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Effect of lignin on properties NR/SBR blends

In the present work research concerning the application of calcium lignosulfonate in NR/SBR rubber blends used to coating cords is reported. Commercially available lignosulfonate Borremment CA120 was tested as replacement of carbon black, rubber and the both of these components in range from 0 to 30% in real rubber blends. Influence of lignin on cure characteristics, crosslink density, physical-mechanical properties and interface compatibility of lignin and rubber matrix were studied. Increasing of lignin content causes increase of optimum cure time and decrease of crosslink density of rubber blends where rubber or rubber and carbon black were replaced. In case of these blends there was also observed significant decline of tensile strength at break of vulcanizates with lignin content over 5%. However, measurements of physical-mechanical properties shown that lignin acts as good replacement of carbon blacks in quite wide range of concentrations, because there is minimal change in properties in comparison with lignin-free compound. Scanning electron microscopy confirmed very good compatibility between lignin and rubber matrix even at high lignin content.

Key words: lignin, rubber blends (NR/SBR), replacement of carbon black or rubber

Wpływ ligniny na właściwości mieszanek NR/SBR

W przedstawionej pracy opisano badania nad zastosowaniem lignosulfonianu wapnia w mieszankach gumowych używanych do powlekania kordów. Dostępny w handlu lignosulfonian Borremment CA120 był testowany jako zamiennik sadzy, kauczuku lub obu tych składników w zakresie od 0 do 30% w stosowanych w przemyśle mieszankach gumowych. Badano wpływ ligniny na właściwości wulkanizacyjne, gęstość usieciowania i właściwości wytrzymałościowe oraz zdolność jednorodnego mieszania się faz ligniny i osnowy kauczukowej. Zwiększenie zawartości ligniny kosztem kauczuku bądź kauczuku i sadzy powodowało wydłużenie optymalnego czasu wulkanizacji i zmniejszenie gęstości usieciowania mieszanek gumowych. W przypadku tych mieszanek można było także zaobserwować znaczące zmniejszenie wytrzymałości na rozciąganie przy zerwaniu wulkanizatów zawierających ponad 5% ligniny. Jednakże pomiary właściwości wytrzymałościowych dowiodły, że lignina jest dobrym zamiennikiem sadzy w dość szerokim zakresie ilościowym, gdyż ich zmiany w stosunku do mieszanek niezawierających ligniny były niewielkie. Badania SEM potwierdziły bardzo dobre powinowactwo kauczuku i ligniny nawet przy dużym udziale ilościowym tej ostatniej.

Słowa kluczowe: lignina, mieszanki gumowe (NR/SBR), zastępowanie sadzy lub kauczuku

1. Introduction

Lignin is one of the main constituents in wood and also one of the most abundant renewable raw materials available on earth. It is estimated that amount of lignin on the earth is about 300 Gt [1]. Lignin is natural, non-toxic, three-dimensional aromatic polymer consisting of phenylpropane units (Fig. 1) linked together with ether or carbon-carbon bonds. Wide variety of functional groups, variable composition of lignin, different methods of extraction and the treatments applied during its isolation have marked influence on lignin reactivity and properties [2].

The major sources of lignin are cooking liquors generated in wood pulping processes, from which lignin can be isolated through different extraction methods, resul-

ting in various types of lignin (alkali, hydrolysis, kraft, organosolv, sulphite lignin). Almost all of the lignin extracted from lignocellulosic materials is burned to generate energy and recover chemicals. It has been estimated that only 1-2% of lignins are used commercially [3]. Due to this fact lignin is still viewed as low quality and low

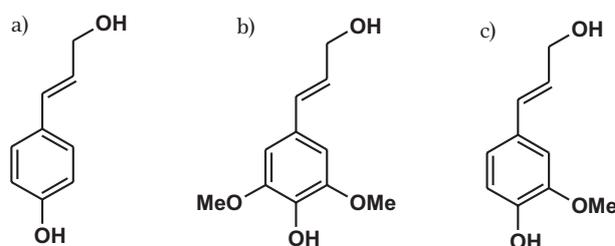


Fig. 1. Monolignol monomer species: a) p-coumaryl alcohol, b) sinapyl alcohol, c) coniferyl alcohol

Rys. 1. Rodzaje monomerów monolignolu: a) alkohol p-kumarylowy, b) alkohol sinapylowy, c) alkohol koniferylowy

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added value material although its complex chemical structure and unique characteristics allow for use in wide range of applications. For example there is well known its utilization in phenolformaldehyde resins, polyurethane foams, epoxy resins, biodispersants and also many studies proved potential use of lignin in polyolefin blends as UV stabilizer or such as low-cost substitute for carbon black in the rubber blends [4].

