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The Influence of Strontium Ferrite on Curing and Properties of BR-Composites

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Abstract

The focus of the work was to prepare elastomeric magnetic composites based on a highly elastic polymer matrix (1,4-cis butadiene rubber). Three modifications of the same type of strontium ferrite $SrFe_{12}O_{19}$, type FD8/24 were applied as magnetic fillers. The applied ferrites differed in particle size distribution and other structural and magnetic characteristics. The work is focused on the preparation of rubber compounds for making elastomeric magnetic composites and evaluation of magnetic fillers influence on curing characteristics, physical-mechanical and magnetic properties of prepared composites. The study is also dedicated to the cross-link density of vulcanizates.

KEY WORDS:
elastomeric composites
magnetic filler
physical-mechanical properties
strontium ferrite

KLJUČNE RIJEČI:
elastomerni kompoziti
fizičko-mehanička svojstva
magnetno punilo
stroncijev ferit

Utjecaj stroncijeva ferita na umreživanje i svojstva kompozita butadienskoga kaučuka

Sažetak

Cilj rada je pripremiti elastomerne magnetne kompozite na temelju visokoelastične polimerne matrice (1,4-cis butadienski kaučuk). Tri su modifikacije istog tipa stroncijeva ferita $SrFe_{12}O_{19}$, tip FD8/24, primijenjene kao magnetna punila. Primijenjeni feriti razlikovali su se po raspodjeli veličine čestica te drugim strukturnim i magnetnim svojstvima. Rad obrađuje pripremu spojeva kaučuka za izradu elastomernih magnetnih kompozita i daje ocjenu utjecaja magnetnih punila na svojstva umreživanja, fizičko-mehanička i magnetna svojstva pripremljenih kompozita. Ispitivanje također obrađuje gustoću umreživanja vulkanizata.

Introduction

Nowadays, more and more attention is given to the preparation and study of elastomeric composites with magnetic properties. One of the possibilities how to prepare such materials is using fillers with magnetic characteristics.[1-3] The final properties of composites are strongly dependent especially on characteristics of polymer matrix. However, by integration of magnetic materials new properties and technological abilities can be provided. Such magnetic fillers include ferrites. Ferrites are compounds of iron oxide with the oxides of some other metals of general formula $MFe_{12}O_{19}$ (M is divalent cation such as Sr, Ba, etc.). In term of technological applications one may distinguish between two main types of ferrites, hard ferrites and soft ferrites. Magnetic soft materials have low coercivity and also low value of remanent magnetic induction B_r. Magnetic hard ferrites have wide hysteresis loop and coercivity H_c > 2.5 kA/m. They also express high value of remanent magnetic induction B_r and high value of maximum energy product $(BH)_{max}$. These ferrites with hexagonal structure and strong magneto-crystalline anisotropy are suitable for producing of permanent magnets.[4-6] Because of low price and very good chemical stability ferrites are included in the most important magnetic materials which cannot be easily replaced. Ba and Sr ferrites are the most common applied magnetic powder fillers.

The advantage of elastomeric magnetic composites is that their properties can be modified for the requirements of specific applications. Because of their elasticity and easy mouldability they are suitable for additive devices, where elasticity and flexibility are additional and important parameters. Moreover, they have very good magnetic properties. Rubber magnets can absorb shock and sound, so they can be applied in DC motors, motor parts, memo holders, intelligent tyres, in microwave and radar technology, and also in other technological applications.

