Rubber composites with incorporated magnetic filler**⁾

Ján Kruželák[1), *], **Rastislav Dosoudil**[2)], **Richard Sýkora**[1)], **Ivan Hudec**[1)]

Abstract: In this study, rubber magnetic composites were prepared by incorporation of strontium ferrite into non-polar and polar rubber matrices. The aim was to investigate the influence of magnetic filler content on the cross-linking and properties of the tested materials. The results demonstrate that the presence of strontium ferrite in rubber matrices leads to a significant increase in the magnetic characteristics of composites. The physical properties of the tested systems seem to be less dependent on magnetic filler content although the improvement of evaluated characteristics with increasing content of ferrite was achieved.

Keywords: rubber magnetic composites, strontium ferrite, curing characteristics, cross-link density, physical and magnetic properties of composites.

Kompozyty elastomerowe z napełniaczem magnetycznym

Streszczenie: Badano wpływ udziału napełniacza magnetycznego na przebieg sieciowania i wybrane właściwości kompozytów wytworzonych na bazie niepolarnego kauczuku butadienowego (BR) lub polarnego kauczuku butadienowo-akrylonitrylowego (NBR) z dodatkiem ferrytu strontu. Wykazano, że obecność takiego napełniacza w matrycy elastomerowej wyraźnie poprawia charakterystykę magnetyczną wytworzonych kompozytów, natomiast ich właściwości fizyczne tylko w niewielkim stopniu zależą od zawartości ferrytu strontu w układzie.

Słowa kluczowe: magnetyczne kompozyty elastomerowe, ferryt strontu, charakterystyka sieciowania, gęstość usieciowania, właściwości fizyczne i magnetyczne kompozytów.

Rubber magnetic composites have become a well known group of smart materials with unique properties combining the elasticity of the rubber matrix and magnetic characteristics of the fillers [1—3]. In composite magnetic materials, the polymer matrix and the magnetic powder as filler affect the processability and physical properties of the final product. The obtained materials have interesting mechanical and magnetic properties, chemical resistance and are suitable for producing flexible magnets. Compared to ceramic magnets, rubber magnetic composites offer a greater degree of design flexibility and adaptability. By selecting a suitable rubber matrix, magnetic fillers can be incorporated to produce composites with required properties [4, 5].

Ferrites as magnetic fillers remain one the best magnetic materials ever discovered and they cannot be easily replaced by any other magnetic materials because of their low cost, good chemical stability and variability of technological applications [6]. Hard ferrites are ceramic materials with hexagonal crystal structures. Their formula composition can be represented as $n(MeO)\cdot m(Fe_2O_3)$, where n and m are natural numbers and Me is a divalent metal. For n=1 and m=6 one obtains the formula so-called M-type ferrites, $MeO\cdot6(Fe_2O_3)$, which can also be written as $MeFe_{12}O_{19}$. The most common M-types ferrites are those where Me = Ba, Sr or Pb [7]. These substances are often used as powders for producing permanents magnets [8, 9].

The aim of the present work was to investigate the influence of strontium ferrite content on the curing characteristics and cross-link density of composites based on non-polar (butadiene rubber) and polar (acrylonitrile butadiene rubber) elastomers. Subsequently, the physical and magnetic properties of the prepared materials were investigated.

EXPERIMENTAL PART

Materials

Butadiene rubber BUNA CB 24 (BR, Lanxess, Germany) as a non-polar rubber matrix and acrylonitrile butadiene rubber EUROPRENE N3330 (NBR, Polimeri, Italy,

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[1)] Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Polymer Materials, Department of Plastics and Rubber, Radlinského 9, 812 37 Bratislava, Slovakia.

[2)] Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Electromagnetic Theory, Ilkovičova 3, 812 19, Bratislava, Slovakia.

