Magnetic and Mechanical Properties of Strontium Ferrite – Rubber Composites

Rubber blends · Magnetic filler · Magnetic properties · Ferrite-rubber composites

The influence of hard magnetic strontium ferrite filler on the morphology, the vulcanization characteristics, the magnetic and mechanical properties of rubber blends was studied. Four different types of strontium hexagonal ferrites powders $SrFe_{12}O_{19}$ were incorporated in different concentrations into a rubber matrix. The variation in the characteristics of the rubber/ferrite composites were evaluated as a function of the ferrite loading. Several parameters including the particle size, the porosity and surface area of the fillers were studied. The results are correlated with the cure time, the hardness, the tensile strength, the elongation at break, and the moduli as well as the magnetic properties of the blends.

Magnetische und mechanische Eigenschaften von Strontiumferrit/Kautschuk-Verbundsystemen

Kautschukverschnitte · magnetische Füllstoffe · magnetische Eigenschaften · Ferrit-Kautschuk Verbundwerkstoffe

In der vorliegenden Arbeit wird der Einfluss von Strontiumferriten auf die Morphologie, den Vulkanisationsverlauf sowie die magnetischen und mechanischen Eigenschaften der gefüllten Elastomere untersucht. Vier verschiedene Typen von Strontiumhexaferrit ($SrFe_{12}O_{19}$), die in unterschiedlicher Dosierung in die Kautschukmatrix eingearbeitet wurden, kamen zur Anwendung. Die Eigenschaften der Kautschuk/Ferrit-Verbundwerkstoffe wurde in Abhängigkeit Füllstoffgehalts, der Teilchengröße, der Porosität, der spezifischen Oberfläche der Füllstoffe untersucht. Die Ergebnisse korrelieren mit der Vulkanisationszeit, der Härte, der Zugfestigkeit, der Bruchdehnung, den Moduli und den magnetischen Eigenschaften der entsprechenden Mischungen.

Rubber/ferrite composites are materials with ferromagnetic fillers as one of the constituents and a rubber or rubber blend as the polymer matrix. Rubber-ferrite composites are important from the point of view that they are suitable for adaptive devices where flexibility and elasticity is an additional and important parameter. Such composite materials can be moulded into complex shapes. In magnetic composite materials where the magnetic filler is well distributed in a polymer matrix, new and unexpected mechanical, chemical and rheological properties can be observed. In rubber blends the magnetic powder as well as the polymer affect the processability and the physical properties of the final vulcanizate. The materials obtained demonstrate interesting mechanical and magnetic properties, chemical resistance and they are suitable for producing of flexible magnets [1, 2].

Ferrites are a very well established family of magnetic materials. They are important because they are inexpensive and chemically stable. In addition they have a wide range of technological application. The ferrites form a large class of ceramic materials [3]. In terms of technological applications one may distinguish between the two major types of ferrites, the soft and the hard ones. Soft magnets are materials characterized by domain walls (Bloch walls) which easily can be moved when a magnetic field is applied. Those with less mobile domain walls are termed hard magnets. Magnetic hard fillers represents chemical compounds of metal oxides with strong magnetic properties, which are ideal for permanent magnets [4]. The magnetic hard ferrites have hexagonal crystal structure. The high values of magneto-crystalline anisotropy and saturation magnetization ensure a wide application of these so called M-phase ferrites as permanent magnets. The formula of such magnetic hard ferrites can be generally represented as $(MeO).(Fe_2O_3)_6$, where Me is a bivalent metal (eg. Sr, Ba, Pb or of mixture of them). These substances are often used as powder for producing permanent magnets [5, 6]. Recently strontium ferrite $SrFe_{12}O_{19}$ has received a wider attention as permanent magnet than barium ferrite Ba $Fe_{12}O_{19}$ although both compounds are relatively close if magnetic properties are concerned. In addition the latter has a high chemical stability and low price then the former [7].

The present work reports the structural characteristics of four different types of strontium ferrites and the incorporation of these as fillers into a rubber matrix. The final properties of the composites depend not only on the properties of the fillers but also on the properties of the matrix. Several parameters including particle size, porosity and surface area of the ferrite fillers and the influence of the strontium ferrite content on the vulcanization characteristics, the mechanical and the magnetic properties of rubber matrix were studied. The results are correlated with the curing characteristics, the hardness, the tensile strength, the elongation at break, the moduli and the magnetic properties of corresponding rubber blends.

