Characterization of composite materials based on Fe powder (core) and phenol–formaldehyde resin (shell) modified with nanometer-sized SiO₂

M STREČKOVÁ^{a,*}, J FÜZER^b, L' MEDVECKÝ^a, R BUREŠ^a, P KOLLÁR^b, M FÁBEROVÁ^a
and V GIRMAN^b

^aInstitute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic

^bInstitute of Physics, Faculty of Science P. J. Šafárik University, Park Angelinum 9, 040 01 Košice, Slovak Republic

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Abstract. Soft magnetic composites based on Fe powder and phenol–formaldehyde resin (PFR) modified with tetraethylorthosilicate are investigated in detail. The chemical synthesis of PFR, its modification with nanometer-sized SiO₂ particles created by sol–gel method and subsequent coating, enables a preparation of insulating PFR–SiO₂ (PFRT) layer on the surface of Fe particles. Thermal degradation and FTIR analysis of PFR and PFRT with different amount of SiO₂ was examined. Mechanical hardness and flexural strength of FePFRT composites was studied depending on the amount of nanosized-SiO₂ in the coating. SEM serves in evidence of a defectless microstructure if the coating contains at least 2% of silica particles. The morphology of Fe particles implies uniform coating without any visible exfoliation. A presence of fine SiO₂ particles was verified by TEM. The best magnetic properties were found in Fe–PFRT composite with 2% of SiO₂ in the insulating layer on behalf of its uniform arrangement and homogeneity.

Keywords. Thermosetting resin; magnetic properties; microstructures; heat treatment.

1. Introduction

The ideal insulating soft magnetic composite (SMC) is formed by ferromagnetic core, which is perfectly coated with a very thin electrically insulating layer. The main advantage of SMC in comparison with conventional laminated materials is that magnetic properties and electrical resistivity are isotropic in the bulk, whereas they may be also pressed to a net shape with tight tolerances and this reduces the constraints on a design (Gilbert *et al* 2004). Apart from this fact, the low eddy current loss and total core loss at medium to high frequencies allows one to use SMC materials for a lot of electromagnetic applications (Bas *et al* 2003; Balaji Thattai parthasarathy *et al* 2008; Egelkrauta *et al* 2010; Narasimhan *et al* 2010). The preparation of microcomposite materials based on Fe powder covered by organic shell is one of the most promising approaches for a design of SMC materials. The primary disadvantage lies in their low mechanical strength, because they cannot be sintered. Moreover, micro- and macro-defects are observed in the composites after curing process due to the evaporation of initially existing water and other volatile by-products formed during crosslinking reaction (Kaynak and Cem Tasan 2006). Therefore, the considerable effort has been devoted to improve the magnetic performance of SMCs by designing hybrid

inorganic–organic insulating coating through different additives (Strečková *et al* 2012) or surface modifications of base metal material (Taghvaei *et al* 2009a, b). However, any structural defect may basically affect the magnetic properties of prepared SMCs. The structural studies, magnetic properties and loss separation in iron-phenolicsilane SMCs were studied in detail by Taghvaei *et al* (2010a, b) and Strečková *et al* (2013). This study serves in evidence that the hysteresis loss coefficient does not dramatically change for different samples, but the current loss coefficient is much higher in composites with 0.7% resin in the sample without any coupling agent. The enhancement of the oxidation resistance of carbonyl iron by polyaniline coating and its consequent changes in electromagnetic properties are described in the work of Abshinova *et al* (2008). Ziğbowicz *et al* (2007) studied an influence of the shape and the size of powder particles on magnetic properties of SMCs.

The preparation of SMC materials with outstanding electrical, magnetic and mechanical properties is a very difficult task, because the chemical modification of Fe base powder should simultaneously improve various properties such as density, dimensional and shape stability, wear and corrosion resistance, etc. In addition, the prepared SMCs should also obey demanding environmental and economical requirements.