[*)] Author for correspondence; email: jan.kruzelak@stuba.sk

T a b l e 1. Strontium ferrite characteristics

Characteristics	Values
Density, g/cm^3	4.73
Specific surface area, m^2/g	4.06
Total porosity, %	55.62
Total volume of pores, cm^3/g	0.254
Coercivity H_c, kA/m	117
Remanent magnetic induction B_r, T	0.17
Maximum magnetic induction B_m, T	1.26

content of acrylonitrile — 33 %) as a polar rubber matrix were chosen for the experiments. Strontium hexaferrite provided by Magnety, Světlá Hora, Czech Republic, was dosed to elastomeric matrices in a concentration ranging from 0 to 100 phr in order to prepare rubber magnetic composites. The structural and magnetic characteristics of the applied ferrite are given in Table 1. Besides rubber and filler, the rubber compounds contained only ingredients that support the curing process (sulphur, zinc oxide, N-cyclohexyl-2-benzothiazole sulfenamide and stearic acid). The content of these additives was kept constant in all experiments.

Samples preparation

The rubber compounds were prepared in a Brabender laboratory mixer in two mixing steps. In the first step, the rubber together with activators and fillers were compounded (9 min, 90—95 °C), in the second step (4 min, 90—95 °C), the curing system was introduced. After that, the rubber compounds were homogenized in a two-roll calender.

The curing characteristics of the prepared rubber compounds were determined from the corresponding curing isotherms measured in a Rheometer, Monsanto R100 at 150 °C. The curing process was performed at 150 °C for the optimum cure time t_{c90} by using a hydraulic press, Fontune.

Methods of testing

The physical properties of the prepared vulcanizates were measured in accordance with the valid technical standards (ISO 37), on double side dumbbell-shaped test specimens (length 10 cm, width 6.4 mm, thickness 2 mm), using a Zwick Roell/Z 2.5 appliance at a cross-head speed of 500 mm/min. The hardness was measured using a durometer and the unit was expressed in Shore A (ISO 7619-1).

Magnetic measurements of composites were determined with a magnetometer TVM-1 at room temperature and maximum intensity of magnetic field of H_m = 750 kA/m. The basic principle of measurement is the induction method of scanning of scattering magnetic flux Φ

induced by magnetic vibrating sample. The magnetic field is generated by means of two cores of a Weiss electromagnet at a minimum distance of pole adapters 7.5 mm. The specimens were of a prism shape (8 × 4 × 4 mm).

The cross-link density of vulcanizates was evaluated based on the equilibrium swelling of samples in xylene or acetone. The Flory-Rehner equation (1), modified by Krause for filled vulcanizates, was then applied [10]:

$$\nu = -\frac{V_{r0}}{V_S}\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_r^{1/3}V_{r0}^{2/3}-0.5V_r} \tag{1}$$

where: ν — cross-link density (mol/cm^3), V_{r0} — volume fraction of rubber in equilibrium swelling sample of vulcanizate in absence of fillers, V_r — volume fraction of rubber in equilibrium swelling sample of filled vulcanizate, V_S — molar volume of solvent (for xylene = 123.45 cm^3/mol, for acetone 73.519 cm^3/mol), χ — Huggins interaction parameter (for BR-xylene χ = 0.3900, for NBR-acetone χ = 0.3692).

RESULTS AND DISCUSSION

Influence of ferrite content on curing characteristics and cross-link density

The influence of ferrite content on the curing process of prepared rubber compounds was considered on the basis of their curing characteristics, the scorch time t_{s1}, the optimum cure time t_{c90} and the difference between the values of maximum and minimum torque ΔM. From Fig. 1, it is obvious that the scorch time decreased when 20 phr of ferrite was incorporated in rubber compounds based on both BR and NBR. With increasing ferrite content, the values of t_{s1} fluctuated in a small range almost independently on the amount of ferrite.

