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

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

Utjecaj stroncičeva ferita na umreživanje i svojstva kompozita butadienskoga kaučuka

Sažetak

Cilj rada je pripremiti elastomerne magnetne kompozite na temelju visokoelastične polimerne matrice (1,4-cis butadiene kaučuk). Tri modifikacije istog tipa stroncičeva ferita SrFe$_{12}$O$_{19}$, tip FD8/24, bili su primjenjeni kao magnetni punila. Primijenjeni feriti razlikovali su se po raspoloživoj veličini čestica te drugim strukturnim i magnetnim svojstvima. Rad obrađuje pripremu spojeva kaučuka za izrada elastomernih magnetnih kompozita i daje ocjenu utjecaja magnetnih punila na svojstva umreživanja, fizičko-mehanička i magnetna svojstva pripremljenih kompozita. Ishćitanje 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. 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.4-8 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., Svetlá 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 ferite 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 ferite were reduced. For the purpose of further reduction of particles size, ferite 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 ferite particles were determined by application of mercury porosimetry in POROSIMETER 2000 instrument (Carlo Erba, Milan, Italy). Particle size distribution of ferite 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.
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

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>FD0</th>
<th>FD1</th>
<th>FD2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>4.13</td>
<td>4.73</td>
<td>4.77</td>
</tr>
<tr>
<td>Specific surface area, m²/g</td>
<td>3.30</td>
<td>4.06</td>
<td>4.46</td>
</tr>
<tr>
<td>Total porosity, %</td>
<td>54.94</td>
<td>55.62</td>
<td>49.91</td>
</tr>
<tr>
<td>Coercivity, kA/m</td>
<td>116</td>
<td>117</td>
<td>108</td>
</tr>
<tr>
<td>Remanent magnetic induction, T</td>
<td>0.116</td>
<td>0.170</td>
<td>0.183</td>
</tr>
</tbody>
</table>

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 (Vízort, Prague, the Czech Republic) at room temperature.

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

- equilibrium swelling in xylene ($v_{ch}$ - chemical cross-link density), using the Krause modified Flory-Rehner equation (1) for filled vulcanizates:

$$v_{ch} = \frac{V_{r_0}}{V_5}\ln(1 - V_c) + V_c + \chi V_c^2$$

where:

- $v_{ch}$ - cross-link density (mol/cm³),
- $V_{r_0}$ - volume fraction of rubber in equilibrium swelling sample of vulcanizate in absence of fillers,
- $V_c$ - volume fraction of rubber in equilibrium swelling sample of filled vulcanizate,
- $V_5$ - molar volume of solvent (for xylene = 123.45 cm³/mol),
- $\chi$ - Huggins interaction parameter (for measuring conditions $\chi = 0.39$),

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

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

where:

- $\sigma$ - tension,
- $\alpha$ - relatively extension
- $C_1$, $C_2$ - constants

$$v_c = 2C_1 / RT$$

$R = 8.314$ 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 $t_S$, optimum cure time $t_C$, and the difference between the values of maximum and minimum torque $\Delta M$. 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 $t_C$. 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 $t_C$ from about 28 to approximately 15 minutes (for the composite with 100phr of ferrite). The $t_C$ of BR compounds filled with FD1 and FD2 also decreases with the increase in magnetic fillers loading, but $t_C$ 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.

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.
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.

\[ J_s = \frac{\Phi_s}{S} \cdot D \]  \hspace{1cm} (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):

\[ B_r = \mu_0 \cdot H + J_r = B_s = J_r \]  \hspace{1cm} (6)

\( \mu_0 \) - vacuum permeability

\( H \) - intensity of magnetic field \((H = 0 \text{ kA/m})\)

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).

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 \( H_c = 750 \text{ kA/m} \).

The experimentally measured values of maximum magnetic flux \( \Phi_m \) and remanent magnetic flux \( \Phi_r \) 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 \( \Phi_m \) and \( \Phi_r \) values using equations (4) and (5):

\[ J_m = \frac{\Phi_m}{S} \cdot D \]  \hspace{1cm} (4)

\[ J_r = \frac{\Phi_r}{S} \cdot D \]  \hspace{1cm} (5)

FIGURE 9 – Influence of ferrites content on hardness of vulcanizates
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 \( \nu_c \) as well as the chemical cross-link density \( \nu_{ch} \) was determined. The determination of both densities allowed the evaluation of the physical cross-links \( \nu_f \) 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 \( \nu_c \) of FD1 and FD2 ferrites filled vulcanizates seem to be independent of the magnetic fillers content (Figure 12). The \( \nu_c \) 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, \( \nu_c \) values fluctuate in the low range, almost independently of the amount of magnetic filler.

The physical cross-link density \( \nu_f \), which represents the difference between the total and the chemical cross-link density \( \nu_c - \nu_{ch} \), is much lower than \( \nu_{ch} \) (Figure 14). The \( \nu_f \) 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).

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.

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 $\text{SrFe}_5\text{O}_{19}$, 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 hardiness, 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**

*This work was supported by grant agency VEGA, Project No. 1.0575/09.*

**REFERENCES**


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**Ekstrudiranje troslojno krijevnog filma u Muraplastu**

U Muraplastu je puštena u pogon linija za ekstrudiranje troslojno krijevnog PE-LD filma. Linija njeomačkog proizvođača Windmüller & Hólscher kapaciteta je proizvodnje do 300 kg/h. Linija je opremljena najmodernijom opremom poput automatskog sustava hlađenja glave s pomićnim mjernim debljine i unutrašnjih vrednosti; esthetickim načinom načinom zraka, temperatura; kondicioniranja; gravimetrijskim dozmernim mjerenjem debljine i unutrašnjih vrednosti. Specifičnost linije nju je posebno hlađena valjci za FFS film, čime se postižu optimalna mehanička svojstva potrebna za uspješno uporabni proizvod.

Davor UJLAKI

**Promjene u vodstvu DIOKI grupa**


**Rast tržišta sintetskog kaučuka**

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