

The Influence of Selected Physico-Chemical Factors on Physico-Mechanical Properties of Studied Vulcanizates

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Abstract. The focus of the presented study was set on the influence of physico-chemical factors on the physico-mechanical properties of the investigated vulcanizates containing carbon black filler substitution by mixing alternative fillers. Relating to the alternative partial substituents of fillers, the fine fractions of bentonite, polylactide, polypropylene and coffee grounds have been chosen. The prepared vulcanizates were exposed to various environment conditions which were based namely on DCSBD, plasma discharge (Diffuse Coplanar Surface Barrier Discharge), organic solvent and fungus extract of *Piptoporus betulinus*. The main objective of the study was to investigate the influence of the selected environment conditions on the physico -mechanical as well as dynamical and mechanical properties of the studied vulcanizates. The effect of chosen alternative fillers and physico-chemical factors on the physico-mechanical properties (elongation, tensile strength and hardness) was evaluated for the studied vulcanizates. Taking into account the chosen environment conditions, the viscoelastic behaviour of the prepared vulcanizates with alternative fillers and reference vulcanizate were evaluated on the basis of the results of the dynamical and mechanical analysis which was resulting from measurements. The measured results show that selected physico-chemical factors in combination with selected alternative fillers affect the physico-mechanical as well as dynamical and mechanical properties of the studied vulcanizates.

1 Introduction

Nowadays, the rubber industry produces high-quality tire treads for cars and trucks, while the given tire treads are mainly based on composite materials. The given introduced composite consists of a rubber matrix with added additives [1-4]. The filler is one of the main additives and it which significantly affects the physico-mechanical properties of the final car tire product. Fillers are important components of rubber compounds that have a major impact on the properties of the compounds and final products and they can be modified or their quality and quantity can be adjusted [5 -7]. These are mostly solids used

in the form of powder (carbon black, clay, silica, etc.) or short fibers (carbon fibers, polymers, etc.) [8-11]. Fillers help to improve mechanical properties (e.g. toughness, tensile strength, stiffness, etc.). They also improve resistance to abrasion, to heat, fire, corrosion, aging and moreover, they affect the appearance or design of products [5, 6, 12, 13]. Fillers efficiency is closely connected with different variables of fillers, for example: particle size, shape, dispersion and surface, surface reactivity, filling structure, filling ability to form bonds with the rubber matrix and many others [1, 4, 7, 14]. At present, the final rubber products are not based only on quantity, but quality as well as environmental protection represent the prevailing or dominant aspect. The mentioned statement stands for the fact that rubber companies have to use different types of environmentally acceptable fillers in a blend and it leads to the green production of the car tires, while maintaining the quality of the resulting products. The current trend is based on the selection of various alternative fillers, such as suitable clay minerals, their modified forms, as well as clay rocks, including the fillers based on various polymers of natural or synthetic materials. Furthermore, the waste from any production process can fulfil the required and suitable properties to be used in the function of the fillers [11-19].

This work mainly deals with a partial replacement of commercial carbon black filler by selected alternative fillers, including the modification of prepared vulcanizates of selected physico-chemical parameters.

2 Experimental

2.1. Materials

The four different fillers were investigated. Selected materials, namely polypropylene (PP) waste, polylactide waste (PLA), coffee grounds after drying (K) and bentonite-clay rock (B), were mixed into the rubber compound as alternative fillers. Alternative fillers were used instead of the commercial filler - carbon black N339, as a partial replacement. The particle size of the studied fillers was up to 0.04 mm.

2.2. Rubber composites realization process

According to standards, the rubber blend and vulcanizates (v) in order: standard – v (S) and its adapted forms: v polypropylene (PP), v polylactid (PLA), v coffee grounds (K) and v bentonite (B) were mixed in a Plastograph® EC-Brabender laboratory mixer device by a two-step mixing. The volume of the mixing chamber was 70 cm³ and operating speed was 50 rpm [20]. At the temperature of 120 °C was performed the first step of mixing, where were used fillers, separately: carbon black, polypropylene, polylactid, grounds from the coffee grains and bentonite. The second step of mixing process was performed at the temperature of 100 °C. In the second step was common vulcanization agent (sulphur) and accelerator of vulcanization mixed into the blend [7]. As the modified fillers were applied polypropylene and polylactid fibres, both of them based on waste, then dried coffee grounds and clay rock – bentonite containing montmorillonite mineral. These fillers were used as a sectional replacement of the N339 carbon black, which is mostly used in worldwide rubber industry nowadays.

