The influence of silane on the physico-mechanical properties of vulcanizates using bentonite fillers

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Abstract. Layered phyllosilicate fillers have received attention in the polymer industry due to their unique nanoscale sheet-like structure. Adding a small amount of bentonite nanofiller gives rise to improved mechanical, thermal, and gas barrier properties of rubber mixtures. Depending on the application, natural bentonite is often modified by physical processes or by chemical processes (intercalation, cation exchange process, functionalization, pillaring, etc.). Chemical modification increases the size of the interlayer spaces and provides a hydrophobic environment. Functionalization (e.g., silanization), which encompasses the chemical grafting of thermally stable silane coupling agents onto the clay platelets, make inorganic bentonite and the organic polymer matrix compatible. In the introduced study, commercial bentonite P130 from Lieskovec deposit was modified by silane treatment. Different techniques such as infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to characterize modified and raw bentonite sample. Silanized P130s and raw product P130 were added to the natural rubber matrix to examine the influence of chemically functionalized bentonite on curing characteristic ($M_H$, $M_L$, $t_{90}$, $t_{90}$, $\Delta M$) and mechanical properties (TS, $E_b$, hardness) of rubber vulcanizates. Organo-bentonite was mixed into a rubber blend in particular ratio of 5, 10, 15, 20 phr in various combination with silane (3-aminopropyl triethoxysilane), Perkasil and carbon black. The highest maximum torque values were obtained with the sample using 20 phr of silanized P130s. The tensile strength (TS) values decreased with increasing P130 content, as well as non-silanized and silanized P130. However, when 20 phr P130s was used, value of TS was higher. The most enhanced properties of rubber blends were found with the addition of 20 phr of silanized bentonite P130s.

1. Introduction
The inorganic fillers based on clay are important ingredients which affect the characteristics of polymer rubber mixtures. Mineral fillers were used because of reduced price as well as achievement of the white color of rubber products. The current trend is to use the clay (kaolin, montmorillonite, mica) as nanofillers in the polymer mixtures because their small amount can affect the required properties. The conditions employed in the preparation of these materials depend on the inorganic or organic matrix [1]. Montmorillonite is the main mineral (approximately 50-80% w/w) of bentonite clay. Montmorillonite particles reach a size of 0.1 to 1 μm. The density is in the range of 2 - 3 g/cm³. The color ranges from white to brown. Bentonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. Isomorphous substitutions of SiIV+ cation by AlIII+ cation in the tetrahedral layer and those of AlIII+ cations by MgII+, FeII+ etc. cations in the octahedral layer of the aluminosilicate structured clay minerals result in a negative charge which is balanced by the cations such as K+, Na+,
Ca	extsuperscript{II} etc. [2, 3]. Bentonite can accept not only exchangeable cations between its layers, but also various organic compounds and water. Outstanding feature of this clay structure is that water and other organic/inorganic molecules can enter between the layers to expand basal spacing (“c” crystallographic direction). The volume of the interlayer varies according to the volume of the substance received. As a result, the distance between the layers is variable. After removal of the received substance, the reduction occurs again. This property is called expandability [4]. Inorganic ions can be exchanged with other cations. Recently, there has been interest in montmorillonite mainly due to its ability to expand and thus accept various organic molecules into the structure through ion exchange reactions. This also changes its surface character, hydrophilic changes to hydrophobic. The chemical modification is necessary for making natural clays suitable for specific adsorption and catalysis [5, 6]. Intercalation is a reversible process and it can involve exchange of cations from interlayer, adsorption of polar molecules through ion-dipole interactions, hydrogen bonding, and protonation [7].

Rubber mixtures are often loaded with different amounts of fillers that are either reinforcing or non-reinforcing. The term reinforcement is defined as the increases in the mechanical properties, such as tensile strength, tear strength, hardness, abrasion resistance and modulus, process properties and so on. Carbon black and precipitated silica are usually used as reinforcing fillers in the rubber composites, but the price is higher than that of other fillers [8, 9].

This work deals with modification of bentonite sample with commercial designation P130 by silane (3-aminopropyl)triethoxysilane. The properties of bentonite and its modified form were characterized by Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). This study investigates the effect of modified bentonite on cure properties (minimum torque, maximum torque and cure time) and mechanical properties (hardness, tensile strength at break, and elongation at break) of natural rubber mixtures.