Phenol–formaldehyde resins (PFR) are well known in many industrial applications in different sectors because of their low cost, aging endurance, dimensional stability

*Author for correspondence (mstreckova@imr.saske.sk)

and high-tensile strength. They belong to the most useful substrates for the encapsulation of inorganic nanoparticles into polymeric networks (Padron *et al* 2006). An incorporation of inorganic silica particles into PFR matrix leads to a preparation of the hybrid PFR/SiO₂ resin, which represent convenient insulating spacer because of a good control of its chemical design. Much attention has been paid to the preparation, characterization and general properties of organic–inorganic PFR/SiO₂ nanocomposite materials prepared by the sol–gel method (Chiang *et al* 2003). The sol–gel process leading to a preparation of SiO₂ nanoparticles, which may simultaneously occur with PFR polymerization, is illustrated in scheme 1.

An aggregation of SiO₂ nanoparticles of approximate size 100 nm has been observed in the prepared hybride composites. The silica-containing hybride composites have a higher thermal stability and char yield, excellent fire-resistant properties, improved flexural strength and flexural modulus compared to that of the net resin. Impervious, resistance and anticorrosive property of resinous-SiO₂ coating were achieved by the sol–gel synthesis of finely disseminated SiO₂ colloidal particles, which are trapped inside functionalized or unfunctionalized resin polymer network (Padron *et al* 2003, 2006). The influence of the SiO₂ content on the physical, mechanical and anticorrosive properties of urushiol formaldehyde polymer/multihydroxypolyacrylate/SiO₂

nanocomposites (UFP/MPA/SiO₂) was investigated by Baia and Lin (2011). The antiultraviolet tests showed that the prepared coatings improved ultraviolet resistance of UFP/MPA/SiO₂. The best anti-ultraviolet and anticorrosive properties were achieved in the samples with SiO₂ content of about 5 wt%. Many investigations have also been focused on the different types of polymers, whose flame retardancy (Ji *et al* 2009) and/or thermal degradation (Periadurai *et al* 2010) can be essentially improved by the SiO₂ nanoparticles embedded by means of the sol–gel process.

In this article, the design of core–shell composites composed of Fe powder particles (core) and PFR–SiO₂ (PFRT) insulating coating (shell) is examined by employing the sol–gel method used for a preparation of organic–inorganic PFRT polymer. It should be noticed that the applied conditions allowed us to synthesize the SiO₂ particles *in situ* with PFR prepolymer. Hybride polymers and also SiO₂ nanoparticles isolated from the PFRT were verified by FTIR spectroscopy. The size and morphology of particles were determined by TEM analysis. The thermal properties of the PFRT coatings with different amount of silica were investigated in particular along with an effect of SiO₂ content on mechanical, electrical and magnetic properties of the final microcomposites. The morphology of microcomposite hybride powder and the microstructure of the final samples were examined by SEM and EDX analyses.

Scheme 1. Sol–gel process leading to a preparation of SiO₂ particles.

Table 1. Composition of prepared samples and methods of characterization.

Samples	Fe (wt%)	PFR (wt%)	Si _(exp) (%)	Methods
PFR	–	100	–	FTIR, TG, DSC
FePFR	97	3	–	HV10, TRS, SEM, EDX
SiO ₂	–	–	–	TEM, FTIR
PFRT ₁	–	98.5	1.50	TG, DSC, FTIR
PFRT ₂	–	98.03	1.97	TG, DSC, FTIR
PFRT ₃	–	96.72	3.28	TG, DSC, FTIR
FePFRT ₁	97	2.955	0.045	TG, DSC, HV10, TRS, SEM, EDX, ER ⁺ , M [#]
FePFRT ₂	97	2.941	0.059	TG, DSC, HV10, TRS, SEM, EDX, ER, MM
FePFRT ₃	97	2.902	0.098	TG, DSC, HV10, TRS, SEM, EDX, ER, MM

⁺ ER, electric resistivity.

[#] MM, magnetic measurements.

Table 2. Curing schedule applied for each sample.

Temperature/°C	40	60	80	90	100	110	120	130	150	180
Time/h	24	24	8	1	16	0.5	1	1	0.5	0.25

2. Experimental

2.1 Materials

Iron powder (ASC 100.29 Höganäs) with the size fraction in the range from 45 to 212 μm was used as the basic ferromagnetic material for the preparation of microcomposites. Phenol (99%, Sigma-Aldrich, Germany), formaldehyde (37% aq., Sigma-Aldrich, Germany), ammonia (26% aq., Sigma-Aldrich, Germany), tetraethylorthosilicate (TEOS, 99%, Merck, Germany) and ethanol (absolute 99.5%, Sigma-Aldrich, Germany) were analytical grade without further purification.

