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Elastomeric magnetic composites — physical properties and network structure

Summary — The two types of magnetic elastomeric composites were prepared by incorporation of ferrite alone as well as ferrite in combinations with carbon black in rubber matrix based on natural rubber. The influence of applied fillers and thermo-oxidative ageing on basic physical and magnetic properties of elastomeric composites was studied. Together with the study of properties, the crosslink density and sulfur crosslink structure of prepared vulcanizates were analyzed. The results of the study showed that ferrite alone as well as in combinations with carbon black affects the evaluated properties in various ways. The presence of magnetic filler leads to an increase value of stress at 300 % elongation (S_{e300}) and hardness of composites, the elongation at break by contrast decreases. The values of tensile strength practically do not change in the presence of applied filler. The values of magnetic properties of vulcanizates significantly increase with increasing of ferrite content. In generally one can say that prepared vulcanizates have suitable magnetic and elastic properties.
Keywords: elastomeric magnetic composites, strontium ferrite, physical properties, magnetic properties, thermo-oxidative ageing.

MAGNETYCZNE KOMPOZYTY ELASTOMEROWE — WŁAŚCIWOŚCI FIZYCZNE I STRUKTURA SIECI

Streszczenie — Wytworzono dwa rodzaje magnetycznych kompozytów elastomerowych, które otrzymano przez wprowadzenie ferrytu lub ferrytu w połączeniu z sadzą do matrycy z kauczuku naturalnego. Zbadano wpływ użytych napełniaczy i termooksydacyjnego starzenia na podstawowe właściwości fizyczne i magnetyczne kompozytów elastomerowych. Wraz z badaniem właściwości analizowano gęstości sieciowania i struktury wiązań poprzecznych w przygotowanych wulkanizatach. Wyniki badań wykazały, że dodatek samego ferrytu, jak i w połączeniu z sadzą wpływa na badane właściwości w różny sposób. Obecność wypełniacza magnetycznego prowadzi do zwiększenia wartości naprężenia przy wydłużeniu 300 % (S_{e300}) i twardości kompozytów, natomiast wydłużenie przy zerwaniu zmniejsza się. W przypadku wytrzymałości na rozciąganie praktycznie nie obserwuje się jego zmian pod wpływem dodanego wypełniacza. Wartości właściwości magnetycznych wulkanizatów znacznie zwiększają się wraz ze wzrostem zawartości ferrytu. Podsumowując można stwierdzić, że otrzymane wulkanizaty mają dobre właściwości magnetyczne i mechaniczne.
Słowa kluczowe: magnetyczne kompozyty elastomerowe, żelazian(III) strontu, właściwości fizyczne, właściwości magnetyczne, starzenie termooksydacyjne.

The preparation of elastomeric magnetic composites is possible by incorporation of magnetic fillers in polymer matrix. The final properties of composites are strongly dependent on characteristics of polymer matrix. However, by integration of magnetic materials new properties and technological abilities can be provided.

Ferrites represent well established family of magnetic materials. Metal ferrites of general formula $MFe_{12}O_{19}$ (M is divalent cation such as Ba, Sr, *etc.*) belong to widely used magnetic materials. They have domain structure, which terminates over the Curie temperature. Due to high values of magneto-crystalline anisotropy and saturation magnetization these materials can be widely applied as permanent magnets [1, 2]. In term of technological applications one may distinguish two main types of ferrites, hard ferrites and soft ferrites. Magnetic soft materials with coercivity $H_c < 1$ kA/m have narrow hystere-

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sis loop and low value of remanent magnetic induction (B_r). Magnetic hard materials have wide hysteresis loop and value of coercivity H_c > 2.5 kA/m. They also exhibit high value of B_r and high value of maximum energy product [$(BH)_{max}$]. Ferrites may occur in several crystallographic modifications, but in term of possible applications ferrites with hexagonal structure are of the biggest interest [3]. Ferrites with hexagonal structure become very important materials as media for magnetic and magnetic-optical recording, as well as components for reproducers, engines and generators in automobile industry. Low price and very good chemical stability together with suitable magnetic characteristics include ferrites in the most important magnetic materials, which cannot be easily replaced. Ba and Sr ferrites are the most common applied magnetic powdery fillers.

Nowadays it is well known, that by incorporation of magnetic ferrites into various polymer matrices it is possible to prepare polymer magnets, or ferrite polymer magnets [4—8]. The results of these works showed also the possibility of preparation of magnetic composites with applicable properties. The advantages of elastomeric magnetic composites are, 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 find their application in dc-motors, motor parts, memo holders, electromagnetic absorbers, intelligent tyres, sensors of magnetic fields, in microwave and radar technology, and in many other technological applications.

