MAGNETIC AND PHYSICAL-MECHANICAL PROPERTIES OF POLYMER COMPOSITES WITH SOFT MAGNETIC FILLERS

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1. Introduction

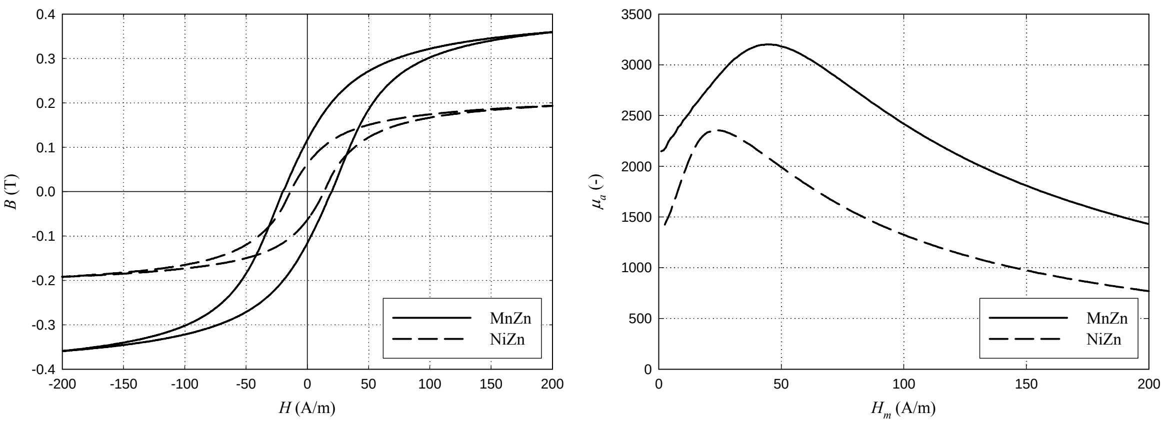
In this paper the influence of soft magnetic ferrite fillers on magnetic and physical-mechanical properties of the prepared composite samples based in natural rubber matrix was studied. The soft magnetic ferrite materials with the chemical composition $Mn_{0.37}Zn_{0.57}Fe_{2.06}O_4$ and $Ni_{0.33}Zn_{0.67}Fe_2O_4$ were used as magnetic filler in various concentrations. Further, the effect of thermo-oxidative ageing on the prepared composite materials was investigated. Magneto-rheological elastomers are solid analogues to magneto-rheological fluids. These materials are considered as smart materials comprising of micro- or submicro-sized magnetic particles dispersed in non-magnetic matrix. The problem of magneto-rheological fluids - particle sedimentation, is well eliminated by replacing the fluid matrix by solid one, such as the rubber, etc. [1, 2]. The magnetic ferrite powders filled into various polymer matrixes allow preparing new magneto-polymer composite materials which properties characteristics for polymers (elasticity, mouldability) are combined with good magnetic parameters. These properties can be modified using adequate magnetic filler or polymer matrix in various concentrations for prepared composites available in required specific applications. The soft magnetic materials, such as spinel ferrites are known for many years thanks to good absorbing properties. The magneto-polymer composites, in which the ferrite is incorporated into polymer matrix, enable to utilise the spinel ferrites as electromagnetic wave (EM-wave) absorbers in GHz frequency region. Using EM-wave absorbers is an effective way to minimize EM interferences arising in wireless communication systems (mobile phones, WiFi LANs, radar or satellite systems, etc.) by the transformation of undesired electromagnetic energy into thermal energy. Moreover, the ferrite-polymer absorbers are characterised by their lightweight, low cost and good design flexibility [3, 4].

