

# **SERINOL: A BIOSOURCED BUILDING BLOCK FOR BETTER MECHANICAL REINFORCEMENT AND SUSTAINABLE VULCANIZATION OF RUBBER COMPOUNDS**

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## ABSTRACT

Serinol and serinol derivatives were used to promote the mechanical reinforcement and the sulphur based crosslinking of rubber compounds. Reaction of serinol was performed with aldehydes and ketones, such as cinnamaldehyde, acetone, 2,5-hexanedione and camphor, obtaining the regiospecific synthesis of either imines or oxazolidines. Paal-Knorr reaction was as well carried out between serinol and 2,5-hexanedione, obtaining a serinol derivative containing a pyrrole ring, 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol, named as serinolpyrrole. All the reactions were performed in the absence of solvents and catalysts and were characterized by high and also quantitative yields. Thanks to the reactions' specificity, pure substances were obtained, with controlled atoms hybridization. The aromatic pyrrole ring was exploited to form adducts of serinolpyrrole with carbon allotropes. Adducts of SP with carbon black promoted the reduction of filler networking in silica based compounds. Serinol and imine as well oxazolidine derivatives were efficient secondary accelerators in silica based compounds and are thus suitable substances for the replacement of DPG. Tuning of vulcanization kinetics was performed.

## INTRODUCTION

“The preparation of innovative polymers and composite materials from biosourced chemicals is a hot research topic [1]”. This was the *incipit* of the proceeding n. 16 for the Fall 186<sup>th</sup> Technical Meeting of the Rubber Division of the American Chemical Society in Nashville (TN) [2]. Research on materials from renewable sources should be inspired to the basic principle of sustainable chemistry: it should not have impact on the food chain, reactions, processes and products should adhere to the principles of green chemistry [3] and the whole technology should have reasonable economic perspective.

The 2014 paper to the Nashville ACS meeting was based on 2-amino-1,3-propanediol, also known as serinol, as the starting building block for the preparation of innovative materials. Serinol is a glycerol [4-5] derivative and is an odourless, non-toxic, biodegradable substance, which can be obtained from natural and petrochemical feedstocks [6]. In particular, serinol becomes easily available when is obtained from glycerol. Indeed, glycerol has been long investigated as the building block for a C3 platform alternative to the oil based one. Serinol is characterized by the presence of hydroxyl and amino functional groups, hence it belongs to the class of amino alcohols and is a chemoselective prochiral molecule. Serinol exhibits a multitude of applications in medicine and chemical industry [6, 7] and, since 1940s, has been investigated in organic chemistry with its C-substituted analogs, particularly for pharmaceutical applications [6]. The crucial aspect is the control of functional groups' chemistry, that means the selective ability of amino and hydroxy groups to promote either independent reactions or to cooperate to form heterocyclic products. Largely investigated are the reactions of amino alcohols with ketones and aldehydes [8-10]. The condensation reaction of a carbonyl compound with a beta amino alcohol leads to imine but also to 1,3-oxazolidine. Imines (Schiff bases) are chemical compounds with a double carbon–nitrogen bond [11]. The oxazolidine ring [12] is present in many biologically active compounds and is also in chemicals with important pharmaceutical activity, as in antitumor drugs [13].

In our research group, in the last years, the study of chemoselectivity of reactions on serinol has been focused on the preparation of derivatives suitable to promote better mechanical reinforcement and sustainable vulcanization of rubber compounds. In this work, the reaction of serinol has been performed with aldehydes and ketones, aliphatic and aromatic, containing one or two carbonyl groups, such as cinnamaldehyde, acetone, 2,5-hexanedione, camphor. Aim was the specific preparation of either imines or oxazolidines. Further aim was the introduction of an aromatic ring in the serinol derivative. In the frame of our research, an aromatic derivative of serinol was obtained through the Paal-Knorr reaction [14, 15] of serinol with 2,5-hexanedione, transforming the amino group into a pyrrole ring and obtaining 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol, named as serinolpyrrole (SP) [16-19]. First data were presented at the Nashville ACS Meeting [2] and have been then published. In the present work, serinol pyrrole has been used for the preparation of adducts with carbon allotropes. Preparation, characterization and application in rubber compounds is reported. In particular, in this paper the use of SP adduct with CB to reduce the filler networking phenomenon in silica based compounds is discussed.