The focus of the work was the study of influence of ferrite content and thermo-oxidative ageing on basic physical and magnetic properties of cured natural rubber model compounds and on capability of NR composites to retain their magnetization and magnetic properties after ageing.

EXPERIMENTAL

Materials

In this work following materials were used:

— natural rubber (NR) under the trade name SMR 20 (Mardec, Malaysia),

— sulfur (Siarkopol, Poland),

— zinc oxide (SlovZink, Slovak Republic),

— Stearin 2 which is a mixture of saturated fatty acids, mainly stearic and palmitoleic acid (Setuza, Czech Republic),

— *N*-cyclohexyl-2-benzothiazole sulfenamide under the trade name Sulfenax (CBS/MG, Duslo, Slovakia),

— strontium ferrite FD 8/24 ($SrFe_{12}O_{19}$, Magnety, Czech Republic),

— carbon black under the trade name Sterling V, type N-660 (CABOT Corporation),

— xylene (Lachema, Czech Republic),

— *n*-hexane-1-thiol (Fluka Chemie AG CH-947, Germany),

— *n*-propane-2-thiol (Merck, Germany),

— *n*-heptane (Merck, Germany),

— petroleum ether (Mikrochem, Slovak Republic),

— piperidine (Merck, USA).

Preparation of rubber compounds

In this work, elastomeric magnetic composites were prepared by incorporation of ferrite alone (F) as well as ferrite in combinations with carbon black (CB) in the rubber compounds based on natural rubber (NR). A standard sulfur-based vulcanization system (sulfur — 2 phr, CBS/MG — 1 phr, ZnO — 5 phr, stearin — 1 phr) was used. In the first type of composites, filled only with ferrite (type A), the content of magnetic filler changed in range from 0 to 100 phr. Anisotropic strontium hexaferrite FD 8/24 was prepared by wet milling. It is a product with additional polyvinyl alcohol, which covers the surface of ferrite particles. The amount of polyvinyl alcohol ranged for about 3—3.5 %. Detailed characterization of applied ferrite is presented in Table 1. Elastomeric composites, specified as type B, were filled with combinations of ferrite and carbon black. The total content of both fillers was kept constant (60 phr), only the weight fraction of ferrite in combination of both fillers [$w_f = m_F/(m_F + m_{CB})$] changed.

T a b l e 1. Strontium ferrite characteristics

Property	Values
Density	4.13 g/cm^3
Specific surface area	3.30 m^2/g
Total porosity	54.94 %
Total volume of pores	0.264 cm^3/g
Coercivity	116 kA/m
Remanent magnetic induction	0.116 T
Maximum magnetic polarization	0.205 T

The rubber compounds were prepared in the laboratory mixer FARREL BR 1600 in two mixing steps. In the first step the rubber and the fillers were compounded (at 140 °C for 6 minutes), in the second step (at 90 °C for 1 minute) curing system was added. The compounds were cured at 150 °C for the optimum cure time (t_{C90}) by using the hydraulic press FONTUNE.

Methods of testing

Physical properties of the prepared vulcanizates were measured in accordance with the valid technical standards, on the double side blade specimens (width 6.4 mm, length 10 cm, thickness 2 mm).

Room temperature magnetic measurement were carried out by using TVM-1 magnetometer at maximum coercivity of H_m = 750 kA/m. The basic principle of measurement is induction method of scanning of scattering magnetic flux Φ induced by magnetic vibrating sample. Magnetic field is generated by means of two cores of Weiss electromagnet at a minimum distance of poles adapters equals to 7.5 mm. The specimens were of prism shape with dimensions 8 × 4 × 4 mm.

For ageing test the Geer method was used. The tests were carried out in air atmosphere at 70 °C, exposure time was equal to 72 or 168 h, respectively.

Two different methods were used in order to determine crosslink density of vulcanized samples. In the first method the chemical crosslink density (ν_{ch}) was determined based on equilibrium swelling in xylene. The Flory-Rehner equation modified by Krause for filled vulcanizates [9] was used:

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

where: *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 V_S = 123.45 cm^3/mol), χ — Huggins interaction parameter (for measuring conditions χ = 0.4106).*

In the second method based on a deformation measurements [the total crosslink density (ν_c)] was calculated by means of the Mooney-Rivlin equation (2) [10]:

$$\nu_c = 2C_1 / RT \quad (2)$$

$$\frac{\sigma}{2(\alpha-\alpha^{-2})} = C_1 + \frac{C_2}{\alpha} \quad (3)$$

where: $R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$, $T = 293.15$ K, σ *— tension,* α *— relatively extension, C_1, C_2 — constants.*

The measurements were carried out using the INSPEKT desk 5 kN apparatus (Metrotest), up to 100 % deformation with deformation velocity of 10 mm/min.

