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USING ZEOLITES AS A NANOADDITIVES IN THE RUBBER COMPOUNDS

POUŽITÍ ZEOLITŮ JAKO NANOADITIV V KAUČUKOVÉ SMĚSI

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Abstract

The present work deals with the preparation and study of physical and mechanical properties modified rubber compounds. In a function of filler was used natural zeolite which is from a group of hydrated aluminosilicates. The prepared modified polymer compounds were characterized by physical-mechanical properties of vulcanizates. The found values were compared with the values of commercially used polymer materials with the original filler carbon black [1,2].

Key words: natural zeolites, filler, physical-mechanical properties

1. Introduction

The basic polymer compound includes natural rubber, vulcanization system and plasticator. One of important additives of rubber compound are filler too. Inorganic materials are adding in polymer materials in form of filler. The application of inorganic materials in organic polymers is one of usual way to improve up of mechanical properties for example hardness, tensile strength, module of polymer materials [1].

Present paper studies possibility of applications of natural zeolite in preparation of modified rubber compounds and evaluate the influence of addition light filler on properties of resultant vulcanizer. Following measure give the information about rheology, vulcanization performance and physical-mechanical properties modified rubber compound on the base of natural zeolites.

2. Experimental

The sample of natural zeolite was used in a function of filler in rubber compound. The model compound was select on the base of natural rubber (SMR-20) [2]. As a reference 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 Condition of prepared model rubber compound in g

| Ingredient of compound | sample 1 | sample 2 | sample 3 |
|------------------------|----------|----------|----------|
| SMR 20 | 59,40 | 59,40 | 59,40 |
| ZnO | 2,73 | 2,73 | 2,73 |
| CBS | 0,89 | 0,89 | 0,89 |
| N660 | 5,94 | 0 | 2,97 |
| Zeolite | 0 | 5,94 | 2,97 |
| Sulphur N | 0,89 | 0,89 | 0,89 |

After waiting 24 hours 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.

For determination of physical-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 values of prepared modified rubber compounds was compared with the standard (commercial rubber compound).

3. Results and discussion

The results of measurements are given in Table 2 and in Figs. 1-2.

Table 2 Vulcanization performance of modified rubber compounds

| | M_L [dN/m] | M_H [dN/m] | t_{02} [min] | t_{90} [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 |

The values of vulcanization performance remitted, that the used type of zeolite influences as an inactive filler in compare with a carbon black (N660) in rubber compound. A viscosity decreases with an increasing amount of natural zeolite in rubber compound (see a lower values of M_L and M_H (Fig. 1)) and extend optimal time of vulcanization (t_{90}). 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. 2). The values of rate coefficients (R_v), 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 SiO₂ is till 70 % in natural zeolite and this use as „inactive filler“, so called a diluent in rubber compounds [7,8].

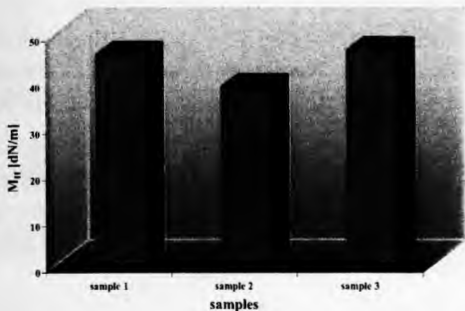


Fig. 1 Maximal torque moment

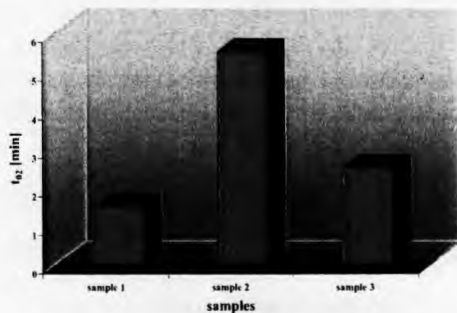


Fig. 2 Scorch of time of model rubber compounds

The measured values of physical-mechanical properties prepared vulcanizates are mentioned in Table 3.

Table 3 Physical-mechanical properties of prepared vulcanizates

| | Tensile strength [MPa] | Tensibility [%] | 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, where was the substitution of carbon black by natural zeolite 50 %, shows the best values of physical - mechanical parameters. The sample has the highest value of tensile strength and tensibility too, what can be caused by relative synergy between carbon black and the used natural zeolite. The value of hardness (Fig. 3) is a bit lower than the value at sample 1, where was used only carbon black, what can be connected with lower „activity“ of used natural zeolite in compare with carbon black. The measured values of physical-mechanical parameters at sample 2 aren't suitable of technological point of view. The sample has a lower value of tensile strength to the prejudice of a high sensibility (Fig. 4), what confirm of 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.

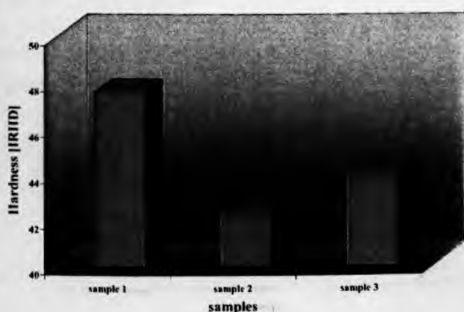


Fig. 3 Hardness of vulcanizates

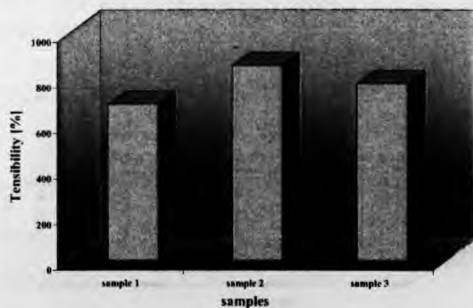


Fig. 4 Tensibility of vulcanizates

4. Conclusion

In the prepared rubber compounds with modified composition was studied rheological and vulcanization performances and physical-mechanical properties. There was tested three model rubber compounds, where was original filler carbon black N660 substituted by inorganic filler on the base of natural zeolite.

From study of properties of modified rubber compounds with the addition of natural zeolite nanofiller follow that natural zeolite – clinoptilolite may be used for the application in the rubber compounds improving the physical-mechanical properties.

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