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Antioxidant properties of lignin in rubber blends

The present work studied the antioxidant properties of different lignin samples in carbon black filled NR/SBR blends. The commercial calcium lignosulfonate and two types of lignins with different botanical origin which were isolated from black liquors using diluted sulfuric acid were used. The lignin samples were characterized in terms of the elemental analysis and FTIR spectroscopy. The content of phenolic hydroxyl groups of each sample was determined using UV spectroscopy. Efficiency of these “natural stabilizers” was compared with common used rubber stabilizer *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD). Rubber vulcanizates with addition of chosen stabilizers were submitted to accelerated thermo-oxidative aging for 72 and 168 hours and the mechanical properties of prepared vulcanizates before and after aging were measured. The obtained results showed that lignin exhibits stabilizing effect in tested rubber blends and its effect is comparable with conventional antioxidant IPPD. However, it was revealed that stabilizing effect depends greatly on total content of phenolic hydroxyl groups. Moreover, the amount of phenolic structures significantly influences antioxidant properties of lignins in mixtures with IPPD.

Key words: lignin, stabilizing effect, rubber blends, thermo-oxidative aging

Właściwości przeciwutleniające ligniny w mieszankach gumowych

W niniejszej pracy badano właściwości przeciwutleniające różnych próbek ligniny w napełnionych sadzą mieszankach NR/SBR. Do badań użyto komercyjnego lignosulfonianu wapnia oraz dwóch rodzajów ligniny o różnym pochodzeniu botanicznym, wyizolowanych z tugu posiarczynowego za pomocą rozcieńzonego kwasu siarkowego. Próbkę ligniny scharakteryzowano metodami analizy elementarnej i spektroskopii FTIR. Zawartość grup hydroksylowych pochodzących z fenolu w każdej z próbek określono za pomocą spektroskopii UV. Skuteczność tych „naturalnych stabilizatorów” porównywano z efektywnością powszechnie stosowanego w mieszankach gumowych stabilizatora – *N*-izopropyl-*N'*-fenylo-*p*-fenylenodiaminy (IPPD). Zwulkanizowane próbki zawierające dodatek wybranych stabilizatorów poddano przyspieszonemu starzeniu termooksydacyjnemu w ciągu 72 i 168 h oraz zmierzono ich właściwości mechaniczne przed i po starzeniu. Uzyskane wyniki dowodzą, że w przypadku badanych mieszanek gumowych lignina działa stabilizująco, zaś pod względem skuteczności jest porównywalna z konwencjonalnym przeciwutleniaczem – IPPD. Okazało się także, że efekt stabilizujący ligniny zależy w dużym stopniu od całkowitej zawartości fenolowych grup hydroksylowych. Co więcej, ilość struktur fenolowych znacząco wpływa na właściwości przeciwutleniające ligniny w mieszaninach z IPPD.

Słowa kluczowe: lignina, działanie stabilizujące, mieszanki gumowe, starzenie termooksydacyjne

1. Introduction

The aging of rubber vulcanizates caused by oxidative degradation is an undesirable phenomenon which leads to irreversible changes in properties of elastomeric materials such as softening or hardening, crazing effects, fa-

tigue and finally decline in physical properties and performance characteristics. The reasons for the rubber's sensitivity to the oxygen, which increases with temperature, are unsaturated groups in rubber molecule. In an effort to improve oxidative stability of rubbers and to avoid aging processes the antioxidants are usually used. Antioxidants are materials which activity consists in inhibiting or retarding of oxygen effects. The antioxidants have different effectiveness in dependency on their molecular structure, chemical reactivity and their compatibility and miscibility with rubber matrix [1]. Typical antioxidants include substituted phenols and amine materials which usually act as radical scavengers. The most widely used stabilizers in rubber industry are *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD) and

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N-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine (6PPD), but there is a trend and demand for longer-lasting and non-staining products [2].

In recent years, natural polymers are receiving increasing attention for their renewability, large annual biomass stock and special properties as well [3]. In terms of antioxidant activity, the most interesting biopolymer is lignin.

Lignin represents the second most abundant biopolymer in nature and also one of the main by-products of the treatment of lignocellulosic materials in pulp and paper industry. However, its utilization is still limited, because the most of produced lignin is burned for steam and power generation and only less than 2% of the lignin is used in another commercial applications as a raw material [4].