Experimental

Materials

The 1, 4-cis butadiene rubber (*Buna CB 24*, *Lanxess*, Leverkusen, Germany) was filled with ferromagnetic particles in order to prepare rubber compounds for elastomeric magnetic composites. A standard sulfur-based vulcanization system (sulfur - 1.3 phr, CBS - 1.5 phr, ZnO – 3 phr, stearin – 2 phr) was used. Three modifications of the same type of strontium ferrite $SrFe_{12}O_{19}$, type *FD8/24* (*Magnety* a.s., Světlá Hora, Czech Republic) were used in our work. Anisotropic strontium hexaferrite was prepared by wet milling. It is a product with additional polyvinyl alcohol, which covers the surface of ferrite particles. This type of ferrite is in our work specified as FD0. Second modification of ferrite (FD1), which was used in our experiments, was prepared by dissolution of polyvinyl alcohol by extraction in hot water. After removal of polyvinyl alcohol, particles the size of ferrite were reduced. For the purpose of further reduction of particles size, ferrite without polyvinyl alcohol was next milled in the ball mill (FD2). The content of ferrites in both types of rubber compounds varied from 0 to 100 phr. Specific surface area and total porosity of ferrite particles were determined by application of mercury porosimetry in *POROSIMETER 2000* instrument (*Carlo Erba*, Milan, Italy). Particle size distribution of ferrite fillers was investigated by using the apparatus *CILAS 1064L* (*Cilas*, France). Fine particles are measured by scanning of scattering reflection, which is formed by examined sample. The time of detection is 20 seconds in liquid state. Measuring is performed in the attenuation range of the laser beam from 5 to 28%. The detailed specification of magnetic fillers is mentioned in Figures 1-3 and Table 1.

TABLE 1 – Characteristics of strontium ferrites

Characteristics	FD0	FD1	FD2
Density ρ, g/cm^3	4.13	4.73	4.77
Specific surface area, m^2/g	3.30	4.06	4.46
Total porosity, %	54.94	55.62	49.91
Coercivity, kA/m	116	117	108
Remanent magnetic induction, T	0.116	0.170	0.183

