

## MORPHOLOGY AND SURFACE MODIFICATION OF WASTE PHOSPHOGYPSUM UTILIZED AS MINERAL FILLER FOR POLYMER COMPOSITE MATERIALS

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### Abstract

*The waste calcium sulfate (phosphogypsum) is a solid by-product generated from phosphoric acid production processes. The phosphogypsum (PG) represents a serious ecological problem that isn't solved globally. A potential possibility for its utilization is using as a mineral filler for polymer composite materials. The aim of present work is research on morphological diversity of phosphogypsum that offers opportunities to obtain mineral filler for polymers with optimum morphological characteristics and the ability to regulate its dispersion composition. The second purpose of current research is study on possibility for surface modification of phosphogypsum using cheap low molecular compounds. It is clear proved that phosphogypsum is effective mineral filler for polymer composites and the surface modification by sodium metasilicate significant increases the properties of the composites.*

### 1. Introduction

The modification of the polymer by filling is one of the most widely used methods for improving the physical and mechanical characteristics and a reduction in price of polymer materials. The mechanical properties of synthetic rubbers in the unfilled state have very low values. This requires the use of highly active fillers such as various types of carbon black.

At the phosphoric acid production process fall away great amounts of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  known like phosphogypsum [1, 2]. At 1 ton phosphoric acid production falls out around 4 – 5 tons phosphogypsum. Annually in the world drop off 133 million tons, in Bulgaria – 1.5 – 2.0 million tons phosphogypsum. In the 1990 the amount of produced phosphoric acid increases compared to 1976 twice. This tendency keeps his growth and the phosphogypsum became a serious ecological problem. The transportation of a phosphogypsum to his depots bound up with great capital expenses and fill of big areas, pollution of the air and underground waters.

The phosphogypsum is a synthetic by-product for which are spend million tons concentric sulfur acid and his utilization is interesting mainly by practical and ecological point of view. The problem in the world still is unsolved [1, 2].

The commercial applications of elastomers often require using of disperse fillers for obtaining of desired reinforcing effect which makes rubber articles suitable in different exploitation areas. The fillers also reduce the rubbers articles prices and improve many characteristics such Young modulus, tear resistance, tensile strength etc [3 - 7].

The filling of the synthetic rubbers with high-activity fillers such soot is a basic modification method. The goal is the increasing of mechanical behavior. In many cases for obtaining of white and color vulkanizates are used mineral fillers like SiO<sub>2</sub>, chalk, clays, lithopone, talcum etc [8].

The mineral fillers improve mainly technological properties of rubber mixtures and own light reinforcing effect [9]. The using of light fillers requires especially attention in choosing of accelerators, activators and their dosing together with the vulcanization agent [10].

There are many ways to improve mineral filler's effectiveness using surface modification with different chemical compounds [12-13]. The sodium metasilicate is a good choice because of their ability to form polysilicic acid during the modification process and adsorption on the phosphogypsum particles [14-18].

The aim of present work is research on phosphogypsum modification process by sodium metasilicate and characterization of obtained modificates. The resulting fillers are studied as mineral reinforcement agents for two types of vulkanizates based on styrene-butadiene rubber (grade Bulex 1500) and ethylene-propylene rubber (grade Keltan 512).

## 2. Experimental

### 2.1. Materials

The used rubbers like a matrix in obtained vulkanizates filled with different content of phosphogypsum and its modificates are:

1. Styrene-butadiene rubber, grade Bulex 1500 (Bulgaria) – copolymer of butadiene and styrene, produced by emulsion copolymerization process. The main characteristics of Bulex 1500 are:

- free organic acids, %	5 – 7.25
- linked organic acids, %	to 0.5
- ash, %	to 0.6
- viscosity by Mooney (at 100 °C)	38 – 53
- Fe content, %	0.01
- weight loss at 105 °C	0.5

2. Ethylene-propylene rubber, grade Keltan 512 (Holland) – copolymer of ethylene and propylene, obtained by polymerization in solution with catalytic complex of alcyllaluminium and vanadium oxichloride. The main characteristics of Keltan 512 are:

