Modification of the Filler based on Kaolin and its Use in the Polymer Composites

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Abstract. Light mineral fillers are the natural inorganic materials of various compositions that have been used in a practical way since the beginning of the rubber industrial processing. Depending on the application, the natural kaolin is often modified by physical processes or by chemical processes (pillaring, adsorption, intercalation, functionalization, acid activation, etc.). It is important to modify kaolin due to improvement of its properties in order to adsorb the inorganic as well as organic molecules. In the introduced study, kaolin from Kaznějov deposit was modified by potassium acetate or dimethylsulphoxide and subsequently functionalized by accelerator dibenzothiazyldisulphide and its last modification was performed by silane treatment. Different techniques, such as the thermal (DTA) and spectral (FTIR) analysis were used to characterize modified kaolin samples. The main aim of the article is to observe the influence of modified kaolin forms on the physico-mechanical properties and structural changes of rubber mixtures. Combined with the carbon black, the given modified kaolin was mixed into a rubber blend in a particular ratio, which was5, 10, 24 phr. The effect of the modified kaolinite on the cure characteristics (minimum torque – M_L, maximum torque – M_H, optimal cure time – t_{90}, scorch time t_{s2})and mechanical properties (tensile strength at break – TS_b, elongation at break – E_b and hardness)in sulphur-cured rubber composites was investigated. In images from a scanning electron microscope (SEM), we observed the incorporation of modified forms of kaolin into the matrix of the rubber mixture.

1 Introduction

Hydrous aluminosilicate minerals have sheet structures with variously arranged layers of alumina and silica and are found as stacks of these layers. The main clay mineral, used in the polymer industry, is kaolinite, which represents the majority mineral of kaolin clay. Kaolinite is a 1:1 type clay mineral composed of stacked layers of SiO_4 tetrahedral (silica) sheets and $AlO_2(OH)_4$ octahedral (alumina) sheets [1, 2]. Kaolin clay is suitable for use as a functional filler to modify the properties of rubber composites and other polymer materials properties because of its fine particle size, layered structure and low heat, whiteness and electric conductivity. Polymer/layer alumino-silicate composites have recently acquired significant research attention because they exhibit notably improved material properties when compared with conventional composites. Rubber products are often loaded with large 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. In contrast, the purpose of the non-reinforcing fillers is only to increase bulk and reduce the cost of the rubber [3-5]. Carbon black and precipitated silica are usually used as reinforcing fillers in the rubbercomposites, but the price is higher than that of other fillers[3].Although the cheap clay fines are non-reinforcing for the rubbers, because of the similarity, such as SiO_4 units and OH groups in clays and fumed silicas, they can be converted to the filler both reinforcing and structuring by using the physico-chemical treatment [6].

The natural kaolin has slight negative charge and it causes that the kaolin surface is not inert. Depending on the application, natural kaolin is often modified by physical processes (milling, calcification) or by chemical processes (adsorption, intercalation, functionalization, acid activation, etc.).It is important to modify kaolin due to enhancing its capacity to be able to adsorb organic or inorganic molecules. It was proven that kaolin could be used as a substitute agent for carbon black or silica, because it is relatively inexpensive as well as non-carcinogenic [7].Similar to silica, the kaolin surface possesses OH groups, which make it polar and moisture adsorbent. Progress in the preparation of hybrid organic-inorganic materials by chemical treatment of organic molecules for kaolinite can improve its dispersion in a non-polar matrix (rubber) as well as it can improve the interactions with rubber components[8]Kaolin has the potential to be functionalized via Al-O-R bonds. Number of polar organic molecules, such as dimethyl sulfoxide, formamide, fatty acid salt, potassium acetate, and silane, are reportedly able to disrupt the interlayer bonding between the adjacent siloxane and hydroxy aluminium surfaces[9, 10].