2.2 Synthesis of PFRT

The initial molar reaction ratio of phenol/formaldehyde/ammonia/tetraethylorthosilicate (Ph/F/NH₃/TEOS) was 1/1.5/0.35/(0.06, 0.08 or 0.17). A predetermined amount of TEOS was added to the binary liquid mixture of phenol and formaldehyde. The mixture was cooled in ice bath and the ammonia was added dropwise. The white precipitate resulted from the chemical reaction of those reactants. The reaction mixture was refluxed for 45 min at 85 °C. The water phase was immediately removed under vacuum for 45 min at 95 °C. The PFRT prepolymer with the honey-like viscosity was not as transparent as the pure PFR due to the incorporation of nano-SiO₂ particles into the polymer matrix. The composition of prepared samples, the methods of their analyses and testing are listed in table 1. The main difference between the samples, PFRT₁, PFRT₂ and PFRT₃ lies in the content of SiO₂ nanoparticles embedded in the prepared polymer. The ratio of Fe powder and the polymer matrix modified by SiO₂ nanoparticles remains the

same, i.e. 97 wt% of Fe powder and 3 wt% of modified PFRT polymer, whereas the content of SiO₂ nanoparticles inside the polymer varies as specified in table 1. The Si content was determined by spectrophotometrically via Si–Mo–V complex.

2.3 Coating and curing

The prepared PFR or PFRT resins were dissolved in a small amount of ethanol, whereas the obtained solution had the water-like viscosity. A slightly milky yellow suspension was observed by dissolving PFRT resin. The fine SiO₂ particles for FTIR analysis were extracted by 300 ml of ethanol and dried in air. The iron powder particles were added to those solutions. The suspension was manually mixed by glass rod until the complete evaporation of ethanol from the suspension was achieved. In order to prepare the final microcomposites Fe–PFR and Fe–PFRT_{1–3}, the coated powder was pressed at 800 MPa into the required shapes for mechanical, electrical and magnetic testing. The prepared samples were cured under ambient pressure according to the schedule described in table 2.

2.4 FTIR and TG, DSC analysis

Fourier transform infrared spectra (FTIR) were recorded by FTIR spectrophotometer (Shimadzu, IRAffinity, KBr pellets 1 mg sample + 300 mg KBr) before and after curing. 100 scans with the resolution of 2 cm^{–1} at the 4000–400 cm^{–1} were signal-averaged. The thermal degradation of pure PFR and three modified polymers PFRT_{1–3} were analysed by differential scanning calorimeter (METTLER 2000 C) on air. The samples were heated up to 700 °C at a heating rate of 10 °C/min.

2.5 SEM, TEM, mechanical testing, specific resistivity and magnetic properties

The microstructure and morphology of all samples were examined by scanning electron microscope SEM (JEOL JSM-7000F) equipped with the energy dispersive X-ray analyser (EDX) after the carbon coating. SiO₂ nano-particles were placed in Cu carbonated grid and explored by transmission electron microscopy TEM (JEOL 2100F). The bright-field TEM image was obtained at 200 kV and high-magnification were taken at 20,000 $\times$.

Vickers hardness test HV10 was measured according to STN EN ISO 6507-1 (42 0374), MPIF 43. For this purpose, the samples were prepared in cylindrical shape with dimensions of 10 $\times$ 3 mm (d $\times$ h). The flexural strength was measured on samples of a prism shape 5 $\times$ 4 $\times$ 20 mm (w $\times$ h $\times$ l) according to standard STN (42 0891-4), MPIF 41.

The electrical resistivity was measured on the samples of a cylindrical shape with the dimensions of 10 $\times$ 3 mm (d $\times$ h) by Teraohmmeter-Picoampermeter Sefelec M1501P. The magnetic measurement were performed on the toroid-shaped samples with outer diameter of 24 mm, inner diameter of 17 mm and height of 2 mm. The toroid with 33 turns was wound for AC complex permeability measurement. Complex permeability spectra were measured by an impedance analyzer (HP 4194A) from 1 kHz to 40 MHz with the contact electrodes in two-terminal connection configuration. The AC hysteresis loops were measured using MATS-2010SA and MATS-2010M AC hysteresisgraphs, respectively. All measurements were carried out at room temperature. Total losses, W_t were calculated directly from the measured hysteresis loops.