Lignin is cross-linked polyphenolic material which arises from copolymerization of three monomer structures – coniferyl, sinapyl and *p*-coumaryl alcohols – with different degree of oxygen substitution on phenyl ring. High content of various functional groups (phenolic and aliphatic hydroxyl groups, carbonyls, carboxyls, etc.) and its phenylpropanoic structure provides antioxidant characteristics of lignin. Lignin can act as an inhibitor in oxidation process, stabilizing reactions induced by oxygen radicals and their derived species. However, these stabilizing properties depend greatly on structure of lignin which varies with botanical origin, the environmental conditions of growth and also methods of extraction from lignocellulosic materials [5, 6].

In the present work, we studied antioxidant properties of commercial calcium lignosulfonate and 2 types of lignins isolated from black liquors with different botanical origin. Those lignin samples were characterized in terms of elemental analysis, infrared and UV spectroscopy and incorporated into NR/SBR blends filled with carbon black. Rubber compounds were exposed to accelerating thermo-oxidative aging and mechanical properties of vulcanizates before and after aging were measured. The stabilizing effect of lignin samples were compared with common used rubber stabilizer IPPD.

2. Materials

2.1. Lignin samples

The tested lignins were extracted from different sources. *Lignin 1* was isolated from black liquor (modified alkaline anthraquinone cooking) obtained from the annual plants, which was kindly supplied by OP Papirna Ltd. (Olsany Czech Republic). *Lignin 2* – wood lignin – was extracted from kraft black liquor, which was kindly supplied by Bukoza Holding Inc. (Hencovce, Slovak Republic). The properties of black liquor are in Table 1.

Lignin recovery from black liquor was carried out in cooperation with Department of Chemical Technology of Wood, Pulp and Paper. Lignins were precipitated from black liquor using diluted acid solution (5% w/w).

100 ml of the black liquor was treated with different amount of diluted sulfuric acid to obtain a final pH value 3. After complete precipitation the content of each flask was filtered through a pre-weighed oven-dry filter paper using a vacuum filtration unit. The precipitated lignin was twice washed with hot water to remove impurities. Then the lignin was dried at 25°C for 24 hours, using lyophilisation equipment (LYOVAC TG) up to reaching constant weight [7]. A commercial calcium lignosulfonate Borrement CA 120 (Borregaard, Germany, $M_w = 24000$, pH of 10% solution = 4.5, Ca content 5%) was also studied.

Table 1. Characteristics of black liquor

Tabela 1. Właściwości ługu posiarzynowego

Sample	pH	Density (g/ml)
Lignin 1	12.9 ± 0.3	1.242
Lignin 2	12.8 ± 0.4	1.358

2.2. Components of rubber blends

The batch of natural rubber SMR 5 (Mardec, Malaysia), styrene-butadiene rubber Kralex 1502 (Synthos Kralupy, Czech Republic) and carbon black N550 (CS Cabot, Czech Republic) was used. Zinc oxide and stearic acid were used as activators. The vulcanization system was composed of sulfur and sulphenamide accelerator CBS (N-cyclohexyl-2-benzothiazole sulphenamide). A commercial rubber antioxidant IPPD (*N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine) was also used.

3. Methods

3.1. Compounding

Rubber compounds were prepared in mixing chamber of Plasticorder Brabender at 80°C and rotor speed of

Table 2. Formulation of rubber blends (phr)

Tabela 2. Skład mieszanek gumowych (phr)

	B1	B2	B3	B4	B5	B6	B7	B8
SMR 5	80	80	80	80	80	80	80	80
SBR	20	20	20	20	20	20	20	20
N550	40	40	40	40	40	40	40	40
ZnO	5	5	5	5	5	5	5	5
St. acid	2	2	2	2	2	2	2	2
Sulfur	2	2	2	2	2	2	2	2
CBS	2	2	2	2	2	2	2	2
IPPD	0	1	0	0	0	1	1	1
Lignin 1	0	0	1	0	0	1	0	0
Lignin 2	0	0	0	1	0	0	1	0
CA 120	0	0	0	0	1	0	0	1

70 rpm in two steps. In the first step, the batch of SMR 5/SBR Krallex 1502/N550, activators (ZnO and stearic acid) and stabilizers were mixed together for 6 minutes and then the blend was calendered. In the second step, the calendered blend was dosed into the mixing chamber and the curatives were added and compounded for 3 minutes. After the second step, all blends were calendered into thick sheets. The rubber formulation is listed in Tab. 2.