- ethylene content, %	55
- third monomer content, %	4
- viscosity by Mooney (at 125 °C)	46
- density, kg/m <sup>3</sup>	860

The rubber compounds were prepared on open mixing rolls, and vulcanization was conducted in accordance with the requirements of standard ISO 2393:1994. The stress-strain characteristics of the rubber compositions with different content of phosphogypsum were obtained according to the requirements of standard ISO 37:1994 on a mechanical testing machine INSTRON 4002. The compositions of the studied rubber mixtures based on SBR (Bulex 1500) and EPDM (Keltan 512) are shown in Table 1. The process conditions of vulcanization of both types of mixtures are as follows: temperature 160 ° C and time 15 minutes.

SBR (Bulex 1500)		EPDM (Keltan 512)	
Ingredient	Content, wt. %	Ingredient	Content, wt. %
Bulex 1500	100	Keltan 512	100
ZnO	4.0	ZnO	3.0
Stearic acid	2.0	Glyceryl tristearate	1.0
Vulcazit CZ	1.0	Thiuram	1.25
1,3-Diphenylguanidine	0.2	2-Mercaptobenzothiazole	0.75
Antioxidant 4010NA (IPPD)	1.5	Antioxidant 4010NA (IPPD)	1.0
Sulphur	2.0	Sulphur	1.5
Triethanolamine	2.0	Triethanolamine	1.25
Phosphogypsum	0 – 150	Phosphogypsum	0 – 150

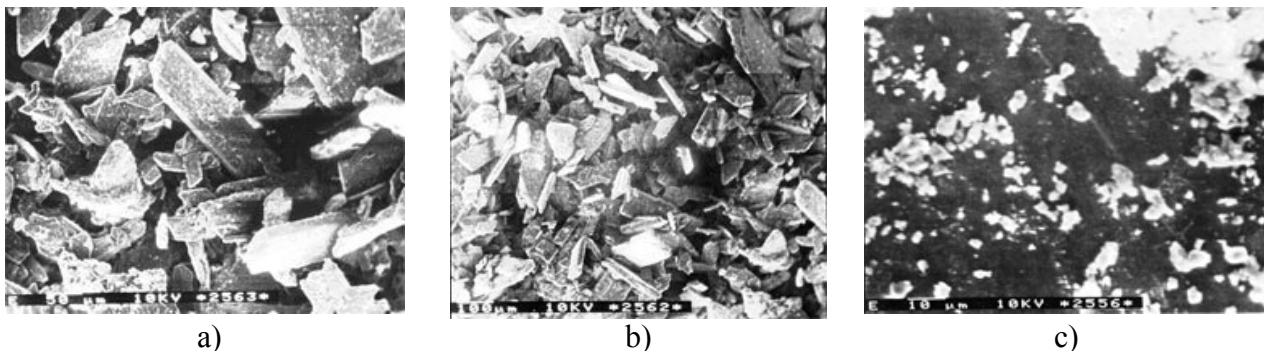
**Table 1.** Composition of rubber mixtures based on SBR (Bulex 1500) and EPDM (Keltan 512).