This work deals with modification of kaolin by silane (3-aminopropyl) triethoxysilane, potassium acetate ordimethylsulphoxide and accelerator dibenzothiazyl disulfidetreatment. The properties of kaolin and its modified forms were characterized by thermal (DTA) analysis and Fourier transformed infrared spectroscopy (FTIR).This work investigates the effect of modified kaolin on vulcanizates properties (minimum torque, maximum torque and cure time) and mechanical properties (hardness, tensile strength at break, and elongation at break) of natural rubber composites. Dispersion of the kaolin filler and its incorporation into the vulcanizates were investigated by scanning electron microscopy (SEM), observing the vulcanized fracture surfaces.

2 Experiment

2.1. Materials used

Kaolin was obtained from Kaznějov deposit CzechRepublic. APTS (3-aminopropyl)triethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$ was obtained from Sigma Aldrich, Ltd. Dimethylsulphoxide (C_2H_6OS) and potassium acetate (CH_3COOK)were purchased from Centralchem, Ltd. Natural rubber (SMR 10),Carbon black (N339),2,2'-benzothiazyl disulfide (MBTS), Sulfenax CBS (N-cyklohexyl-2benzothiazole sulfenamide), elemental sulphur and TMQ (2,2,4-trimethyl-1,2-dihydroquinoline) were obtained from CMR Púchov Ltd., Slovak republic. Stearic acid (SA) and zinc oxide (ZnO) were purchased from local supplier (Centralchem, Ltd.). DTPD (N,N'-Diphenyl-p-phenylenediamine) and Dusantox 6PPD N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylendiaminewere obtained from DUSLO Inc., Slovak republic.

2.2. Modification of kaolin

The raw kaolin sample was placed into an oven and it was left at 80°C for 24 h to remove the moisture. In relation to the modification with dimethylsulfoxide, sample of raw kaolin was mixed with 30 %wt. solution of DMSO at temperature of 50°C under vigorous stirring for 40 h. The resulted suspension was decanted three times with solution of ethanol and water. Then, the sample was dried in the vacuum oven at 60°C for 10 h and it was designated as K_{DMSO}. Next, the 2,2'-benzothiazyl disulfide was solubilized in toluene and the K_{DMSO} sample was added and stirred for 4 h. Excess solution was washed by ethanol. The $K_{D\text{-}MBTS}$ sample was dried in vacuum oven at 60°C for 10 hours.

In relation to the modification with potassium acetate, sample of raw kaolin was mixed in 0.5 M solution of CH_3COOK at temperature of 60°C under vigorous stirring for 4 h. The resulted suspension was decanted three times with distilled water. The sample was dried in the vacuum oven at 60°C for 10 h and it was designated as K_K. Next, the 2,2'-benzothiazyl disulfide was solubilized in toluene and the K_K sample was added and stirred for 4 h. Excess solution was washed by ethanol. The $K_{K\text{-}MBTS}$ sample was dried in vacuum oven at 60°C for 10 hours.

Silane(APTS) was hydrolyzed in mixture of distilled water and ethanol (in a ratio of 1:9) for 15 minutes. Kaolin was added to this hydrolyzed APTS solution and heated to 50 °C under the continuous stirring for 4 hours. Excess silane solution was removed by washing it three times with ethanol. Prepared sample was dried in an oven at 60°C for 10 hours and it was designated as K_{APTS}.

2.3. 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}wavelenght range at a resolution of 4 cm^{-1},at the workplace of the CEDITEK, FPT Púchov. Using the Derivatograph MOM Hungary, the DTA measurements were carried out from room temperature up to 600°C in an air atmosphere at heating rate of 10°C/min.

The morphology of modified kaolin/NR composites was characterized using a scanning electron microscopy –VEGA 3; TESCAN with BSE detector and 40 mm field of view with Wide Field Optics, which was also used to study the dispersion of kaolin particles in the rubber matrix.

Using the PRPA 2000 rheometer Alpha Technologies, the cure characteristics (M_L, M_H, t_{90}) of modified kaolin/NR composites were studied at temperature of 150°C for 30 min. The rubber compounds were vulcanized in a hydraulic press (LabEcon 600; Fontijne) at cure temperature of 150°C and at pressure of 20 MPa.