Vulcanization of samples was carried out in hydraulic press at 150°C, pressure 20 MPa and time corresponding to optimum cure time (t_{c90}). Cure characteristics – optimum cure time t_{c90} and scorch time t_{s1} – were obtained using RPA 2000 at 150°C.

3.2. Mechanical testing

Tensile strength at break and elongation at break of vulcanizates were measured using Zwick Roell at crosshead speed of 500 mm/min according STN ISO 37. Tested dumbbell specimens for tensile test were obtained by cutting the vulcanized plates of 2 mm thickness.

3.3. Swelling measurements

Crosslink density of prepared vulcanizates was determined on specimens with dimensions 10×10×2 mm, immersed in 1% solution of IPPD in xylene at room temperature to reach swelling equilibrium. The crosslink density ν_{ch} ($\text{mol} \cdot \text{cm}^{-3}$) was calculated using Flory-Rehner equation:

$$\nu_{ch} = -\frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_s (V_r^{1/3} - 0.5V_r)} \quad (1)$$

where V_r is volume fraction of rubber in the swollen network, V_s is the molar volume of the xylene ($123.45 \text{ cm}^3 \cdot \text{mol}^{-1}$), χ is the Huggins interaction parameter. The volume fraction of rubber V_r was calculated using the following equation:

$$V_r = \frac{V_k}{V_k + V_n} \quad (2)$$

where V_k is volume of rubber defined as

$$V_k = \frac{m_o}{\rho_r} \cdot \frac{100}{100 + x} \quad (3)$$

and V_n is volume of absorbed xylene in sample

$$V_n = m_o \left(\frac{\Delta V}{m_o} \right) \quad (4)$$

where m_o is weight of unswollen specimen (g), ρ_r is rubber density, x is weight of all compounding ingredients without rubber and $(\Delta V/m_o)_r$ is equilibrium degree of swelling.

Huggins interaction parameter was calculated according following equation:

$$\chi = 0.35 + \frac{V_s (\delta_{xylene} + \delta_r)^2}{RT} \quad (5)$$

where δ_{xylene} is solubility parameter of xylene and δ_r is solubility parameter of rubber.

3.4. Elemental analysis

Total amount of nitrogen (N), carbon (C), hydrogen (H) and sulfur (S) of all lignin preparates (Lignin 1 and 2, calcium lignosulfonate CA 120) was determined by dry combustion using a Vario Macro Cube C/H/N/S – analyser (Elementar, Hanau, Germany).

3.5. Accelerated aging

Accelerated thermo-oxidative aging was carried out in an air-circulating oven. The vulcanized sheets with dimension 150×150×2 mm were exposed to temperature 70°C for 72 and 168 hours. After aging dumbbell shaped specimens were cut from sheets and the mechanical properties as well as crosslink density after aging were measured.

3.6. UV-spectroscopy–determination of total amount of phenolic hydroxyl groups

According to work of Gartner and Gellersted [8], the modified UV-spectroscopy method was used for determination of total content of phenolic hydroxyl groups. UV spectroscopy is a simple method based on the difference in absorption between lignin in alkaline solution and lignin in neutral or acid solution. In alkaline solution, phenolic hydroxyl groups are ionized and the absorption changes towards longer wavelengths and higher intensities. Phenolic structures can be divided (according Gartner and Gellersted [8]) into six structural types (Fig. 1). Unconjugated phenolic structures (A and C) are expected to reach the maxima at 300 nm and 350-360 nm. Maximum at 350-370 nm is assigned to conjugated structures (B and D).