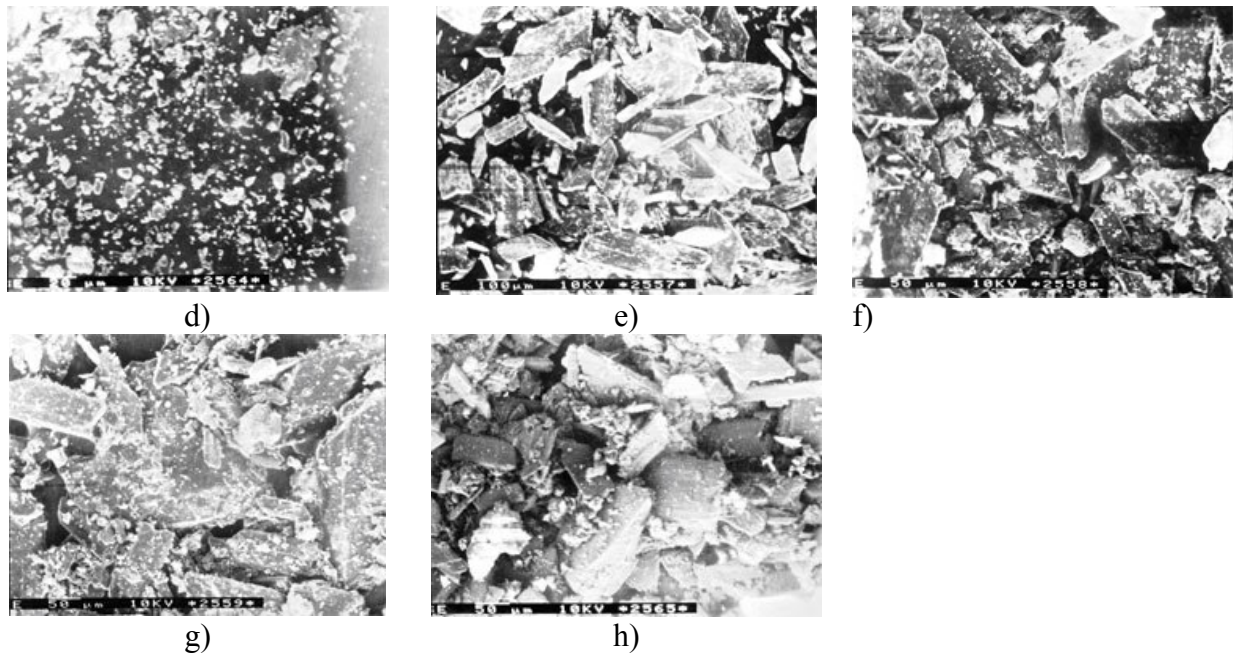
### 2.2. Technology for modification of phosphogypsum by sodium metasilicate

In a reactor, slurry is prepared from 1000 g of neutralized and dried at ambient temperature phosphogypsum (PG) in 5000 ml of water with vigorous stirring. To the suspension was added the required amount of sodium metasilicate (SMS) in portions with stirring. With dilute hydrochloric acid the pH of the medium was adjusted to values of 4-5, and the stirring was continued for 60 minutes. In these conditions, sodium metasilicate decays to silicic acid, which is adsorbed on the particle surface of the phosphogypsum and under these conditions polymerize into a polysilicic acid. The suspension was neutralized with dilute sodium hydroxide to pH=7, and allowed to "ripen" for several hours. Then the product was filtered and dried at an ambient temperature. The conversion of the dihydrate to hemihydrate becomes as the modifier was heated at 140 °C for few hours. The hemihydrate was stored in polyethylene bags, sealed to protect from moisture in the air.

### 3. Results and discussion

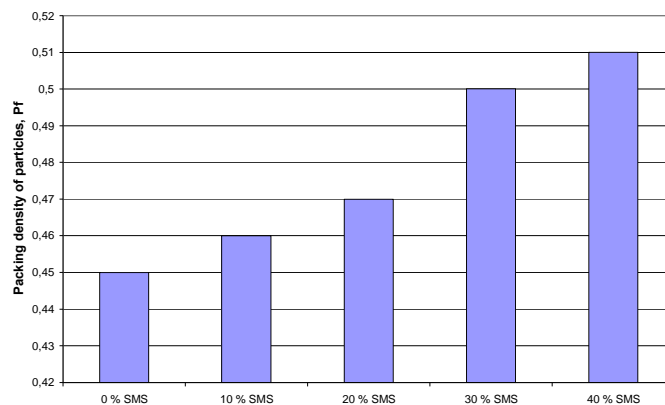
During the reinforcement of the synthetic rubbers with phosphogypsum obtained materials have a relatively low modulus of elasticity as phosphogypsum itself has nasty hardness in the range of about 2 to 3 in Mohs scale [19]. The modification of phosphogypsum with sodium metasilicate changes chemical composition, mainly by importing a new component of colloidal polysilicic acid. The modifier strongly changes the disperse composition among adsorbed onto particles of phosphogypsum polysilicic acid remains as a separate phase, particularly by increasing the amount of sodium metasilicate. The described modification of phosphogypsum with sodium metasilicate affords a combination of phosphogypsum and colloidal polysilicic acid according to the degree of modification of such material and changes the distribution of particle size as shown on fig. 1.