The values of torque difference showed increasing tendency with increasing content of magnetic filler (Fig.
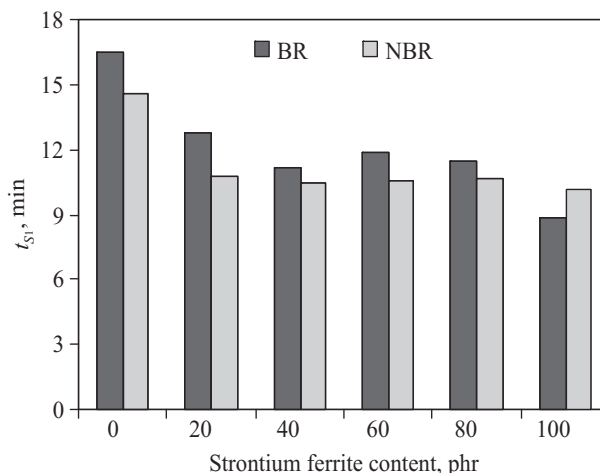
Fig. 1. Influence of strontium ferrite content on scorch time t_{s1} of rubber compounds based on BR and NBR
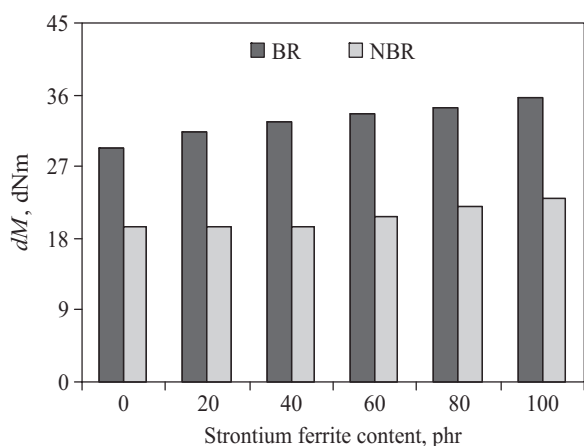
Fig. 2. Influence of strontium ferrite content on torque difference ΔM of rubber compounds based on BR and NBR
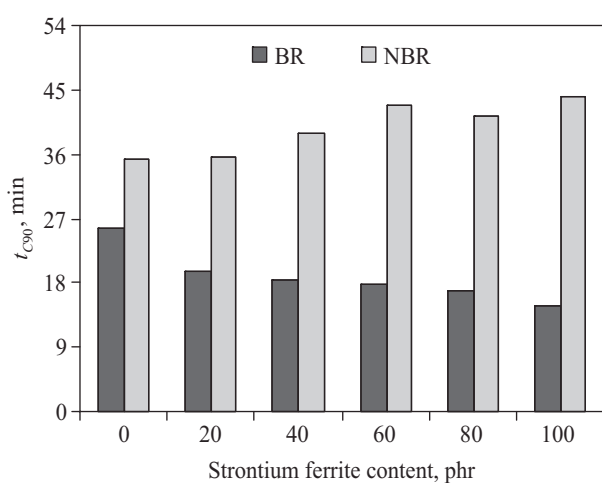

Fig. 3. Influence of strontium ferrite content on optimum cure time t_{c90} of rubber compounds based on BR and NBR

when the amount of ferrite increased from 0 to its' maximum content.

The cross-link density ν of cured rubber compounds was determined based on equilibrium swelling of samples in a suitable solvent. The non-polar solvent, xylene, was used for vulcanizates based on BR and polar solvent, while acetone was used for vulcanizates based on NBR. First, the samples were swollen in the selected solvents until equilibrium swelling was reached. The cross-link density was calculated based upon equilibrium swelling degree by applying the Flory-Rehner equation (1). As shown in Fig. 4, the cross-link density of both BR and also NBR vulcanizates exhibited a decreasing trend in dependence on ferrite content, although the differences between the values ν for reference samples and samples
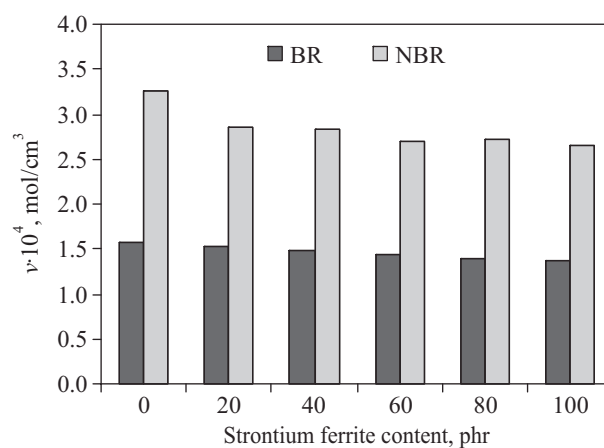