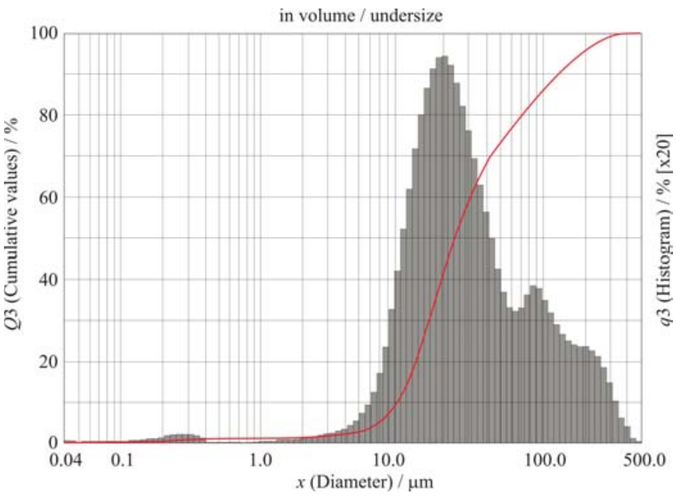

FIGURE 1 – Particle size distribution of strontium ferrite FD0

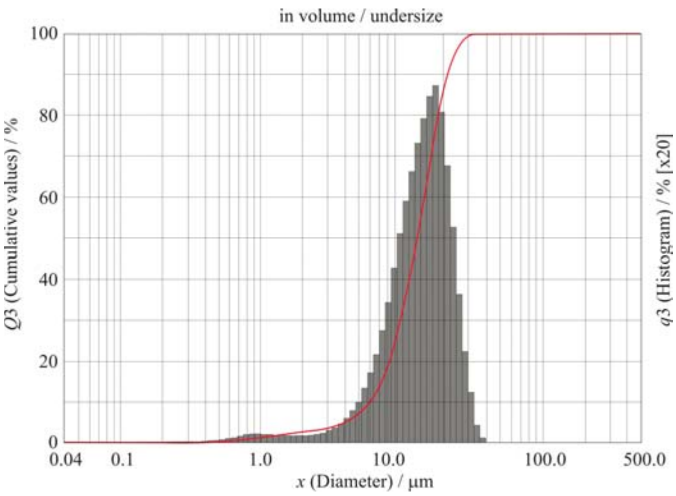

FIGURE 2 – Particle size distribution of strontium ferrite FD1

Procedures

The rubber compounds were prepared in the laboratory mixer *BRABENDER* (*Plasti-Corder*, Duisburg, Germany) in two compounding steps. In the first step the rubber and the fillers were compounded (9 min, 90 °C), in the second step (4 min, 90 °C) curing system was added. The curing characteristics were investigated from the curing isotherms measured by *Rheometer MONSANTO R100* (*Eagle Polymer Equipment*, Akron, USA), at 150 °C. The prepared compounds were cured at 150 °C for the optimum cure time t_{C90} by using the hydraulic press *FONTUNE* (*N.V. Machinefabriek*, Vlaardingen, Holland). Physical-mechanical properties of the prepared vulcanizates were measured in accordance with the valid technical norms, on the double side blade specimens (width: 6.4 mm, length: 10 cm, thickness: 2 mm). Magnetic measurements of vulcanizates were determined on the magnetometer *TVM–1* (*Vúzort*, Prague, the Czech Republic) at room temperature.

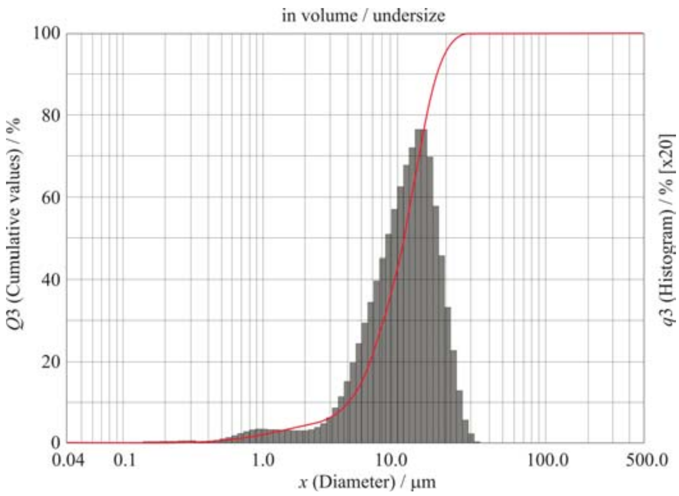

FIGURE 3 – Particle size distribution of strontium ferrite FD2

Two different methods were used in order to determine the cross-link density of vulcanized samples:

– equilibrium swelling in xylene (ν_{ch} - chemical cross-link density), using the Krause modified Flory-Rehner equation (1) for filled vulcanizates:[7]

$$\nu_{ch} = -\frac{V_{r0}}{V_S}\frac{\ln(1-V_r)+V_r+\chi V_r^{\,2}}{V_r^{\,1/3}V_{r0}^{\,2/3}-0{,}5V_r} \tag{1}$$

where:

ν_{ch} - 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),

χ - Huggins interaction parameter (for measuring conditions χ = 0.39),

– deformation measuring (ν_c - total cross-link density) by means of the Mooney-Rivlin equation (2), utilizing relation (3), too:

$$\frac{\sigma}{2\left(\alpha-\alpha^{-2}\right)} = C_1 + \frac{C_2}{\alpha} \tag{2}$$

σ - tension, α - relatively extension

C_1, C_2 – constants

$$\nu_c = 2C1 / RT \tag{3}$$

R = 8.314 J/K mol, measuring temperature T = 293.15 K

The measurements were carried out in the *INSPEKT* desk 5kN apparatus (*Hegewald & Peschke*, Nossen, Germany) up to 100% deformation, deformation velocity of 10 mm/min.

Results and discussion

Influence of ferrites content on curing process of rubber compounds

The influence of ferrites content on curing of the BR compounds was assessed on the base of their curing characteristics, e.g. the scorch time t_{S1}, optimum cure time t_{C90} and the difference between the values of maximum and minimum torque ΔM. They were determined from corresponding curing isotherms measured at 150°C. As seen in Figure 4, the presence of ferromagnetic fillers leads to decrease of the optimum cure time t_{C90}. The BR compounds filled with FD0 ferrite required the shortest time essential for their vulcanization. In comparison with unfilled sample used as reference, the addition of FD0 caused a reduction of t_{C90} from about 28 to approximately 15 minutes (for the composite with 100phr of ferrite). The t_{C90} of BR compounds filled with FD1 and FD2 also decreases with the increase in magnetic fillers loading, but t_{C90} of rubber compounds filled with FD1 ferrite seems to be much longer than the optimum cure time of the other two types of rubber compounds.