**Fig.1.** Electron microscopic images of phosphogypsum (PG) modified by sodium metasilicate (SMS) a – pure PG (x50), b – pure PG (x100), c – SMS, d – polysilicic acid, e – PG modified by 10 wt. % SMS, f – PG modified by 20 wt. % SMS, g – PG modified by 30 wt. % SMS, h – PG modified by 40 wt. % SMS.

The change of the dispersion composition of the phosphogypsum after its modification with sodium metasilicate most strongly affects the packing density of particles of the obtained modificates – Pf [13]. By increasing of the modification rate the polydispersity of filler increases. This helps to increase the packing density of particles Pf. The mechanical properties and the overall efficiency of the fillers significantly increase as the density of the packing rises [3]. The expected significant change in the packing density of particles Pf with increasing of the polydispersity of phosphogypsum modificates was observed (Fig. 2).

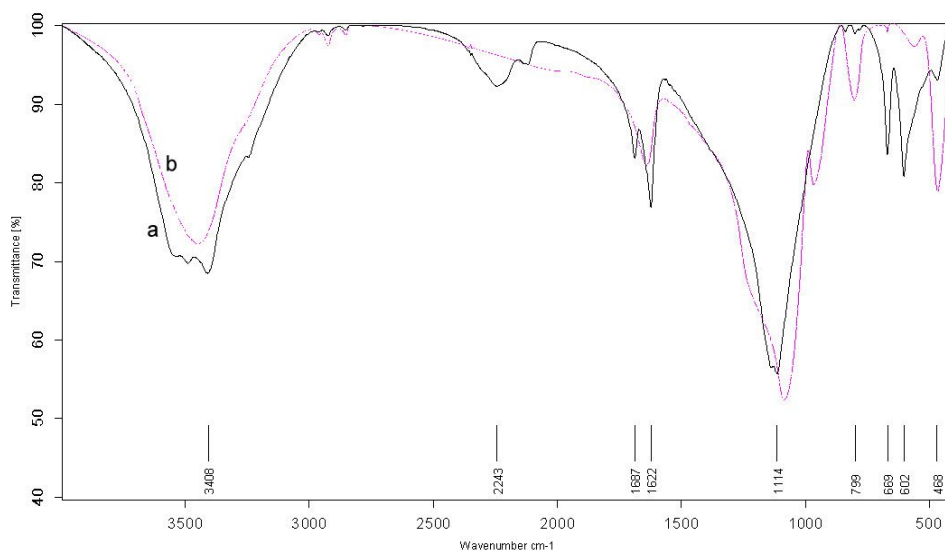


**Fig. 2.** The effect of the modifier content on filler packing density of particles.

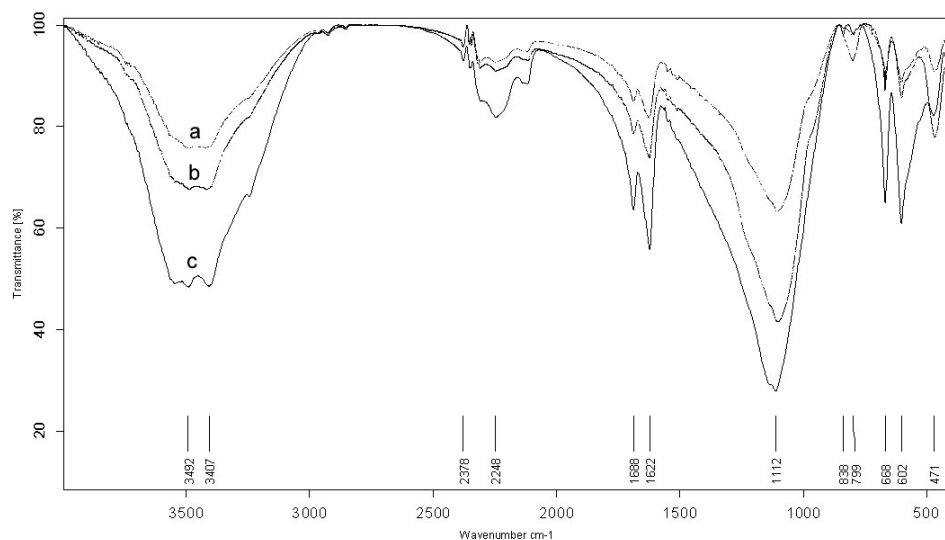
This may be explained by the fact that at lower amounts of the modifying agent and the resulting monosilicic acid and polysilicic acid are largely adsorbed onto particles of phosphogypsum (fig. 1 d, e). Only when larger quantities of sodium metasilicate were used, after saturation of the surface of the phosphogypsum, polysilicic acid is separated as a distinct phase. However, by increasing the degree of modification the effectiveness of the modifier increases. Modification of phosphogypsum with sodium metasilicate leads to partial

adsorption of the received monosilicic acid, which is polymerized under the same conditions to the polysilicic acid. The electron microscopic photographs show that at the beginning in low concentrations range of substantially all of the modifiers of the polysilicic acid remains adsorbed onto the particle surface of the phosphogypsum (fig. 1 e, f). With increasing amount of the saturation degree of the modifier on the surface of