The homogenization of prepared rubber blends was carried out by the LaboWalz W80T double drum. Rotation speed of the roller was predetermined at 20 rpm.

In this paper, 5 rubber blends were prepared, with different content of filler. The standard or reference blend comprised 87 phr of N339 carbon black filler. The prepared rubber blends with selected alternative fillers contained 77 phr of commercial carbon black (N339) and 10 phr of the modified filler. All of the vulcanizates were prepared from the rubber

mixtures by curing process. The prepared vulcanizates were labelled or designated as follows: standard vulcanizate v (S), vulcanizate v (PP) with the content of polypropylene PP, vulcanizate v (PLA) with the content of polylactide PLA, vulcanizate v (K) with the content of dried coffee grounds K and vulcanizate v (B) with the content of clay rock bentonite B. Test specimens (double-sided blades) were cut from the prepared vulcanizates and subsequently, they were exposed to selected physico-chemical factors. The prepared samples of vulcanizates were exposed to an organic solvent - isopropyl alcohol (IPA) and then to an extract from the fungus *Piptoporus betulinus* in isopropyl alcohol (IPAPB), at room temperature and for 6 months. Plasma modification of the vulcanizates samples was performed with a KPR 20 device. The samples were treated at a power set at 400 watts, at distance from the ceramic dielectric of 0.25 mm for 20 seconds.

The hardness of the prepared vulcanizates before and after the action of physico-chemical factors was measured with an IRHD equipment in the range from 30 to 85 IRHD. The vulcanizate samples were 6 mm thick. The physico-mechanical properties namely tensile strength and tensibility etc. of studied vulcanizates were determined using Shimadzu Autograph AG-X universal testing machine at a settled temperature of 25 °C and the test rate of 100 mm.min⁻¹, according to standards.

Thermal analysis – Dynamical and mechanical analysis (DMA) was carried out by DMA Q800 thermal analysis device by TA Instruments. Temperature of DMA experiment was set in the range of -75 °C to 75 °C, frequency of 1 Hz and the rate of heating was 3 °C/min.⁻¹.

3. Results and discussion

3.1 The physico-mechanical properties of studied vulcanizates

The effect of the isopropyl alcohol (IPA) organic solvent and the extract from the fungus of *Piptoporus betulinus* in isopropyl alcohol (IPAPB) on the hardness of prepared vulcanizates, containing the common N339 carbon black filler (S) and vulcanizates, containing alternative fillers (PP), (PLA), (K) and (B) was studied. The values of hardness of prepared vulcanizates ST, PP, PLA, K and B were determined according to standards. The hardness results for the studied vulcanizates before and after their exposure to IPA/IPAPB are shown in Figure 1. All prepared vulcanizates with specified content of alternative fillers have to be compared with the reference (standard) vulcanizate – v (S).

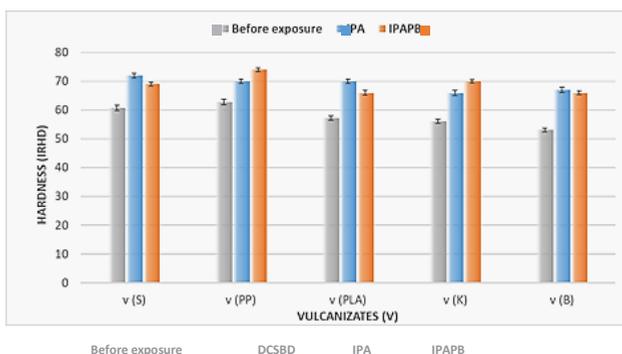


Fig. 1. Hardness changes of prepared vulcanizates: v (S), v (PP), v (PLA), v (K) and v (B).

