Effect of low-temperature plasma-treated bentonite on rubber compounds properties

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Abstract: The influence of low-temperature plasma modification of bentonite on the dynamic-mechanical properties and vulcanization of rubber mixtures was examined. EDX, FTIR and TGA analysis were used to evaluate the filler. IR spectra of modified bentonite indicate lower intensity of the bands associated with OH groups and water. TGA confirms a smaller weight loss of samples subjected to plasma treatment, which also proves a lower water content in the mineral, confirming the effectiveness of the plasma treatment used.

Keywords: bentonite, plasma treatment, rubber compounds, vulcanization.

Wpływ bentonitu modyfikowanego plazmą niskotemperaturową na właściwości mieszanek gumowych

Streszczenie: Zbadano wpływ modyfikacji bentonitu plazmą niskotemperaturową na właściwości dynamiczno-mechaniczne oraz wulkanizację mieszanek gumowych. Do oceny napełniacza zastosowano analizę EDX, FTIR i TGA. Widma IR modyfikowanego bentonitu wskazują na mniejszą intensywność pasm związanych z grupami OH i wodą. TGA potwierdza mniejszy ubytek masy próbek poddanych obróbce plazmowej, co również świadczy o mniejszej zawartości wody w minerale, potwierdzając skuteczność zastosowanej obróbki plazmowej.

Słowa kluczowe: bentonit, obróbka plazmowa, mieszanki gumowe, wulkanizacja.

The advancements in material development have driven tires manufacturers to incorporate new raw materials in tire compound production. These materials directly influence essential performance parameters such as wear resistance, tread longevity, rolling resistance, and wet grip. Achieving progress in these areas requires a delicate balance, as improvements in one aspect can potentially impact another. One commonly used filler for reinforcing rubber is carbon black, which is well-known for its considerable influence on the dynamic mechanical properties [1, 2]. Fillers are incorporated into polymer systems to enhance mechanical strength, electrical or thermal properties, or to reduce costs of expensive polymer systems while minimizing significant alterations to the rheological characteristics of the material [3, 4].

However, the use of petroleum-based carbon black has raised concerns regarding environmental pollution, soaring prices, and sustainability issues. As an alternative, researchers have explored various mineral deposits from the earth that can serve as both reinforcing and non-reinforcing fillers in rubber compounds. One such filler studied is clay, which can be sourced from minerals like montmorillonite, kaolinite, or quartz [1, 5]. Clay minerals can be described as naturally occurring, crystalline substances with a fine particle size (less than 2 μm). They are primarily composed of hydrated aluminum silicates, but may also contain essential constituents such as magnesium, iron, calcium, potassium, or sodium. These constituents are arranged in various configurations, forming alternating layers within the clay minerals [6]. Bentonite is a type of clay that primarily consists of montmorillonite, an expansive mineral, and it is characterized by its multi-layered structure. Within these layers, isomorphic substitution takes place, leading to the formation of negative surface charges. The lamellae of bentonite are held together by weak van der Waals forces, which allow for easy penetration of water molecules and expansion of the interlayer space. This swelling capability of bentonite results in an increased surface area and reduced voids. These exceptional characteristics make bentonite a highly versatile material suitable for a wide range of applications [7]. Clays, particularly bentonite, have gained increasing

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attention due to their affordability, widespread availability, high cation exchange capacity, and large surface area. These desirable attributes have made clays, especially bentonite, a popular choice in various applications [8, 9]. Clay minerals are often chemically modified to enhance their compatibility with organic materials. One common method of modification involves ion-exchange reactions with cationic surfactants, such as primary, secondary, tertiary, and quaternary alkylammonium cations. This chemical modification changes the polarity of the clay minerals and increases the interlayer spacing, facilitating the intercalation and exfoliation of polymers within the clay structure. Traditionally, this modification process is carried out in wet organic conditions [10, 11].