3. Results and discussion

3.1 FTIR

The FTIR spectra of the pure PFR and PFRT₃ for both uncured as well as cured samples are shown in figure 1(a, b). The FTIR analysis of pure SiO₂ particles, which were isolated from PFRT₃ sample, is also presented in this figure. First, let us take a closer look at SiO₂ spectra. The typical asymmetric and symmetric vibrations of Si–O–Si are located at 1092 cm^{−1} and 800 cm^{−1}, which correspond to the ring structure of SiO₄ tetrahedra. A band at 1630 cm^{−1} can be attributed to overtone SiO₂ vibration and stretching vibration of OH in physisorbed water molecules (Costa *et al* 1997). The signal at 959 cm^{−1} can be assigned to the Si–O–(H $\cdot$ · H₂O) bending vibration (Singh *et al* 2011) and vibrations at 2922 cm^{−1} and 2850 cm^{−1} comes from –CH₃, –CH₂ organic groups of resin remainder (Pecksook and Shelds 1990). The band at 462 cm^{−1} represents deformation vibration of Si–O–Si. This band can also be clearly visible in the sample PFRT₃ due to the presence of SiO₂ nanoparticles in the composite. The similar effect is

also observable in the FTIR spectrum of cured PFRT₃ sample (figure 1b).

The signals of the pure PFR are described in detail in our previous work (Strečková *et al* 2012). Let us therefore focus only upon the most significant changes, which occur in PFRT₃ sample on behalf of the presence of SiO₂ nanoparticles. When comparing the spectra of PFR and PFRT₃ samples, the effect of SiO₂ nanoparticles is the most obvious in the region around 1100 cm^{−1} connected by straight dotted line in figure 1. According to Fang and Suo (2011), the reason for a band broadening in this region lies in an overlap of the symmetric Si–O–Si stretching peak, C–O stretching peak and a new possible band between organic and inorganic parts Si–O–C at 1092 cm^{−1}. This effect is also evident in the cured form of PFRT₃ sample displayed in figure 1(b). The chemical incorporation of SiO₂ particles into the polymer matrix was described through the interaction between free OH groups of the resin and OH groups of the silica particles (Padron *et al* 2003). Abundance of phenolic and alcoholic –OH groups can be observed in the intense OH stretching vibrations, which form a broad peak at 3386 cm^{−1}. It is difficult to find a new absorption bands formed by the reaction of PFR and silica, but the absorption intensities in this region are significantly influenced by the incorporation of silica into the PFR matrix.

The crosslinking reaction is evident mainly from narrowing of a broad peak of phenolic and alcoholic OH groups in cured resins and their simultaneous shift toward higher wavenumbers (figure 1b). The condensation reaction is responsible for a decrease of the total number of OH groups, which is confirmed by the complete vanishing of a signal at 1370 cm^{−1} (OH in plane bend (Poljansek and Krajnc 2005)) in each cured resin.

3.2 Thermal analysis

Figure 2 depicts TG and DSC analyses of the pure PFR and three polymeric samples PFRT_{1–3} including different amount of nanometer-sized SiO₂ particles. Two significant regions can be observed during the heat treatment. The first region from 150 to 250 °C relates to a crosslinking reaction of PFR, which is responsible for building of the polymeric network. The second region from 450 to 700 °C corresponds to the pyrolysis and the overall collapse of polymer structure. Regardless of whether the pure PFR or modified PFRT_{1–3} samples are considered, both parts of thermal treatment are characteristic by similar exothermic reactions (figure 2b), which serve in evidence that SiO₂ nanoparticles are not chemically bonded in the polymeric network and form native agglomerate. Extensive studies about thermal stabilities and heat resistance (Chen *et al* 2008; Abou Msallem *et al* 2010) of hybride polymers modified by silica nanoparticles have been performed in the literature yet, but only a little attention was focused on influence of silica in the temperature region corresponding to the polycondensation reaction (see zoom in figure 2a). Moreover, this part of

Figure 1. FTIR spectra of (a) Si particles, uncured samples PFR and PFRT₃ and (b) cured samples PFR and PFRT₃.