UV absorption spectra of lignin solution was registered using a CECIL spectrophotometer, at absorption region 200-450 nm, scan speed 5 nm/s and resolution

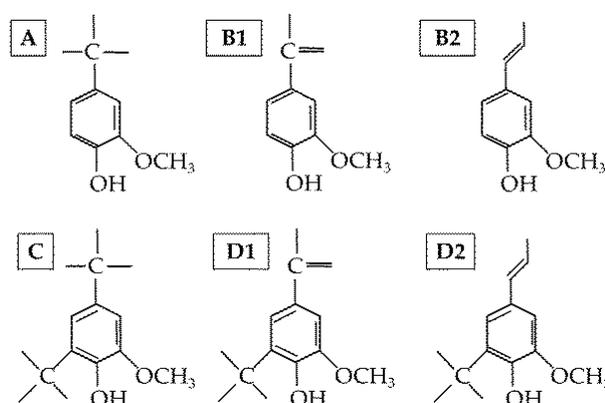


Fig. 1. Types of phenolic structures in lignin
Rys. 1. Rodzaje struktur fenolowych w ligninie

1 nm. Lignin samples were dissolved in diluted solution of dioxane and 0.2 mol/l NaOH to reach the final concentration of lignin about 0.08 g/l. The absorbance of the alkaline lignin solutions was measured against the lignin solution with pH value 6 used as a standard.

The content of non-conjugated phenolic structures was calculated using the absorbance at 300 and 350 nm (Eq. 6), while the conjugated phenolic structures B and D were quantified using only absorbance at 350 nm (Eq. 7). In order to determine the total amount of phenolic hydroxyl groups, the absorbance at 300 and 350 nm was used (Eq. 8).

Non-conjugated phenolic structures (A+C)

$$\text{OH(A + C)} = [0.250 \times A_{300 \text{ nm}}(\text{NaOH}) + 0.0595 \times A_{350 \text{ nm}}(\text{NaOH})] \times 1/(c \times l) \text{ [mmoles/g]} \quad (6)$$

Conjugated phenolic structures (B+D)

$$\text{OH(B + D)} = 0.0476 \times A_{350 \text{ nm}}(\text{NaOH}) \times 1/(c \times l) \text{ [mmoles/g]} \quad (7)$$

Total amount of phenolic hydroxyl groups

$$\text{OH(A + B + C + D)} = [0.250 \times A_{300 \text{ nm}}(\text{NaOH}) + 0.107 \times A_{350 \text{ nm}}(\text{NaOH})] \times 1/(c \times l) \text{ [mmoles/g]} \quad (8)$$

Eq. 6-8: *A* – absorbance, *c* – concentration in g/l, *l* – path length through the sample in cm [8]

4. Results and discussion

4.1. Lignin characterization

In order to investigate the composition and structure of lignin samples as well as their antioxidant properties, we have determined several characteristics of tested lignin powders extracted from different biological origin. The weight percentages of elements C, H, N, O and S of precipitated lignins and commercial calcium lignosulfonate CA 120 are listed in Tab. 3.

Table 3. *Elemental analysis*

Tabela 3. *Analiza elementarna*

Lignin samples	Elemental analysis (% wt)				
	N	C	H	S	O
Lignin 1	1.18	63.64	5.93	0.49	28.34
Lignin 2	0.28	55.68	4.62	3.91	31.65
CA 120	0.14	46.63	5.35	5.62	28.96

It is evident that content of each element in tested samples is different. Lignin 1 derived from annual plants has higher content of C and N atoms and lower content of sulfur in comparison with Lignin 2 and CA 120 extracted from wood. It is well known that lignins found in annual plants contain predominately H structures (4-hydroxy phenyl) while wood lignins normally contain S (syringyl) and G (guaiacyl) structures [9]. The heterogeneity, various origin as well as various monomer units in the tested lignins and also different delignification

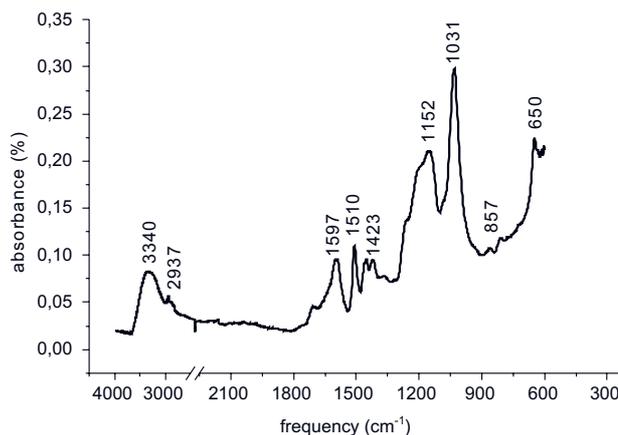


Fig. 2. *FTIR spectra of Borremet CA 120*

Rys. 2. *Widmo FTIR lignosulfonianu Borremet CA 120*

and isolation processes are probably the reasons of differences in elemental analysis of the lignin preparates.