The crosslink structure was investigated using the thiol-amine method in argon atmosphere, at laboratory temperature for 2 or 48 h, respectively [11—13].

RESULTS AND DISCUSSION

Influence of ferrite content and ageing on properties of elastomeric composites

Composites were prepared based on natural rubber SMR 20 type. No antioxidant and antiozonants were added, but SMR 20 contained some amounts of natural antiageing substances. Therefore, soft thermal conditions for ageing were chosen, namely 70 °C for 72 or 168 hours in air, respectively.

Based upon experimental data it was concluded that ferrite applied alone as well as its combinations with carbon black influences evaluated properties of prepared composites in various ways. The results of study of physical properties of vulcanizates A (only with ferrite) showed that ferrite present in rubber compounds affects particularly values of stress at 300 % elongation (S_{e300}). A significant increase of S_{e300} with increasing content of ferrite filler is observed in Figure 1. The increase of S_{e300} value of sample with maximum ferrite loading represents more than 105 % of the corresponding S_{e300} value of reference ferrite free sample. After exposure of test samples to the conditions of thermo-oxidative ageing the values of S_{e300} rised in depending on the length of exposure time. The specific values of S_{e300} after 72 hours ageing increased in the range from 6 to 27 % in comparison with corresponding S_{e300} values of vulcanizates before thermo-oxidative degradation. The extension of ageing to 168 hours led to the next increase of the S_{e300} values.

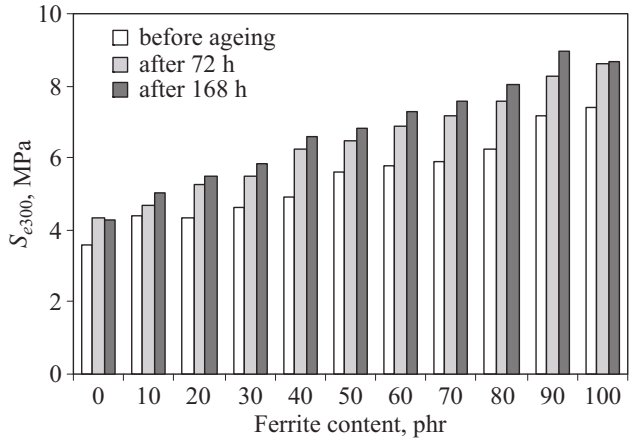

Fig. 1. Influence of ferrite content and ageing time on stress at 300 % elongation (S_{e300}) of vulcanizates A (filled only with ferrite)

The hardness of composites was also found to increase with increasing content of magnetic filler (from 34 °Sh A for the reference unfilled sample up to 43 °Sh A for the sample with maximum ferrite content). The reason

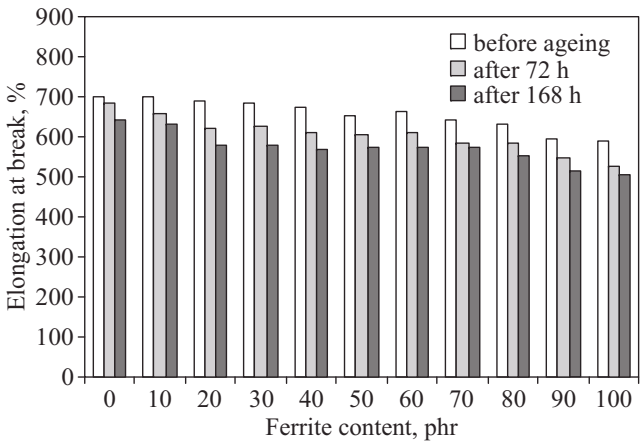

Fig. 2. Influence of ferrite content and ageing time on elongation at break of vulcanizates A (filled only with ferrite)

for the increase of hardness of composite is that the hardness of ferrite particles is higher than that of natural rubber.

On the other hand the elongation at break shows decreasing tendency with increasing amount of ferrite. The variation of elongation as a consequence of ferrite loading and ageing period is shown in Figure 2. At maximum ferrite loading 16 % decrease of observed property compared to unfilled vulcanizate was spotted. During elongation rearrangement or orientation occurs to form crystallites, and this stress-induced crystallization gives natural rubber high elongation. This rearrangement or orientation of rubber can be inhibited in the presence of applied magnetic particles, and so the elongation at break decreases with increase in loadings [6]. The next decline of elongation at break values was recorded after thermo-oxidative degradation.