2. Experimental details

Two types of soft magnetic materials; commercially available MnZn and laboratory prepared NiZn ferrite [5] were used as the fillers. Both raw ferrite materials were prepared by grinding in the agate mill and sieved in order to get required powder grain fraction below 40 µm. The size, shape and distribution of prepared ferrite particles were investigated by scanning electron microscope (SEM) and laser particle size analyzer. The density ρ, specific surface area S_A and total porosity p_t of ferrite fillers were measured by means of mercury porosimetry method. The magnetic properties of prepared ferrites (coercivity H_c, remanence B_r, initial permeability μ_i, etc.) were examined on sintered ferrite samples having toroidal form with outer diameter of 12 mm, inner diameter of 6 mm and thickness of roughly 4 mm by means of tailor-made computer controlled experimental equipment based on commercially available instruments. The Curie temperature of ferrite filler T_C was found from the temperature dependencies of the magnetic susceptibility measured by means of bridge method within the temperature range of 30-400°C with constant temperature increase rate of 4°C/min. The magnetic ferrite fillers incorporated into the natural rubber matrix (SMR 20) with standard sulphur-based vulcanisation system (S - 1.3 phr, CBS - 1.5 phr, ZnO - 3 phr, stearine - 2 phr) by mixing in Brabender laboratory mixer were used for the production of magneto-polymer composites to be studied [6]. The ferrite filler content in the composite samples changed within the range from 0 to 600 phr; this corresponds to the volume concentration of magnetic filler from 0 to 50 vol.%. Physical-mechanical properties of the composites were investigated using double-sided blade specimens of the width 6.4 mm, length 100 mm and thickness about 2 mm in accordance with valid technical standards. The influence of thermo-oxidative ageing on prepared composite materials was evaluated on the samples with the same shape by Geer method. The composite samples were subjected to artificial ageing in the air atmosphere at 70°C with the exposure time of 72 hours.

3. Results and discussion - properties of composite constituents

Magnetic and structural properties of both types of ferrite fillers were examined. Various magnetic parameters were determined from the families of hysteresis loops of MnZn and NiZn ferrite samples measured at sinusoidal exciting field $H(t)$ waveform with the frequency $f = 50$ Hz, changing the exciting field amplitude from its maximum value $H_m = 200$ A.m^{-1} down to 1 A.m^{-1}, step -1 A.m^{-1}. Thus, 200 minor loops were obtained for each sample. The hysteresis loops measured at the highest exciting field are shown in Fig.1a; the dependencies of amplitude permeability μ_a upon exciting field amplitude H_m are in Fig.1b. The initial permeability was found as an extrapolation of these dependencies to zero exciting field. Important magnetic and structural parameters are summarised in Table 1. The values of T_C are sufficiently high to allow application of both materials in various devices at elevated operating temperatures.



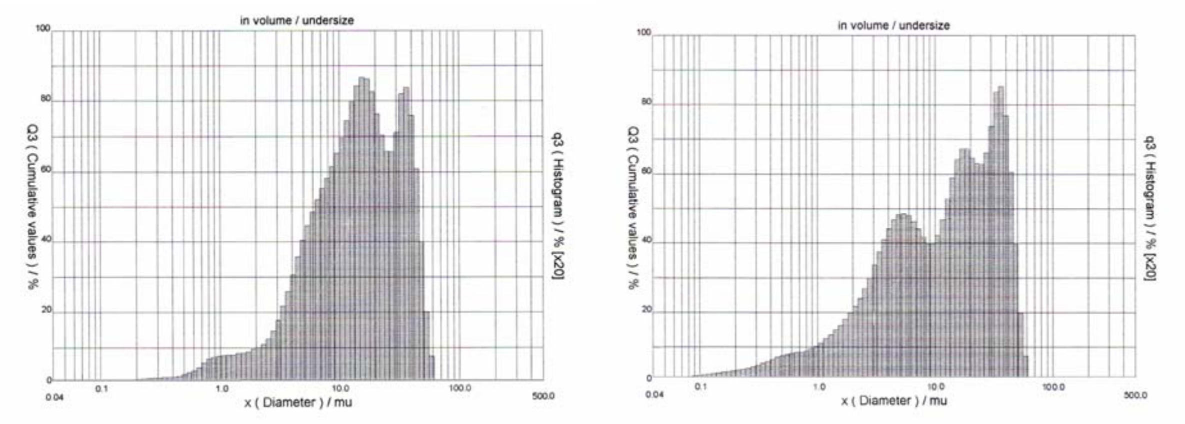
a) *b)*

Fig.1: *The hysteresis loops of MnZn and NiZn ferrite (a) and the amplitude permeability μ_a of MnZn and NiZn ferrite as a function of exciting field amplitude H_m (b).*

Laser particle size distribution curves in Fig.2 show that the ferrite powders contain the particles with the sizes up to 40 μm with the dominance of particles above 20 μm for MnZn ferrite and above 5 μm for NiZn ferrite. These results are in agreement with SEM analysis published in [7]. The structural properties of both types of fillers, such as the specific surface area S_A, density ρ and total porosity p_t are given in Table 1.

