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ANALYSIS OF NETWORK STRUCTURE IN ELASTOMERIC MAGNETIC COMPOSITES

Denisa Bellušová* — Gabriela Kyselá* — Eva Ürögiová* — Ivan Hudec*— Rastislav Dosoudil**

The incorporation of magnetic fillers (strontium hexaferrites) in the elastomeric matrix on the base of unsaturated elastomers for general use provides magnetic properties of their cross-linked elastomeric composites considerably. The properties of these crosslinked elastomeric composites are dependent on the level of magnetic fillers and carbon black loading, too. The magnetic fillers and carbon black also have influence on their network structure and its possible change in process of accelerated thermo–oxidative aging. Crosslink density of prepared composites was determined from receives results of the kinetics study of their swelling in xylene using the modified Flory-Rehner equation according to Kraus for filled vulcanizates.

Keywords: hard magnetic materials, strontium hexagonal ferrite, permanent magnet, aging, network structure

1 INTRODUCTION

The composites composed of ferrimagnetic particles dispersed in elastomeric matrix susceptible to elastic deformation give an interesting group of magnetic composite materials. Elastomeric magnetic composites have gained considerable commercial importance thanks to their wide applications in clamps, refrigerator door latches, bearing sleeves, intelligent tyres, etc. Compared to the ceramic magnets, the elastomeric magnetic composites offer a greater degree of design flexibility and improved processibility. By selecting an appropriate elastomeric matrix, magnetic fillers can be incorporated to form a composite with required properties. In fact all elastomeric composite properties can be related to their crosslink structure [1-2].

Ferrites as magnetic fillers remain one of the best magnetic materials ever discovered and cannot be easily replaced by any other magnetic materials because they are inexpensive, stable and have wide range of technological applications [3-5]. Hard ferrites are ceramic materials that have hexagonal crystal structures. Their formula composition can be represented as $n(MeO).m(Fe_2O_3)$, where n and m are natural numbers and Me is a divalent metal. For n=1 and m=6 one obtains the formula for the so-called M-type ferrites, $MeO.6(Fe_2O_3)$, which can also be written as $MeFe_{12}O_{19}$. The most common M-type ferrites are those where Me = Ba, Sr, or Pb. These substances are often used as powder for producing permanent magnets [6].

The aim of this article is to present a way of preparing and the results of investigations of magnetic properties and network structure of prepared elastomeric magnetic composites and its possible change in process of accelerated thermo-oxidative aging in dependence on the level of magnetic fillers and carbon black loading.

2 EXPERIMENTAL

Composite materials were filled with carbon black (N-330 and N-550 types) and strontium hexagonal ferrite $SrFe_{12}O_{19}$. Hard magnetic filler $SrFe_{12}O_{19}$, type FD 8/24, with coercive force 155 kA/m, remanent magnetization Br = 235 mT and average particles size ranges from 1 to 30 μm was prepared by wet milling (Stamag a.s., Světlá Hora, Czech Republic).

Natural rubber (SIR 20), butadiene rubber (SKD-2) and styrene-butadiene rubber (KRALEX 1500) were used as elastomeric matrix. For their curing the standard sulfur vulcanization system was used. The content of strontium hexaferrite was changed from 10.74 to 53.87 phr and the content of carbon blacks was changed from 15.11 to 53.71 phr.

The composites were prepared in laboratory mixer FARREL BR 1600. Blends were cured in a hydraulic heated press at 150 °C and 20 MPa into cylinder sheets. Cured elastomeric composites were conditioned for 24 h, prior to testing.

The room temperature magnetic measurements of cured elastomeric magnetic composites were carried out using TVM-1 magnetometer at a vibration frequency of 80 Hz and sensitivity of 10-11 Wb. The crosslink density ν_c was determined from the results of the kinetics study of their swelling in xylene at 25°C using the modified Flory-Rehner equation according to Kraus [9] for filled crosslinked composites. The crosslink structure was investigated by using the thiol-amine method (in argon atmosphere) according to the literature [10-12].

The crosslinked composites were exposed to influence of thermo-oxidative aging (according STN 621522).

*Slovak University of Technology, Faculty of Chemical and Food Technology, Department of Polymer Technology, Radlinského 9, 812 37 Bratislava, Slovakia, E-mail:denisa.bellusova@stuba.sk

**Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Electromagnetic Theory, Ilkovičova 3, 812 19 Bratislava 1, Slovakia.

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3 RESULTS AND DISCUSSION

The aim of this work is the investigation of the influence of the combination strontium hexaferrite $SrFe_{12}0_{19}$ (F) and carbon black (C) on magnetic characteristics and network structure of elastomeric magnetic composites.
The morphologic and magnetic properties of used ferrite are mentioned in Fig.1 and Tab. 2. Fig.1 shows the microstructure of ferrite powder particles coated with PVA (polyvinylalcohol). It is clear that PVA provides spherical shape of particles in the range of size from 10 to 200 μm.