Despite the fact, the dependence of the evaluated characteristics on magnetic filler content is noticeable, the tensile strength at break changes slightly what is shown in Figure 3. The tensile strength first increases at initial loadings up to 10 phr of ferrite. Thereafter, with increasing content of ferrite, its values fluctuate in the low range,

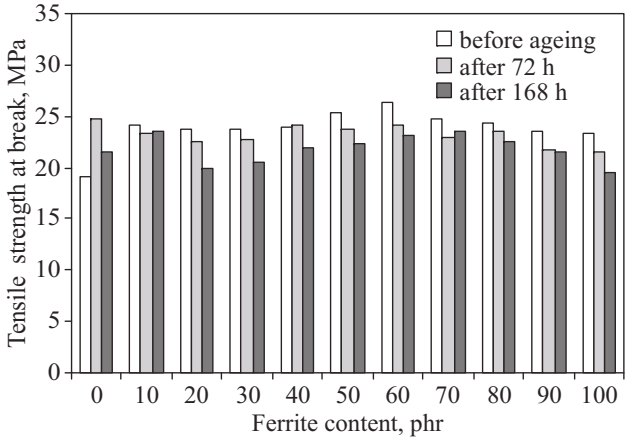

Fig. 3. Influence of ferrite content and ageing time on tensile strength at break of vulcanizates A (filled only with ferrite)

almost independently on the amount of magnetic filler. As a result of thermo-oxidative ageing the values of tensile strength declined (except reference sample without ferrite). In most cases the extension of ageing to 168 hours is connected with stronger deterioration in this physical property. The decrease of tensile strength after thermo-oxidative degradation did not exceed 17 % of equivalent tensile strength values of original non-ageing vulcanizates.

From the above mentioned changes it can be concluded that ferrite exhibits only low reinforcement effect on crosslinked elastomeric materials as it was also described in the work [14] for elastomeric composites based on natural and butadiene rubber filled with different strontium ferrites. Reinforcement effect was insignificantly observed even in case of vulcanizates with maximum ferrite loading.

This is probably caused by very low compatibility and a weak mutual interactions between ferrite and polymer matrix with many voids existing between two phases. The inner voids lead to stress concentration within the sample, which may result in rupture at a low stress [15]. The poor bonding forces on phase interface, weak adhesion between magnetic filler and elastomeric matrix and increasing internal defects are the main reason why ferrite does not exhibit the character of reinforcing filler in rubber materials.

The influence of fillers combinations (ferrite and carbon black) on physical properties of vulcanizates B is presented in Figures 4—6. As it can be seen in Figure 4 the S_{e300} was found to decrease with increasing of ferrite loading in fillers combinations. More than 250 % decline of S_{e300} was recorded for vulcanizate filled with ferrite only in comparison to S_{e300} value of vulcanizate filled

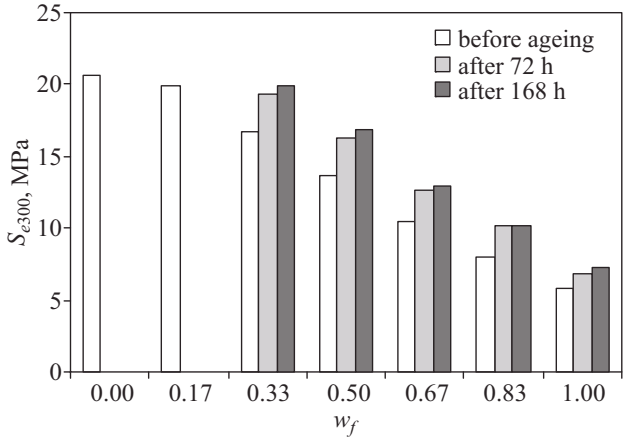

Fig. 4. Influence of ferrite weight fraction (w_f) and ageing time on S_{e300} of vulcanizates B (filled with combinations of ferrite and carbon black)

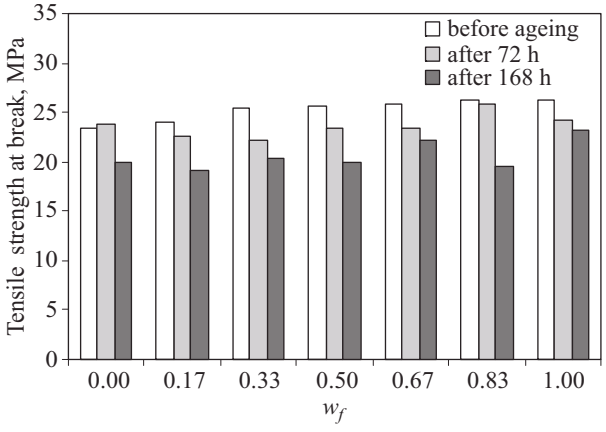

Fig. 5. Influence of ferrite weight fraction w_f and ageing time on tensile strength at break of vulcanizates B (filled with combinations of ferrite and carbon black)