The mechanical properties of modified kaolin/NR composites with various proportions of modified kaolinfillers were studied and compared with standard sample which contains the conventional carbon black filler (N339). The mechanical properties (tensile strength at break TS_b, elongation at break E_b) were determined, using universal testing machine (Shimadzu Autograph AG-X plus 5kN) at a crosshead speed of 500 $mm.min^{-1}$ 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. The experiments were carried out at the workplace of the CEDITEK.

2.4. Preparation of NR rubber composites

Natural rubber (SMR 10) was used as a polymer matrix. Composites were prepared with different amounts of modified kaolin samples ($K_{D\text{-}MBTS}$, $K_{K\text{-}MBTS}$, K_{APTS}) at 5, 10 and 24 phr in order to investigate them as a replacement for standard filler carbon black (N339). The basic formulation of the composites used in the study is given in the Table 1.

Table 1. Prescription for NR composite filled with modified kaolin.

Ingredients	Standard (St) phr*	$K_{D\text{-}MBTS}$, $K_{K\text{-}MBTS}$, K_{APTS} phr*
SMR 10	100	100
ZnO	3	3
6PPD	1.5	1.5
TMQ	1	1
Stearic acid	2	2
DTPD	2.1	2.1
N339	49	44; 39; 25
modified kaolin	-	5;10;24
Sulphur	1.7	1.7
CBS	1	1

* phr - parts per hundred rubber

The model NR/$K_X$composites were blended by two-step mixing in PlasticorderBrabender®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 min.) and at 90°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 composites were homogenized in laboratory double-rolled device (LaboWalz W80T; Vogt, 300 X 200), with a friction ratio of 1:1.2. The experiments were carried out at the workplace of the CEDITEK, FPT Púchov.

3 Results and discussion

3.1. Characterization of kaolin samples

The DTA curve of raw kaolin sample in Figure 1a) has a typical course in relation to kaolin. The DTA curve shows an endotherm in the range of ~ 510 - 600 °C, with the maximum at temperature of ~ 560 ° C, which represents the loss of dehydroxylation of coordinated and structural water molecules in kaolin [11]. Mass of the sample was reduced by about 7.22 wt. %.The DTA curve of $K_{D\text{-}MBTS}$ (c) shows an endotherm in the range of ~ 505 - 600 °C, with the maximum at temperature of ~ 570 °C. Small endothermic effect was also observed in the range of ~ 210 - 300°C, with a maximum at temperature of ~ 272°C, corresponding to the thermal decomposition on the surface-bounded modifying agent. The mass of the sample was reduced by about 8.38 wt. %.The DTA curve of $K_{K\text{-}MBTS}$ (b) has a similar course with two endothermic effects. The first endothermic peak was observed at ~ 290°C and it was due to the thermal decomposition of the surface-bounded potassium acetate. Subsequently, there was a faster endothermic decrease at temperatures of ~ 509–

600°C, with a maximum at temperature of ~ 565°C. Mass loss of sample was 8.41 wt. %. As it can be seen in see Figure 1 (d), the highest 9.35 wt.% weight loss of the sample was observed for the K_{APTS} sample, although there was a slight endothermic effect in the range from 200-400°C. In addition, the amount of hydroxyl groups of modified kaolin samples displays a rather marked dihydroxylation peaks and a shift of the dihydroxylation maximum temperature in 5-10°C.