To circumvent the need for chemistry modification this research is conducted. The aim is to modify clay surface using a plasma treatment technique. According to authors best knowledge, plasma treatment can effectively modify the surface of clay minerals. It is an environmentally friendly process that eliminates the requirement for further manipulation of clay particles. The plasma technique introduces new chemical features to the clay surface, which can influence the interaction between the treated surface and the rubber matrix [12].

EXPERIMENTAL PART

Materials

In this study, a sample of bentonite sourced from a Slovak deposit, namely the Lieskovec deposit, was utilized, featuring an average volume particle size of 4,5 μm. The rubber compounding components used in this study included natural rubber elastomer (SMR 10), carbon black (N339), cure activators (ZnO and stearic acid), plasticizer (residual aromatic extract), and the cure system (N-tert-butyl-2-benzothiazyl sulfonamide and sulfur). These materials were sourced from CMR Púchov Ltd., Slovak Republic.

Preparation of plasma

The bentonite surface treatment was carried out on a KPR 200 mm low-temperature plasma reactor (Research Institute for Man-Made Fibers, Svit, Slovak Republic). The procedure involved placing a powdered form of a clay rock, bentonite, on a planar electrode. The bentonite was then applied to the active surface of the electrode using a brush. The plasma electrode used had a power of 350 W, while the bulk density of the plasma was maintained at a minimum of 800 W/cm^3. To protect the sample surface, a 3D frame with stretched foil was placed over the electrode, ensuring that the foil did not come into direct contact with the sample. During the experiment, air at atmospheric pressure was used as the working gas. Surface treatment of bentonite was performed by applying DCSBD (Diffuse Coplanar Surface Barrier Discharge) plasma to the filler for 1 minute and 3 minutes. The process of bentonite treatment, serving as a filler for elastomeric blends, was captured in Figure 1. It involved preparing the planar ceramic dielectric by gradually increasing the power to the desired level, turning off the plasma reactor, applying the filler, installing the custom-designed frame for handling loose materials, sealing the system with a counterpart and foil, activating the plasma reactor for the required exposure time, and finally collecting the plasma-treated filler.

Preparation of rubber compounds

Rubber compounds were prepared on a laboratory Brabender Plastograph kneader (Duisburg, Germany), at an initial temperature of 55°C and a speed of 50 rpm. The
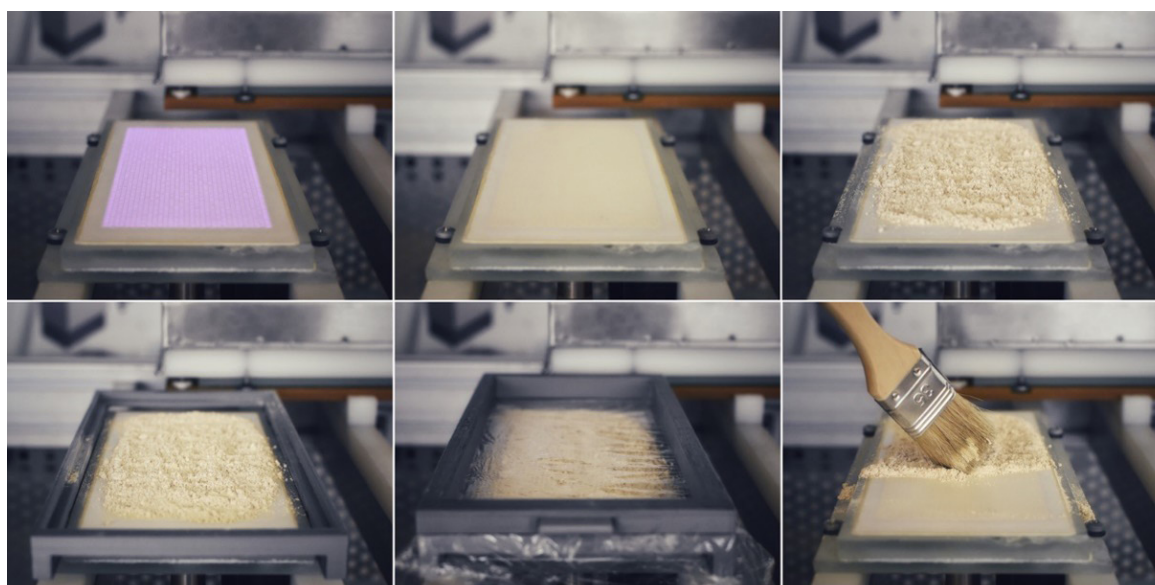