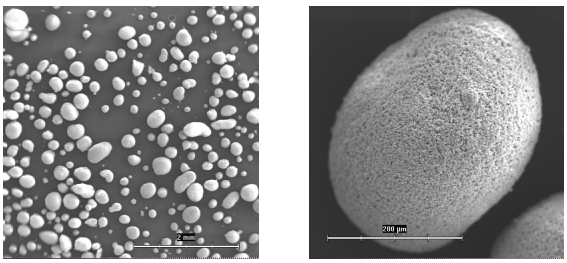

Fig. 1. SEM micrograph of Sr ferrite FD 8/24

They have a porous surface. In Tab. 2 magnetic characteristics of strontium ferrite are summarised.

Table 1: Magnetic characteristics of strontium ferrite

Magnetic property	Value
H_c (kA/m)	105
Φm (n Wb)	259
Φr (n Wb)	135
J_m (10^{-1} T)	1.33
$J_r = B_r$ (10^{-2} T)	6.99
B_m (T)	1.06

3.1 Magnetic properties

The study was based on two-factor five-level planning experiment. It was applied in order to study effects of two factors: weight ratio of strontium ferrite to carbon black (x_1 = F/C) and total content of strontium ferrite and carbon blacks (x_2 = F+C) in the rubber compounds on remanent magnetisation B_r of cured composites. Conditions for experimental design are shown in Table 2, where coded levels are recalculated to real values for both factors.

Table 2: Condition for experimental design

Factor		
Coded level	Real values	
	x_1 = F/C	x_2 = F + C (phr)
- 1.414	0.20	50.00
- 1	0.61	54.23
0	1.60	64.45
1	2.59	74.67
1.414	3.00	78.90
Step	0.99	10.22

The experimental determined Br values were treated by complete regression analysis, using the statistical program of Microsoft Excel and the general regression equation (1) in the form:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 \qquad (1)$$

Where $Y = B_r$
$b_0, b_1, b_2, b_{12}, b_{11}, b_{22}$ = regression coefficients
x_1, x_2 = choice factors on the coded levels

The variability of B_r due to the experimental error of its estimation (characterised by the mean square error s_e) as well as its variability due to the inaccuracy of the used regression model (S_{LF}) were specified by means of a variance analysis. The adequacy of the regression equation was evaluated by applying a F-test (F_{LF}), on the significance level α = 0,05. The results the statistical treatment are summarised in Table 3. From these data it becomes obvious that the adequate

Table 3: Results of regression analysis

Coeff.	Value	Crit. coeff.	Value
b_0	19.8625*	$b_{crit\ 0}$	3.4465
b_1	8.5673*	$b_{crit\ i}$	2.7249
b_2	3.1476*		
b_{11}	-2.2309	$b_{crit\ ii}$	2.9226
b_{22}	3.3983*		
b_{12}	4.0075*	$b_{crit\ ij}$	3.8533
s_e = ± 2.2776		F_{LF} = 4.3737	
S_{LF} = ± 5.8050		F_{crit} = 6.5914	

* statistically significant coefficient

regression equation for the change of B_r with F/C as well as F+C was founded ($F_{LF}<F_{crit}$). It described adequately the change of B_r with the change of both independent variables in the selected experimental place. The space diagram for B_r change of with the change of weight ratio of magnetic and nonmagnetic fillers and with total content of fillers in elastomeric compounds is illustrated in Fig. 2.

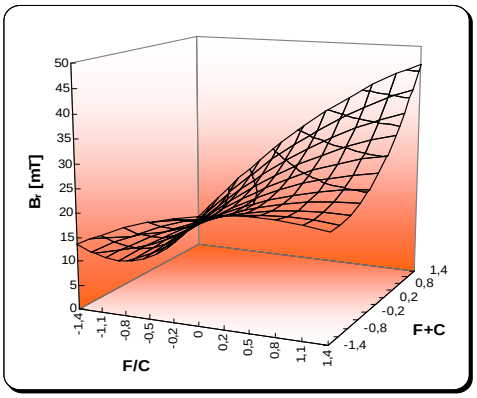

Fig. 2. The influence of F/C and F+C on remanent magnetization B_r of cured elastomeric composites

From of these results can be seen that remanent magnetization Br of prepared elastomeric composites nonlinear increased mainly in the area of higher total content of both fillers F+C and weight ratio of magnetic and nonmagnetic fillers F/C, too. Because the B_r values are relatively high, it can be predict that in this way prepared elastomeric magnetic composites have appropriate magnetic properties usable in suitable application.