the particles increases and the proportion of polysilicic acid remains as a separate phase. This amount increases with the amount of the modifier (fig. 1 f, g, h). The resulting modification of phosphogypsum poses significantly altered chemical composition and significantly broadened distribution of particle size and increased packing density of particles Pf.

The characterizations of modificates by the Fourier transform infrared spectroscopy show that although the active functional groups silica in the chemical interactions between the two components are absent due to the low reactivity of the calcium sulfate. On figure 3 the infrared spectra of phosphogypsum, polysilicic acid and modificates of phosphogypsum with 5, 20 and 50 wt. % of sodium metasilicate are shown. The bands of the polysilicic acid increase its intensity as well as amount of sodium metasilicate is higher.



**Fig. 3.** Infrared spectra of the source compounds: a – phosphogypsum; b - polysilicic acid.



**Fig. 4.** Infrared spectra of the obtained phosphogypsum/sodium metasilicate modificates: a – PG + 5 wt % SMS; b – PG + 20 wt % SMS; c – PG + 50 wt % SMS.

The stress-strain curves of SBR (Bulex 1500) and EPDM (Keltan 512) on figure 5 show an increasing of the Young modulus with increasing degree of filling and changes due to the modification of phosphogypsum with different amounts of modifier. On the figure, it can be seen that the stress in the vulcanizates of SBR (Bulex 1500) varies quite a wide range, while at EPDM (Keltan 512), it is very narrow distributed. Naturally, with increasing amount of phosphogypsum modulus of elasticity has to increase, especially after the 60 wt. % of filler content. The Young modulus increases and by increasing the degree of modification of phosphogypsum. The increasing of the amount of polysilicic acid as filler also increases the Young modulus. From the curves, it appears that SBR (Bulex 1500) has a wide range of deformation than the vulcanizates of EPDM (Keltan 512). The same applies for the tensile strength of both types of vulcanizates.

