SUBSTITUTION OF CARBON BLACK BY ZEOLITE NANOFILLERS IN THE RUBBER COMPOUNDS

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Abstract
The present work deals with the preparation and study of environmentally friendly modified polymer compounds with the replacement of carbon black by nanofillers on the base of zeolite. Zeolites form a group of aluminosilicate nanoporous materials with wide possibilities for applications, that are environmentally friendly. Zeolites can be used in the role of fillers in the polymer materials too. The prepared modified polymer compounds were characterized by the methods of thermal analysis and their vulcanization performance and physical-mechanical properties of vulcanizates were measured. The found values were compared with the values of commercially used polymer materials with the original composition.

Keywords: Zeolite nanofiller, carbon black, rubber compound, thermal analysis, physico-mechanical properties

1 Introduction

One of the main priorities in the current rubber industry is production of environmentally friendly rubber compounds in according with high quality of products. The environmental requirements are narrowly connected with the environmental protection and mainly with the human health protection. So in the first position comes substitution of some problematic substances with their ecological substituents. The basic polymer compound includes natural rubber, vulcanization system and plasticizers and additives. One of important additives in rubber compound are fillers and in the function of filler in the real rubber compounds carbon black is currently used. Carbon black (Fig. 1) is a problematic substance because of its negative impact not only on environment but mainly on health of workers.

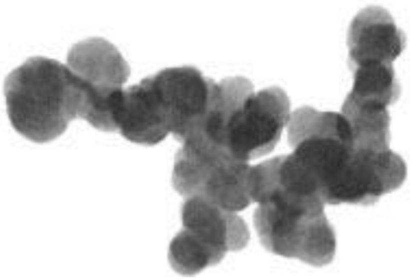

Fig. 1 *Electron microscope image of carbon black*

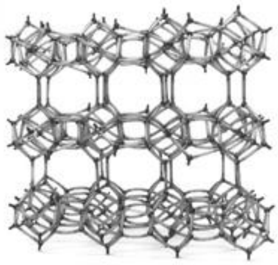

Fig. 2 *Structure of zeolite*

This problem can be solved by the way of substitution of carbon black with some ecological additive. The application of inorganic materials in organic polymers is one of usual way to improve up of mechanical properties for example hardness, tensile straight, module of polymer materials [1].
Natural zeolites form a group of hydrated aluminosilicates with the porous structure (Fig 2). The best known type of zeolites is clinoptilolite. Its structure is based on threedimensional framework composed of tetrahedral SiO_4 and AlO_4 units, which are connected by shared oxygen atoms. The special porous structure of zeolite has lots of practical applications as an ion-exchange, adsorbent, material for reversible hydratation and dehydratation and also as a ecological nanofiller in polymer materials [2].

2 Experimental

The natural zeolite clinoptilotite was used in a function of filler in rubber compounds. The model compounds were select on the base of natural rubber (SMR) [2]. As a comparative filler was used a carbon black (N660), because a size of their particles was approximately equal as a size of particles of used natural zeolite.

The model rubber compounds were prepared by two-step mixing on laboratory mixer Plastograf-Brabender by standard procedure. The first step was made at the temperature 140 °C and a rate of rotation pinions was 50 rpm/min. [3]. At the preparation of modified rubber compounds were used an activator of vulcanization (ZnO) and an accelerator of vulcanization N-cyclohexyl-2-benzothiazolsulfenamid (CBS) besides the natural rubber. In the second step, which was made at the temperature 110 °C and at same rate was added a polymer sulphur in function of vulcanization agent (Sulphur N). A composition of prepared modified rubber compounds is given in Table 1. Sample 2 – modified rubber compound with the substitution of all amount of filler clinoptilolite. Sample 3 – modified rubber compound with the substitution of 1/2 amount of filler clinoptilolite.

Table 1 *Compositon of modified model rubber compounds (samples 2, 3) and commercial rubber compound (sample 1)*

Ingredient of compound	Sample 1	Sample 2	Sample 3
SMR (g)	59,40	59,40	59,40
ZnO (g)	2,73	2,73	2,73
CBS (g)	0,89	0,89	0,89
N660 (g)	5,94	0	2,97
Zeolite (g)	0	5,94	2,97
Sulphur N (g)	0,89	0,89	0,89

After 24 hours waiting of prepared rubber compounds at laboratory temperature were made vulcanization curves by vulcameter MONSANTO 100 STN 62 1416 at the temperature 150 °C during 60 min. [4]. Rheological and vulcanization performances (M_L, M_H, t_S, t_{90}, R_V) of prepared rubber compounds with the addition of nanofiller clinoptilolite were tested and thermal properties by the methods of TG – DTA were studied.