Fig. 1. The process of bentonite treatment

T a b l e 1. The chemical composition of bentonite

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	SO_3	MgO
Content, wt%	65.43	21.90	6.23	2.03	1.67	0.97	0.96

additives used were added in the following order: rubber SMR 20, activators – ZnO and stearic acid, filler – carbon black type N339, plasticizer RAE and the last additive was the vulcanization system: sulfur and TBBS. The reference compound (R) was prepared by this procedure. The other rubber compounds were prepared by the same procedure, changing only the filler – carbon black, which was partially replaced by bentonite and plasma-treated bentonite. Seven rubber compounds were prepared. One compound was the reference (R) and contained the standard filler, carbon black, specifically type N-339. In three compounds, the carbon black was partially replaced by bentonite in quantities 10, 20 and 30 wt% (Ben_10, Ben_20, Ben_30). In the last three compounds, the carbon black was partially replaced by plasma-treated bentonite (Ben_plasma_1min) in quantities of 10, 20 and 30 wt% (Ben/P_10, Ben/P_20, Ben/P_30).

Methods

The chemical composition of the bentonite sample was analyzed using an Energy Dispersive X-ray (EDX) analyzer. Thermal stability of the prepared samples was analyzed using a TGA/DSC 2 STARe (Mettler Toledo, Greifensee, Switzerland) system in the temperature range from 30°C to 1000°C and was performed under a nitrogen atmosphere. The infrared spectra of prepared samples were collected using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The spectra were acquired using the attenuated total reflectance (ATR) diamond accessory. The measurements were performed in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

The curing parameters of the unvulcanized rubber compounds (Ben_10, Ben_20, Ben_30 and Ben/P_10, Ben/P_20, Ben/P_30) were evaluated using a rubber pro-

Fig. 2. IR spectra of Ben, Ben/P/1 min and Ben/P/3 min samples

cess analyzer (PRPA 2000, Alfa Technologies, Akron, OH, USA). The measurements were performed following the guidelines outlined in ASTM 5289 standard. The curing characteristics of the composites were determined at an oscillating frequency of 1.67 Hz and a temperature of 160°C. DMA (Dynamic Mechanical Analysis) analysis was conducted on vulcanized samples (Ben_10, Ben_20, Ben_30 and Ben/P_10, Ben/P_20 and Ben/P_30) using a DMA Q800 instrument from TA Instruments (Waters, Milford, MA, USA). The analysis was performed over a temperature range from -70°C to 70°C, with a heating rate of 3°C per minute. The testing was carried out at a frequency of 10 Hz, using an amplitude of 15 μm, and under atmospheric pressure.

RESULTS AND DISCUSSION

EDX analysis

The EDX analysis of the bentonite (Ben) sample confirmed the presence of several significant constituents. Samples of bentonite contains mostly SiO_2, Al_2O_3, while other oxides such as Fe_2O_3, CaO and K_2O, SO_3, MgO are present in lower amounts. Table 1 presents the chemical composition of the bentonite powder, including the weight percentages of the identified oxides.

FTIR analysis

FTIR analysis was performed on the bentonite samples (Ben, Ben/P/1 min and Ben/P/3 min) to investigate any changes in the smectite structure, chemical composition, and surface properties due to plasma treatment of the bentonite. Figure 2 shows the IR spectrum of bentonite and both plasma treated bentonite.