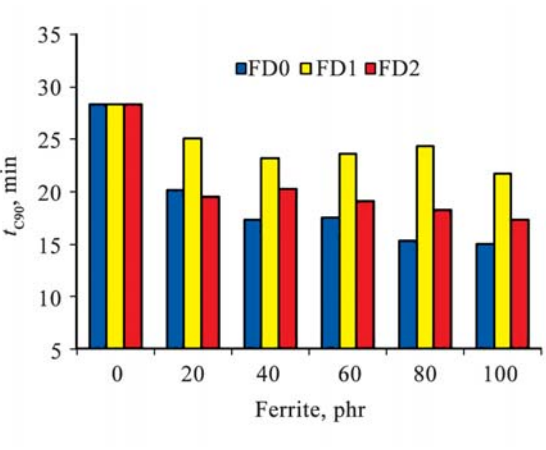

FIGURE 4 – Influence of ferrites content on optimum cure time t_{C90} of rubber compounds

The scorch time t_{S1} shows a similar decreasing tendency with the increasing content of applied ferrites as t_{C90} (Figure 5). The lowest values of t_{S1} were recorded also in case of compounds filled with FD0 filler. Figure 6 shows the extension of ΔM values with increasing of ferrites loading in rubber compounds, but the type of used fillers has no significant influence on ΔM values.

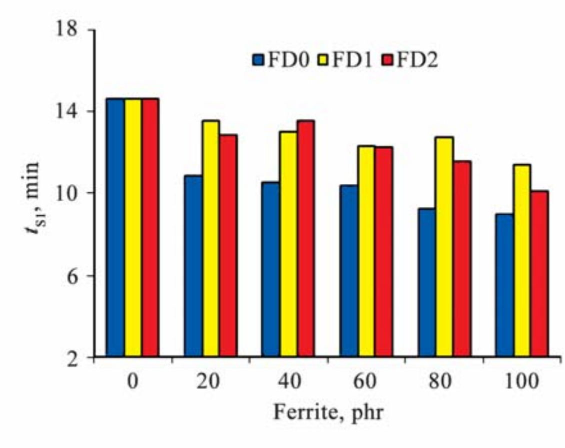

FIGURE 5 – Influence of ferrites content on scorch time t_{S1} of rubber compounds

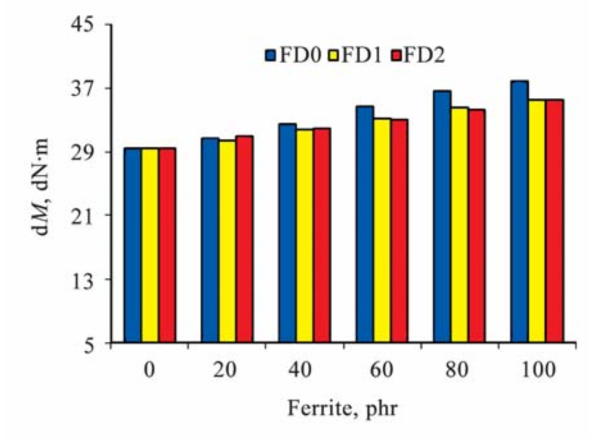

FIGURE 6 – Influence of ferrites content on ΔM values of rubber compounds

Influence of ferrites content on elastomeric composites properties

This work was also focused on the study of the influence of ferrites on physical and mechanical properties of cured BR compounds. Despite of the relatively small values of the physical and mechanical properties, from the experimental data it is obvious that the presence of ferrites in elastomeric matrix leads to enhancement of evaluated characteristics. Figure 7 shows the non-linear increase of the tensile strength at break as a function of ferrites loading in vulcanizates based on butadiene rubber. The increase of the tensile strength value of vulcanizate filled with maximum FD0 ferrite content represents more than 105% in comparison with tensile strength value of ferrite free vulcanizate. The similar increase of tensile strength values with increasing of magnetic fillers content could be seen also in case of vulcanizates filled with ferrites FD1 and FD2, namely 75% in case of vulcanizate with maximum FD1 content and 72% in case of vulcanizate with maximum FD2 content compared to the reference unfilled sample.