Serinol and serinol derivative such as imines and oxazolidines have been used as secondary accelerator for sulphur based vulcanization of silica based compounds. Objective was to replace diphenylguanidine and to modulate the kinetic of vulcanization. Vulcanization results are presented.

It is worth emphasizing that all reactions for the preparation of serinol derivatives were inspired to the principles of sustainable chemistry, avoiding the use of solvents and catalysts.

## EXPERIMENTAL SECTION

### Materials

#### *Reagents and chemicals*

Serinol was kindly provided by Bracco.

Imines and oxazolidines derivatives of serinol were prepared as reported in [21].

Serinol pyrrole was prepared as reported in [16-19] and in [22-24].

*Carbon black for the preparation of adduct with SP.* It was carbon black N326 from Cabot, with 30 nm as mean diameter of spherical primary particles.

*Rubbers for the compounds of Table II.* Synthetic poly(1,4-*cis*-isoprene) (IR) was SKY3 from Nizhnekamskneftechim Export, with 70 Mooney Units (MU) as Mooney viscosity ( $M_L(1+4)_{100^\circ\text{C}}$ ), synthetic poly(1,3-butadiene) (BR) was neocis BR 40 from Versalis, with a 43 Mooney Viscosity ( $M_L(1+4)_{100^\circ\text{C}}$ ).

*Rubbers for the compounds of Table III.* Natural rubber was SMR GP (from Lee Rubber), SBR was solution poly(styrene-co-butadiene) Styron 4630 (from Styron), with 25% as styrene content, BR was Neocis 40 from Versalis.

*Other ingredients for the compounds.* Carbon black was CBN326 from Cabot. Silica was Zeosil 1165 from Solvay, TESPT Si69 was Bis(triethoxysilylpropyl)tetrasulfide from Evonik, Stearic acid from SOGIS, Aliphatic MES Oil from ENI, ZnO from Zincol Ossidi, 6PPD was *N*-(1,3-dimethylbutyl)-*N'*-fenil-p-fenilendiammina from Crompton, Sulphur was from Solfotecnica, CBS was *N*-Cyclohexylbenzothiazol-2-sulphenamide from Flexsys, TBBS was *N*-terz-butyl-2-benzotiazil sulfenammide from Flexsys, DPG80 was Difenilguanidina (Rhenogran® DPG80), from Rhein Chemie Additives

*Preparation, crosslinking and dynamic-mechanical characterization of rubber compounds*

*Compounds based on IR/BR and CB/silica, with CB-SP*

*Compounds of Table II.*

*Preparation* Compounds were prepared via melt blending in a Brabender® internal mixer with a mixing chamber with a volume of 50 cc. Fill factor of the mixing chamber was 80% and during mixing rotors rotated at 30 rpm. 16.1 g of BR and 16.1 g of IR were fed into the mixer and masticated at 140°C for 1 minute. 8.1 g of silica and 1.1 g of TESPT were added, performing further mixing for 4 minutes and discharging the composite at 145°C as the temperature. Composite was fed again to the mixer at 80°C, masticated for 1 minute, adding then 1.3 g of ZnO and 0.6 g of stearic acid and 0.6 g of 6PPD. Further mixing was performed for 2 minutes. 0.5 g of sulfur and 0.6 g of CBS were finally added, mixing for further 2 minutes. Compound was discharged at 50°C. Compound was finally homogenized by passing it 5 times on the two roll mill, kept at 50°C, with a rolls rotating at 38 and 30 rpm, with 1 cm nip between the rolls.

The same procedure was followed with CB-SP, except that CB-SP was added in place of CB.

*Crosslinking.* Crosslinking was performed with a Monsanto RPA 2000 rheometer, at 170°C for 20 minutes, with a frequency of 1.667 Hz and an angle of 6.98 % (0.5 rad).