In the first region, ranging from 4000 to 3000 cm^{-1}, the bands correspond to valence vibrations involving changes in bond lengths of structural OH-groups associated with octahedral cations, as well as water molecules linked through hydrogen bonds. The second region, spanning from 1400 to 400 cm^{-1}, contains absorption bands specifically characteristic of the silicate structure [13–15]. The sharp band observed at 3620 cm^{-1} corresponds to the typical OH stretching region of structural hydroxyl groups for dioctahedral smectites. The broad band at 3445 cm^{-1}, is assigned to the stretching vibrations of structural OH groups and water present in the mineral. This suggests the possibility of hydrogen bonding between the octahedral and tetrahedral layers. As can be seen, the intensity of this band marginally reduces after plasma treatment
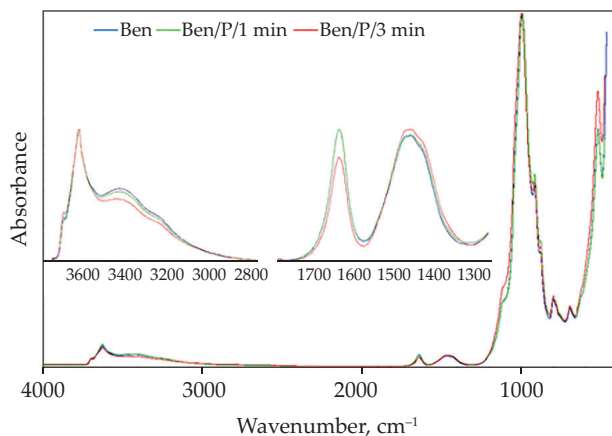
of bentonite. The band observed at 1636 cm^{-1} is attributed to the asymmetric bending vibrations of water molecules and is a structural part of the mineral [16, 17]. The strong band observed at 989 cm^{-1} corresponds to the valence Si-O vibration specific to smectite. The presence of this absorption band, which is shifted towards lower frequencies compared to most valence Si-O bands, can be attributed to the substitution of Si^{4+} ions in the tetrahedral position by trivalent cations [18]. Additionally, bands observed at 912 cm^{-1} and 876 cm^{-1} are assigned to the deformation vibrations of Al-Al-OH and Al-Fe-OH, respectively [13].

TG analysis

Figure 3 shows the TG curves of bentonite and both plasmas treated bentonite. The TG curve for bentonite exhibited a weight loss of approximately 5.75% between 35–200°C. In comparison, the weight losses for plasma-treated bentonite samples over the same temperature interval were approximately 5.25% for Ben/P/1 min and 4.24% for Ben/P/3 min. This mass loss can be attributed to the release of water molecules, which were adsorbed on the surface and coordinated with exchangeable cations within the clay structure. The lower weight losses observed in the plasma-treated bentonite samples suggest a reduction in the water content compared to the unmodified bentonite, indicating the effectiveness of plasma treatment in altering the clay's water-binding characteristics [9]. The second weight loss, which occurred between 300–700°C, was 5.92% in the bentonite. Plasma-treated bentonite samples showed weight loss of approximately 6.15% (Ben/P/1 min) and 5.92% (Ben/P/3 min). This weight loss can be attributed to the dehydroxylation of clay minerals present in the bentonite samples. Dehydroxylation refers to the removal of hydroxyl groups from the clay minerals because of the heating process. The slightly higher weight loss observed in the plasma-treated bentonites suggests that the plasma treatment may have influenced the dehydroxylation process in the clay minerals to some extent [19].