2. Experiment

2.1. Materials used

Bentonite P130 was obtained from Envigeo, Ltd. (deposit Lieskovec) Slovak Republic. APTS (3-aminopropyl)triethoxysilane ($\text{H}_2\text{N}($CH$_2$)$_2$Si(OC$_3$H$_7$)$_3$ was obtained from Sigma Aldrich, Ltd. Natural rubber (SMR 10), Carbon black (N339), TMQ wax, Perkasil KS 207 (nonreinforced), Paramo (MES 15) oil, Sulfenax CBS (Ne-cyclohexyl-2-benzothiazole sulfuramide), elemental sulfur and DPG (1,3-diphenylguanidine) were obtained from CMR Púchov Ltd., Slovak republic. Stearic acid (SA) and zinc oxide (ZnO) were purchased from local supplier (Centralchem, Ltd.).

2.1.1. Modification of bentonite. Silane APTS was hydrolyzed in mixture of distilled water and isopropyl alcohol (CH$_3$)$_2$CHOH (in a ratio of 1:9) for 15 minutes. 50 g of bentonite P130 was added to prepared hydrolyzed APTS solution and heated to 50°C under the continuous stirring for 5 hours. Excess silane solution was removed by washing it three times with isopropyl alcohol. Prepared sample was dried in an oven at 60°C for 10 hours and it was designated as P130s.

2.1.2. Preparation of NR rubber composites. Natural rubber (SMR 10) was used as a polymer matrix. Mixtures were prepared with different amounts of P130 non-silanized (marked P1, P2, P3, P4) and silanized P130s (marked Ps1, Ps2, Ps3, Ps4) at 5, 10, 15 and 20 phr in order to investigate them as a replacement for silica filler Perkasil. The basic formulation of the mixtures used in the study is given in the Table 1. The model NR/P130 mixtures were blended by two-step mixing in Plasticorder Brabender® EC plus (chamber volume was 80 cm$^3$), with speed of 50 rpm, at temperature of 120°C in step I (mixing time was 7.5 min) and at 100°C temperature in step II (mixing time was 5 min). The given mentioned mixing process was carried out according to ASTM D15-627. The rubber mixtures were homogenized in laboratory double-rolled device (LaboWalz W80T; Vogt, 300 X 200), with a friction ratio of 1:1.2.
Table 1. Prescription for NR mixtures filled with bentonite P130 samples.

| Ingredients    | Standard (ST) phr* | P1, P2, P3, P4 phr* | Ps1, Ps2, Ps3, Ps4 phr* |
|----------------|-------------------|---------------------|------------------------|
| SMR 10         | 100               | 100                 | 100                    |
| N339           | 40                | 40                  | 40                     |
| Perkasil       | 20                | 15;10;5;0           | 15;10;5;0              |
| bentonite      | -                 | 5; 10; 15;20        | 5; 10; 15;20           |
| silane APTS    | 1.5               | 1.5                 | 1.5                    |
| TMQ            | 1                 | 1                   | 1                      |
| ZnO            | 2.5               | 2.5                 | 2.5                    |
| stearic acid   | 1.5               | 1.5                 | 1.5                    |
| oil            | 15                | 15                  | 15                     |
| Sulphur        | 1.7               | 1.7                 | 1.7                    |
| CBS            | 1.5               | 1.5                 | 1.5                    |
| DPG            | 0.5               | 0.5                 | 0.5                    |

* phr - parts per hundred rubber

2.2. Characterization

FT-IR Nicolet iS50 Thermo Scientific spectrometer was used for FTIR/ATR experiments. The results were obtained from the spectra in the range from 4000 to 400 cm\(^{-1}\) wave length range at a resolution of 4 cm\(^{-1}\). The morphology of bentonite P130 and P130s was characterized using a scanning electron microscopy – VEGA 3; TESCAN with BSE detector and 40 mm field of view with Wide Field Optics. Using the PRPA 2000 rheometer Alpha Technologies, the cure characteristics of bentonite/NR mixtures were studied at temperature of 160°C for 30 min. The rubber compounds were vulcanized in a hydraulic press (LabEcon 600; Fontijne) at cure temperature of 160°C and at pressure of 20 MPa. The mechanical properties of bentonite/NR composites with various proportions of P130 fillers were studied and compared with standard sample which contains the conventional filler carbon black (N339). The mechanical properties were determined, using universal testing machine (Shimadzu Autograph AG-X plus 5kN) at a crosshead speed of 500 mm/min according to ASTM standard D 412 87. Using the Shore A Durometer hardness tester and samples which were 6 mm thick, the hardness of the vulcanizates was measured according to ASTM D 2240 86.