Infrared spectroscopy has been used for lignin characterization for a long time. In our work we used this method for characterization of commercial calcium lignosulfonate Borremet CA 120 (Fig. 2). FTIR spectra of CA 120 showed typical bands corresponding to the functional groups expected to be found in lignin sample. The strong wide band between 3500-3100 cm^{-1} assigns to OH stretch vibrations. This band is caused by presence of alcoholic and phenolic hydroxyl groups. Especially phenolic hydroxyl groups are the one that can most affect the antioxidant properties of lignin. The peak at 2937 cm^{-1} attributes to C-H stretching vibration of the methoxyl groups. Absorption band located around 1600 cm^{-1} and 1500 cm^{-1} are referred to vibration of aromatic rings present in calcium lignosulfonate. OH stretching vibration of secondary alcohols (around 1160 cm^{-1}) and OH vibration of primary alcohols (1030 cm^{-1}) are found as well.

Table 4. *Content of phenolic hydroxyl groups*

Tabela 4. *Zawartość fenolowych grup hydroksykowych*

Lignin samples	Unconjugated phenolic structures (A+C) [Eq.6]	Conjugated phenolic structures (B+D) [Eq.7]	Total amount of phenolic hydroxyl groups [Eq. 8]
	mmol/g	mmol/g	mmol/g
Lignin 1	2.238	0.312	2.550
Lignin 2	3.129	0.393	3.521
CA 120	1.437	0.129	1.565

In Table 4, the content of phenolic hydroxyl groups of studied lignin samples is shown. It is seen, that the highest amount of phenolic hydroxyl groups was determined for Lignin 2, followed by Lignin 1 extracted from annual plants and finally by the commercial calcium lignosulfonate CA 120. The content of conjugated as well as unconjugated structures decreases with decreasing of total

amount of phenolic groups. These results also revealed that alkaline (kraft) lignin samples (Lignin 1 and 2) precipitated using diluted sulfuric acid contain more phenolic hydroxyl groups than the commercial CA 120 obtained using sulfite process. These results reflect the different delignification process of tested lignins. The higher content of phenolic structures in case of kraft lignins can be explained by generating of free phenolic hydroxyl groups during the kraft delignification, when the linkages holding the phenylpropane units together are cleaved [10]. In terms of antioxidant properties of lignin, the content of these groups is very important and has therefore of special interest. Phenolic structures play a central role in photo-yellowing reactions, due to their ability to absorb ultraviolet light and participate in photo-oxidation reactions [8]. Thus, it might be expected that alkaline Lignin 1, which presented the highest total amount of phenolic hydroxyl groups than the other analyzed lignins, could exhibit the most significant antioxidant properties and could be used as a stabilizer in rubber blends. In order to investigate the possibility of lignin application as an antioxidant additive and to affirm a meaning of phenolic groups, we studied the tested lignins as stabilizers in NR/SBR blends, which were submitted to thermo-oxidative aging.

4.2. Application of lignins in rubber blends

The effect of commercial stabilizer IPPD as well as tested lignin samples on cure characteristics and mechanical properties of NR/SBR blends filled with carbon black before aging is shown in Table 5. Based on the obtained results it wasn't observed significant influence of used stabilizers on evaluated properties. The scorch time and the optimum cure time of prepared blends remained almost the constant. In addition, the elongation at break of vulcanizates was changing minimally with addition of different antioxidant additives. On the other hand, addition of stabilizers caused slight decrease of

Table 5. Cure characteristics and mechanical properties of vulcanizates before aging