Curing parameters of rubber compounds

Based on the graphical results (Figure 4), it can be deduced that the prepared rubber compounds (Ben_10, Ben_20, Ben_30 and Ben/P_10 Ben/P_20 and Ben/P_30)
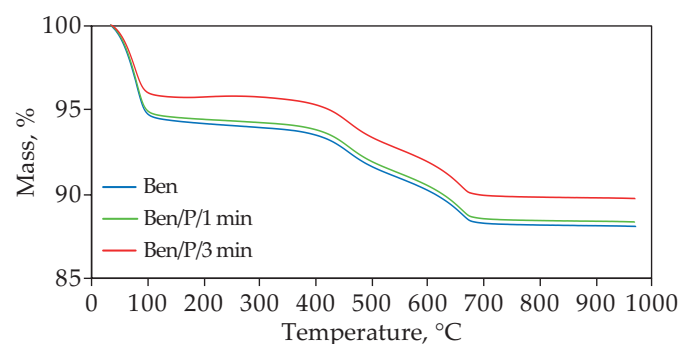
exhibited decreased minimum torque (M_L) values compared to the M_L values of the reference compound R. This decrease can be attributed to the observed reduction in viscosity in the rubber compounds [1, 20]. Among the rubber compounds tested, the Ben_20 and Ben_30 compounds showed the lowest minimum torque (M_L) values.

Additionally, the graphical analysis of the maximum torque (M_H) results presented in Figure 4 revealed a noticeable reduction in the maximum torque (M_H) values when compared to the reference compound R. As the content of the modified filler increases, the maximum torque (M_H) values decrease significantly. This decrease in maximum torque (M_H) is attributed to the lower stiffness of the model mixtures containing modified filler in comparison to the reference compound R [21, 22]. The reduction in M_H indicates that the presence of both untreated and treated filler results in overall increased flexibility and reduced rigidity in the vulcanizates [9].

Based on the graphical evaluation of the scorch time (t_{s2}) as shown in Figure 5, it can be observed that the prepared rubber compounds exhibit increasing t_{s2} compared to the reference rubber compound R. As the content of modified filler increases, the value of scorch time (t_{s2}) decreases. The rubber compounds Ben/P_10, Ben/P_20 and Ben/P_30 containing plasma modified bentonite achieved the highest values of scorch time (t_{s2}) among all the tested samples. This indicates that the vulcanizates with plasma-treated bentonite as the filler demonstrate enhanced safety characteristics and better performance in terms of the mixture stability compared to other formulations with different fillers.

Based on the graphical comparison of the results of the optimum cure time (t_{90}) as shown in Figure 5, it is evident that the values of the optimum cure time (t_{90}) increased for the rubber compounds in comparison to the reference compound R. The most significant increase can be observed for the rubber compound containing the filler modified by plasma with 30 wt% (Ben/P_30) content. From an economic standpoint, this increase in the optimum cure time (t_{90}) translates to higher energy costs [23]. The longer curing time required for the rubber compounds, especially those with plasma-treated bentonite filler and higher 30 wt% content, would result in increased energy consumption during the curing process, potentially impacting production costs.
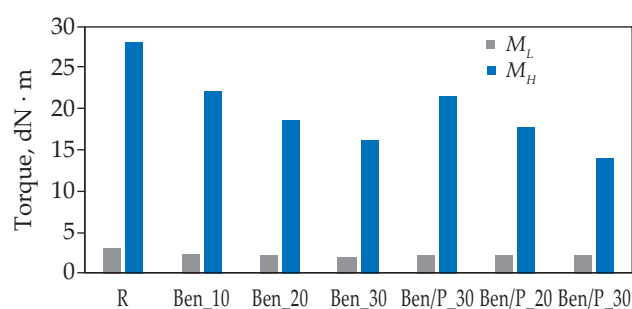

Fig. 3. TG curves of Ben, Ben/P/1 min and Ben/P/3 min samples
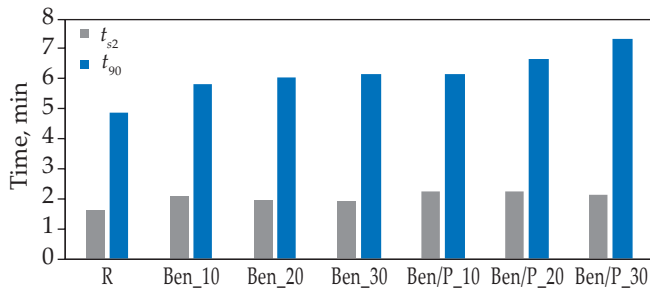