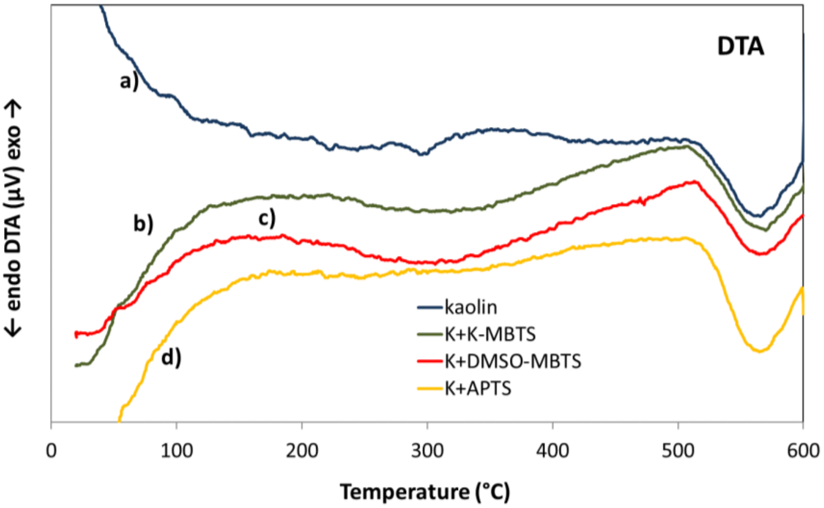


Fig. 1. DTAcurves of modified kaolin samples.

FTIR microscopy was used to observe changes in structure, while the given changes were caused by chemical modification of the kaolin samples. The infrared spectra of samples are characterized by deformation and valence vibration bands of structural OH groups, which occurred in the range of 3700 - 3600 cm^{-1} and 900 - 450 cm^{-1}[12, 13]. Deformation and valence vibrations of Si-O groups are located in the range of 1200 - 850 cm^{-1} and 800 - 150 cm^{-1}.In relation to the IR spectrum of kaolin, the vibrations at 3685, 3668, 3650and 3618 cm^{-1} correspond to the valence vibrations of the surface OH groups. The deformation vibration of the inner OH groups is located at 910 cm^{-1} and correspond to the AlAlOH bond. The absorption bands at 1024 and 1113 cm^{-1} correspond to the valence vibration of tetrahedral Si-O cations. The bending vibrations of the Si-O group correspond to the absorption band at 456 and at 529cm^{-1}[14, 15]. In the IR spectrum of the modified kaolin, there was a slight shift of the valence and deformation vibrations of the Si-O groups, compared to the sample of unmodified kaolin.

3.2. Characterization of modified kaolin/NR rubber composites

3.2.1 Cure characteristics

Figure 2 shows the effect of$K_{D\text{-}MBTS}$, $K_{K\text{-}MBTS}$, K_{APTS} doses (5, 10 and 24 phr) on optimal time of cure (t_{90}) of the modified kaolin/NR composites, in comparison with (St)standard sample. 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 theM_{90} value, while$M_{90}= 0.9 (M_H – M_L) + M_L = M_L + 0.9x\Delta M$ [16]. 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[17, 18]. The t_{90} value of kaolin/NR composites decreased significantly with increasing amounts of modified kaolin, compared with standard sample. The elasticity and tensile strength were improved and facilitated the curing up to the optimal properties in a short sulphurisation time and it advanced the processing energy [18]. In contrast, the silane modification increased the t_{90} to value of 9.72 min. and it was evident that K_{APTS} retarded the cure. The results may be attributed to the incorporation of the rubber chains between the modified kaolin particles as well as the physical interactions of other rubber auxiliaries and modified kaolin during curing. 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 [19].