Before exposing the vulcanizates to IPA/IPAPB, the values of hardness for vulcanizates with the content of B, K or PLA alternative filler were lower as the hardness values of the standard (S). Lower hardness values can be related to the good incorporation of an alternative filler (polypropylene, bentonite, or polylactide) into the rubber compound [9, 15]. Before exposing the vulcanizates to IPA or IPAPB, the lowest hardness value was achieved by vulcanizate B where an alternative filler was on the base of bentonite and the highest hardness was achieved by vulcanizate PP with the addition of polypropylene, compared with the reference sample (S). All vulcanizates with the content of alternative fillers achieved lower hardness values in the IPA, compared with the standard vulcanizate (S). The studied PLA and B vulcanizates achieved lower hardness values in extract IPAPB, compared with the standard vulcanizate (S). The results of the assessment of the hardness show that the content of the alternative filler affects the hardness of the vulcanizates before and after their exposure to IPA/IPAPB (Figure 1). Subsequently, the influence of the alternative filler (polypropylene, polylactide, coffee grounds and bentonite) and the influence of physical and chemical factors on the tensile strength and elongation was evaluated for the studied vulcanizates v (S), v (PP), v (PLA), v (K) and v (B). The results of the mechanical properties before and after exposure to IPA, IPAPB and after modification with DCSBD plasma discharge are in Figures 2 and 3.

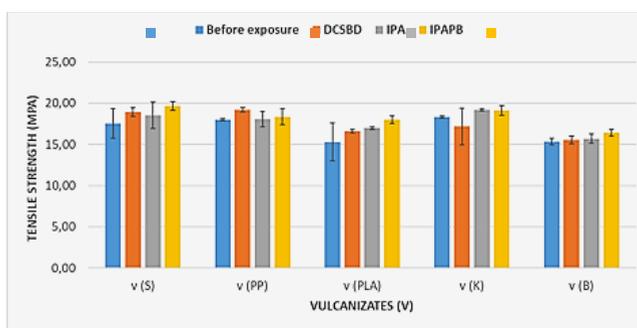


Fig. 2. Change in tensile strength of studied vulcanizates before and after exposure to organic solvents (IPA and IPAPB) and exposition to DCSBD by plasma discharge.

The obtained values of the tensile strength of the studied vulcanizates with alternative K or PP fillers were comparable. Compared with the vulcanizate standard sample (S), they slightly increased. This may be related to the more homogeneous structure of the prepared samples of vulcanizates v (PP), v (K) and v (S) [17, 12].

For samples of rubber containing polylactide or bentonite filler (B), the tensile strength values were lower, compared with the vulcanizate reference sample (S) (Figure 2). The v (PLA) and v (B) vulcanizates achieved lower values of tensile strength, compared with the standard v (S). From the tensile strength results before IPA, IPAPB and DCSBD plasma discharge exposure, it can be observed that v (PLA) and v (B) vulcanizates with alternative fillers based on polylactide and bentonite clay rock, achieved lower values of

tensile strength, compared with the standard v (S). The decrease in values of tensile strength is probably related to the weaker interaction of the filler particles with the rubber matrix. In the case of bentonite, it is a clay filler with a hydrophilic surface. To improve the interaction, it is possible to modify this surface, and thus change its surface to hydrophobic [14 – 16, 21]. After exposing to IPA/IPAPB and DCSBD, the values of the tensile strength for all vulcanizates were higher in comparison with the values of the tensile strength before exposing the vulcanizates to IPA/IPAPB and DCSBD. The highest values of tensile strength were achieved for vulcanizate v (S) after the effect of IPA, vulcanizate v (PP) after exposure to DCSBD and vulcanizate v (K) after the effect of IPA and IPAPB.

The results show that all of the measured values of elongation (Figure 3.) for the studied vulcanizates v (PP), v (PLA), v (K), and v (B) are higher after the effect of IPA, IPAPB and after exposure to DCSBD – compared with standard vulcanizate v (S). Higher values of elongation of the vulcanizates with the content of alternative fillers leads to indication of their increased elasticity and it predetermines the selected vulcanizates for elastic applications.

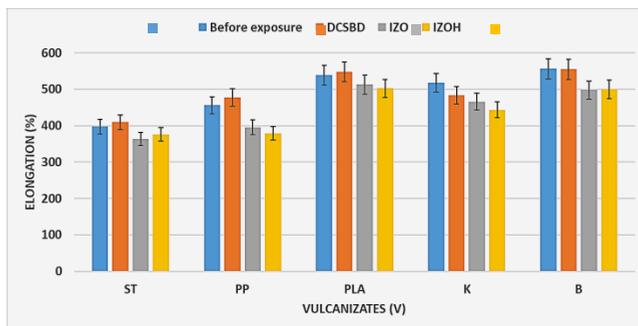


Figure3. Elongation of studied vulcanizates before and after exposition to organic solvents (IPA, IPAPB) and DCSBD plasma discharge.