*Dynamic-mechanical characterization.* It was carried out in the torsion mode with a Monsanto R.P.A. 2000 rheometer. A first strain sweep (0.1–25% strain amplitude) was performed at 50°C on un-cross-linked samples, to cancel their thermo mechanical history. The samples were then kept in the instrument at the minimum strain amplitude (0.1%) for 10 min to achieve fully equilibrated conditions. A strain sweep (0.1–25% strain amplitude) was then performed with a frequency of 1 Hz. Curing was carried out at 150°C with a frequency of 1.67 Hz and an angle of 6.98%. Curing time was 30 min. On cross-linked samples, a first strain sweep (0.1–25% strain amplitude) was performed at 50°C, then the sample was kept in the instrument at the minimum strain amplitude (0.1%) for 10 min, to achieve fully equilibrated conditions. Finally a strain sweep (0.1–25% strain amplitude) was performed with a frequency of 1 Hz.

*Compounds based on SBR/NR/BR and silica, with serinol and serinol derivatives*

*Compounds of Table III*

*Preparation.* Compounds were prepared via melt blending, using the same type of Brabender® internal mixer and the same fill factor and rotors rotation rpm. Rubbers were fed to the mixer and masticated at 90°C for 1 minute. Silica was added together with silane, stearic acid and oil, performing mixing for 4 minutes. The compound was discharged at a temperature of about 140°C. After 16 hours, the composite was fed again to the mixer, mixing was performed at 60°C for 1 minute, ZnO and 6PPD were added and mixing was performed for further 2 minutes., discharging then the composite. Finally, sulphur and vulcanizers were fed and compound was unloaded after 2 minutes mixing, at 90°C. Homogeneization was performed, as reported above.

*Crosslinking.* Crosslinking reactions were performed at 170°C for 20 minutes in a Monsanto rheometer, with a frequency of 1.667 Hz and an angle of 6.98 % (0.5 rad). Data are shown in **Table IV**. The following parameters were measured.  $M_L$ : minimum value of torque,  $M_H$ : maximum value of torque. Torque was measured in dNm.  $t_{S1}$ : time required to have torque increase of 1 dNm, with respect to  $M_L$ .  $t_{90}$ : time required to achieve 90% of time required to have the maximum torque value, taken as  $M_H$ .

*Scorch time test at 127°C.* Scorch test was performed with a Monsanto RPA 2000 rheometer. Samples were fed to the rheometer, kept at 127°C, and a sinusoidal stress with a frequency of 0.5 Hz was applied, by keeping deformation at 50%, for 60 minutes. The following parameters were measured.  $M_L$ : minimum value of torque. Scorch time  $t_{S5}$ : time needed to have an increase of torque of 5 dNm with respect to  $M_L$ .

## RESULTS AND DISCUSSION SECTION

### Synthesis of serinol derivatives

Various carbonyl compounds were selected for the reaction with serinol: aldehydes and ketones, aliphatic and aromatic, containing one or two carbonyls. As mentioned in the Introduction, reactions were inspired to the basic principles of green chemistry. Hence, solvent free approach was selected, in the absence of any catalyst. In particular, acidic catalyst, which is traditionally used for the reaction of primary amines with carbonyl compounds, was avoided. The study on the reactivity of carbonyl compounds and hypothesis on the mechanistic pathway, to account for the formation of either imines or oxazolidines, will be reported in a forthcoming manuscript [20]. In this paper, examples of molecules suitable for promoting either the reinforcement or the vulcanization of rubber compounds is reported. Synthesis of serinol derivative is described in the experimental part and is summarized in **Table I**. In brief, reaction temperature, in the range from 25°C to 170°C, was suitable to have reagents in the liquid state. Reaction was stopped when constant conversion was obtained and products were isolated by removing the excess of reagents, collecting oils or washing crystals.

### TABLE I

1,3-oxazolidine was obtained from the reaction of serinol with acetone and a bis-oxazolidine from the reaction with a dicarbonyl compound such as 2,5-hexanedione. These findings and results from other experiments [20, 21] support the hypothesis that 1,3-oxazolidines are selectively obtained with ketones (and also aldehydes [20, 21]) without steric hindrance. Only imines are obtained when the carbonyl compound is aromatic [20, 21] and/or sterically hindered and when conjugated double bonds are formed, as it is shown by the reactions of serinol with cinnamaldehyde and with camphor. Reaction yields were high, of at least 70% and also quantitative, as in the case of 2,5-



hexanedione. It is definitely worth underlining that mixtures of imine and oxazolidine were never observed. The synthetic procedure adopted in the present work allows thus the selective preparation of either imines or oxazolidines, with high reaction yield. Reaction pathways followed and products obtained are shown in **Figure 1**.