Tab.1. *Magnetic and structural parameters of ferrite fillers.*

ferrite filler	T_C (°C)	μ_i (-)	H_c ($A.m^{-1}$)	B_r (T)	S_A ($m^2.g^{-1}$)	ρ ($g.cm^{-3}$)	p_t (%)
MnZn	213.7	2143	21.7708	0.12683	0.50	4.70	49.36
NiZn	118.0	1316	13.6732	0.06232	0.61	5.11	45.65

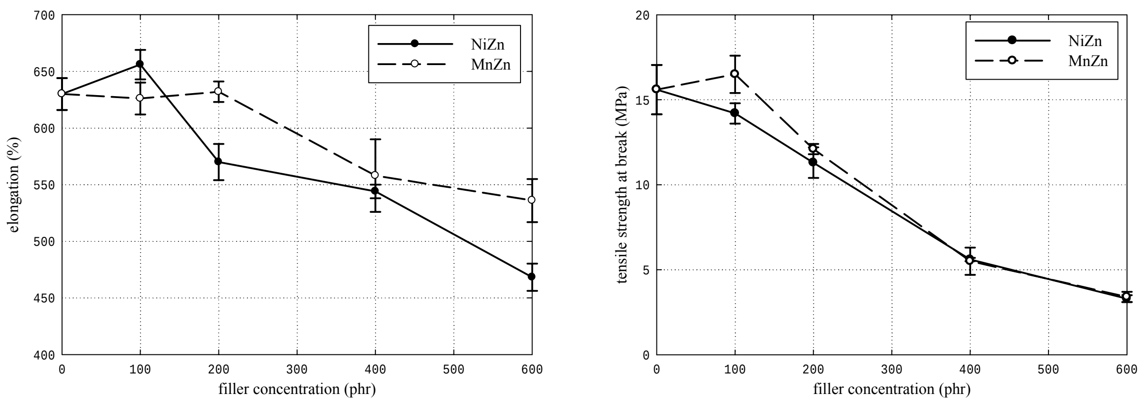


a) *b)*

Fig. 2: *Particle size distribution of MnZn (a) and NiZn (b) ferrite filler*

4. Results and discussion - properties of final composites

The influence of the soft magnetic ferrite fillers on some physical-mechanical properties, such as i.e. the elongation and tensile strength at break were investigated (Fig.3). The dependence of the elongation at break decreased for maximum filled composite samples nearly 15% for MnZn ferrite filled composites and 26% for NiZn composites in comparison with the elongation values of pure matrix material. The value of tensile strength at break sharp decreased with increasing of filler concentrations, for the MnZn ferrite filled composites firstly rises up slightly from 15.60 to 16.50 MPa and then decreased to 3.40 MPa (78%), for NiZn composites from 14.20 to 3.30 MPa (79%).



a) *b)*

Fig.3: *The influence of ferrite concentration on the elongation (a) and tensile strength at break (b) of MnZn and NiZn ferrite filled composites.*

The increase of soft magnetic filler content significantly affects the magnetic properties of composite samples - e.g. the initial permeability values increase from 2.3 to 8.9 for MnZn ferrite filled composites and from 2.6 to 8.2 for NiZn composites. On the other hand, the resonant frequency shifts towards higher values as the ferrite filler content in composite samples decreases. In case of composites with ferrite filler concentration of 100 phr the resonant frequency achieved value 3 GHz for MnZn ferrite filler and 1.4 GHz for NiZn ferrite filler. These values are approximately 3 times higher than for the composites with 600 phr ferrite filler concentration, [7].