Fig. 4. Influence of strontium ferrite content on cross-link density ν of vulcanizates based on BR and NBR

2). Values of ΔM were noted to be higher in the case of rubber compounds based on BR. The different character of dependences on ferrite content was recorded in case of optimum cure time. As seen in Fig. 3, the presence of magnetic filler in rubber compounds based on BR leads to a decrease of t_{c90}. In comparison with the unfilled sample used as a reference, the addition of magnetic filler caused the reduction of t_{c90} from about 26 to approximately 15 minutes (for the sample with 100 phr of ferrite). Taking into consideration that rubber compounds differed in ferrite loading only, it is supposed that ferrite tends to slightly accelerate the sulfur curing process. Ferrites are compounds of iron oxides and oxides of other metals. The presence of these oxides in the rubber matrix might have a similar effect on the curing process as zinc oxide, which acts as an activator of sulfur vulcanization. This presumption is supported by the decrease of scorch time for both types of rubber compounds and reduction of optimum cure time of rubber systems based on BR when magnetic filler was included. However, the t_{c90} of rubber compounds based on NBR was found to increase with a larger content of ferrite. The t_{c90} prolonged to about 9 min

with 100 phr of ferrite were not very significant. With increasing ferrite content, ferrite particles could act as a steric hindrance against the formation of cross-links between macromolecular chain segments, thus contributing to the decrease of cross-link density. The higher values of cross-link density of vulcanizates based on NBR can be attributed to the longer optimum cure time of equivalent rubber compounds. During a longer curing period, more intermolecular linkages could be formed.

Influence of ferrite content on the properties of rubber magnetic composites

The experimentally obtained values of physical properties for the examined composites are illustrated in Figs. 5—8. As seen in Fig. 5 and Fig. 6, the values of stress at 100 % elongation (S_{e100}) and tensile strength at break were improved with an increased content of ferrite. The improvement of both characteristics points to the stiffening of the rubber matrices with increased content of magnetic filler. Whereas the values of S_{e100} were found to be higher in the case of composites based on BR, higher
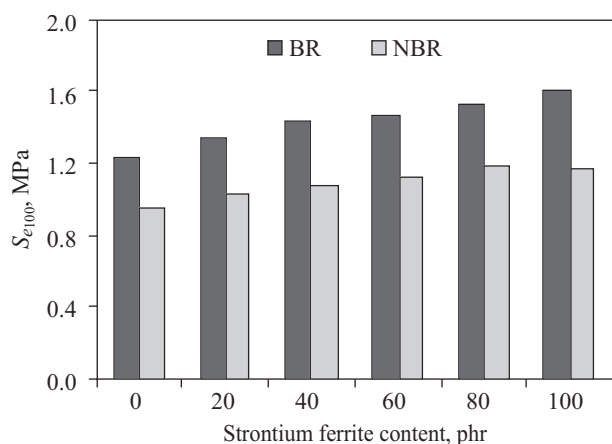
Fig. 5. **Influence of strontium ferrite content on stress at 100 %**
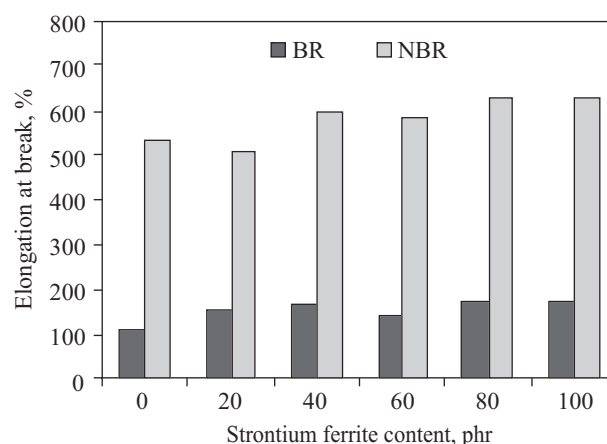**elongation S_{e100} of composites based on BR and NBR**