3. Results and discussion

3.1. Characterization of bentonite samples

Figures 1a) and 1b) show the FTIR spectra of the bentonite P130 and the silanized P130s. In the recorded spectra of bentonite P130 (Figure 1a)), a sharp peak at 3621 cm\(^{-1}\) was due to Al–OH stretching vibration of the structural hydroxyl groups while the AlAl–OH and AlMg–OH bending bands are observed at 940 and 841 cm\(^{-1}\), respectively in Figure 1b). A strong band at 985 cm\(^{-1}\) is attributed to the stretching vibrations of Si–O groups of the tetrahedral sheets. The bands at ~3424 and 1634 cm\(^{-1}\) correspond to the –OH stretching and bending vibrations of water molecules present in the bentonite [10, 11]. In the silanized P130s we observed the increase of intensities of the stretching vibrations of Si–O groups and bending vibrations of –OH groups. In comparison with P130, the silanized sample exhibit several rather small vibration bands assigned to C–H stretching of methylene groups around 2935 cm\(^{-1}\) (Figure 1a)), the deformation vibration band of CH\(_2\) groups (in Figure 1b)) at 1449 cm\(^{-1}\) [12], and band at 695 cm\(^{-1}\) is attributed to the CH\(_2\) groups rocking vibration of Si–CH\(_2\)R [13]. These findings evidence the presence of the silane moieties in APTS modified sample P130s.
Figure 1. FTIR spectra of natural bentonite P130 and modified P130s in region 3800-2900 cm\(^{-1}\) a) and in region 2000-500 cm\(^{-1}\) b).

3.2. **SEM analysis of bentonite samples**

The thermoemissive scanning electron microscope was used to detect micromorphological changes for bentonite P130 samples. The SEM image of both P130 and P130s are presented in Figure 2. The bentonite physical structure (Figure 2 a)) based on the SEM image is like bulk structure with fine surface. However, after APTS modification, the surface of the P130s (Figure 2 b)) is covered with silane reagents and thus the surface of the individual grains is smoothed. As can be seen in the figures, before silanization, the grains of montmorillonite had a more pronounced morphology, which proves the binding of silane to the surface of the filler.

Figure 2. The SEM micrographs of P130 a) and silanized P130s b), magnified at 10.000x.

3.2. **Characterization of bentonite/NR rubber mixtures**

3.2.1. **Cure characteristics.** The cure characteristics (\(M_h\), \(M_L\), \(t_{90}\), \(t_{90}\), \(\Delta M\)) of the prepared bentonite/NR rubber mixtures are given in Table 2. Figure 3 a) shows the effect of bentonites P130 (P1, P2, P3 and P4) and silanized P130s (Ps1, Ps2, Ps3, Ps4) doses (5, 10, 15 and 20 phr) on optimal cure time (\(t_{90}\)) of the prepared bentonite/NR mixtures, in comparison with (ST) standard sample without bentonite. Optimal cure time (\(t_{90}\)) is the period which is necessary to achieve a 90% of the maximum achievable
value of torque or crosslink density at the given temperature, which corresponds to the torque $M_{90}$ value [14]. $M_H$ is the highest torque value in the curing curve and it is proportional to the value of cured sliding modulus of blend at the given temperature characterizing the stiffness of vulcanizate at the end of the curing process. $M_L$ is the lowest torque value and it was obtained during the cure tests, carried out in oscillating disc rheometer. The $t_{90}$ corresponds to the formation of maximum crosslink density and it is responsible for the highest possible physical and mechanical properties [15].

Table 2. Vulcanizing characteristics of the bentonite/NR mixtures.

| mixture | $M_L$ (dNm) | $M_H$ (dNm) | $t_{S2}$ (min) | $t_{90}$ (min) | $\Delta M$ (dNm) |
|---------|-------------|-------------|----------------|----------------|-----------------|
| ST      | 1.38        | 14.25       | 0.63           | 1.59           | 12.87           |
| P1      | 1.01        | 12.06       | 0.83           | 1.66           | 11.05           |
| P2      | 1.13        | 12.55       | 0.83           | 1.61           | 11.42           |
| P3      | 1.19        | 12.8       | 1.06           | 1.95           | 11.61           |
| P4      | 1.32        | 13.2        | 0.87           | 1.91           | 11.88           |
| Ps1     | 1.19        | 12.97       | 1.15           | 2.3            | 11.78           |
| Ps2     | 1.21        | 12.37       | 1.31           | 2.22           | 11.16           |
| Ps3     | 1.4         | 12.98       | 1.11           | 2.15           | 11.58           |
| Ps4     | 1.48        | 13.64       | 0.94           | 2.00           | 12.16           |