Experimental

Four different types of strontium ferrites were used for preparing of ferromagnetic rubber composites. Strontium hexagonal ferrites $SrFe_{12}O_{19}$ was prepared by wet milling (Motorpal a.s., Světlá Hora, Czech Republic). The Sr ferrite with coercitive force

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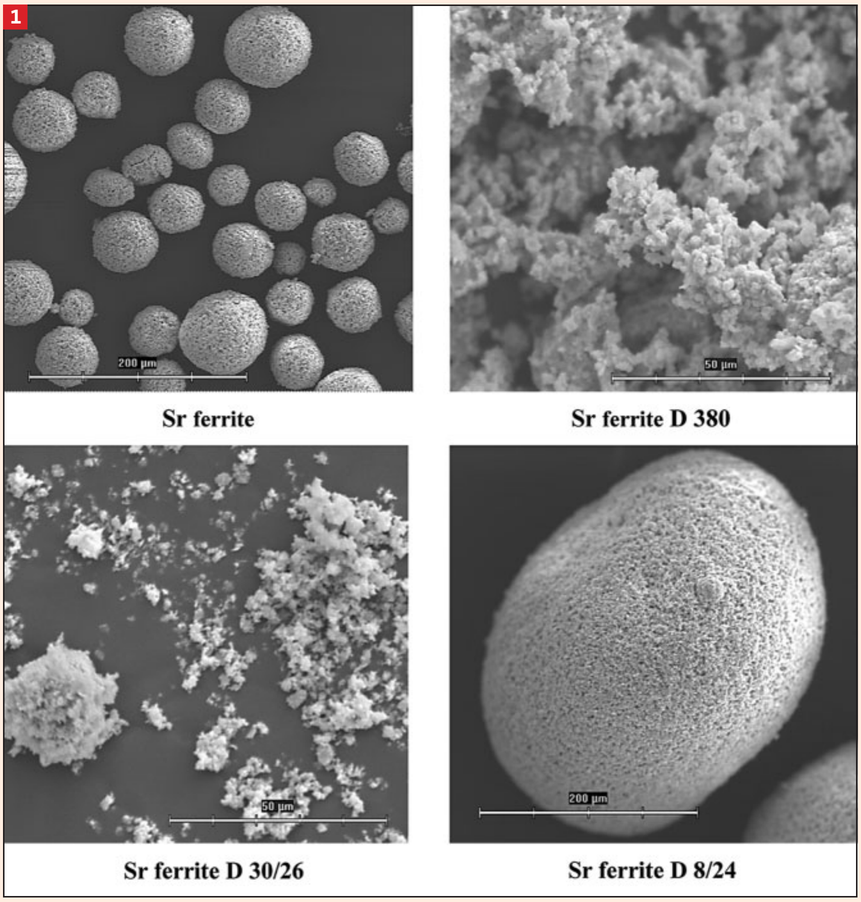


1 SEM micrograph of Sr ferrites

112 kA/m was removed after the first heat treatment – ferritizing, and dried with PVAL. The type FD 8/24 is an anisotropic strontium ferrite with coercitive force of 105 kA/m. The type FD 30/26 is a anisotropic strontium ferrite with coercitive force 131 kA/m and the type D380 is a vibrated calcinate with coercitive force 137 kA/m. These compounds were used as a hard magnetic filler [8]. The SEM micrographs show the morphology and particle size distribution of the used Sr ferrites as illustrated in Figure 1. To investigate the particle size, porosity and surface specific area of the ferrite fillers mercury porosimetry was employed by using the Porosimetro 1500 (Carlo Erba, Milano).

The rubber blend was prepared from natural rubber (SIR 20) and butadiene rubber (SKD). A standard sulphur-based vulcanization system was used.

The composite materials in concentration ranging from 30 to 50 wt.% of the ferromagnetic filler were prepared in a laboratory mixer at 80°C and 40 rpm for 10 min. The composite materials were calendered after mixing. The prepared mixtures were vulcanized at 150°C for the optimum cure time (tc_{90}) in a hydraulic press. The specimen thickness was 2 mm.

The degree of dispersion of ferromagnetic particles in the polymer matrix was measured by using the Disper Grader 1000.

The vulcanization characteristics were investigated according to ISO 3417-77. The physical properties were measured according to the following standards: hardness Shore A – ISO 868, tensile properties – ISO 37.