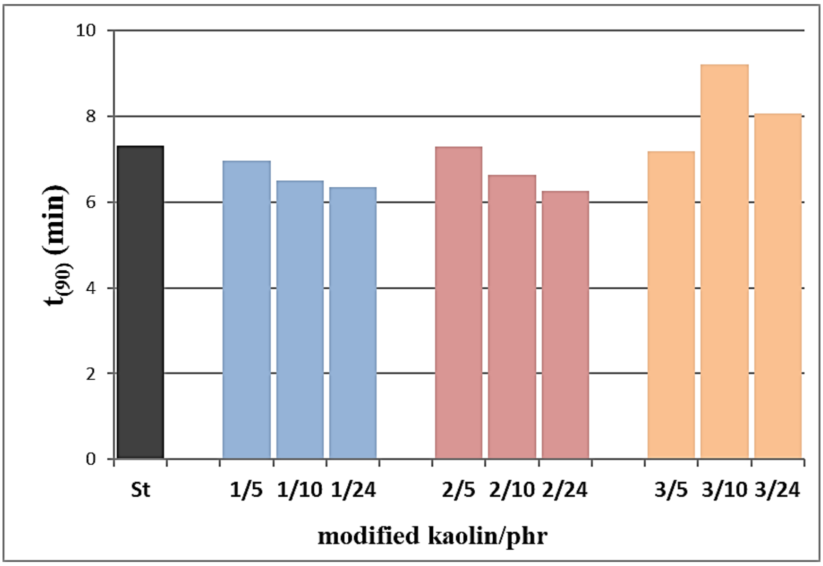


Fig. 2. Optimal cure time of kaolin/NR composites with modified kaolin: 1-$K_{D\text{-}MBTS}$, 2 -$K_{K\text{-}MBTS}$, 3 -K_{APTS}.

The M_L of modified kaolin/NR composites (Figure 3a), which determines the viscosity of rubber, was decreased slightly because of incorporation of kaolin particles between the rubber chains. However, the M_H (Figure 3b), which represents the stock modulus, presented a reduction by various degrees. The decrease in the maximum torque values means a lower stiffness of the mixtures and thus a lower viscosity at the end of the vulcanization [17].The Δ torque for modified kaolin/NR composites was decreased as the loading of the modified kaolin was increased from 5 phr to 24 phr. This revealed the damaging effect of kaolin on the crosslink density.

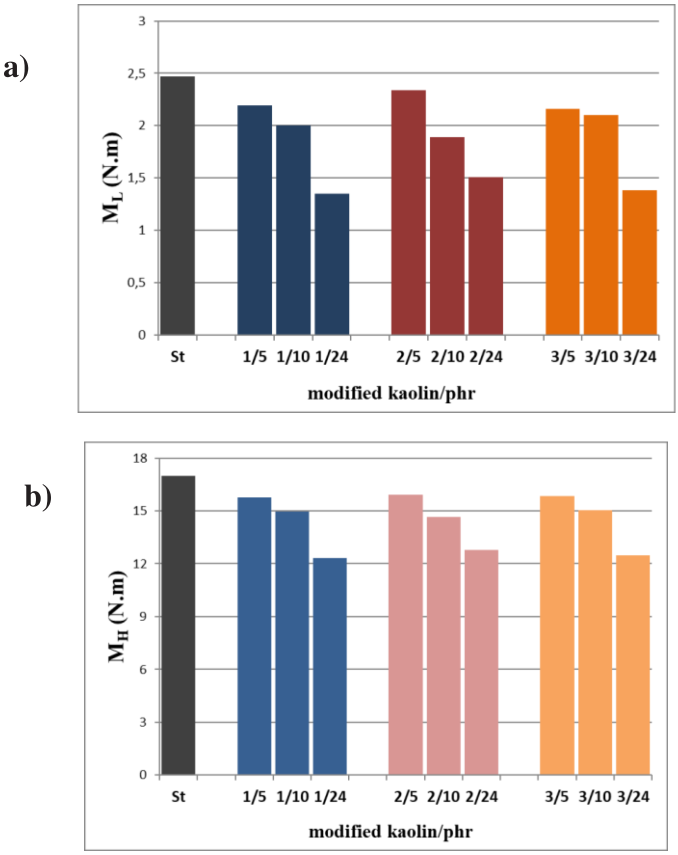


Fig. 3. Minimum a) and maximum b) torque of kaolin/NR composites with modified kaolin: $K_{D\text{-}MBTS}$, 2 -$K_{K\text{-}MBTS}$, 3 -K_{APTS}.

3.2.2 *Mechanical characteristics*

The mechanical properties of modified kaolin/NR composite, filled with different modified kaolin, are presented in Figures 4 and5. Figure 4 shows that the tensile strength of the modified mixtures is decreased in comparison with the standard sample. When the amount of modified filler in the rubber compound is increased, the tensile strength is decreased in all samples. Composites with the highest content (24 phr)of kaolin show the lowest values of tensile strength (MPa). However, it is possible to conclude that the tensile strength is not decreased significantly, compared with the standard sample, it is most reduced in blend with24 phr of K_{APTS}(18%). The most balanced tensile strength results were obtained for the compounds with the content of $K_{D\text{-}MBTS}$.