The determination of physico-mechanical properties of vulcanized rubber - stress-strain properties (tensile strength, modulus 300, tensibility) was made by instrument INSTRON at the temperature 23 ± 2 °C by STN 62 1436 (ISO 37) [5]. Hardness was measured by hardness tester IRHD by STN 62 1433 at the temperature 23 ± 2 °C [6]. The evaluated values of prepared modified rubber compounds were compared with the values of commercial rubber compound.

3 Results and discussion

The results from determination of rheology and vulcanization performance of prepared rubber compounds are given in Table 2 and in Figs. 3-4.

Table 2 *Rheology and vulcanization performance of modified rubber compounds 2, 3 and commercial rubber compound 1*

	M_L [dN/m]	M_H [dN/m]	t_{02} [min]	t_{c90} [min]	R_v [min^{-1}]
Sample 1	5,0	45,0	1,5	3,5	50,00
Sample 2	4,0	38,0	5,5	7,5	50,00
Sample 3	8,0	46,0	2,5	4,5	50,00

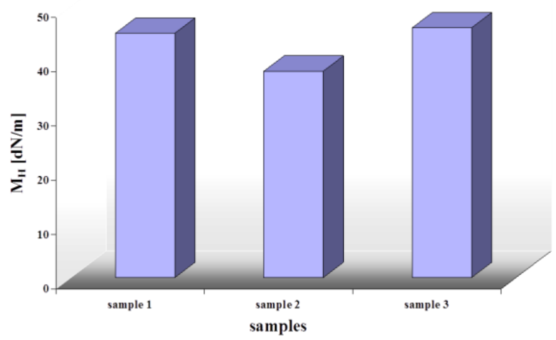

Fig. 3 *Maximal torgue moment* M_H *of model rubber compounds*

The values of vulcanization performance remitted, that the used type of zeolite influences as an inactive filler compared with carbon black (N660) in rubber compound. Viscosity decreases with an increasing amount of natural zeolite in rubber compound (see a lower values of M_L and M_H (Fig. 3)) and extend optimal time of vulcanization (t_{90}).

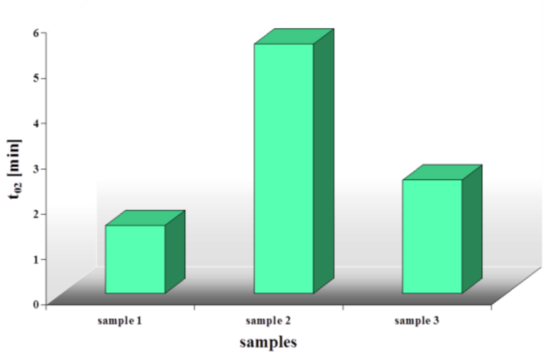

Fig. 4 *Scorch of time* t_{02} *of model rubber compounds*

At sample 2, were is a complete substitution of carbon black is that more than 200 % and the scorch of time (t_{02}) is expressively higher (Fig. 4). The values of rate coefficients (Rv), which characterize „activity“ of ingredients in compound are equal. Vulcanization curves had equally steep „gradient“, what indicate, that the used natural zeolite is partially also „active filler“. That can be caused by present of a little amount of oxides (mainly CaO and MgO). Both maybe use as an activators of vulcanization too. Their content is very little in compound, so don´t have distinct influence on vulcanization parameters. Further, content of SiO_2 is till 70 % in natural zeolite and this use as „inactive filler“, so called a diluent in rubber compounds [7,8]. The results of measurements of physico-mechanical properties of prepared vulcanizates are given in Table 3.

Table 3 *Physico-mechanical properties of prepared vulcanizates*

	Tensile strength [MPa]	Elongation [%]	Modulus 300 [MPa]	Hardness [IRHD]
Sample 1	13,17	685	5,77	47,6
Sample 2	11,12	854	3,91	42,3
Sample 3	13,65	774	5,29	44,0

The sample 3, with the 50 % substitution of carbon black by natural zeolite, shows the best values of physico-mechanical parameters. The sample shows the highest value of tensile strength and elongation at break too, what can be caused by relative synergistic effect of carbon black and natural zeolite combination.

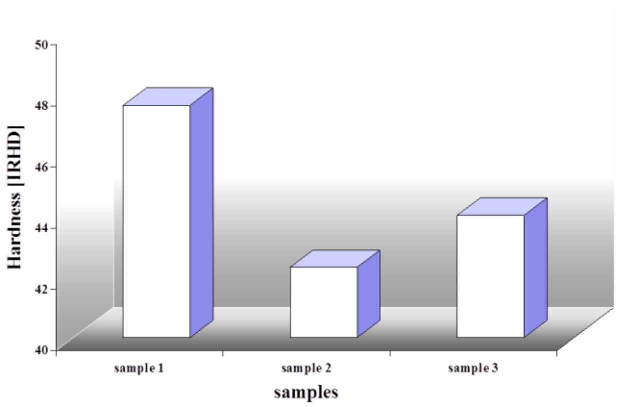

Fig. 5 *Hardness (IRHD) of vulcanizates*

The hardness values of modified vulcanizates with zeolite filler (Fig. 5) are a bit lower than the value of standard sample 1, where was used only carbon black, what can be connected with lower „activity“ of used natural zeolite in comparison with carbon black. The measured values of physicol-mechanical parameters at sample 2 aren´t suitable of technological point of view.