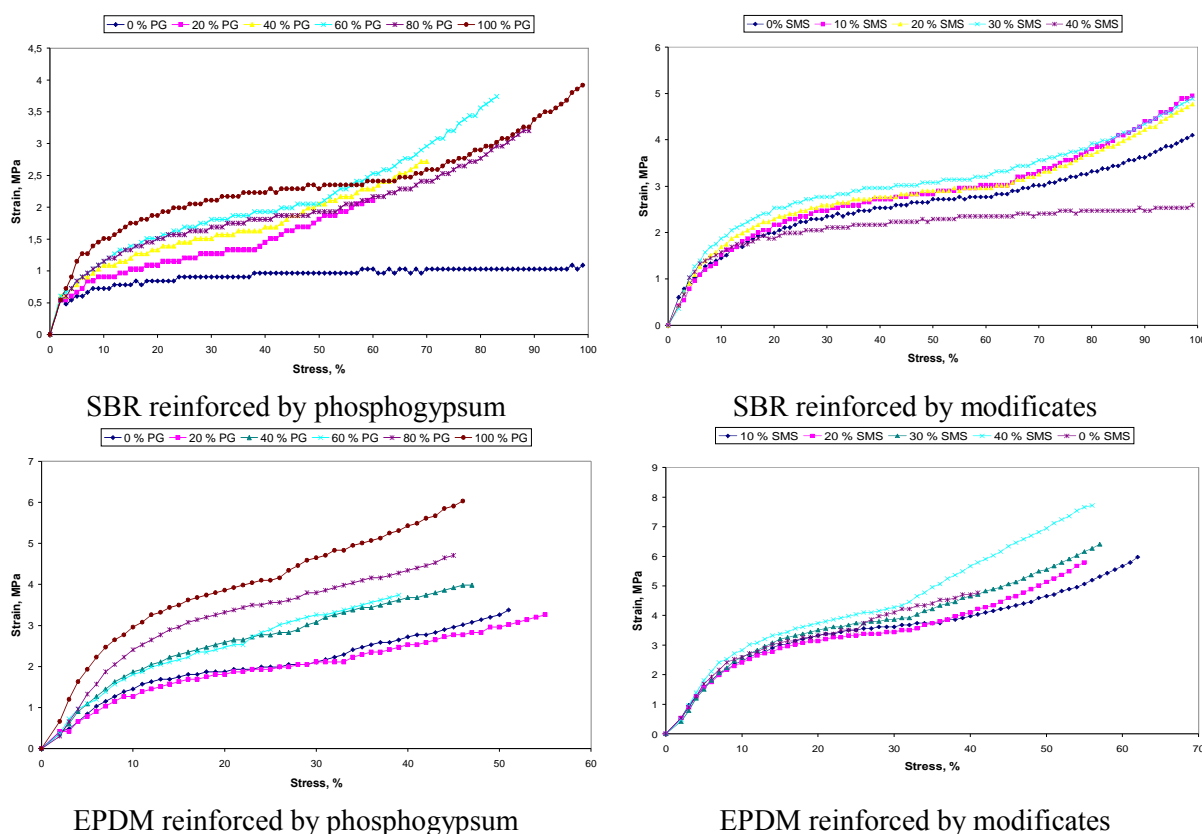


Fig. 5. Stress-strain curves of the studied vulcanizates of SBR and EPDM.

The reinforcement of SBR (Bulex 1500) and EPDM (Keltan 512) with phosphogypsum show that the tensile strength increases slowly with increasing the degree of filling of such a high strength are observed at SBR vulcanizates. The optimum degree of filling in both the rubber is in the range of 80 – 100 wt. %. This is typical for a lot of synthetic rubbers reinforced by minerals fillers [16]. The reinforcement optimum of 80 wt. % was chosen in this work. The studies of the mechanical properties of vulcanizates by modified phosphogypsum were conducted with the adopted optimum of 80 wt. %. The modification of phosphogypsum with sodium metasilicate leads to significant changes in the tensile strength. The strength of unfilled SBR (Bulex 1500) has very low values of 1.98 MPa. When unmodified phosphogypsum was introduced in content of 80 wt. % the tensile strength increases to 3.1 MPa. The tensile strength increased substantially reworking phosphogypsum with sodium metasilicate. By increasing the amount of the modifier 10, 20, 30 and 40 wt. % to the tensile strength increases up to 3.6 MPa. This is most likely due to the modified particles of phosphogypsum and free polysilicic acid influence. When the amount of the modifier is less