On the basis of experimentally obtained results in our previous work [5] there was decided to examine the effect of calcium lignosulfonate as replacement of carbon black, rubber and both of these components on properties of NR/SBR blends used to coating cords.

2. Materials

Mixture of natural rubber (NR) SMR 5 and styrene-butadiene rubber (SBR) Kralex 1502 (Kaucuk Kralupy, Czech Republic) was used as an elastomeric matrix in experimental work. Carbon black N550 (CS Cabot, Czech Republic) was used as a filler. Powdered lignosulfonate Borremont CA120 (Borregaard, Germany) with properties which is shown in Table 1 was used as potential replacement of carbon black, rubber or both of these components in range from 0 to 30 vol. % in NR/SBR blends. The vulcanization system was composed of sulphur and sulphenamide accelerators.

Table 1. *Borremont CA120 properties*
Tabela 1. *Właściwości ligniny Borremont CA120*

Calcium content (%)	5
Sulphur content (%)	7
pH of 10% solution	4.5
M_w ($\text{g} \cdot \text{mol}^{-1}$)	24000
Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	3.9

3. Methods

3.1. Compounding

Rubber blends were prepared in mixing chamber (75 cm^3) of Plasticorder Brabender in two steps at mixing temperature 80°C and a rotor speed of 70 rpm. In the first step rubbers, activators (ZnO, Stearin III) and fillers were mixed together for 6 minutes, in second step the curatives were added and compounded for 3 minutes. After the second step, all compounds were calendered into thick sheets. Vulcanization of samples was carried out at 150°C using hydraulic press at pressure 20MPa and time corresponding to optimum cure time (t_{c90}).

Calcium lignosulfonate as a polymer product in powder form were applied in NR/SBR blends by different ways for partially replacement of fillers or rubber:

- 1) Lignosulfonate was used as replacement of carbon black;
- 2) Lignosulfonate was used as replacement of rubber;

- 3) Lignosulfonate was used as replacement of both of these components in rubber blends.

3.2. Cure characteristics

Cure characteristics of the rubber blends (scorch time t_{c1} , optimum cure time) were obtained using Rheometer Monsanto 100S at 150°C .

3.3. Mechanical testing

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

3.4. Swelling measurements

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

3.5. Scanning electron microscopy

Morphology of surface fractures of vulcanizates was studied using Tesla BS 300 scanning electron microscope. All samples were measured directly after fracture in liquid nitrogen as well as after extraction of lignosulfonate from fracture surface in contact with boiling water during 4 hours.

4. Results and discussion

4.1. Cure characteristics

At the first the influence of calcium lignosulfonate on cure characteristics of NR/SBR blends was studied. As is shown in Fig.2, lignosulfonate has minimal effect on scorch time even at high concentration in case of all three types of replacement. The same trend is seen from Fig.3 where optimum cure time remains almost constant in full concentration range, but only for compounds in which carbon black are replaced with lignin. However, this parameter significantly increases with increasing lignin content if lignin is applied as it was mentioned in point 2 and 3 (lignosulfonate is used as replacement of rubber or rubber and carbon black). Optimum cure time of rubber blends, in which rubber was partially substituted with lignin, was lengthened substantially from 17 min (standard compound) to almost 40 min (compound with maximal substitution of rubber). It is quite difficult to describe reasons of significant increase of t_{c90} , because there are a number of factors (pH of lignosulfona-

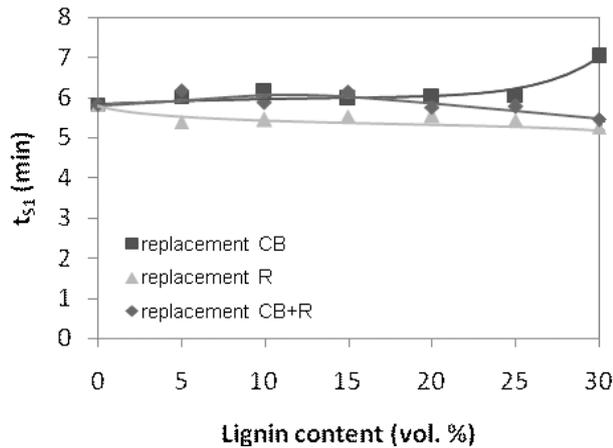


Fig. 2. Dependence of scorch time on lignin content and ways of application

Rys. 2. Zależność czasu podwulkanizacji od zawartości i sposobu zastosowania ligniny