The sample 2 shows a lower value of tensile strenght to the prejudice of a high sensibility (Fig. 6), what confirms the theory of high elasticity [9,10], but complete substitution of carbon black by this type of natural zeolite isn´t possible of point of view of rubber technology. The used type of natural zeolite is „inactive filler" in this case.

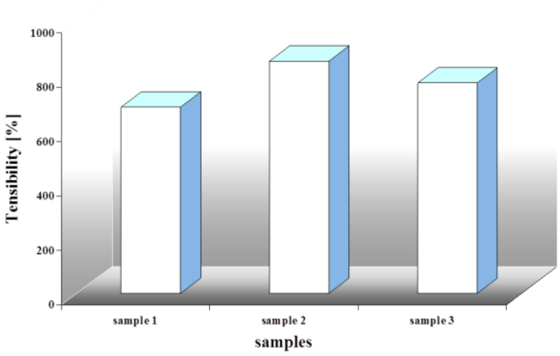

Fig. 6 *Tensibility of vulcanizates*

Samples of newprepared modified rubber compounds with zeolite filler were studied by methods of thermal analysis – DTA and TG in the temperature range of 40 °C – 900 °C (Figs. 7 and 8) [11].

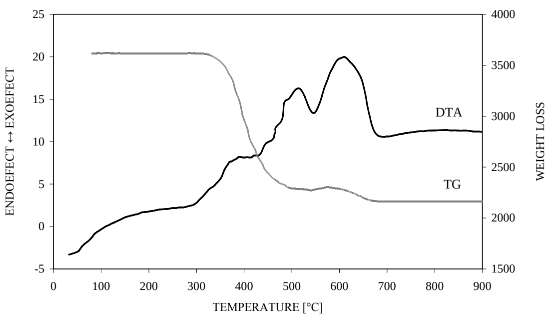

Fig. 7 *DTA-TG of commercial rubber compound with carbon black*

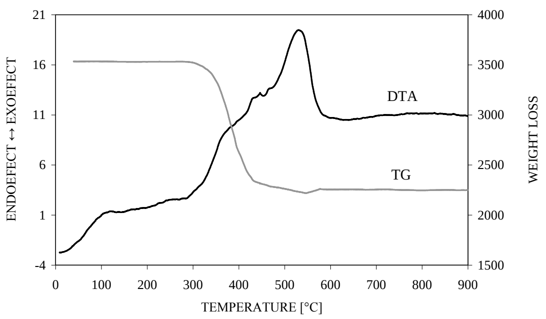

Fig. 8 *DTA-TG of rubber compound with zeolite filler*

4 Conclusion

At the prepared rubber compounds with environmentally friendly modified composition the rheological and vulcanization performances and physico-mechanical properties was studied. There was tested three model rubber compounds, where the original filler carbon black N660 was substituted by inorganic filler on the base of natural zeolite. From the study of modified rubber compounds with the addition of natural zeolite nanofiller follow that natural zeolite – clinoptilolite may be used as environmentally friendly substituent of carbon black for application in rubber compounds improving the physico-mechanical properties.

References

[1] JESENÁK, K.: *Prírodné ílové nanokompozity*, *Chem. Listy* 101, (2007), 657-664.
[2] ŠAMAJOVÁ, E.: *Z histórie výskumu zeolitových surovín Slovenska*, Seminár Prírodné a syntetické zeolity, FCHPT STU Bratislava, 2003.
[3] DUCHÁČEK, V.: *Polymery - výroba, vlastnosti, zpracování, použití.* 2. vyd. Vysoká škola chemicko - technologická v Praze, Praha, (2006), 154.
[4] *Príprava gumárenských zmesí* STN 62 1425.
[5] *Stanovenie vulkanizačných charakteristík* STN 62 1416.
[6] *Stanovenie ťahových vlastností* STN 62 1436 (ISO 37).
[7] *Stanovenie tvrdosti* STN 62 1431.
[8] DUCHÁČEK V.: *Gumárenské suroviny a jejich zpracovávání*. VŠCHT Praha, (1999), 96.
[9] PREKOP Š. a kol.: *Gumárska technológia I.* Žilinská univerzita Žilina, (1998), 78.
[10] CIESELSKI A.: *An Introduction to Rubber Technology.* Rapra Technology, Schawbury, (1999), 37.
[11] ONDRUŠOVÁ D. a kol.: *Preparation and properties of ecologically modified rubber compounds.* Chemické Listy 102, 733-740, 2008.

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