Fig. 7. **Influence of strontium ferrite content on elongation at**
break of composites based on BR and NBR
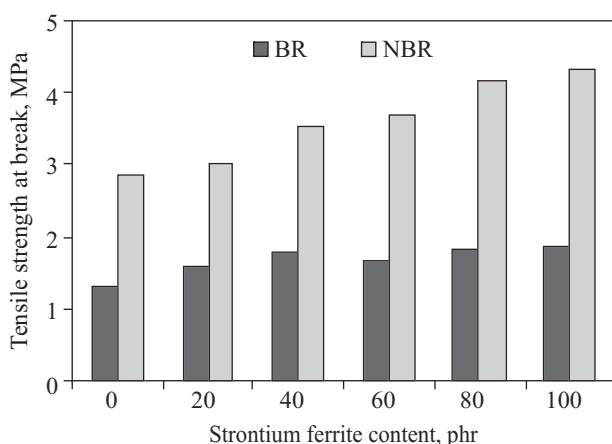

Fig. 6. **Influence of strontium ferrite content on tensile strength at**
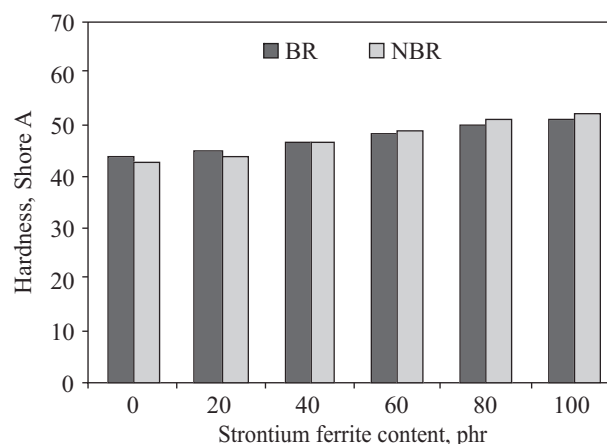**break of composites based on BR and NBR**

Fig. 8. **Influence of strontium ferrite content on hardness of com-**
posites based on BR and NBR

values of tensile strength at break were exhibited by composites based on NBR. Also, the dependence of tensile strength at break on magnetic filler content was more pronounced in the case of composites based on NBR. From Fig. 6 it is possible to observe that increased ferrite content from 0 to 100 phr results in the tensile strength at break of the composites based on BR to increase from 1.31 to 1.88 MPa and the tensile strength at break of composites based on NBR to increase from 2.84 to 4.33 MPa.

The increasing tendency on magnetic filler content was possible to observe also in the case of elongation at break although there are big differences in the values of this physical property of both types of composites (Fig. 7). Composites based on NBR showed much higher elongation at break. The increase of elongation at break on the dependence of magnetic filler content can be attributed to the decrease of cross-link density with increased content of ferrite. The fewer cross-links between macromolecular chains are formed, the less restricted are the chain mobilities. Therefore, a higher elongation at break of composites is achieved.

From the graphical dependence of hardness on magnetic filler content (Fig. 8), it becomes evident that the

hardness of both types of composites was improved by incorporation of ferrite, as the hardness of ferrite is greater than that of BR and NBR. Ferrite particles can also fill various microcavities in the rubber matrices, which also contributed to the increase of hardness. The type of elastomer has almost no influence on the hardness of the tested materials.