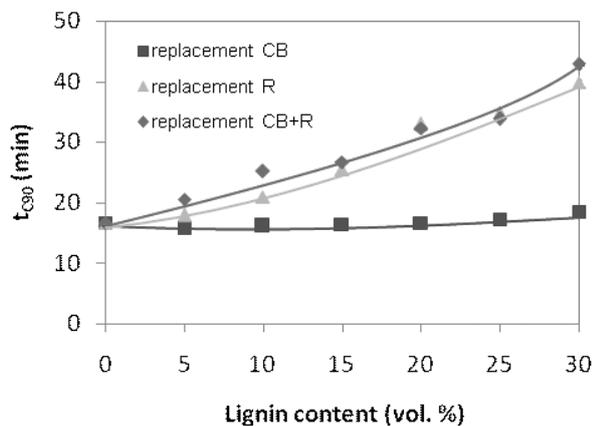


Fig. 3. Dependence of optimum cure time on lignin content and ways of application

Rys. 3. Zależność optymalnego czasu wulkanizacji od zawartości i sposobu zastosowania ligniny

te, lignin reactivity) which can affect vulcanization process. One of the reasons can be mutual interactions between lignosulfonate and components of vulcanization system.

4.2. Swelling properties

Effect of lignosulfonate on vulcanization process was evaluated by measuring the crosslink density of vulcanizates as well. Dependence of crosslink density on lignin content and different ways of application is illustrated in Fig. 4. The obtained results indicate that increasing of lignin content causes decline of crosslink density in all cases of replacement.

4.3. Mechanical properties

The mechanical properties of the prepared vulcanizates are shown in Fig. 5 and 6. It is evident that substi-

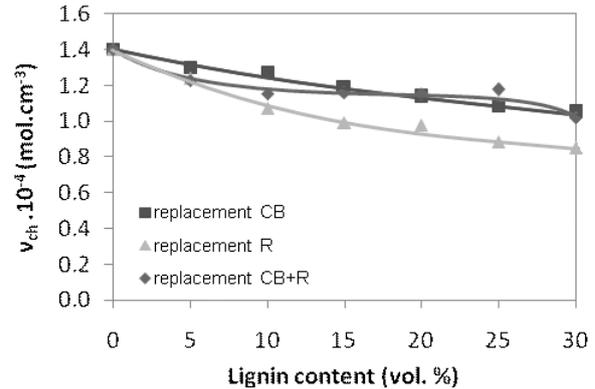


Fig. 4. Dependence of crosslink density on lignin content and ways of application

Rys. 4. Zależność gęstości usieciowania od zawartości i sposobu zastosowania ligniny

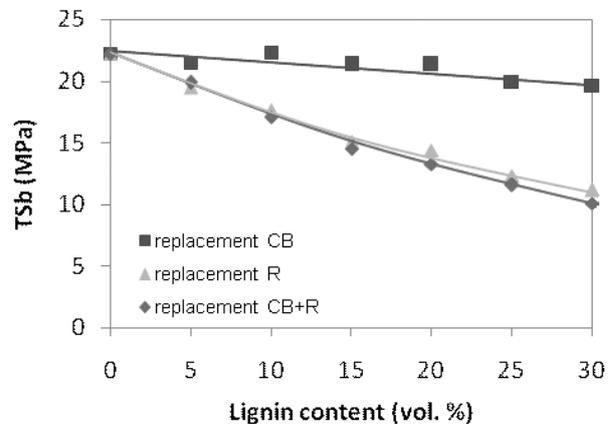


Fig. 5. Dependence of tensile strength at break of vulcanizates on lignin content and ways of application

Rys. 5. Zależność wytrzymałości na rozciąganie wulkanizatów od zawartości i sposobu zastosowania ligniny

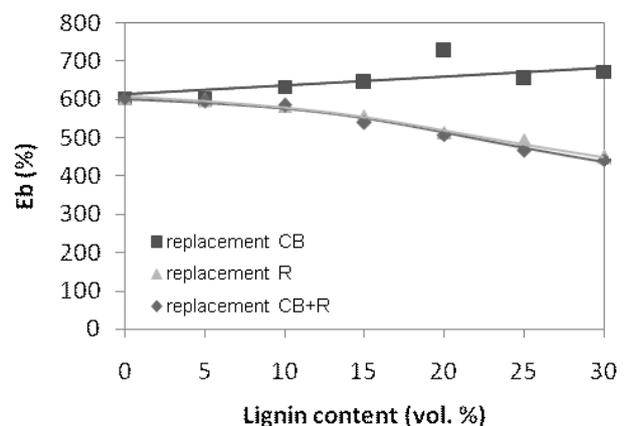


Fig. 6. Dependence of elongation at break of vulcanizates on lignin content and ways of application