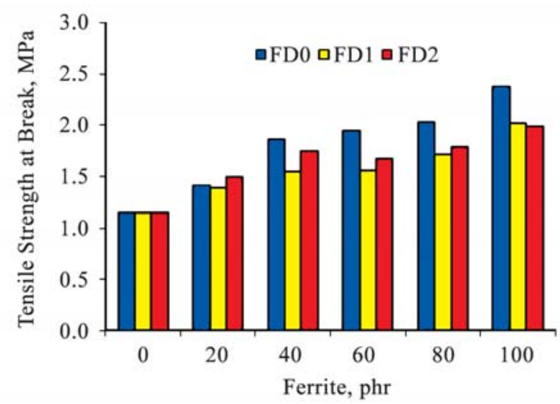

FIGURE 7 – Influence of ferrites content on tensile strength at break of vulcanizates

The increasing tendency of magnetic fillers content was detected also in case of elongation at break (Figure 8). The highest values of elongation at break were achieved by using ferrite FD2. At maximum ferrite loading nearly 150% increase of observed property in comparison to the ferrite free vulcanizate has been observed. The positive effect of magnetic filler on the elongation at break values was recorded in case of BR vulcanizates filled with FD0 and FD1 ferrites as well. The hardness of elastomeric composites seems also to have an increasing tendency with increasing of magnetic fillers content (Figure 9). The type of applied ferrite has no significance influence on the hardness of samples with lower ferrites content, in case of samples with higher ferrites content (60 phr and more), the best values of observed property were achieved by using ferrite modification FD0.

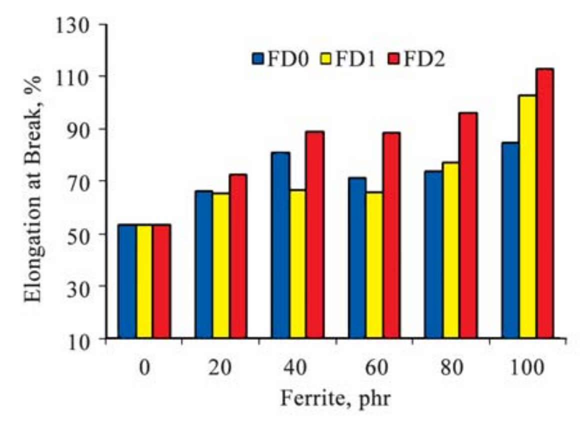

FIGURE 8 – Influence of ferrites content on elongation at break of vulcanizates

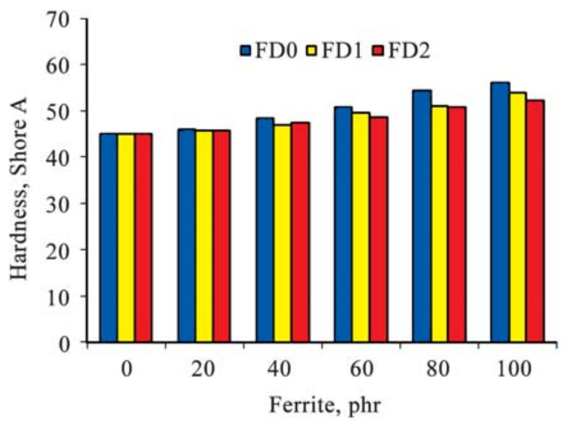

FIGURE 9 – Influence of ferrites content on hardness of vulcanizates

The values of modules could not be measured, because the vulcanizates were ruptured at deformation of less than 100%. From the above mentioned changes it becomes obvious that ferrites exhibit only low reinforcing effect on cross-linked elastomeric materials. The reinforcing effect was not significantly observed even in case of vulcanizates with maximum ferrites loading.

From the practical point of view it is interesting to know whether ferrite capability of magnetization retains magnetic properties of prepared materials after removal of magnetic field. Therefore, this effect was investigated. The magnetic properties of both types of vulcanizates were evaluated at laboratory temperature and maximum coercivity of H_m = 750 kA/m. The experimentally measured values of maximum magnetic flux Φ_m and remanent magnetic flux Φ_r increase markedly with the increasing amount of ferrites in vulcanizates.