### FIGURE 1

#### **Serinol derivative for the mechanical reinforcement of rubber compounds**

The bisoxazolidine obtained from the reaction of serinol with 2,5-hexanedione, 4a,6a-dimethyl-hexahydro-1,4-dioxo-6*b*-azacyclopenta[*cd*]pentalene, shown in **Figure 1**, was isomerized to the aromatic pyrrole derivative 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol, serinolpyrrole, by simply increasing the reaction temperature. The whole process was characterized by a yield of about 95% and by a high atom efficiency, of about 80% [16-19]. The whole process is shown in **Figure 2**.

### FIGURE 2

Serinolpyrrole has been used for the controlled functionalization of  $sp^2$  carbon allotropes [22-24]. Procedure, summarized in **Figure 3**, is simple indeed. SP and the carbon allotrope are mixed, optionally with the help of a solvent, and then energy, either mechanical or thermal, is given to the solid mixture.

### FIGURE 3

Different types of carbon allotropes were used: furnace carbon black, high surface area nanosized graphite and carbon nanotubes. Functionalization yields were very high, of at least 80% and, by appropriately tuning the reaction conditions, were also quantitative, larger than 95%.

The introduction of SP on carbon allotropes allowed the preparation of stable dispersions of carbon fillers in polar solvents, namely in water. This allowed to isolate few layers graphene from water dispersions [18]. Stable dispersions of few layers graphene and of carbon black were prepared in natural rubber (NR) latexes and, by coagulating the composite, very good dispersion of carbon fillers in NR matrix was observed [23, 24]. Polar groups allowed also the compatibilization of carbon black with silica.

Rubber compounds were prepared with carbon black functionalized with SP (CB-SP). In this paper, compounds based on either NR or IR/BR blend as the rubber matrices and with only CB or CB/silica as the filler systems were used.

#### COMPOUNDS BASED ON IR/BR AND CB/SILICA

Recipes of the composites are in **Table II**.

#### TABLE II

The same amount of CB was used in all the composites. The amount of SP, added with CB in Compounds 2 and 3, corresponds to 0.6 and 0.9 phr, indeed a pretty low amount. Strain sweep experiments were carried out on crosslinked samples, at 50°C. The dependence of storage modulus  $G'$  on strain amplitudes and the dependence of loss modulus  $G''$  on  $G'$  are shown in **Figure 4** and in **Figure 5**, respectively.

#### FIGURE 4

## FIGURE 5

The addition of CB-SP leads to the reduction of the Payne Effect [25], though to a minor effect. The Cole-Cole plot in **Figure 5** shows that CB-SP allows to have lower loss modulus for a given level of dynamic stiffness. Indeed, as commented, the reduction of Payne Effect is not that remarkable, as compared to the one provided by silane in silica filled compound [26] and by functionalized polymers [27]. Aspects such as the effect of SP amount and the filler-polymer interaction have to be investigated, to account for these differences.

### **Serinol and serinol derivatives for the vulcanization of rubber compounds**

Serinol and serinol derivatives such as the imines and oxazolidine reported in **Table I** were used as secondary accelerators for the sulphur based vulcanization of silica based compounds. As mentioned in the introduction, the use of serinol and different serinol derivatives as secondary accelerator had the primary objective to replace diphenyl guanidine but had also the objective to tune the kinetic of vulcanization.

Recipes of the compounds are in **Table III**. Recipes are typical of a silica based compound which could be used for tyre tread application. Standard compound was with DPG as secondary accelerator, used in a traditional amount. Serinol and serinol derivatives were used in the same molar amount. All the compounds containing the secondary accelerator are compared with a compound without any secondary accelerator.