The achieved results demonstrate that ferrite incorporated into rubber matrices acts as a reinforcing filler although the degree of reinforcement is not very high. Despite this, an improvement in the physical properties dependent on ferrite content was observed. Although ferrite seems to be an inactive filler, it is estimated that some physical interactions between the rubber matrix and the particles of ferrite are formed, which subsequently leads to the enhancement of adhesion at the phase interface. Ferrite seems to be a more active filler for polar elastomers. As already mentioned, ferrites are compounds of iron oxide with oxides of some other metals. The structural units of hexagonal ferrites are formed from spinel and hexagonal blocks. The coupling forces of ferrite crystals are caused by electrostatic attractions between positive metal ions that are captured inside the ferrite structure

and negative oxygen ions, which are then placed at the edge of structural units. Due to the presence of oxygen ions on the surface of ferrite crystals, it is expected that some polar interactions are formed between particles of ferrite and the cyano groups of acrylonitrile structural units of NBR. This presumption is supported by a better improvement of tensile strength at break of composites based on NBR, when the amount of ferrite increased from 0 to 100 phr. The results obtained by the study demonstrated that although the physical properties of vulcanizates are dependent mainly on the chemical structure of elastomers, these characteristics can be positively modified by incorporation of ferrite filler.

The dependences of magnetic induction B on the intensity of the magnetic field H are called magnetizing curves, which provide complete information about the technical properties of magnetic substances. Fig. 9 illustrates the dependence of magnetic induction B in the material, with an intensity of magnetic field H, when the sample is cyclically magnetized in the presence of an external magnetic field. The remanent magnetic induction
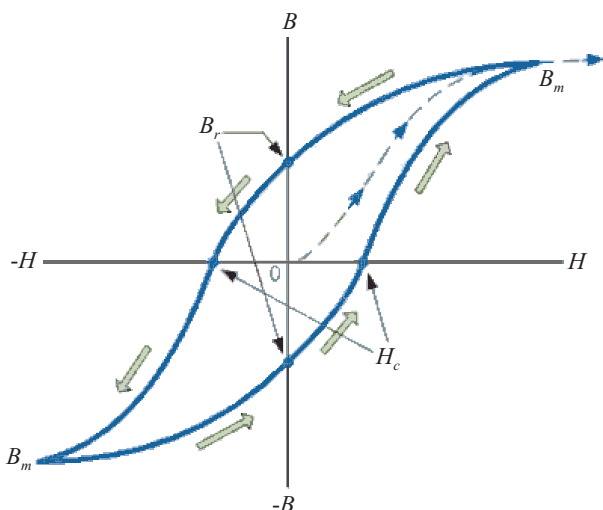
Fig. 9. **Magnetizing curve of magnetic materials**

B_r, which represents the value of residual magnetism of the material when an external magnetic field is removed, and the coercive intensity of magnetic field (coercivity, H_c), which represents energy needed to abolish the remanent magnetic induction, are the most important parameters of permanents magnets. Magnetic hard materials, like ferrites, usually exhibit high values of both magnetic characteristics. The values of maximum magnetic induction B_m of remanent magnetic induction B_r and coercivity H_c for all prepared composites are graphically illustrated in Figs. 10—12.