The maximum magnetic polarization J_m and the remanent magnetic polarization J_r were computed on the basis of experimentally determined Φ_m and Φ_r values using equations (4) and (5):

$$J_m = \frac{\Phi_m}{S} \cdot D \qquad (4)$$

$$J_r = \frac{\Phi_r}{S} \cdot D \qquad (5)$$

S - surface area of the sample, D - constant of the used apparatus TVM-1 (D = 16.4)

The remanent magnetic induction B_r was calculated utilizing equation (6):

$$B_r = \mu_0 \cdot H + J_r => B_r = J_r \qquad (6)$$

μ_o - vacuum permeability

H - intensity of magnetic field (H = 0 kA/m)

From Figures 10 and 11 it becomes evident that the maximum magnetic polarization J_m as well as the remanent magnetic induction B_r exhibit significant increasing tendency with increasing of ferrites content in vulcanizates. The highest increase of the most important magnetic characteristics, the remanent magnetic induction, was obtained in case of vulcanizates filled with FD0 filler. The difference between values B_r of samples with 20 and 100 phr of FD0 ferrite was more than 380%. The lowest values of B_r were observed in case of vulcanizates filled with FD2 ferrite; despite that about 326% increase of B_r of maximum FD2 filled vulcanizate was detected compared to B_r value of the least magnetic active sample (vulcanizate with 20 phr of ferrite).

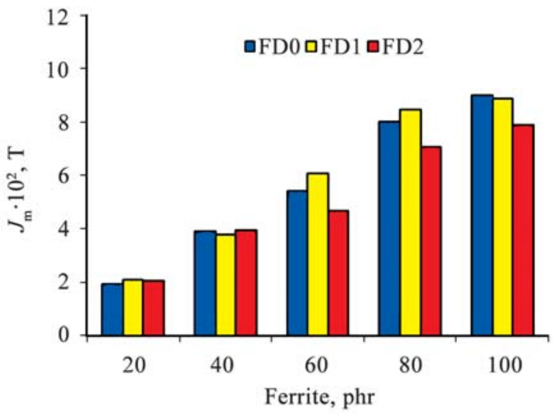

FIGURE 10 – Influence of ferrites content on maximum magnetic polarization J_m of vulcanizates

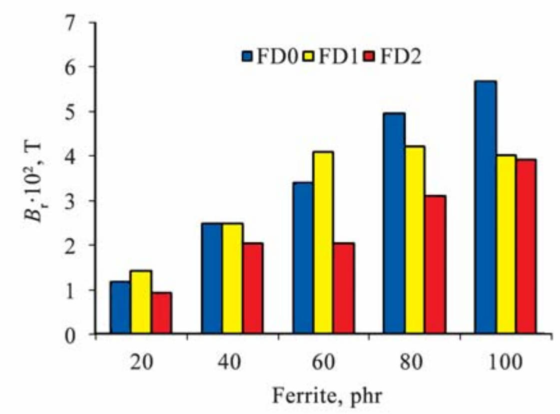

FIGURE 11 – Influence of ferrites content on remanent magnetic induction B_r of vulcanizates

Influence of ferrites content on cross-link density of vulcanizates

Simultaneously, among the study of properties of ferrites filled elastomeric composites, the cross-link density of vulcanizates was analyzed, too. The total cross-link density ν_c as well as the chemical cross-link density ν_{ch} was determined. The determination of both densities allowed the evaluation of the physical cross-links ν_f of prepared samples as well. Polymer-polymer physical interactions, polymer-filler physical interactions, and also various intramolecular and intermolecular entanglements are involved in the physical cross-link density.

The results of measurements showed that the total cross-link density ν_c of FD1 and FD2 ferrites filled vulcanizates seem to be independent of the magnetic fillers content (Figure 12). The ν_c of FD0 ferrite filled system was found to increase in the presence of 20 and 40 phr of filler, but with the next increasing of ferrite loading, ν_c values fluctuate in the low range, almost independently of the amount of magnetic filler.