### TABLE III

### TABLE IV

The exam of data in **Table IV** allows the following comments. The effect of secondary accelerator is particularly evident on  $t_{90}$  values: all the compounds with a secondary accelerator have  $t_{90}$  lower than  $t_{90}$  of silica based compound without secondary accelerator. Particularly lower is  $t_{90}$  value with DPG. With serinol,  $t_{90}$  is 2 minutes lower than  $t_{90}$  of the compound without ant secondary accelerator.  $t_{s1}$  values appear substantially similar for all the compounds, with slightly lower values for compounds with serinol and with serinol oxazolidine. DPG and the serinol imine with camphor, which is indeed the most hydrophobic serinol derivative, bring about the lowest  $M_L$  value, which is slightly higher only with serinol as the secondary accelerator.  $M_H$  values are larger for compounds containing the secondary accelerator, in particular for compounds with serinol and DPG. It is worth commenting that serinol, a substance which can be easily derived from glycerol or even from renewable sources shows the typical behaviour of a secondary accelerator for silica based compound. Indeed, data obtained from rheometric tests are pretty similar for compounds with either DPG or serinol as the secondary accelerator.

Study was also performed on induction time of vulcanization and  $M_L$  at 127°C. Objective was to investigate the behaviour of the silica based compound with innovative secondary accelerator in conditions which could simulate those experienced by the compounds during processing. Data of  $M_L$  and of the so called scorch time, that means the time needed to have an increase of torque of 5 dNm, are in **Table V**. are shown

#### **TABLE V**

At 127°C, secondary accelerators, either DPG or the serinol based ones, lead to reduction of compound viscosity, as indicated by the lower  $M_L$  values. Scorch time of compounds with serinol and serinol derivatives, with the exception of the compound with serinolcamphor, appears to be in line with the scorch time of DPG based compound and is thus suitable to allow compounds' processability. The compound with serinolcamphor shows remarkably higher value of scorch time.

Preliminary interpretation of results shown in **Table IV** and in **Table V** makes reference to the chemical structure of serinol and serinol derivatives. The presence of primary amine in serinol is responsible for the low values of  $t_{s1}$  in the vulcanization at 170°C and of  $t_{s5}$ , in the test performed at 127°C. Highest values of these parameters are obtained for the imine derivative with camphor. These results could be attributed to the stability of the imine derivative with camphor. However, it is worth observing that SCam brings about  $t_{s1}$  value larger than the value of silica compound without any secondary accelerator, but lower  $t_{90}$  value. This suggests that the imine bond could be opened during the vulcanization process. Lower values of  $t_{s1}$ ,  $t_{90}$  and  $t_{s5}$ , both with respect to the compound without any secondary accelerator and with respect to the compound with Scam are obtained with SCin, i.e. with the serinol imine with cinnamaldehyde. These findings appear to support the hypothesis that the imine can be opened during the crosslinking reaction. Interesting results were obtained with oxazolidine: vulcanization was indeed accelerated without having critical value of scorch time at 127°C, and viscosity of the compound was either in line or decreased. By properly selecting the carbonyl compound for the reaction with serinol, it is thus possible to tune the kinetics of vulcanization of silica based compound.

## CONCLUSIONS

Serinol and serinol derivatives were used to control the filler networking and to promote the sulphur based vulcanization of silica based compounds.

Reactions of serinol with carbonyl compounds, aldehydes and ketones, performed in the absence of solvents and catalysts, allowed the specific preparation of either imines or oxazolidines. In particular, bisoxazolidine was obtained from the reaction of serinol with 2,5-hexanedione and was isomerized, by simply heating, to a serinol derivative containing an aromatic ring, serinolpyrrole. Hence, reactions inspired to the principle of sustainable chemistry are also endowed with specificity. This results is unprecedented for the reactions of aminoalcohols with carbonyl compounds.

The reaction specificity and the control of atoms' hybridization allowed the specific use of serinol derivatives in silica based rubber compounds.

Serinol pyrrole was used for the functionalization of  $sp^2$  carbon allotropes and the adduct with carbon black, used in minor amounts (0.6 and 0.9 phr of SP) promoted the reduction of filler networking of the silica based compounds.

Serinol and serinol derivatives such as imines and oxazolidines were efficient secondary accelerators. In particular, data obtained with serinol as the secondary accelerator of induction vulcanization,  $t_{90}$  and scorch time measured at  $127^\circ\text{C}$ , are in line with those collected with diphenyl guanidine. The use of either imines or oxazolidines of serinol allows to tune the vulcanization kinetics.