The magnetic measurements of the ferrite powders, the un-vulcanized rubber mixes and the cured rubber blends were carried out in a TVM-1 magnetometer at a vibration frequency of 80 Hz and a sensitivity of 10^{-11} Wb.

Results

The characterization of the ferromagnetic fillers includes the determination of morphological, physical and magnetic parameters of the fillers used in this study. In order to clarify the structural characteristics of the ferromagnetic fillers the surface specific area and the porosity of the fillers was determined by using the method of mercury porosimetry. The structural characteristics of different types of strontium ferrites are shown in Table 1. A more detailed picture was obtained from SEM micrographs. The particle size distribution of different types of Sr ferrites is illustrated in Figure 1 and 2.

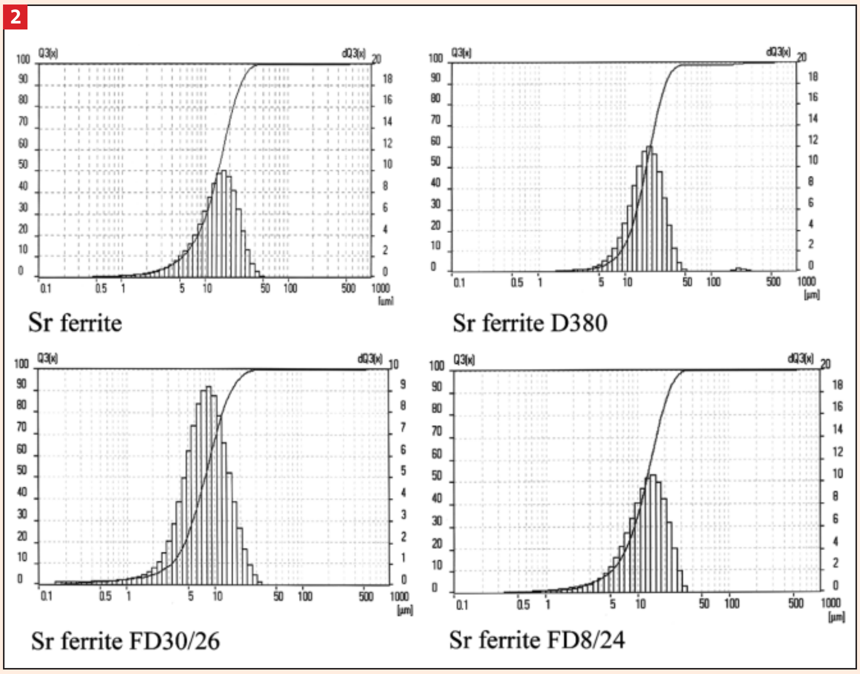
The Curie temperature of a ferromagnetic material, is the temperature above which it loses its characteristic ferromagnetic ability to possess a spontaneous magnetization in the absence of an external magnetic field. At temperatures below the Curie point, the magnetic moments are partially aligned within the magnetic domains in ferromagnetic materials. [9]. The measurement of the temperature dependence of initial magnetic susceptibility γ is therefore a convenient method for determination of the phase of composition and the Curie temperature [10]. The magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field [11]. The values of the Curie temperatures and the remanent magnetisation Br for the ferrites under investigation are listed in Table 2.

1 Structural characteristics of ferromagnetic fillers

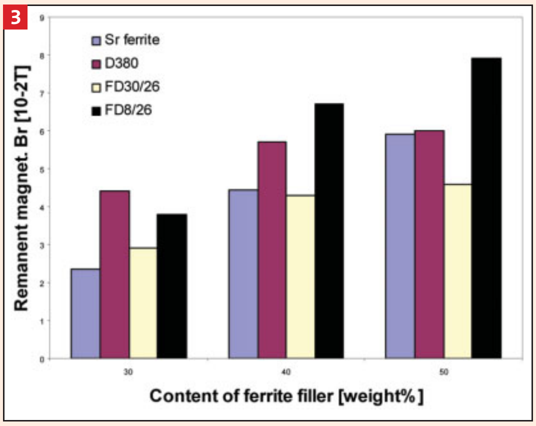
	Sr	D 380	FD 30/26	FD 8/24
Volume of pores less then 10 µm [cm^3/g]	5.01	0.05	0.03	0.14
Total specific surface [m^2/g]	2.11	0.80	6.14	3.39
Total porosity [%]	72.09	59.96	59.97	67.94
Total volume of pores [cm^3/g]	0.24	0.25	0.30	0.42