3.2 Dynamical and mechanical analysis (DMA) of vulcanizates before and after exposure to DSCBD plasma discharge

By dynamical and mechanical analysis was evaluated the viscoelastic behaviour of vulcanizates with a content of PP, PLA, K and B alternative fillers and standard S in the temperature operating range from -75 °C to 75°C. The dependence of the dynamical and mechanical properties – the loss angle ($\tan \delta$) to the temperature is graphically represented in Figure 4 – for the prepared vulcanizates before and after their modification by DCSBD. Max. peak $\text{tg } \delta_{\text{max}}$ indicates the values of the glass transition temperature (T_g). Filler stiffening effect was indicated by max. peaks in relation to size values [17, 19]. The chosen parameters T_g (°C) and $\text{tg } \delta_{\text{max}}$ obtained by DMA measurement are given in Table 1.

Table 1. DMA parameters.

Compounds	Tg (°C)	tg δ_{\max}	Compounds exposed to DCSBD (+DCSBD)	Tg (°C)	tg δ_{\max}
v (S)	- 31.9	0.74	v (S) + DCSBD	- 30.0	0.69
v (PP)	- 30.6	0.63	v (PP) + DCSBD	- 35.6	0.66
v (PLA)	- 30.0	0.69	v (PLA) + DCSBD	- 32.4	0.69
v(K)	- 27.7	0.73	v (K) + DCSBD	- 34.9	0.77
v (B)	- 28.8	0.75	v (B) + DCSBD	- 33.3	0.78

Loss angle tg δ maximum peaks of vulcanizates specify the glass transition temperatures (Table 1.). The values of the glass transition temperatures are higher for all vulcanizates with alternative fillers, compared with the standard vulcanizate v (S) before their modification by DCSBD discharge and there is an increase in the following order: v (S) < v (PP) < v (PLA) < v (B) < v (K) (Table 1.).

The values of the glass transition temperatures are lower for all vulcanizates with alternative fillers, compared with the standard vulcanizate (S) after their modification by DCSBD discharge and there is a decrease in the following order: v (S) > v (PLA) > v (B) > v (K) > v (PP) (Table 1.). The results show that the achieved tg values of examined vulcanizates are affected by the type of alternative filler [19, 22, 23] as well as by the modification of the vulcanizates by plasma discharge DCSBD.

From the resulting evaluations which were obtained by the DMA analysis, especially from the values of the maximum peaks (tg δ) (Figure 4, Table 1), it is possible to predict the stiffening effect of the chosen fillers in the prepared vulcanizates v (PP), v (PLA), v (K) and v (B) in comparison with vulcanizate v (S). The stiffening effect of the filler is related to the restriction of the mobility of the segments of the rubber molecules. The lower the value of tg δ_{\max} , the higher the stiffening effect of the filler. In this case, the interaction of the filler with the rubber matrix [18, 19] increases.

Comparing the values of tg δ_{\max} for vulcanizates v (S), v (PP), v (PLA), v (K) and v (B) before and after vulcanizate modification by DCSBD, it is possible to see that the mentioned discharge affects the interaction of matrix and filler in most cases and it stands for influencing of the reinforcing effect (Table 1, Figure 4). Before modification of vulcanizates by DCSBD, the highest stiffening effect can be spotted for vulcanizates v (PP) and v (PLA), with a certain amount of polypropylene PP or polylactide PLA filler [19]. The values of tg δ_{\max} decrease in the following order: v (B) > v (S) > v (K) > v (PLA) > v (PP).

In the case of modification of vulcanizates by DCSBD discharge, it is as follows: v (B) > v (K) > v (S) = v (PLA) > v (PP). After modification by DCSBD plasma discharge, vulcanizate v (PP) containing polypropylene reached the best stiffening effect. The obtained results show that there is the best interaction of the filler particles with the rubber matrix.