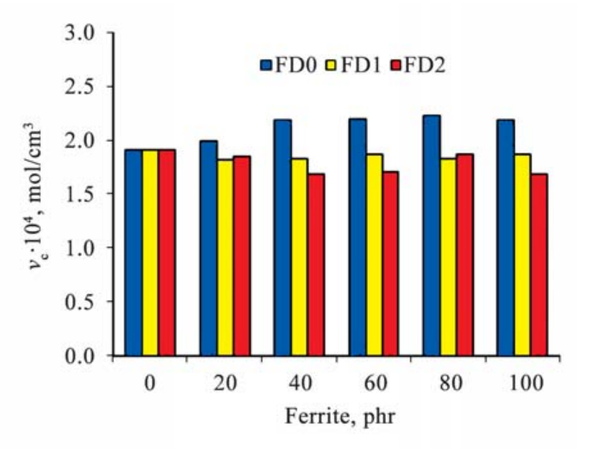

FIGURE 12 – Influence of ferrites content on total cross-link density ν_c of vulcanizates

Figure 13 shows the influence of magnetic fillers content on chemical cross-link density ν_{ch}. It is possible to see the decline of ν_{ch} values with the increase in FD1 and FD2 ferrites content, but in both cases the decrease of ν_{ch} in consequence of ferrites loading increase from 0 to 100 phr does not exceed 20%. On the other hand, the change in ν_{ch} of FD0 filled vulcanizates is different; at lower magnetic filler content there are practically no changes, at higher FD0 loading (60 phr and more) slight increase of ν_{ch} was observed.

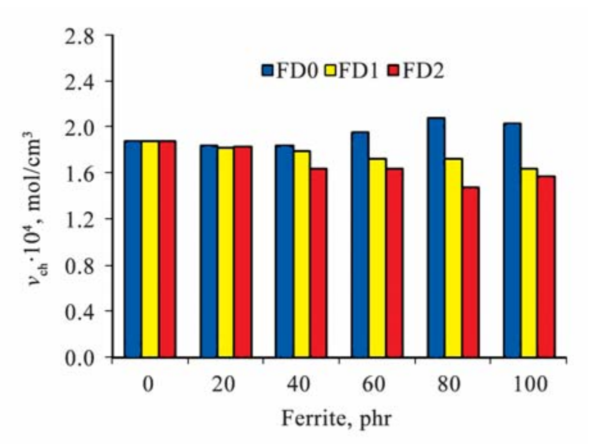

FIGURE 13 – Influence of ferrites content on chemical cross-link density ν_{ch} of vulcanizates

The physical cross-link density ν_f, which represents the difference between the total and the chemical cross-link density (ν_c -ν_{ch}), is much lower than ν_{ch} (Figure 14). The ν_f values tend to have a slight increase with increasing of magnetic fillers FD1 and FD2 content, the physical cross-link density of FD0 filled vulcanizates reaches a slight maximum at medium ferrite contents (40-60 phr).

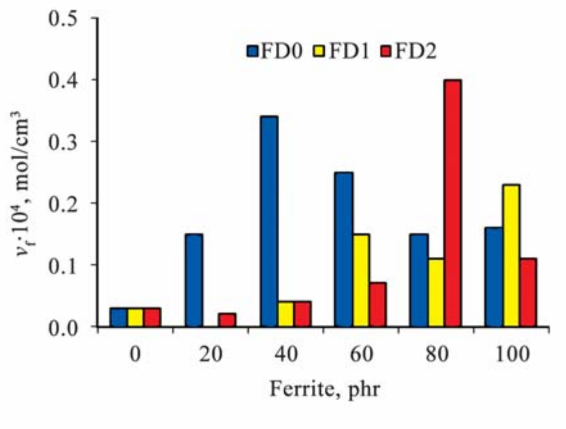

FIGURE 14 – Influence of ferrites content on physical cross-link density ν_f of vulcanizates

In order to investigate the interaction between polymer matrix and magnetic fillers, the content of rubber bound to filler was evaluated. A simple experiment was carried out. Samples of elastomeric composites with different content of ferrites were dissolved in xylene for the 48 hours. After that, xylene together with dissolved rubber was extracted from the equipment. A part of rubber which was not dissolved in the applied solvent represents the part of elastomeric matrix bound to ferrite filler. In this way it was possible to determine the content of rubber bound to filler. From Figure 15 it becomes apparent, that the highest content of rubber bound to filler exhibits composites filled with ferrite modification FD1. At maximum FD1 ferrite content less than 6% of rubber bound to filler could be observed.