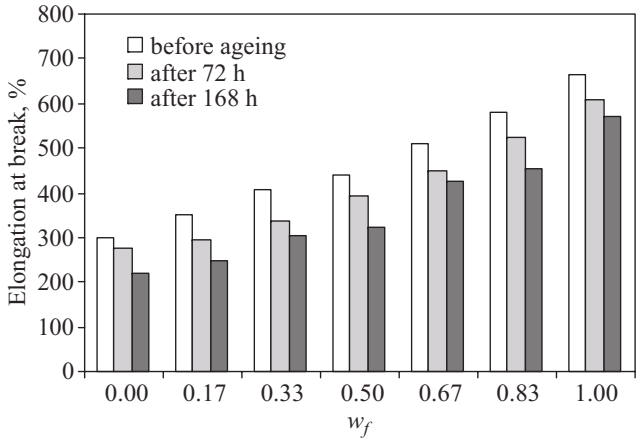

Fig. 6. Influence of ferrite weight fraction w_f and ageing time on elongation at break of vulcanizates B (filled with combinations of ferrite and carbon black)

with carbon black only. The thermo-oxidative ageing has positive effect on the values of observed stress at 300 % elongation. The values of S_{e300} slightly increased depending on ageing period. The S_{e300} of samples with ferrite weight fraction 0 and 0.17 was not possible to measure after ageing, because the vulcanizates were ruptured at deformation less than 300 %.

The linear decreasing tendency with increasing content of ferrite in fillers combinations was observed also in case of hardness (59 °Sh A for the composite filled only with carbon black and 39 °Sh A for the composite filled only with ferrite). This is probably a consequence of decreasing of fillers volume fraction in rubber compounds, because ferrite has essentially higher density in comparison with carbon black. The increasing content of magnetic filler in combinations with carbon black at the same mass content of both fillers led to decrease of fillers volume fraction.

The tensile strength of vulcanizates gently increased in whole examined ferrite concentration range as it is shown in Figure 5. When test samples were exposed to the thermo-oxidative ageing the decrease of the observed property was detected. There was recorded 1—12 % derease of tensile strength values in case of 72 h ageing and 12—25 % decrease of tensile strength values in case of 168 h ageing in comparison with the corresponding values of tensile strength before thermo-oxidative degradation.

From Figure 6 nonlinear increase of elongation at break with increasing content of magnetic filler in fillers combinations can be observed. After exposure of test sample to thermo-oxidative degradation, the decrease of elongation at break values in dependence of ageing period was recorded.

The different dependences of evaluated physical characteristics of composites filled with fillers combinations relate mainly to decreasing content of carbon black in fillers combinations. Carbon black plays an important role as reinforcement filler in rubber materials due to its very good compatibility and adhesion to elastomeric matrix. Carbon black is very well dispersed in polymer matrix so macrohomogeneous structure is formed. It evens out the inner stresses in rubber and lets more molecular chains effectively carry the load [15]. Due to very good interactions and adherence of macromolecular chains to the surface of carbon black particles, their mobility is restricted (the reason for decrease of elongation at break and increase of stress at 300 % elongation with increasing of carbon black in fillers combinations).

Based upon the results obtained by the study of influence of thermo-oxidative ageing, it can be stated, that this process affects the evaluated properties in various ways. But almost all evaluated properties of vulcanizates after ageing remained character of their variations depending on content of ferrite, or fillers combinations. The values of physical properties of vulcanizates after ageing are higher or lower in comparison with corresponding values of vulcanizates before thermo-oxidative degradation.

From 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 also 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) increased markedly with increasing amount of ferrite in vulcanizates A as well as in case of vulcanizates B.

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:

$$J_m = \frac{\Phi_m}{S} \cdot D \tag{4}$$

$$J_r = \frac{\Phi_r}{S} \cdot D \tag{5}$$

where: *S — surface area of the sample, D — constant of the used apparatus TVM-1 (D = 16.4).*

The maximum magnetic induction (B_m) and the remanent magnetic induction (B_r) were calculated from equations:

$$B_m = \mu_0 \cdot H_m + J_m \tag{6}$$

$$B_r = \mu_0 \cdot H + J_r \tag{7}$$

where: μ_0 *— vacuum permeability,* H_m *— maximum intensity of magnetic field (*H_m *= 750 kA/m), H — intensity of magnetic field (H = 0 kA/m hence* $B_r = J_r$*).*