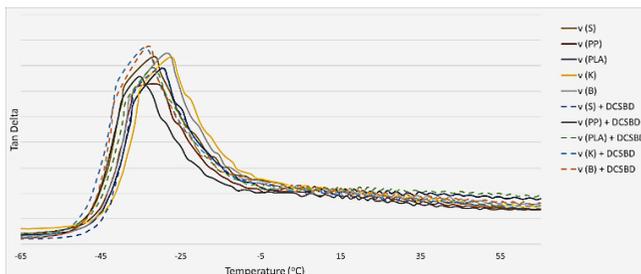


Fig. 4. Loss angle of studied vulcanizates v(S),v(PP),v(PLA),v(K),v(B) before and after DCSBD plasma exposition.

The chosen properties of tire tread vulcanizates, for instance, traction on snow and ice $tg \delta$ (-20 °C), traction on the wet $tg \delta$ (0 °C) and dry $tg \delta$ (0 °C) surfaces and the rolling resistance $tg \delta$ (60 °C) were examined on the dependency of loss angle ($\tan \delta$) on temperature [22] as it is shown in Tables 2, 3 and Figure 4.

Table 2. $Tg \delta$ values at selected temperatures -20 °C, 0 °C, 20 °C, 60 °C for different DMA parameters of studied vulcanizates before DCSBD plasma exposure/modification.

Compounds	$tg \delta$ (-20 °C)	$tg \delta$ (0 °C)	$tg \delta$ (20 °C)	$tg \delta$ (60 °C)
v (S)	0.40	0.24	0.20	0.14
v (PP)	0.34	0.21	0.18	0.14
v (PLA)	0.39	0.21	0.21	0.18
v (K)	0.47	0.24	0.20	0.15
v (B)	0.45	0.23	0.21	0.16

Table 3. $Tg \delta$ values at selected temperatures -20 °C, 0 °C, 20 °C, 60 °C for different DMA parameters of studied vulcanizates after DCSBD plasma exposure/modification.

Compounds exposed to DCSBD plasma discharge (+DCSBD)	$tg \delta$ (-20 °C)	$tg \delta$ (0 °C)	$tg \delta$ (20 °C)	$tg \delta$ (60 °C)
v(S) + DCSBD	0.39	0.22	0.20	0.14
v (PP) + DCSBD	0.29	0.20	0.18	0.14
v (PLA) + DCSBD	0.36	0.22	0.22	0.19
v (K) + DCSBD	0.37	0.23	0.19	0.15
v (B) + DCSBD	0.35	0.22	0.20	0.16

Temperature -20 °C for $tg \delta$ represents the traction of the tire tread on snow and ice. The results show that vulcanizates v (K) and v (B) achieve the best traction on snow and ice compared to the sample vulcanizate v (S) /before DCSBD modification/ (Table 2). The values of $tg \delta$ (-20 °C) increase in order: v (PP) < v (PLA) < v (S) < v (B) < v (K). In the case of vulcanizates, modified by DCSBD discharge (Table 3), the value of $tg \delta$ at -20 °C

decreased and it adversely affects the tread-road adhesion. The vulcanizate v (S) shows the best snow and ice traction. The $\text{tg } \delta$ values ($-20\text{ }^{\circ}\text{C}$) for DCSBD-modified vulcanizates increase in order: v (PP) < v (B) < v (PLA) < v (K) < v (S).

The results of the tire tread wet surface traction $\text{tg } \delta$ for $0\text{ }^{\circ}\text{C}$ show that the vulcanizates v (K) and v (S) exhibit the best values /before DCSBD modification/ (Table 2). The values of $\text{tg } \delta$ ($0\text{ }^{\circ}\text{C}$) increase in order: v (PP) = v (PLA) < v (B) < v (K) = v (S). In the case of vulcanizates modified by DCSBD discharge (Table 3.), the value of $\text{tg } \delta$ at $0\text{ }^{\circ}\text{C}$ significantly decreased. The vulcanizate v (S) shows the best wet surface traction. The $\text{tg } \delta$ values ($0\text{ }^{\circ}\text{C}$) for DCSBD-modified vulcanizates increase in order: v (PP) < v (S) = v (PLA) = v (B) < v (K).