Tabela 5. Charakterystyka wulkanizacji oraz właściwości mechaniczne wulkanizatów po starzeniu

	t_{s1} (min)	t_{c90} (min)	TS_b (MPa)	E_b (%)
B1	4.38	8.23	23.16	460
B2	4.07	7.96	23.28	460
B3	4.57	8.26	22.66	450
B4	4.71	8.60	22.50	450
B5	4.37	7.61	22.35	460
B6	4.45	8.01	23.08	460
B7	4.55	8.18	22.37	470
B8	4.28	8.27	22.00	470

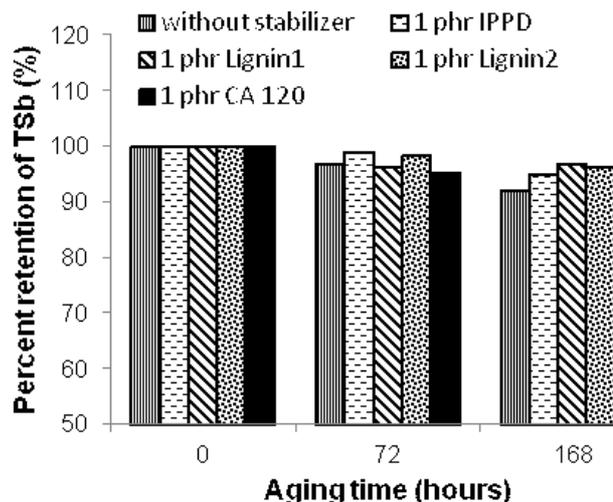


Fig. 3. Percent retention of tensile strength at break vs. aging time of NR/SBR vulcanizates

Rys. 3. Procentowa retencja wytrzymałości na rozciąganie wulkanizatów NR/SBR w funkcji czasu starzenia

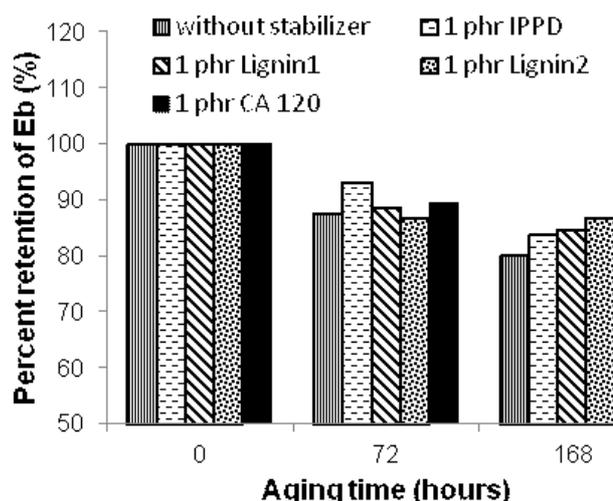


Fig. 4. Percent retention of elongation at break vs. aging time of NR/SBR vulcanizates

Rys. 4. Procentowa retencja wydłużenia przy zerwaniu wulkanizatów NR/SBR w funkcji czasu starzenia

tensile strength at break for all vulcanizates in comparison with reference blend (B1), except the blend B2 with content of 1 phr of IPPD.

Figure 3 and 4 show the influence of thermo-oxidative aging on the tensile properties of NR/SBR compounds stabilized with 1 phr of each antioxidant additive. The obtained results which were determined in percentage as a relative change to original values of each rubber blend are discussed in the following parts.

The tensile strength and elongation at break of non-stabilized vulcanizates decreased with extending aging time, probably because of predominant degradation reactions. Moreover, regardless of the type of antioxidant additive, all of the stabilized blends showed

negative change in tensile strength and elongation at break, indicating a deterioration of these properties with aging. However, obtained results confirmed higher resistance toward accelerated thermo-oxidative aging of samples stabilized with IPPD as well as with lignin. Vulcanizates with addition of IPPD or different types of lignin exhibited comparable values of percent retention of TS_b after 72 hours of aging, whereas in the case of elongation at break the common used IPPD seems to be the best stabilizer. However, based on the obtained results in pictures 3 and 4, it can be seen that Lignin 1 and Lignin 2 exhibit comparable or better stabilizing effect as IPPD after 168 hours of aging. On the other hand, stabilizing effect of calcium lignosulfonate CA 120 is very low, which could be related to low content of phenolic hydroxyl groups in comparison with lignins isolated from black liquors. These results indicate that the main factor that establishes the antioxidant properties of lignin in rubber blends is content of phenolic structures, although the compatibility of lignin and rubber matrix may have a significant effect.