The values of B_r and J_m for magnetic elastomeric composites A are shown in Table 2. The presence of ferromagnetic filler led to significant increase of both magnetic characteristics. The difference between B_r and J_m values of samples with minimum and maximum ferrite loading was approximately 760 % and 710 %, respectively. The

values of these magnetic properties were also found to increase with increasing of ferrite loading in fillers combinations in composites B what is evident from results listed in Table 3. The value of B_r increased more than 690 % and the value of J_m more than 620 % in comparison with the reference (vulcanizate B2 with 10 phr of ferrite and 50 phr of carbon black). It is very interesting, that the B_r and J_m values of vulcanizates A are higher in comparison to the corresponding values of these magnetic parameters of vulcanizates B, filled with ferrite and carbon black, with equivalent content of magnetic filler. This fact is likely connected with dispersion index of ferrite filler.

T a b l e 2. Remanent magnetic induction (B_r) and maximum magnetic polarization (J_m) of vulcanizates A before ageing and after 168 h ageing in the air at 70 °C

Compound	Ferrite content phr	$B_r \cdot 10^2$, T		$J_m \cdot 10^2$, T	
		before ageing	after 168 h	before ageing	after 168 h
A1	0	—	—	—	—
A2	10	0.82	0.68	1.40	1.26
A3	20	1.32	1.44	2.39	2.58
A4	30	2.01	2.27	3.14	4.32
A5	40	3.29	2.89	5.47	4.53
A6	50	3.48	4.17	5.96	6.61
A7	60	4.91	3.90	7.39	6.87
A8	70	4.99	4.37	8.05	8.35
A9	80	5.34	5.33	8.07	9.17
A10	90	6.25	6.36	9.99	9.94
A11	100	7.07	6.71	11.40	10.40

T a b l e 3. Remanent magnetic induction (B_r) and maximum magnetic polarization (J_m) of vulcanizates B before ageing and after 168 h ageing in the air at 70 °C

Compound	Ferrite content phr	Carbon black content phr	$B_r \cdot 10^2$, T		$J_m \cdot 10^2$, T	
			before ageing	after 168 h	before ageing	after 168 h
B1	0	60	—	—	—	—
B2	10	50	0.62	0.78	1.02	1.11
B3	20	40	1.38	1.08	2.08	1.70
B4	30	30	1.90	1.63	2.94	3.20
B5	40	20	2.40	2.44	3.91	3.80
B6	50	10	3.06	4.12	4.81	6.01
B7	60	0	4.91	3.90	7.39	6.87

From Tables 2 and 3 it also becomes evident, that the influence of thermo-oxidative ageing on the values of magnetic characteristics was insignificant in case of both types of prepared elastomeric magnetic composites. The magnetic parameters are dependent only on the amount of magnetic filler.

Influence of ferrite content and ageing on crosslink density and crosslink structure

Together, with the study of properties of elastomeric composites, the crosslink density and the sulfur crosslink structure of prepared vulcanizates were analyzed. The total crosslink density (ν_c) as well as the chemical crosslink density (ν_{ch}) were determined. The determination of both properties allowed to evaluate also the physical crosslink density (ν_f) of prepared samples. Polymer-polymer physical interactions, polymer-filler physical interactions, also various intramolecular and intermolecular entanglements are involved in physical crosslink density.

T a b l e 4. Total (ν_c), chemical (ν_{ch}) and physical (ν_f) crosslink density of vulcanizates A before ageing and after 72 h ageing in the air at 70 °C

Compound	Ferrite content phr	$\nu_c \cdot 10^4$ mol/cm^3		$\nu_{ch} \cdot 10^4$ mol/cm^3		$\nu_f \cdot 10^4$ mol/cm^3	
		before ageing	after 72 h	before ageing	after 72 h	before ageing	after 72 h
A1	0	1.36	1.51	1.33	1.50	0.03	0.01
A2	10	1.56	1.80	1.45	1.45	0.11	0.35
A3	20	1.52	1.89	1.51	1.42	0.01	0.47
A4	30	1.59	1.99	1.50	1.41	0.09	0.58
A5	40	1.60	2.18	1.45	1.49	0.15	0.69
A6	50	1.88	2.32	1.56	1.40	0.32	0.92
A7	60	1.92	2.43	1.56	1.42	0.36	1.01
A8	70	1.88	2.38	1.54	1.37	0.34	1.01
A9	80	1.96	2.63	1.57	1.37	0.39	1.26
A10	90	2.22	2.73	1.69	1.40	0.53	1.33
A11	100	2.39	2.76	1.71	1.46	0.68	1.30

The experimentally obtained values of crosslink density for vulcanizates filled only with ferrite are shown in Table 4. The results of measurements showed that the total ν_c as well as ν_{ch} of vulcanizates A slightly increased with increasing of ferrite loading. The influence of ageing on density ν_{ch} is not very clear in samples with lower ferrite content, but in samples with higher ferrite content (50 phr and more) the decrease of ν_{ch} after thermo-oxidative degradation was observed. The positive effect of ageing was observed in case of ν_c which increased after thermo-oxidative degradation. The rise of ν_c after ageing represented 15—36 % compared to equivalent values of total crosslinking density of original vulcanizates. The ν_f, which represents the difference between the total and the chemical crosslink density ($\nu_f = \nu_c - \nu_{ch}$), was much lower than ν_{ch} and increased gently with increasing of ferrite loading and after thermo-oxidative ageing as well.