Further, the study of the thermo-oxidative ageing in the air atmosphere at 70°C for 72 hours on the magnetic and physical-mechanical properties was carried out for composite samples with NiZn ferrite filler only. No antioxidants and antiozonants were added during composite preparation except that the natural rubber of SMR 20 type contains small amount of natural anti-ageing substances [8]. The influence of ageing on the initial permeability values was almost insignificant, the largest difference was found at the highest filler concentration (see Fig. 4). This can be explained by increased influence of mutual interaction among the ferrite grains settling to each other during the ageing, probably associated with the creeping of rubber matrix material at elevated temperature. Nevertheless, these small variations are within the uncertainty of the permeability measurements. On the other hand the values of the elongation at break as well as the tensile strength showed some changes.

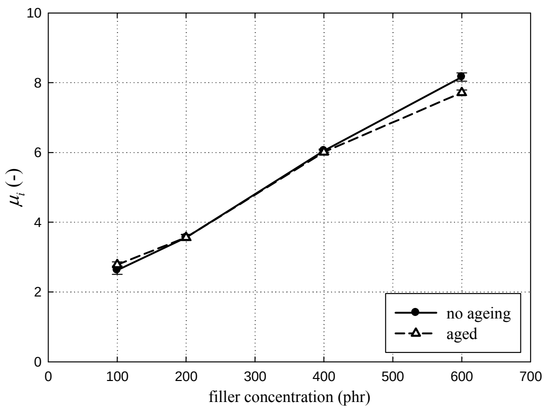
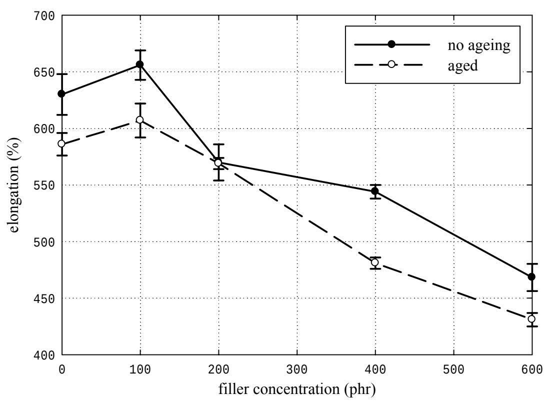
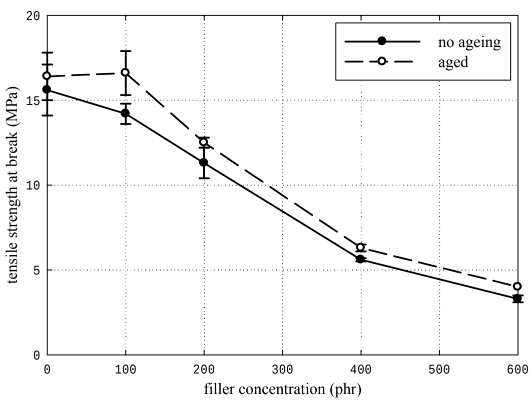


Fig.4: *The influence of thermo-oxidative ageing on the initial permeability of NiZn ferrite filled composites.*



a)



b)

Fig.5: *The influence of thermo-oxidative ageing on the elongation (a) and tensile strength at break (b) of NiZn ferrite filled composites.*

In Fig.5a the reduction of the elongation at break after artificial ageing is apparent, meanwhile the tensile strength values of samples slightly increased in all the range of filler concentrations (Fig.5b). Whereas the thermo-oxidative ageing did not influence the magnetic characteristics of NiZn ferrite filled composites and the physical-mechanical properties were changed only very slightly, we expected the same effect also for the composite samples filled by MnZn ferrite powders.

5. Conclusions

The experiments carried out have confirmed that the thermo-oxidative ageing almost did not affect the magnetic properties of the composites. More evident is the influence upon physical-mechanical properties. This can be explained by the fact, that the ageing temperature was meaningless from the point of view of the grain growth of ferrite particles (where the temperatures above 1000°C are required). On the other hand, 70°C is enough to initiate natural rubber degradation. Also, the decreased viscosity of the rubber matrix probably results in gradual creep process manifested in some reordering or "settling" of ferrite grains.

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