This work demonstrates that a molecule such as serinol which can be easily obtained either from renewable sources or from an industrial by product as glycerol, can be transformed, by means of sustainable technologies, into molecules suitable for the rubber world, obtaining better compound properties and replacing critical ingredients.

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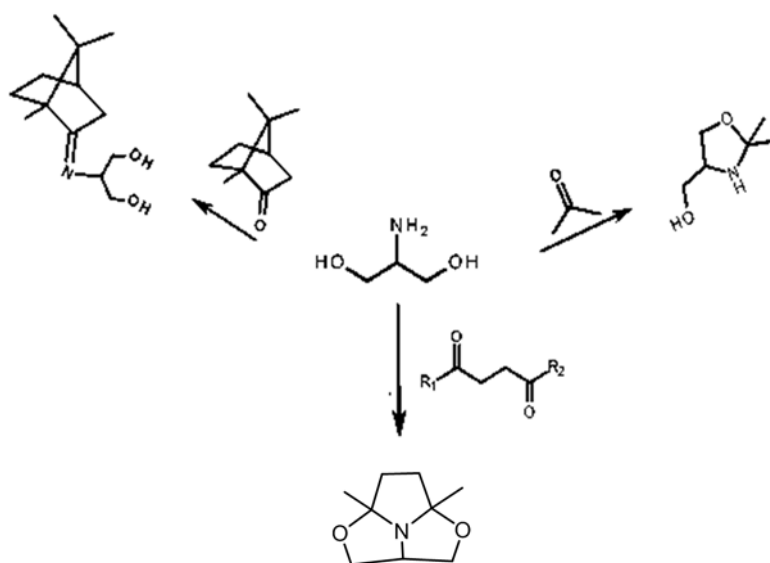
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FIGURE 1