In case of vulcanizates B filled with fillers combinations, vulcanizate filled with carbon black only exhibited the highest ν_c value and vulcanizate filled with ferrite only exhibited the lowest density ν_c value what is evident

T a b l e 5. Total (ν_c), chemical (ν_{ch}) and physical (ν_f) crosslink density of vulcanizates B before ageing and after 72 h ageing in the air at 70 °C

Compound	Ferrite content, phr	Carbon black content, phr	$\nu_c \cdot 10^4$, mol/cm^3		$\nu_{ch} \cdot 10^4$, mol/cm^3		$\nu_f \cdot 10^4$, mol/cm^3	
			before ageing	after 72 h	before ageing	after 72 h	before ageing	after 72 h
B1	0	60	3.61	5.19	2.81	2.47	0.80	2.72
B2	10	50	3.22	4.05	2.77	2.38	0.45	1.67
B3	20	40	3.02	3.62	2.64	2.13	0.38	1.49
B4	30	30	2.65	3.17	2.49	1.98	0.16	1.19
B5	40	20	2.38	2.58	2.36	1.79	0.02	0.79
B6	50	10	2.23	2.38	2.22	1.62	0.01	0.76
B7	60	0	1.92	2.43	1.56	1.42	0.36	1.01

from results presented in Table 5. Therefore the increase of ferrite content in fillers combinations led to consistent linear decrease of the ν_c value. As a consequence of thermo-oxidative ageing the values of ν_c increased in range from 9 % to 44 % in comparison with equivalent ν_c values of original vulcanizates, but the ν_c dependences on ferrite content in fillers combinations were remained. The increase of ferrite content in fillers combinations led also to the decrease of ν_{ch} value. The difference between the density ν_{ch} of sample filled with carbon black only (B1) and sample filled with ferrite only (B7) was more than 80 %. The next decrease of ν_{ch} was recorded after thermo-oxidative degradation. The increase of ferrite weight fraction w_f resulted in decrease of ν_f. The decline became more evident at lower magnetic filler content. At higher ferrite loading only low change of ν_f was observed. The content of physical crosslinks increased after ageing.

Carbon black particles contain various functional groups (carboxyl, phenol, lactonyl, *etc.*), which play important role in physicochemical interactions of carbon black with elastomers. In consequence of mutual interactions with rubber, carbon black can form also chemical bonds with the elastomeric matrix. Therefore, it is supposed that it may contribute to forming of crosslinks. Also very good compatibility and physical adhesion of carbon black to polymer matrix contribute to higher evaluated crosslink densities with increasing content of carbon black in vulcanizates. Ferrite fillers, by contrast, have no functional groups on their surfaces; therefore there is no possibility for ferrites to be chemically bound to macromolecules of elastomeric matrix. It is supposed that the interactions between polymer matrix and ferrite fillers are only of weak physical character due to poor bonds and interactions with polymer matrix as mentioned above.

The analysis of crosslink structure was investigated by using the thiol-amine method. The measurements were performed in argon atmosphere at laboratory temperature (22—25 °C). The results of measurements showed that by using hexane-1-thiol (1-HT), which has ability to decompose polysulfidic and disulfidic crosslinks, the analyzed samples were either completely decomposed or after drying they had powdery form. Therefore it is supposed that the vulcanizates practically do not contain, or contain only a very small part of monosulfidic crosslinks. By using propane-2-thiol (2-PT) the content of polysulfidic crosslinks was quantitatively determined. From the ν_{ch} value and crosslink density corresponding to polysulfidic crosslinks (ν_{Sx}) the ratio of disulfidic crosslinks in the networks of prepared vulcanizates (ν_{S2}) was computed. These results are presented in Figures 7 and 8. In case of vulcanizates A the lowest content of ν_{Sx} in unfilled vulcanizate (about 60 % from ν_{ch}) was found. With increasing of ferrite loading the content of ν_{Sx} increases non-linearly up to 75 % approximately (Fig. 7). During thermo-oxidative degradation part of polysulfidic crosslinks was transformed into disulfidic crosslinks. The more evident change was observed in samples with higher ferrite content. As it can be in Figure 7 in samples with 40—80 % of ferrite the ν_{Sx} content reached the slight maximum. The similar changing tendency of the tensile strength at break of vulcanizates with increasing of magnetic filler loading was also detected. These results point out that there is certain relation between crosslink structure and tensile properties of vulcanizates. The content of ν_{Sx} in vulcanizates B is higher and in most cases

