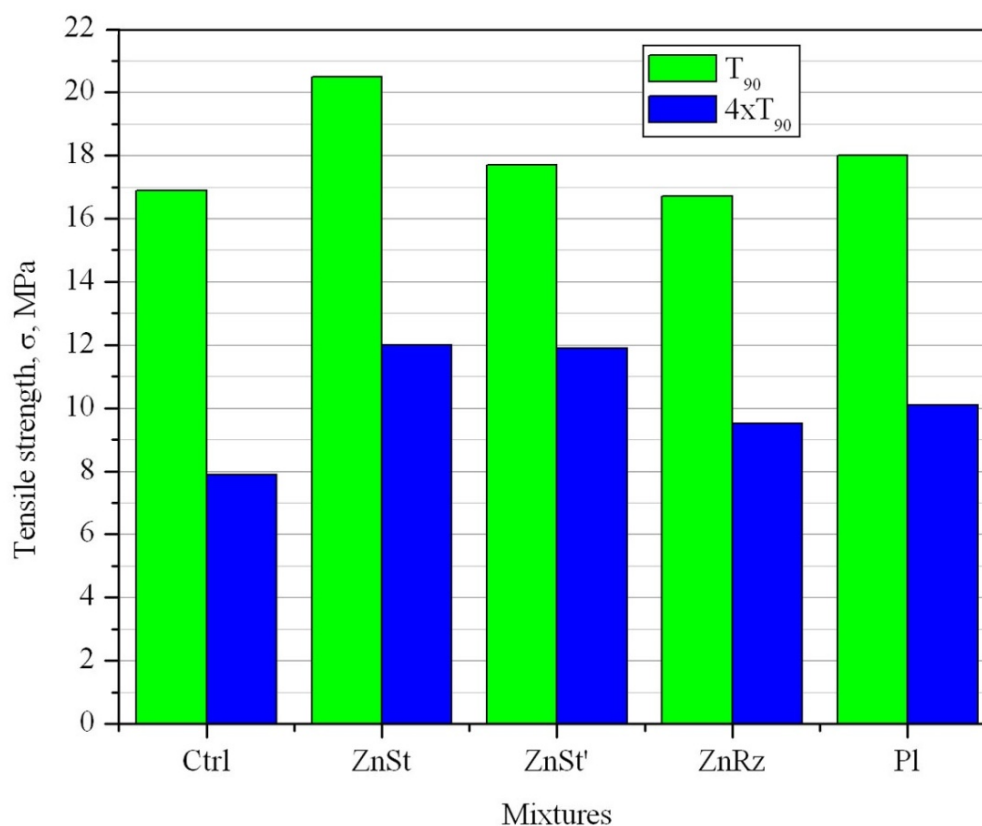


Figure 2. Tensile strength of the vulkanizates studied at optimum curing time (T_{90}) and 4x optimum curing time ($4 \times T_{90}$)

As we can see, for the vulcanizates of all studied compounds, a longer curing time leads to a significant reduction in tensile strength. The tensile strength of the vulcanizate from control mixture (Ctrl), cured in the optimum curing time (T_{90}), is 17 MPa. The presence of zinc stearate and plastikol leads to an insignificant increase of the tensile strength, while the presence of zinc resinate does not have any influence. The tensile strength of vulcanizates in $4 \times T_{90}$ is significantly lower than that of vulcanizates cured in the optimum curing time (T_{90}), while this is most evident with the control substance (Ctrl) vulcanizate. The mechanical and curing properties are in full compliance, i.e. the presence of reversion in the vulcanization isotherms leads to a loss of the properties of the vulcanizates of the studied compounds when there is a longer curing time.