**FIGURE 2**

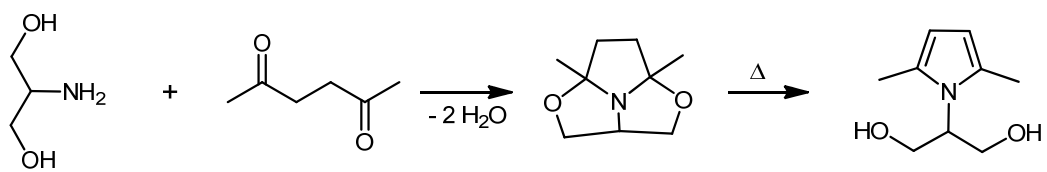


FIGURE 3

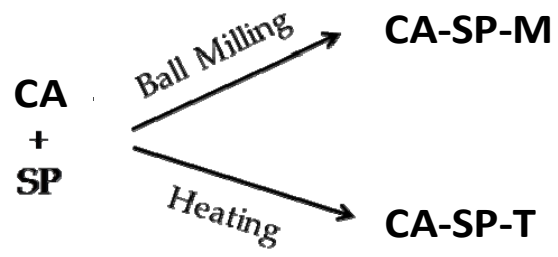


FIGURE 4

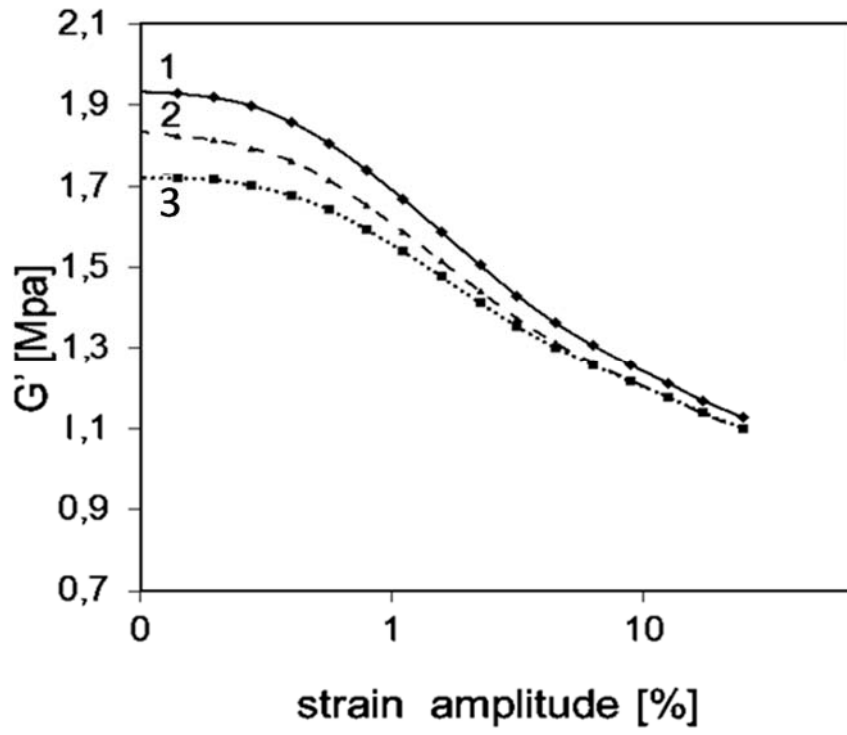
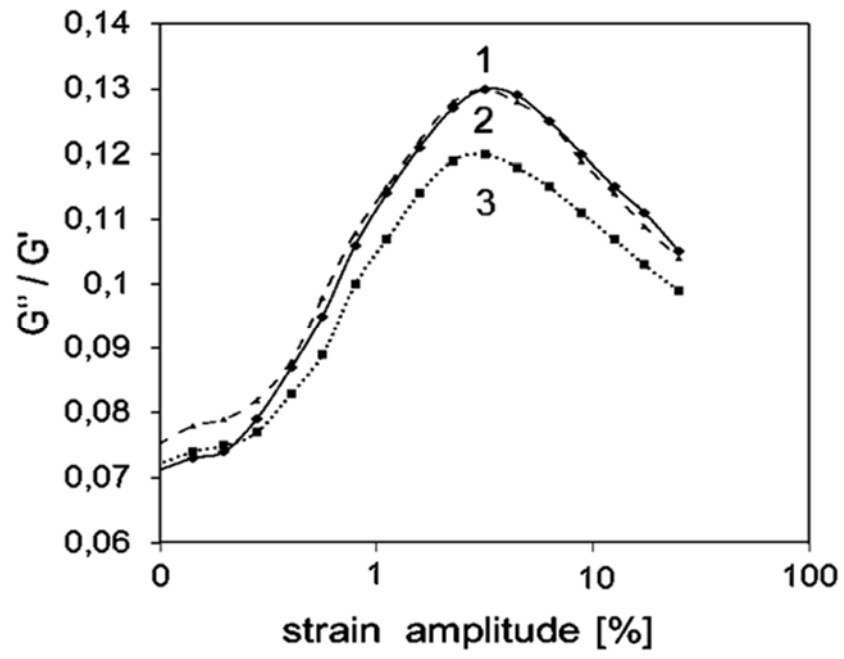


FIGURE 5



## LIST OF FIGURE CAPTIONS

**Figure 1.** Serinol and serinol derivatives as ingredients of rubber compounds.

**Figure 2.** Reaction between serinol and 2,5-hexanedione leading to serinolpyrrole.

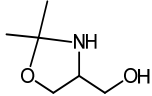
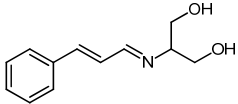
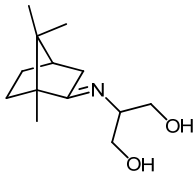
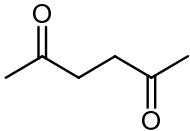
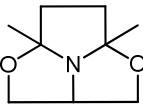
**Figure 3.** Preparation of CA-SP adducts, by using either mechanical or thermal energy.

**Figure 4.** Storage modulus  $G'$  [MPa] versus strain amplitude [%] for Composites of **Table II**. The content of SP was: 1) 0 phr, 2) 0.6 phr, 3) 0.9 phr.

**Figure 5.** Loss modulus  $G''$  versus storage modulus  $G'$  for crosslinked composites of **Table II**. The content of CB-SP was: 1) 0 phr ; 2) 5 phr; 3) 7.5 phr.