Fig. 4. Torque of rubber compounds

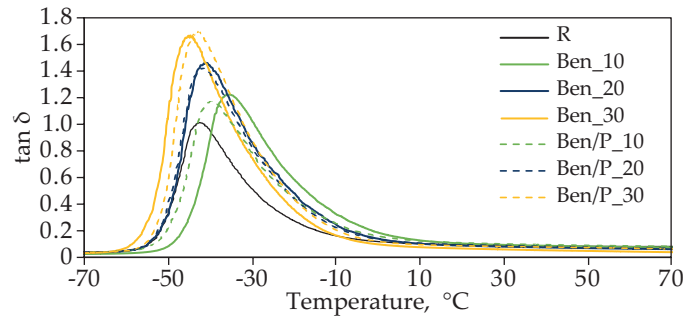Fig. 5. The scorch time (t_{s2}) and optimum cure time (t_{90}) of rubber compounds

Fig. 6. Dependence of loss angle (tan δ) on temperature for vulcanized compounds

Dynamic-mechanical properties

Dynamic-mechanical analyses were performed to evaluate the viscoelastic behaviour of vulcanizate samples (Ben_10, Ben_20, Ben_30, Ben/P_10, Ben/P_20 and Ben/P_30) containing different contents of bentonite and plasma-treated bentonite, along with a reference sample R. The relationship between the dynamical and mechanical properties, specifically the loss angle (tan δ), with respect to temperature is depicted graphically in Figure 6. The maximum peak of tan δ, denoted as tan δ_{max}, corresponds to the glass transition temperature (T_g) [24].

The results show that the glass transition (T_g) for Ben_10 and Ben/P_10 compared to R, is shifted to higher values, which may be due to the higher crosslinking density and stronger polymer-filler interactions [25].

For vulcanizate samples evaluation, tan δ values at -25°C, 0°C and 70°C are used as indicators of adhesion on ice and snow, wet and dry, and rolling resistance (Table 2). A higher tan δ value at lower temperatures is more suitable to ensure sufficient loss deflection, leading to increased hysteresis and better traction. On the other hand, a lower tan δ value at higher temperatures is desirable to avoid unnecessary deformation and hysteresis that would otherwise contribute to higher fuel consumption [2, 26]. From the results, it can be assumed that almost all the prepared vulcanizate samples show better adhesion on snow and ice and adhesion on wet road compared to the reference sample R. Vulcanizate samples Ben_20, Ben_30, Ben/P_20 and Ben/P_30 showed lower values of rolling resistance compared to the reference sample R.

CONCLUSIONS

Natural bentonite has been modified with low-temperature plasma to improve its properties as a filler in rubber compounds. IR spectra indicate reduced intensity of bands associated with structural OH groups and mineral-bound water after plasma treatment of bentonite. TGA confirms lower mass loss in plasma-treated samples, implying decreased water content compared to untreated bentonite, collectively highlighting plasma treatment's effectiveness. The results of curing characteristics and dynamic mechanical analysis showed that plasma-treated bentonite influences the properties of rubber compounds. The analyses conducted on various properties, it can be deduced that plasma-treated bentonite exhibits potential for extended research and utilization in rubber industries.

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T a b l e 2. Glass transition temperature, tan δ_{max} and tan δ at -25°C, 0°C and 60°C

Samples	T_g, °C	tan δ_{max}	tan $\delta_{-25°C}$	tan $\delta_{0°C}$	tan $\delta_{60°C}$
R	-42.4	1.016	0.371	0.116	0.079
Ben_10	-35.4	1.231	0.780	0.192	0.084
Ben_20	-41.1	1.468	0.648	0.144	0.069
Ben_30	-44.6	1.670	0.531	0.105	0.050
Ben/P_10	-39.8	1.178	0.581	0.155	0.081
Ben/P_20	-42.0	1.420	0.612	0.137	0.073
Ben/P_30	-43.1	1.705	0.630	0.121	0.069

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