2 Magnetic characteristics of ferromagnetic fillers

	Sr	D 380	FD 30/26	FD 8/24
Curie temperature [°C]	430	450	445	455
Remanent magnetisation Br [T]	1.09	1.08	0.95	1.06



2 **Particle size distribution of Sr ferrites**



3 **The variation of remanent magnetisation Br with content of ferrite filler in rubber blends**

The vulcanization charakteristics were measuered at 150°C using the Rheometer Monsanto S100. The optimum cure time t_{c90} was investigated.. The difference between the maximum torque value M_H and the minimum one M_L represents the parameter ΔM. The obtained values are shown in Table 3. The presence of the ferromagnetic filler in the rubber compound leads to a decrease of the optimum cure time (t_{c90}) and the torque difference ΔM. By increasing the amount of ferrite filler in the compound the cure time t_{c90} decreases.

All the mechanical properties of the compounds were tested after vulcanization at t_{c90} by using the TiraTest machine according to ISO 37. This method rests in straining of tested material in tension by specified strain rate. The values of measured mechanical properties are shown in Table 4. It becomes evident, that all the mechanical properties besides the elongation at break increase when compared with the unfilled rubber blend. The elongation at break and the tensile strength show a decreasing tendency with the increasing amount of ferrite filler in the composite material. The values of the modulus and the hardness Shore A increase also with amount of ferrite filler, except for some cases, when the decreasing can be caused by inhomogenity and porosity of sample.

The values of remanent magnetisation Br for ferromagnetic rubber composites are shown in Figure 3. From obtained results is evident, that remanent magnetisation Br increase with increasing of magnetic filler content in rubber blend. The higher value of remanent magnetisation $7{,}9.10^{-2}$T accounts strontium ferrite type FD8/24 by 50 % ferrite content in the sample. From point of viev magnetic properties all types of strontium ferrites are suitable as filler for rubber blends. Strontium ferrite of type FD8/24 showed the best parameters and its incorporating into matrix was not difficult.

Conclusion

The influence of hard magnetic fillers content on vulcanization characteristics, mechanical and magnetic properties in filled rubber compounds was studied. Four different types of strontium hexagonal ferrites powders $SrFe_{12}O_{19}$ having the particle size in a range 5–50 μm were incorporated into a rubber matrix with loading levels 30–50 weight %. Results showed that the cure time decreased with the increasing of amount of ferrite filler in the compound. All studied mechanical properties besides

3 **Vulcanisation characteristics of strontium ferrite – rubber composite materials**

Type of filler	Content of filler [w%]	ΔM [Nm]	t_{c90} [min]
Rubber matrix	0	1.58	17.5
Sr ferrite	30	3.33	12.0
	40	3.62	11.0
	50	3.58	9.0
D 380	30	3.83	9.5
	40	3.87	8.3
	50	2.77	6.5
FD 30/26	30	1.95	5.6
	40	0.85	3.4
	50	1.13	3.8
FD 8/24	30	2.51	6.8
	40	2.37	6.3
	50	2.77	5.6

4 Physical and mechanical properties of strontium ferrite – rubber composite materials

Type of filler	Content of filler [w%]	Modulus [MPa]			Elongation at break [%]	Tensile strength [MPa]	Hardness Shore A [°ShA]
		100 %	200 %	300 %			
Matrix	0	1.13	2.08	3.20	649.4	9.80	43
Sr ferrite	30	3.68	7.26	11.20	341.3	12.80	61
	40	3.56	7.02	10.57	338.3	13.44	63
	50	4.37	7.87	0	206.1	7.87	65
D 380	30	2.42	4.90	7.96	465.9	15.07	55
	40	2.63	5.21	8.22	408.8	12.35	57
	50	2.42	4.82	0	302.4	7.72	57
FD 30/26	30	2.61	5.06	8.41	403.3	12.67	45
	40	2.74	5.49	0	209.1	6.09	46
	50	3.77	0	0	136.3	5.49	48
FD 8/24	30	2.65	5.63	9.63	361.7	12.55	53
	40	3.02	6.12	0	239.2	7.76	56
	50	3.96	7.65	0	231.3	9.05	60

ellongation at break increase with filler content in comparison with rubber blend without ferromagnetic filler. The remanent magnetization linearly depends on the weight fraction of the magnetic filler in rubber blends. The changes of monitored properties of ferromagnetic rubber composites in comparison with standard rubber blends are acceptable for their practical application.

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