**TABLE I**

SYNTHESIS OF SERINOL DERIVATIVES THROUGH THE REACTION WITH CARBONYL  
COMPOUNDS <sup>a</sup>

Run	Carbonyl compound	time (h)	Temperature (°C)	Yield (%)	Product
1	Acetone	12	25	90	
2	Cinnamaldehyde	2	100	92	
3	Camphor	4	170	70	
4	 2,5-hexanedione	12	25	99	

<sup>a</sup>Serinol / carbonyl compound molar ratio = 1 / 1



**TABLE II**RECIPES OF COMPOUNDS BASED ON IR/BR AND CB/SILICA<sup>a</sup>

<b>Compound</b>			
<b>Ingredients</b>	<b>1</b>	<b>2</b>	<b>3</b>
IR	50.0	50.0	50.0
BR	50.0	50.0	50.0
CBN326	25.0	20.0	17.5
CB-SP <sup>b</sup>	0.0	5.0	7.5
Silica	25.0	25.0	25.0
TESPT	4.0	4.0	4.0

<sup>a</sup> Other ingredients (phr): ZnO 4.0, Stearic acid 2.0, S 1.5, 6PPD 2.0, CBS 1.8;<sup>b</sup> amount of SP on CB: 12 mass%

**TABLE III**  
 RECIPES OF SILICA BASED COMPOUNDS WITH SERINOL AND SERINOL  
 DERIVATIVES AS SECONDARY ACCELERATORS <sup>a</sup>

	<b>Compound</b>					
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Secondary accelerator</b>	=	DPG	S	SCam	SCin	SOxa
<b>Ingredient</b>						
NR	15.0	15.0	15.0	15.0	15.0	15.0
S-SBR	96.3	96.3	96.3	96.3	96.3	96.3
BR	15.0	15.0	15.0	15.0	15.0	15.0
Silane TESPT Si 69	5.2	5.2	5.2	5.2	5.2	5.2
Silica	65.0	65.0	65.0	65.0	65.0	65.0
Oil MES	10.0	10.0	10.0	10.0	10.0	10.0
Stearic Acid	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	2.5	2.5	2.5	2.5	2.5	2.5
6PPD	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.8	1.8	1.8	1.8	1.8	1.8
Sulphur	1.2	1.2	1.2	1.2	1.2	1.2
DPG80	0.0	2.4	0.0	0.0	0.0	0.0
Serinol (S)	0.00	0.00	0.83	0.00	0.00	0.00
Serinol imine with camphor (SCam)	0.00	0.00	0.00	2.04	0.00	0.00
Serinol imine with cinnamaldehyde (SCin)	0.00	0.00	0.00	0.00	1.87	0.00
Serinol oxazolidine with acetone (SOxa)	0.00	0.00	0.00	0.00	0.00	1.19

**TABLE IV.**  
VULCANIZATION PARAMETERS ( $M_L$ ,  $M_H$ ,  $t_{s1}$ ,  $t_{90}$ ) FROM RHEOMETERIC TESTS AT  
170°C FOR 20 MINUTES FOR COMPOUNDS OF TABLE III.

		<b>Compound</b>					
		<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Secondary accelerator</b>		=	DPG	S	SCam	SCin	SOxa
<b>Parameter</b>							
$M_L$	[dNm]	2.8	2.3	3.1	2.6	2.7	2.8
$M_H$	[dNm]	13.3	15.1	15.0	14.6	13.6	14.8
$t_{s1}$	[min]	2.8	2.9	2.6	3.0	2.7	2.4
$t_{90}$	[min]	11.5	7.1	9.5	10.5	9.2	9.2

**TABLE V**ML AND SCORCH TIME ( $t_{s5}$ ) AT 127°C FOR COMPOUNDS OF TABLE III.

		<b>Compound</b>					
		<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Secondary accelerator</b>		=	DPG	S	SCam	SCin	Soxa
<b>Parameter</b>							
ML	dNm	7.1	6.1	7.0	6.5	6.1	6.6
$t_{s5}$ <sup>a</sup>	min	46.4	28.9	25.7	37.3	27.0	20.6

<sup>a</sup> Scorch time  $t_{s5}$ : = time needed to have an increase of torque of 5 dNm