The results show that the vulcanizates v (PLA) and v(B) exhibit the best dry surface traction $\text{tg } \delta$ for $20\text{ }^{\circ}\text{C}$ compared to sample vulcanizate v (S). The values of $\text{tg } \delta$ increases in the order: v (PP) < v (PLA) < v (S) < v (B) < v(K). In the case of DCSBD-modified vulcanizates, there was not any significant reduction in $\text{tg } \delta$ values at $20\text{ }^{\circ}\text{C}$ (Table 3.). There was even a slight increase in the $\text{tg } \delta$ value for vulcanizate v (PLA) and it stands for a positive effect on tread-dry road adhesion. The PLA vulcanizate shows the best dry surface traction. The $\text{tg } \delta$ values ($20\text{ }^{\circ}\text{C}$) for DCSBD-modified vulcanizates increase in the order: v (PP) < v (K) < v (S) = v (B) < v (PLA).

The $\text{tg } \delta$ for $60\text{ }^{\circ}\text{C}$ signifies the rolling resistance. Rolling resistance is associated with fuel consumption – the lower the value of $\text{tg } \delta$ at $60\text{ }^{\circ}\text{C}$, the lower is the rolling resistance value and it stands for which is positive effect [23]. The results show that the vulcanizates v (S) and v (PP) exhibit the best rolling resistance before DCSBD modification [19]. The values of $\text{tg } \delta$ ($60\text{ }^{\circ}\text{C}$) increase in the order: v (PLA) > v (B) > v (K) > v (PP) = v (S). In the case of modified vulcanizates by DCSBD discharge, the value of $\text{tg } \delta$ at $60\text{ }^{\circ}\text{C}$ increased slightly only for PLA vulcanizate.

In the case of other vulcanizates, there was not increase of the $\text{tg } \delta$ values at $60\text{ }^{\circ}\text{C}$ and it stands for positive effect in relation to the rolling resistance. After the modification by DCSBD, the $\text{tg } \delta$ values ($60\text{ }^{\circ}\text{C}$) for vulcanizates decreased in the following order: v (PLA) > v (B) > v (K) > v (PP) = v (S).

4 Appendices

The given study deals with the application of selected alternative fillers, which were incorporated into a selected blend for tire tread. The four different types of fillers were examined. These investigated non-conventional fillers included waste of plastic (PP, PLA), dried coffee grounds (K) and clay rock – bentonite (B) with the majority of montmorillonite mineral and they were applied as sectional replacement of carbon black (N339) - the high reinforcing filler. The prepared vulcanizates with an alternative filler were exposed to organic solvent IPA, the fungus extract IPAPB and the DCSBD plasma discharge. Selected dynamical and mechanical properties and physico-mechanical properties of prepared vulcanizates before or after the action of selected physico-chemical factors were studied. The results show that the alternative fillers based on polypropylene, coffee grounds, polylactide and bentonite as well as the action of selected physico-chemical factors significantly affect the physico-mechanical as well as dynamical and mechanical properties of the prepared vulcanizates. The obtained results are probably related to the chemical composition, structure, particle size of the alternative fillers as well as to the dispersion and different interaction degree of the alternative filler (PLA, PP, K, B) with the matrix of polymer. Appropriately predetermined amounts of alternative filler and selected physico-chemical factors, can positively affect the properties of tread rubber for passenger car tires or truck tires.