The maximum magnetic induction showed an increasing trend with increasing content of magnetic filler (Fig. 10). From Fig. 11 it becomes clearly evident that remanent magnetic induction of both types of composites was
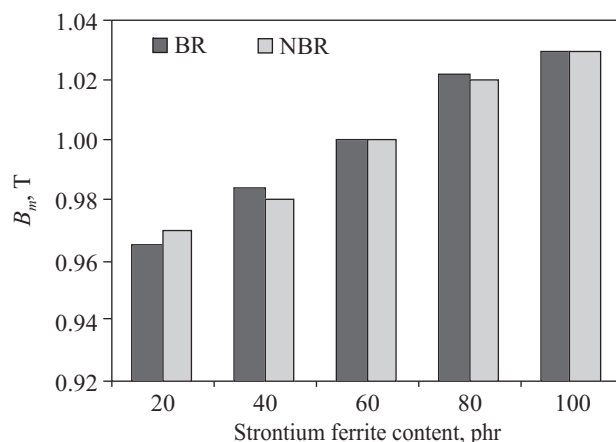
Fig. 10. **Influence of strontium ferrite content on maximum magnetic induction B_m of composites based on BR and NBR**
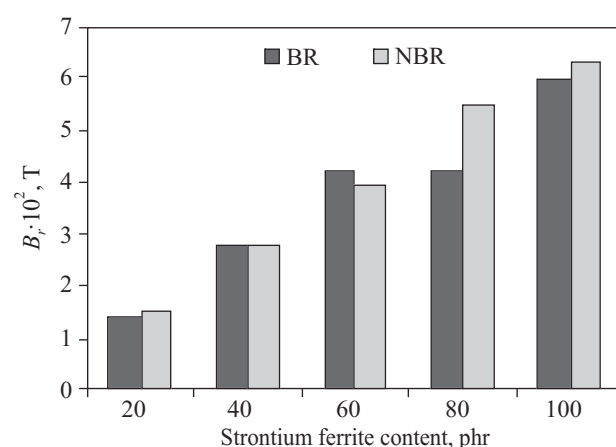
Fig. 11. **Influence of strontium ferrite content on remanent magnetic induction B_r of composites based on BR and NBR**
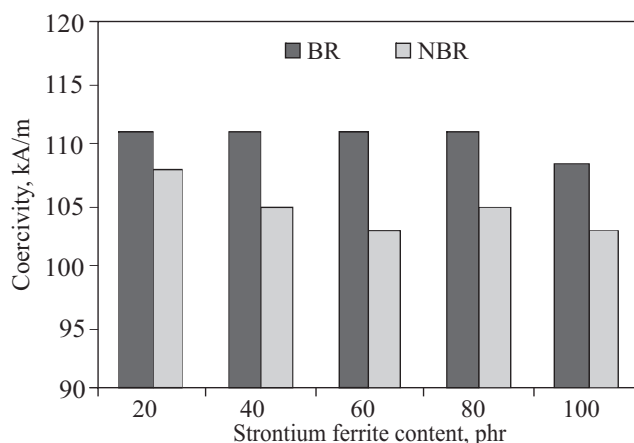
Fig. 12. **Influence of strontium ferrite content on coercivity H_c of composites based on BR and NBR**

found to be strongly dependent on the content of applied strontium ferrite. In the case of both types of composites, there was recorded a more than 400 % increase of the value B_r by increasing of ferrite content from 20 to 100 phr. The type of rubber matrix has almost no influence on the values of the magnetic characteristics; the values of B_m

and B_r are dependent only on the amount of magnetic filler, regardless of the type of tested rubber.

The coercivity of composites based on BR seems not to be influenced by the magnetic filler content, while the coercivity of composites based on NBR tends to decrease with an increased content of ferrite (Fig. 12). The values of H_c are greater in the case of composites based on BR, which is surprising as the magnetic characteristics were found not to be affected by the type of rubber matrix.

CONCLUSIONS

The aim of the work was the preparation of rubber composites with strontium ferrite and an evaluation of the influence of magnetic filler content on the curing process, cross-link density and physical properties of the prepared materials.

The results achieved by the study revealed that ferrite incorporated into the rubber matrices influences both the curing process of rubber compounds and the cross-link density of vulcanizates. Although the physical properties of prepared materials are dependent mainly on the characteristics of rubber matrix, the positive effect of the magnetic filler content on the physical, and especially on the magnetic, properties was observed. This suggests that ferrite provides not only suitable magnetic characteristics to the tested materials but also contributes to the improvement of the physical properties of rubber composites by improving the adhesion between the two phases. This is very promising with a view to the future preparation of rubber composites with incorporated magnetic fillers, especially ferrites.

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