3.2 Analysis of network structure

One of the most popular methods in the rubber industry to measure the crosslink density is the swelling method. This method requires swelling of a small sample of cured compounds (vulcanizates) in the suitable solvent (xylene) to the equilibrium state. For the calculate of cross-link density ν_C (the number of effective network chains per unit volume of cured rubber) Flory-Rehner equation modified according Kraus (3) we used:

$$\nu_C = -\frac{V_0}{V_S}\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_r^{1/3}V_0^{2/3}-0{,}5V_r} \qquad (3)$$

where: ν_C is cross-link density of the network chains,
V_r is volume fraction of rubber in the equilibrium swollen sample of filled vulcanizate
V_0 is volume fraction of rubber in the equilibrium Swollen sample of unfilled vulcanizate
V_s is the volume of solvent in the equilibrium swollen sample of filled vulcanizate
χ is interaction parameter

Together, with the study of the chemical cross-link density, the sulphur cross-link structure of the network, using the thiol-amine method was analysed. The influence of thermo–oxidative aging on the cross-link density and sulphur network structure of prepared composites was determined, too. The network structure of cross-linked composites is affected by weight ratio of ferrite filler to carbon black and the total content of strontium ferrite and carbon black, too. From the results mentioned in Table 4 it becomes evident, that the cross-link density (νc) of cross-linked magnetic composites increases with F/C when the value of F+C is unvaried.

On the base of the results mentioned in Table 4 it is evident that the total cross-link density of the rubber composites, which were submitted to influence of aging condition for 168 hours (ν_c 168) increases in comparison with original composites (ν_c 0). It is very probably due to additional curing of rubber macromolecules during the aging at elevated temperature (70°). It was also shown (Fig. 3 - 4), that the fractions of polysulfidic (S_x) and monosulfidic (S) cross-links is slightly decreasing with the increasing of weight ratio of fillers at constant total content of fillers. Simultaneously the fraction of disufidic cross-links is increasing. At the constant weight ratio of fillers (F/S = 1.6) is the change of monosulfidic fraction

Table 4: The cross-link density and sulphur network structure of cure-delastomeric magnetic composites

F/C	F+C (phr)	$\nu_c.10^5$ (mol/cm^3)		S_x (%)		S_2 (%)		S (%)	
		0	168	0	168	0	168	0	168
0	54.2	15.06	21.11	61	6	16	73	23	22
0.61	54.2	12.47	14.35	56	9	20	70	24	21
2.59	54.2	12.29	11.49	48	13	33	67	19	20
0.61	74.7	12.74	18.02	58	8	20	67	22	25
2.59	74.7	10.37	13.87	51	12	28	61	21	27
0.20	64.5	13.12	23.32	52	10	21	68	27	22
3.00	64.5	10.71	13.18	44	17	35	62	21	21
1.60	50.0	11.05	13.06	55	14	27	63	18	23
1.60	78.9	13.01	16.42	47	18	32	60	21	22
1.60	64.5	11.10	13.98	45	15	24	64	21	21

relatively small, disulfidic fraction is slightly increasing and polysulfidic is increasing with the increasing of F+S, respectively. The aging results in a decreasing of polysulfidic cross-links fraction and increasing of disulfidic cross-links fraction in network structure of composites, respectively.

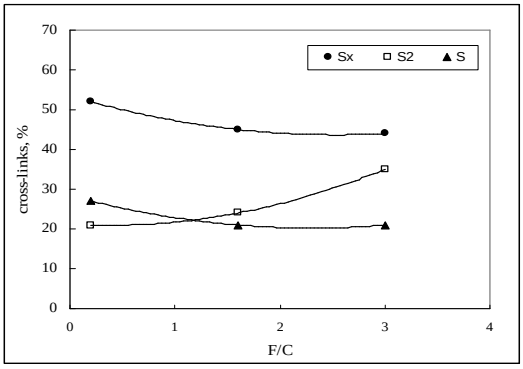

Fig. 3. Influence of F/C on structure of cross-links in elastomeric magnetic composites network at F+C = 64.5 phr

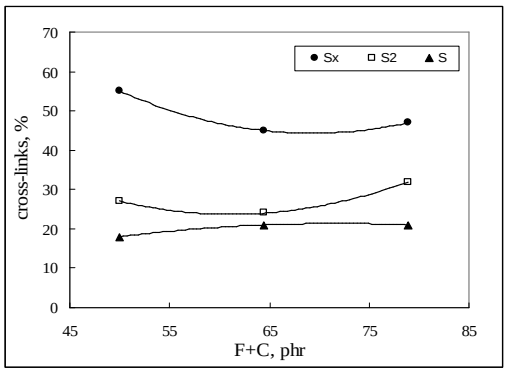

Fig. 4. Influence of F+C on structure of cross-links in elastomeric magnetic composites network at F/C = 1.6

4 CONCLUSIONS

It can be concluded that incorporation of magnetic filler to the typical elastomeric matrix allowed preparing cured elastomeric materials with appropriate magnetic properties. Their remanent magnetization Br depends on the weight ratio of magnetic and nonmagnetic fillers and on the total content of fillers in composites. These factors affected the cross-link density and network structure of prepared composites, too. The extension of aging to 168 h is connected with the modification of the fraction of polysulfidic a disulfidic in the network, predominantly.

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Ivan Hudec (Doc., Ing., CSc.), for biography see page 150 of this issue.

Rastislav Dosoudil (Ing., PhD.), for biography see page 146 of this issue.

Denisa Bellušová (Ing.), **Gabriela Kyselá** (Ing.), **Eva Ürögiová** (Ing., PhD.), biographies not supplied.