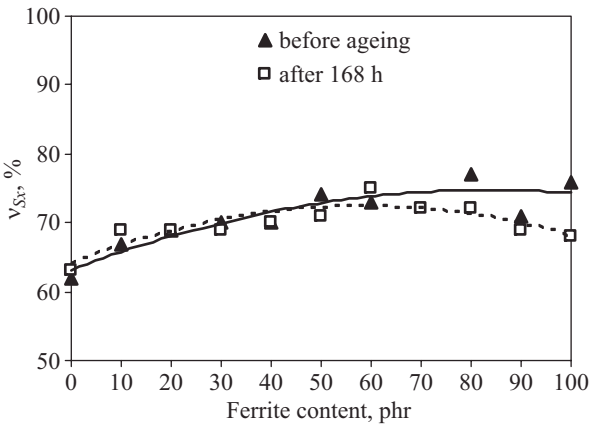

Fig. 7. Influence of ferrite content and ageing time on polysulfidic crosslinks (ν_{Sx}) of vulcanizates A (filled only with ferrite)

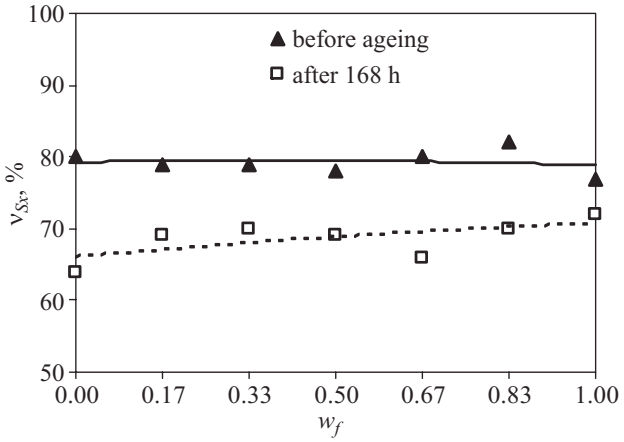

Fig. 8. Influence of ferrite weight fraction (w_f) and ageing time on polysulfidic crosslinks (ν_{Sx}) of vulcanizates B (filled with combinations of ferrite and carbon black)

the amount of ν_{Sx} represents 80 % of chemical crosslink density ν_{ch} (Fig. 8). The evident decrease of polysulfidic crosslinks after thermo-oxidative ageing was detected. The content of polysulfidic crosslinks in the network of vulcanizates after ageing decreased in range from 7 to 20 % in comparison with the ν_{Sx} content of vulcanizates before ageing.

CONCLUSION

The subject of the work was to study of the influence of magnetic filler and ageing on crosslinking and properties of model natural rubber compounds. It was concluded, that ferrite alone as well as in combinations with carbon black affects the evaluated properties in various ways. The presence of ferrite caused the increase of S_{e300} predominantly, which increased considerably with increasing content of ferrite in vulcanizates. The influence on tensile strength was insignificant. After thermo-oxidative ageing the values of S_{e300} increased, the tensile strength at break decreased, however the decreasing was relatively small. In case of vulcanizates filled with combinations of ferrite and carbon black the evaluated characteristics changed additively. Thermo-oxidative degradation caused an increase of S_{e300}, but the tensile strength at break as well as the elongation at break decreased after ageing.

The magnetic characteristics, namely B_r and J_m values showed the significant increasing tendency with increasing amount of ferrite in vulcanizates A as well as with increasing amount of ferrite in fillers combinations in vulcanizates B. The influence of ageing on their values was insignificant in case of both types of vulcanizates. In both case of ferrite as well as ferrite and carbon black combinations filled vulcanizates chemical crosslinks dominated over physical ones. In the crosslink structure disulfidic and polysulfidic crosslinks were experimentally found with dominance of polysulfidic crosslinks. Monosulfidic crosslinks were not spotted experimentally. The part of polysulfidic crosslinks of both types of vulcanizates was transformed into disulfidic crosslinks during thermo-oxidative ageing.

The results achieved by the study point out the possibilities of preparation of elastomeric magnetic composites by the progresses generally used in rubber technologies. The prepared materials have suitable magnetic and elastic properties.

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