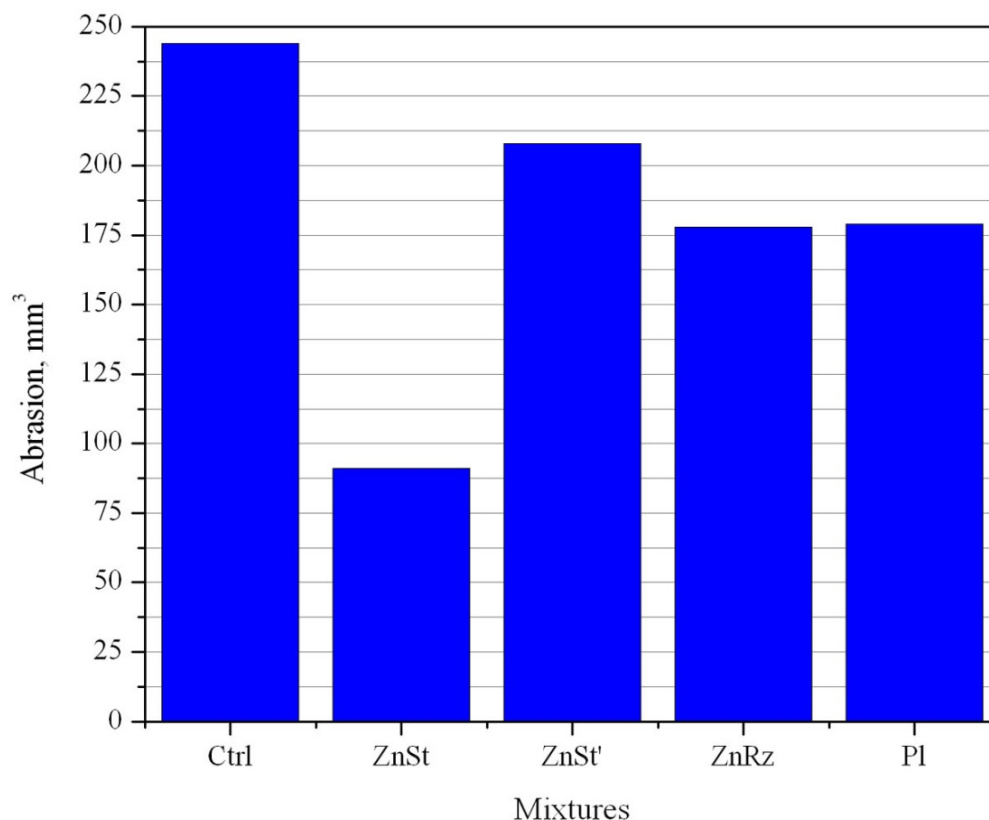


Figure 3. Abrasion of the vulcanizates of the rubber compounds studied.

Figure 3 shows the abrasion of the vulcanizates studied.

Control mixture vulcanizates have the highest abrasion (around 240 mm³). The introduction of zinc soaps leads to a reduction of the abrasion, while this is most evident in vulcanizates containing zinc stearate and 70 phr. SiO₂D (ZnSt'). That cannot be explained, because vulcanizates with a higher amount of SiO₂D containing zinc stearate (ZnSt), have almost 2 times higher abrasion. The higher amount of filler in those compounds leads to an increase in abrasion.

Table 6 shows the mechanical properties of vulcanizates of the studied compounds, cured in the optimum curing time (T_{90}) after accelerated heat aging (72h).

Table 6. Mechanical properties of the vulcanizates of the rubber compounds studied after their accelerated heat aging (72 h) in optimum curing time (T_{90}).

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Modulus 100, M_{100} , MPa	2.4	3.5	4.1	2.3	2.6
Modulus 300, M_{300} , MPa	11.4	14.2	-	9.8	10.1
Tensile strength, σ , MPa	11.4	15.5	10.7	11.9	11.1
Elongation at break, ϵ_{OTH} , %	305	330	230	365	330
Residual elongation, ϵ_{OCT} , %	10	20	15	15	15
K σ , %	-33	-24	-39	-29	-38
K ϵ , %	-35	-28	-43	-31	-32

We can conclude that the tensile strength of vulcanizates cured in the optimum curing time (T_{90}) after accelerated heat aging of 72h, is closer to the tensile strength of vulcanizates cured in $4xT_{90}$ before accelerated heat aging, i.e. the longer curing time has the same effect as aging in atmospheric conditions in a lower temperature and longer time.

Table 7 shows the mechanical properties of vulcanizates of studied compounds, cured in $4x$ optimum curing time ($4xT_{90}$) after accelerated heat aging (72h).

Table 7. Mechanical properties of the vulcanizates of the rubber compounds studied after their accelerated heat aging (72 h) in $4x$ optimum curing time ($4xT_{90}$).

	Ctrl	ZnSt	ZnSt'	ZnRz	Pl
Modulus 100, M_{100} , MPa	1.9	2.0	2.8	1.4	1.5
Modulus 300, M_{300} , MPa	7.3	-	-	5.2	4.7
Tensile strength, σ , MPa	7.7	7.0	7.6	6.7	5.1
Elongation at break, ϵ_{OTH} , %	310	295	255	390	330
Residual elongation, ϵ_{OCT} , %	10	15	10	15	15
K σ , %	-2	-42	-36	-29	-50
K ϵ , %	-30	-37	-30	-25	-31

We can see that control mixture vulcanizates do not age, while vulcanizates containing zinc soaps continue to lose their properties, but the tensile strengths of those vulcanizates after aging are too low to make a conclusion about the influence of the zinc soaps present in them.

CONCLUSION

It was investigated the influence of the solid residue, obtained via pyrolysis-cum-water vapor of waste “green” tires tread, on the properties of natural rubber based composites in the presence of various kinds of zinc soaps and absence of the conventional zinc oxide.

- From the curing properties we can conclude that the ZnO present in the filler (SiO_2D) doesn't have a visible activating effect. During pyrolysis, carbon has probably covered the surface of ZnO, which blocks its effects as an activator. It cannot be seen a combined effect of ZnO and zinc soaps, leading to the forming of a stable crosslink network, which is resistant to reversion when there is a longer curing time.

- The mechanical and curing properties are in full compliance, i.e. the presence of reversion in the vulcanization isotherms leads to a loss of the properties of the vulcanizates of the compounds studied when there is a longer curing time.
- We can conclude that the tensile strength of vulcanizates which are cured in the optimum curing time (T_{90}) after accelerated heat aging of 72h, is closer to the tensile strength of vulcanizates cured in $4 \times T_{90}$ before accelerated heat aging, therefore the longer curing time has the same effect as aging in atmospheric conditions in a lower temperature and longer time.

Having in mind the tendency that SiO_2 is going to replace carbon black both in passenger and truck tires, SiO_2D may be a concurrent substituent for conventional silica. By the other hand the zinc oxide, contained in pyrolyzed solid residue (SiO_2D), is not be able to substitute the properties of conventional zinc oxide as an activator of curing process even in the presence of zinc soaps.

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