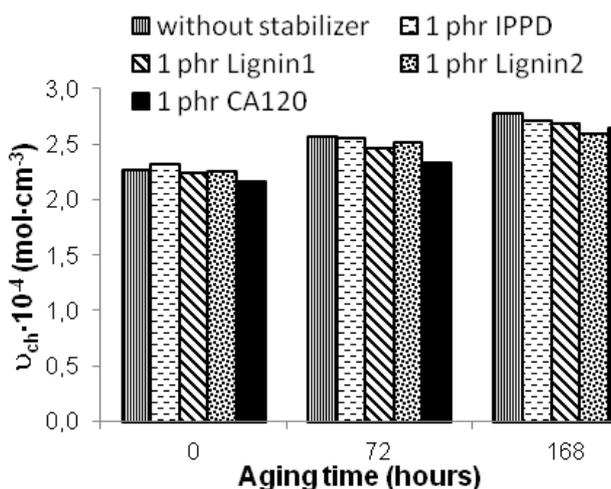


Fig. 5. Crosslink density vs. aging time of NR/SBR vulcanizates

Rys. 5. Gęstość usieciowania wulkanizatów NR/SBR w funkcji czasu starzenia

The crosslink density of vulcanizates stabilized with different stabilizers was studied as well. The influence of aging time on this characteristic is shown in Fig. 5. The crosslink densities of all tested vulcanizates after thermo-oxidative aging increased. This may be explained with formation of new crosslinking bonds and dissociation of existing crosslinks as a result of aging. According to Gregorová et al. [11], it can be suggested that lignin structures containing sulfur formed during the vulcanization can take part in further crosslinking during rubber aging, thereby causing increased retention of tensile properties of the aged samples.

In the second part of our work we tested the stabilizing effect of IPPD mixtures with one of the lignin sam-

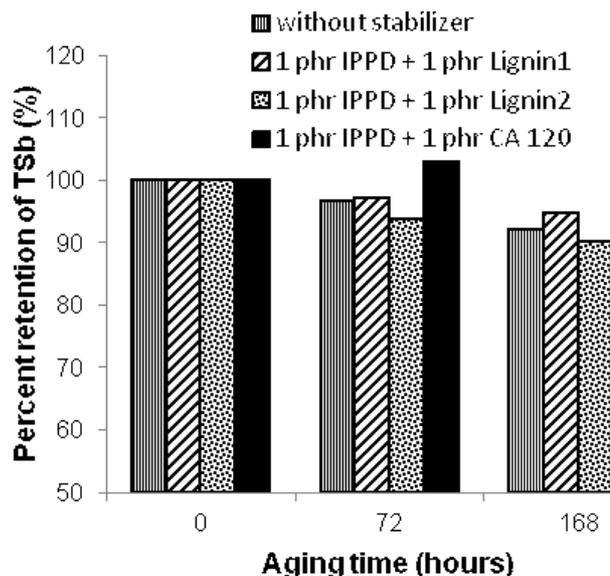


Fig. 6. Percent retention of tensile strength at break vs. aging time of NR/SBR vulcanizates

Rys. 6. Procentowa retencja wytrzymałości na rozciąganie wulkanizatów NR/SBR w funkcji czasu starzenia

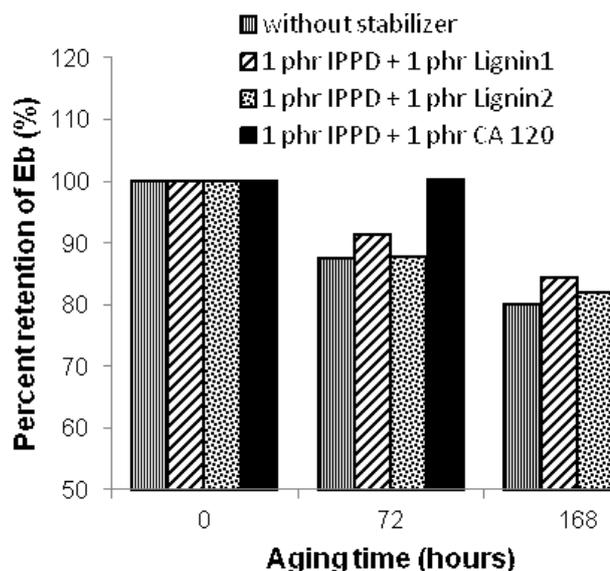


Fig. 7. Percent retention of elongation at break vs. aging time of NR/SBR vulcanizates