The $t_{90}$ value of non silanized bentonite P130/NR mixtures (P1-P4) slightly increased with increasing amounts of P130, compared with standard sample. In contrast, the silane modification (Ps1, Ps2, Ps3, Ps4) in combination with Perkasil increased the $t_{90}$ and it was evident that higher amount of Perkasil (20 phr) in sample Ps1 retarded the cure. The results may be attributed to good physical interactions of Perkasil with silanized bentonite P130s and other rubber auxiliaries. Extending the optimal vulcanization time may be advantageous in such applications which stand for thick-walled rubber products where the slower cure time course is required [16].

![Figure 3. Optimal cure time $t_{90}$ a) and maximum torque $M_H$ b) of bentonite/NR mixtures.](image)

The values of $M_L$ of bentonite/NR mixtures, which determines the viscosity of rubber, are almost invariant and was decreased slightly with decrease of bentonite amount in rubber. It can be caused by incorporation of bentonite particles between the rubber chains. However, the $M_H$ (Figure 3 b)), which represents the stock modulus, presented a slight reduction by various degrees. The decrease in the $M_H$ values means a lower stiffness of the mixtures and a lower viscosity at the end of the vulcanization [17]. The $\Delta M$ of bentonite/NR mixtures was increased as the loading of the bentonite samples was increased from 5 phr to 20 phr. This revealed the damaging effect of both P130 and P130s on the crosslink density.
3.2.2. Mechanical and physical characteristics. The mechanical properties of bentonite/NR vulcanizates, filled with different amount of P130 and P130s, are presented in Figures 4 and 5. The mechanical properties strongly depend on the morphology and structure of the using filler [18]. The interaction of bentonite-NR vulcanizates can be improved by applying silane agent because it could form a film on the mineral surface and reduces the surface energy. Figure 4 shows that the tensile strength $T_{S_b}$ of the mixtures with using both P130 an P130s is lower in comparison with the standard sample. Vulcanizates (P4 and Ps4) with the highest content (20 phr) of P130 and P130s show the highest values of tensile strength. However, it is possible to conclude that the tensile strength is not decreased significantly, compared with the standard sample. The most balanced tensile strength results were obtained for the compounds with the content 20 phr of P130s (mixture Ps4). The improvement of tensile strength by addition of bentonite P130 or P130s is due to the clay minerals which contained alumina and silica layers which can be good distributed in rubber by intercalation [19, 20].

![Figure 4. Tensile strength at break of bentonite/NR vulcanizates.](image)

Figure 4. Tensile strength at break of bentonite/NR vulcanizates.

Figure 5 shows the elongation at break of vulcanizates for various content of bentonite. The $E_b$ was increased throughout the entire range of bentonite dosing in all vulcanizates, whereas the highest elongation was achieved when 20 phr of P130s was added. The results confirmed that the elasticity of the NR vulcanizates was increased with the addition of silanized bentonite that provides the direct evidence on the enhanced polymer-filler interactions. The structure and shape of the fillers are the main factors for the performance discrepancy of different reinforcing agents [19, 21].

![Figure 5. Elongation at break of bentonite/NR vulcanizates.](image)

Figure 5. Elongation at break of bentonite/NR vulcanizates.
The hardness is the most obvious property to be influenced and could be increased with increased cross-link density [20]. Figure 6 shows the hardness of the vulcanizates by varying addition of P130 and P130s. From the results we can see that the hardness of vulcanizates decreases slightly with the addition of bentonite. However, the addition of 20 phr P130s increased the hardness by 13.5% of IRHD compared to the standard.

4. Appendices
This work was focused on study of effect of silanized form of commercial product bentonite P130 on vulcanizing characteristics as well as physical–mechanical properties of bentonite/NR vulcanizates. The results of FTIR of the bentonite samples showed the values which are typical for clay and clay minerals. The addition of bentonite filler and at the same time the reduction of the Perkasil content increased the time required for vulcanization. Extending the optimal vulcanization time may be advantageous in such applications where the slower cure time course is required. The prepared bentonite/NR vulcanizates exhibited slightly the comparable values of studied vulcanizing characteristics and tensile properties with the composite containing only carbon black and Perkasil. This fact can lead to opportunity of the partial replacement of the conventional fillers by the bentonite fillers. In practice, the bentonite can be used in rubber compounds for the bead area of car tires.

5. References

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