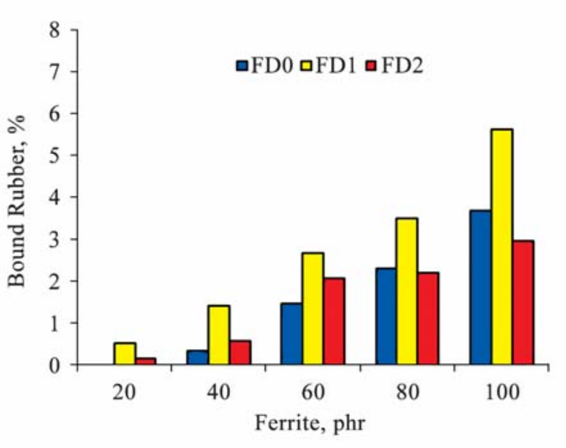

FIGURE 15 – The content of rubber bound to ferrite fillers

Conclusion

The work has been aimed at the study of magnetic fillers influence on curing, properties and cross-link density of model compounds based on butadiene rubber. Three modifications of the same type of strontium ferrite $SrFe_{12}O_{19}$, type FD 8/24 were used in order to prepare elastomeric magnetic composites. The applied ferrites differed in particle size distribution and other physical characteristics. The results of measurements showed, that the presence of ferrites in rubber compounds leads to acceleration of sulfur curing process. The BR compounds filled with FD0 ferrite required the shortest time essential for their vulcanization. The physical-mechanical properties, the tensile strength at break, the elongation at break and the hardness, exhibit non-linear increasing tendency with increasing of ferrites content in vulcanizates. The best values of the tensile strength at break seem to be achieved by using the ferrite FD0, and the highest values of the elongation at break in case of vulcanizates filled with FD2 ferrite were observed. The values of modules could not be measured because the vulcanizates were ruptured at deformation less than 100%. The magnetic characteristics show significant increasing tendency with increase in the ferrites loading. In the network structure of vulcanizates chemical cross-links dominate over physical ones. Their structure depends slightly on the magnetic fillers loading. The best values of evaluated cross-link densities seem to be achieved by using the ferrite modification FD0. The differences among the properties of prepared elastomeric composites caused by using the applied ferrites modifications seem not to be very significant. On the basis of the obtained results one can see that the interaction between the polymer matrix and the ferrite particles is the highest in case of composites filled with FD1 filler. The results achieved by the study point out the possibilities of preparation of elastomeric magnetic composites by the processes generally used in rubber technologies. The prepared materials have suitable magnetic and elastic properties.

Acknowledgements

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Davor UJLAKI

Promjene u vodstvu *DIOKI grupe*

Na sjednici *Nadzornoga odbora* tvrtke *DIOKI grupa* održanoj 7. ožujka 2011. imenovana je nova predsjednica *Uprave* Vidonija Miletić Plukavec, od 17. veljače 2011. i članica *Uprave* te komercijalna direktorica tvrtke *DIOKI* d.d. Na tom je mjestu naslijedila Vatroslava Sablića koji je sporazumno prestao obnašati dotadašnju dužnost.

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Kako je potražnja za sintetskim kaučukom povezana sa stanjem na automobilskom tržištu, i porast te potražnje ovisi o općem oporavku gospodarstva. Smanjena potražnja za automobilima, ali i usporena zamjena isluženih automobilskih pneumatika novima, dovela je do smanjenja potražnje za ovim materijalom. Prvi znakovi oporavka dolaze s kineskoga i indijskoga tržišta, koja prije svega još zadovoljavaju rastuću domaću potražnju i za pneumaticima i za novim automobilima. Očekuje se da će se pozitivni trendovi proširiti na Rusiju, Srednju i Južnu Ameriku te srednjoeuropske i istočnoeuropske zemlje. Stoga se očekuje da će potražnja za sintetskim kaučukom do 2015. narasti na 13,4 milijuna tona.

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