Figure 5 shows the elongation at break of vulcanizates for various samples with modified kaolin as well as for various contents of filler. The Eb was increased throughout the entire range of modified kaolin dosing in all composites, whereas the highest elongation was achieved when 24 phr of kaolin was added. The results confirmed that the elasticity of the NR vulcanizates was increased with the addition of modified kaolin 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.

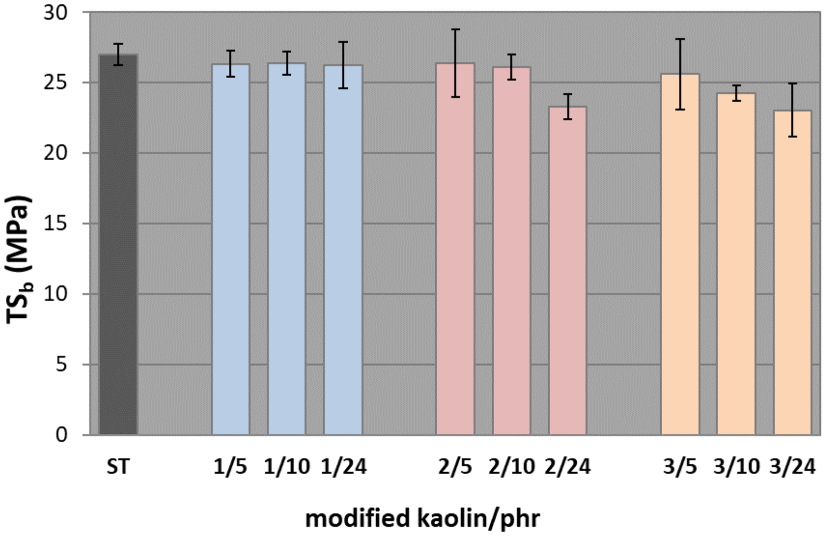


Fig. 4. Tensile strength at break of kaolin/NR composites with modified kaolin:
1 - $K_{D\text{-}MBTS}$, 2 -$K_{K\text{-}MBTS}$, 3 -K_{APTS}.

Kaolin retains its sheet structure and flexibility even after modification and it stands for good rebound elasticity. In this way, the extensibility and elasticity of rubber composites are improved [20]. Due to the fact that the diameter of kaolin sheet reaches the hundreds of nanometers, the layers have a weak binding force and it means the decrease in the tensile strength of the kaolin/NR composites[5].

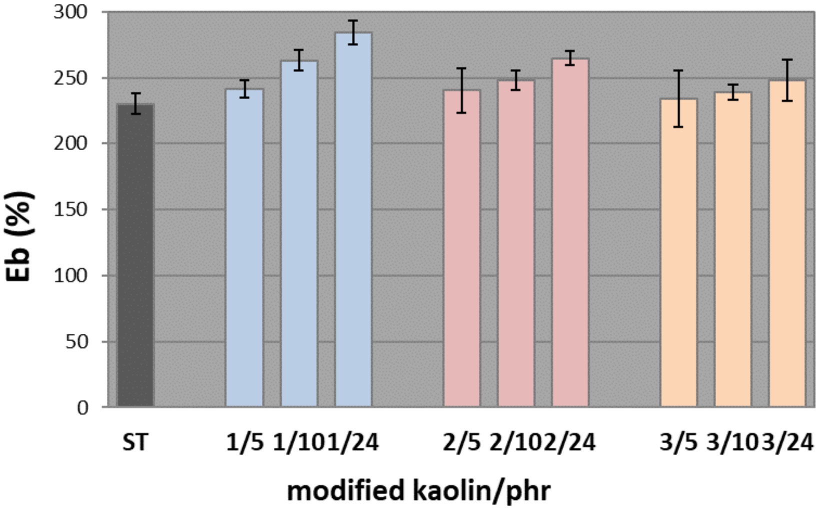
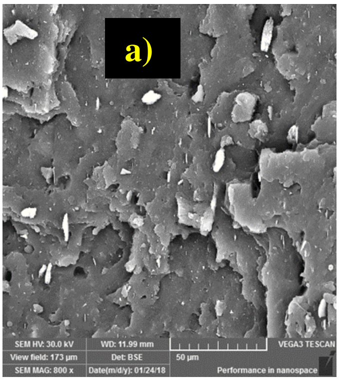
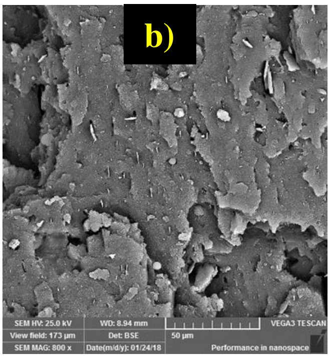