Rys. 6. Zależność wydłużenia przy zerwaniu wulkanizatów od zawartości i sposobu zastosowania ligniny

tution of carbon black with lignosulfonate affects tensile characteristics only moderately, whereas partially sub-

stitution of rubber or both of these components of rubber blends causes significant decrease of tensile strength at break. In comparison with lignosulfonate-free blend decline of tensile strength at break of compound with maximal substitution of components represents almost 50%. Influence of individual ways of application of lignin on elongation at break is not as considerable as in case of tensile strength at break. These results indicate that lignosulfonate does not have positive effect on mechanical properties as it was proved in previous work [5] where model blends based on NR were studied. This can be due to elastomeric matrix of tested compounds in this study was composed of both rubbers – NR and SBR, whereas model blends with significantly improved mechanical properties in work [5] were based only on natural rubber. Alexy et al. [6] found out that lignin in SBR mixtures only slightly improves mechanical properties.

4.4. Scanning electron microscopy

In SEM pictures of fracture surfaces of vulcanizates where rubber was replaced with lignosulfonate (Fig.7) is not seen phase interface between calcium lignosulfonate and rubber matrix, so it suggests good compatibility between these two materials. Pictures which illustrate samples after extraction show that lignosulfonate is dispersed in small and quite good distributed domains. It is clearly seen that amount of lignin domains is increasing with increasing lignin loading.

5. Conclusion

The obtained results show that lignosulfonate does not have so positive effect on evaluated properties of NR/SBR blends as it was in model blends based on NR. However, measurements of physical-mechanical properties shown that lignin acts as good replacement of carbon black in quite wide range of concentrations, because there is minimal change in properties in comparison with lignosulfonate-free compound. Scanning electron microscopy confirmed very good compatibility between lignosulfonate and rubber matrix even at high lignosulfonate content.

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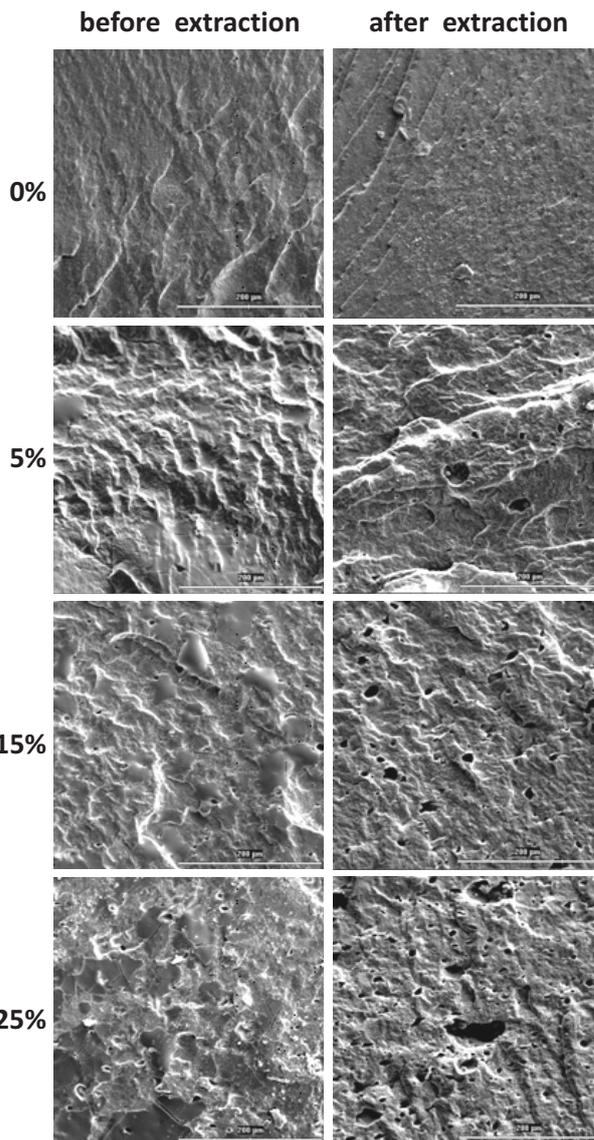


Fig. 7. SEM of fracture surface of vulcanizates where rubber was substituted with calcium lignosulfonate
Rys. 7. Obraz SEM powierzchni przelomu wulkanizatów, w których kauczuk został zastąpiony lignosulfoniem wapnia

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