Rys. 7. Procentowa retencja wydłużenia przy zerwaniu wulkanizatów NR/SBR w funkcji czasu starzenia

ples in rubber blends. Figure 6 and 7 shows the changes in tensile properties of NR/SBR blends, which were exposed to aging for 72 and 168 hours at 70°C. It was revealed that antioxidant properties of lignins in mixture with IPPD are completely different than when the lignin is used alone. It was found out that combination of IPPD with commercial calcium lignosulfonate CA 120 has the best stabilization effect in rubber blends. The best retention of tensile properties after 3 days of aging was displayed by those that were stabilized with the mentioned

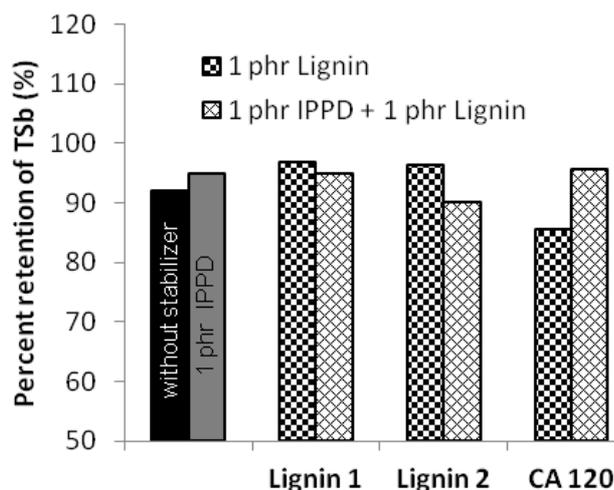


Fig. 8. Percent retention of tensile strength at break of NR/SBR vulcanizates with different type and amount of stabilizers after 168 hours of aging

Rys. 8. Procentowa retencja wytrzymałości na rozciąganie wulkanizatów NR/SBR zawierających różne rodzaje i ilości stabilizatorów po 168 h starzenia

mixture of antioxidants. On the contrary, vulcanizates with addition of IPPD and Lignin 1 or Lignin 2 which contain higher amount of phenolic hydroxyl groups has the lowest stability towards to the thermo-oxidative aging.

The different behavior of lignins in mixture with IPPD can be explained with probable mutual interactions between tested stabilizers either in mixing process, vulcanization process or during the aging. It can be assumed that the higher content of phenolic hydroxyl groups is in lignin sample the higher amount of reactive places is in lignin macromolecule. The same trend can be seen in Fig. 8, where the retention of tensile strength at break of vulcanizates with different type and amount of stabilizers after 168 hours of aging is shown. Mixture of IPPD and Lignin 2 containing the highest content of phenolic structures has the lowest stabilizing effect. On the other hand IPPD and CA 120 together exhibit comparable stabilizing effect as IPPD, Lignin 1 or Lignin 2 alone.

5. Conclusion

In this work it has been proved that different botanical origin and various delignification processes influences the proportion of phenolic hydroxyl groups in lignin samples. Moreover, the study revealed that impor-

tant factor in terms of antioxidant properties of lignins in rubber blends will be in fact the content of these functionalities.

Based on the obtained results it can be concluded that lignin acts as stabilizer in tested rubber blends and its stabilizing effect is comparable with synthetic antioxidant IPPD. The best stabilizing effect was found in case of Lignin 2 with the highest content of phenolic structures. By contrast, the lowest stability toward aging was observed in case of blends stabilized with commercial calcium lignosulfonate. On the other hand, it was found out that high content of phenolic hydroxyl groups negatively influences the stability of vulcanizates with addition of IPPD/lignin mixtures probable because of mutual interactions. The revealed antioxidant properties of lignin in rubber blends could open up new application areas for this natural biopolymer which could contribute to more effective utilization of this material.

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