Fig. 5. Elongation at break of kaolin/NR composites with modified kaolin:
1 - $K_{D\text{-}MBTS}$, 2 -$K_{K\text{-}MBTS}$, 3 -K_{APTS}.

3.2.3 Morphology of modified kaolin/NR composites

Figure 6 a – d shows the SEM micrographs of the tensile-fractured surfaces of standard sample (ST) and modified kaolin/NR composites with 10 phr dosing of kaolin. It is possible to see that the modified kaolin particles at dosing of 10 phr are found to be good dispersed in the polymer matrix in the form of parallel sheets [5, 21]. There was no significant aggregation of kaolin layer-like particles. The substructure sheets of kaolin were separated effectively by the rubber chains. The tightly linked interfaces show that the dispersibility of the modified kaolin sheets in the rubber is very good, and kaolin/rubber composites were formed [22,23]. The directional and parallel arrange of kaolin sheets can improve mechanical properties of composites.





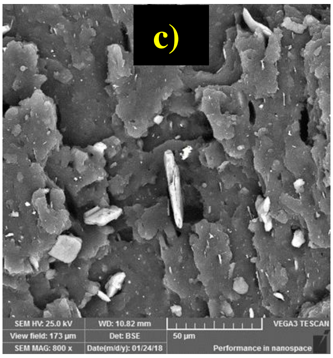


Fig. 6. The SEM images of vulcanisates:a) S_T, b) $K_{D\text{-}MBTS}$/10 phr,c) $K_{K\text{-}MBTS}$/10 phr and d) K_{APTS}/10 phr, magnified at 800x.

4 Appendices

Compared with the standard rubber composite with carbon black filler, the modified kaolin effectively improved the operation in prophase vulcanization and it is also effective from the aspect of the reduction of time to optimum cure (t90). Moreover, there is the enhancement in the productive efficiency and consumption considerable energy is also decreased. The modified kaolin/rubber composites have very good elasticity. The tensile strength is close to that of rubber which is filled with standard carbon black filler. The low cost predestinates kaolin to be used in wide range of applications. The suitable modification can make kaolin platelets dispersed in rubber matrix in direction of parallel arrangements. Good dispersion at nanoscale and strong interfacial interaction are the prerequisites for the rubber/kaolin nanocomposites with excellent properties. In practice, the modified kaolin can be used in rubber compounds for the bead area of car tires. An example is the application into a compound for spraying of bead wires due to the good adhesion to the steel core, the good strength of the vulcanizate and due to increase in the extrusion speed of the mixture. The modified kaolin is also suitable as a filler in the sidewall mixture, as it acts as a barrier against air leakage.

Acknowledgments

The authors would like to thank the Slovak Grant Agency VEGA for financial support (Grant VEGA: 1/0589/17, KEGA 003TnUAD-4/2019). The work was supported by the project Advancement and support of R&D for Centre for diagnostics and quality testing of materialsin the domains of the RIS3 SK specialization, code NFP313010W442.

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