(10 wt. %) and the resulting polysilicic acid is almost totally adsorbed on the particle surface of the phosphogypsum (fig. 1 d, e), the tensile strength increases from 3.1 MPa to about 3.4 MPa. By increasing the amount of free polysilicic acid in an amount of the modifier 40 wt. %, the tensile strength increased to 3.6 MPa. These results clearly show the positive influence on the effectiveness of the modifier of phosphogypsum, compared to the tensile strength before the modification.

Similarly are the changes in the tensile strength of EPDM (Keltan 512) vulcanizates. The unfilled materials have a very low tensile strength with values of 1.9 MPa as in SBR (Bulex 1500), and at filled with 80 wt. % phosphogypsum - 2.25 MPa. After modification of phosphogypsum with 10, 20, 30 and 40 wt. % sodium metasilicate, the tensile strength increases up to 3.40 MPa.

More significant changes were observed in the relative elongation of SBR vulcanizates. For vulcanizates of EPDM the changes in the relative elongation are minimal. Even with the modification with sodium metasilicate changes in this property are negligible. By the modification of phosphogypsum with sodium metasilicate performs against elongation is increased especially for SBR (Bulex 1500).

The Young modulus mainly depends on the type of the rubber matrix and the nature of used filler. The phosphogypsum has low modulus, which leads to the preparation of vulcanizates with relatively low values of this property. The changes in the Young modulus of the vulcanizates of SBR (Bulex 1500) and EPDM (Keltan 512) unfilled and filled with phosphogypsum and its modificates with sodium metasilicate show that the lowest modulus values are for unfilled vulcanizates and those filled with 80 wt.% unmodified phosphogypsum. By increasing of the modifier amount, respectively, with an increase in the quantity of polysilicic acid, the module increases. For SBR (Bulex 1500) the Young module increases from 1.65 MPa for unfilled vulcanizates to 3.9 MPa for those reinforced with 40 wt. % of sodium metasilicate modificate. For EPDM (Keltan 512) Young modulus rises from 1.6 MPa for unfilled vulcanizates to 4.3 MPa for reinforced by phosphogypsum with the maximum degree of modification vulcanizates. The changes in the growth of the module can be traced and the changes throughout stress-strain curves of both rubbers (Fig. 5).

The research made on Bulex 1500 Keltan 512 show that phosphogypsum and its modificates apply as effective light mineral filler for synthetic rubbers. The modification of phosphogypsum by sodium metasilicate contributes significantly to the increase of its efficiency.

#### **4. Conclusions**

The modification of phosphogypsum with sodium metasilicate in order to enhance its effectiveness as mineral filler to two types of synthetic rubbers – SBR (Bulex 1500) and EPDM (Keltan 512) was carried out.

The resulting modificates of phosphogypsum have been characterized by the methods of scanning electron microscopy and Fourier transform infrared spectroscopy. The mechanical characteristics of the rubber vulcanizates were studied too.

The effectiveness of phosphogypsum and its modificates with sodium metasilicate have been demonstrated by analysis of the stress-strain curves and mechanical behavior of the resulting vulcanizates (tensile strength, relative elongation and Young modulus).

The tensile strength of the vulcanizates increased by increasing the degree of filling, as the optimum filling is in the range 80 – 100 wt. %. For SBR (Bulex 1500) the tensile strength increases from 1.98 MPa to 3.10 MPa. After modification with sodium metasilicate, it increases to 3.70 MPa at the same degree of filling. For EPDM (Keltan 512) the tensile

strength increases from 1.89 MPa to 2.25 MPa for unfilled filled with phosphogypsum and 3.43 for the modified phosphogypsum.

The changes of the relative elongation and the Young modulus in both the rubber, particularly for SBR (Bulex 1500), significantly increases by using of filler modificates with sodium metasilicate.

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