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References

1. A. I. Isayev Encyclopedia of Polymer Blends. Weinheim: Wiley-VCH (2011).
2. I. Küçükređeci The investigation of suitable welding parameters in polypropylene sheets joined with friction stir welding. Bull.Pol.Ac.: Tech 67, 1 (2011).
3. P. Krawiec Ł. Warguła, A. Dziechciarz, D. Małozieć, D. Ondrušová Evaluation of chemical compound emissions during thermal decomposition and combustion of V-belts. Przemysł Chemiczny 1, 99, 92–98 (2020).
4. M. Okamoto, R.S. Sinha Polymer/layered silicate nanocomposites: A review from preparation to processing. Prog. Polym. Sci., 28, 1539–1641 (2003).
5. J.S. Dick, Ch.P. Rader Raw materials Supply Chain for Rubber Products: Overview of the Global Use of Raw Materials, Polymers, Compounding Ingredients, and Chemical Intermediates. Munich: HANSER Publisher (2014).
6. Z. Zhenglóng, S. Bin, L. Jiangang, D. Zhiguang, H. Zhongbo Research on ride comfort performance of a metal tire. Bull. Pol. Ac.: Tech. 68, 3, (2020).
7. L.A. Wisojodharmo, R. Fidyarningsih, D.A. Fitriani, D.K. Arti, H. Susanto The influence of natural rubber -butadiene and carbon black type on the mechanical properties of tread compound. Innovation in Polym. Sci. and Technol. 223 (2017).
8. R.N. Rothon Particulate fillers for polymers. 12, 9 Shrewsbury: Rapra Technology p. 154 (2001).
9. L. Yu, K. Dean, L. Li Polymer blends and composites from renewable resources *Prog. Polym. Sci.* **31** 576–602 (2006).
10. I. Vasková, D. Fecko, J. Malík, P. Futáš Physical and chemical clay binder characteristics from various locality and their influence on some technological properties of bentonite moulding mixtures. Arch. Foundry Eng. 10, 211–16 (2010).
11. N. Bitinis, E. Fortunati, R. Verdejo, J. Bras, J.M. Kenny, L. Torre, M.A. López-Manchado Poly(lactic acid)/natural rubber /cellulose nanocrystal bionanocomposites. Part II: Properties evaluation. Carbohydrate Polymers, 96, 621-627 (2013).
12. M. Kawasumi Nanocomposite Based on Organic and Inorganic Materials and Their Unique Properties and Function. R&D Review of Toyota CRDL, 50, 2, 45-61 (2019).
13. M. Bhattacharya, A.K. Bhowmick Synergy in carbon black-filled natural rubber nanocomposites. Part I: Mechanical, dynamic mechanical properties, and morphology. J. Mater. Sci., 45, 6126–6138 (2010).
14. A. Mousa Cure Characteristics and Thermal Properties of Sulfur-cured EPDM-based Composites by Compounding with Layered Nano-Organoclays. Polymer-Plastics Technol. and Eng., 45, 8, 911-915 (2006).
15. A. Ramadhan, M.I. Fathurrohman, B. Soegijono Chemical modification of Upgraded Bentonite as Filler of Natural rubber/organobentonite Composite. Proc. Chem., 16, 85-90 (2015).
16. A. Feriancová et al. The effect of modified Cu(II) kaolinite on interaction with rubberizing components. Appl. Clay Sci. 183, 105313 (2019).

17. M. Pajtašová, Z. Mičicová, D. Ondrušová, S. Božeková, R. Janík, B. Pecušová, L. Raník Use of waste materials in rubber matrix. MATEC Web of Conf. 157, 07009 (2018).
18. A. Das, R. Jurk, K.W. Stöckelhuber, G. Heinrich Effect of vulcanization ingredients on the intercalation-exfoliation process of layered silicate in an acrylonitrile butadiene rubber matrix. Macromol. Mater. Eng., 293, 479–90 (2008).
19. M. Pajtašová, D. Ondrušová, R. Janík, Z. Mičicová, B. Pecušová, I. Labaj, M. Kohutiar, K. Moricová Using of alternative fillers based on the waste and its effect on the rubber properties. MATEC Web of Conf. 254, 04010 (2019).
20. M. Pajtašová, Z. Mičicová, D. Ondrušová, B. Pecušová, A. Feriancová, L. Raník, S. Domčeková Study of properties of fillers based on natural bentonite and their effect on the rubber compounds. Procedia Eng. 177, 470–75 (2017).
21. S.S. Ray, M. Bousmina Effect of Organic Modification on the Compatibilization Efficiency of Clay in an Immiscible Polymer Blend. Macromol. Rapid Commun, 26 1639-1646 (2005).
22. A. Gantowski, P. Palutkiewicz, E. Boceąga Numerical analysis of stress state during single point bending in DMTA examination. J. Achiev. Mater. Manuf. Eng. 28, 47–50 (2008).
23. S. Thongsang, V. Vorakhan, E. Wimolmala, N. Sombatsompop Dynamic mechanical analysis and tribological properties of NR vulcanizates with fly ash/precopitated silica hybrid filler. Tribology International, 53, 134-141 (2012).