Figure 2. (a) TG traces of the samples PFRT₁₋₃ and (b) DSC traces of the samples PFRT₁₋₃.

thermal treatment is responsible for a technologically undesirable evolution of water and other volatile by-products, which was described by Kaynak and Cem Tasan (2006) and Strečková *et al* (2012). This knowledge allowed us to set up the suitable curing schedule for the final PFRT₁₋₃ microcomposite samples reported in table 2.

The first mass loss starts around 50 °C for each sample. The highest mass loss associated with the weakly bonded water is apparent in the sample PFRT₃ with the highest content of silica (zoom of figure 2a). This observation is consistent with the fact that the larger specific surface area of silica nanoparticles in the PFRT₃ sample can release a higher content of adsorbed water compared with the samples PFRT_{1,2} or pure PFR. The rapid evolution of water and other volatile by-products at 175 °C is evident in the pure resin. Hence, it follows that a presence of silica leads to a more gradual release of water and thus, silica prevents the

formation of micro- and macro-voids in the prepared samples FePFRT₁₋₃, as well as the foaming of resin at the surface. Besides, the lower weight loss of the samples PFRT₁₋₃ around the temperature 175 °C is also the most likely caused by the silica particles, which may act as a spherical barrier during the crosslinking. TG results for each polymeric sample imply that the crosslinking finished at 200 °C, which is subsequently followed by local plateau ranging from 200 to 500 °C. The largest thermal stability in this region can be seen in the samples PFRT₁ and PFRT₂, where a more homogeneous distribution of SiO₂ nanoparticles was established in comparison with the sample PFRT₃ with the highest content of silica. The same decomposition temperature of three hybrid polymers PFRT₁₋₃ including the nanometer-sized SiO₂ was observed at 550 °C, whereas the heat resistance of those polymers has increased more than 60 °C compared with the pure PFR.

Figure 3. SEM micrographs of (a) FePFRT₁ microcomposite core-shell powder before curing and (b) detail on the morphology of Fe particle covered by PFRT₁.

Figure 4. SEM image on macrostructure of (a) fractured surface of the sample FePFRT₁ and (b) detail on crack defect.

3.3 SEM, TEM and optical microscope characterization

The morphological and structural characterization of the Fe powder coated by insulating PFRT_{1–3} layer, as well as, the final microcomposite samples obtained after pressing the microcomposite powder into a required shape, enables one to find an optimal composition of FePFRT_{1–3} samples. It has been found that in the final-stage composition, some microstructure defects or imperfections can be basically influenced through the amount of SiO₂ particles in the insulating coating.

The surface morphology of Fe particles coated by PFRT₁ before curing is presented by SEM images shown in figure 3(a, b). It can be clearly seen from figure 3(b) that PFRT₁ coating has a tendency to cover the surface of Fe microparticles completely and quite uniformly. Figure 4 shows SEM micrographs from the fractured surface of FePFRT₁ microcomposite. Although a little number of cracks were observed in this sample, the shape and dimensional stability was significantly improved when compared to FePFR microcomposite containing the pure PFR as an insulating coating. In addition, the negative effect of resin

foaming on the sample surface (which was described in our previous work (Strečková et al 2012)) has been completely suppressed. It should be noticed that no defects or structural imperfection were observed in the FePFRT_{2,3} samples with a higher content of SiO₂ in the polymeric resin. The great advantage of PFR-based polymers acting lies in their viscosity during crosslinking and their ability to bind Fe powder particles. This effect is quite evident from figure 4(b), where structural defects are partially removed due to ability of PFRT₁ resin to bind Fe particle. Thus, this privilege of resin facilitates the preparation of microcomposite samples almost without any pores or structural defects.

Another important observations can be made when comparing the polymeric networks from the polished surface of the samples FePFRT₂ and FePFRT₃ explored by optical microscopy (figure 5a, b). The most uniform and continuous net was achieved in the sample PFRT₂ with about 2% of SiO₂ particles in the coating. Eventhough the most homogeneous distribution of SiO₂ within PFR coating was achieved in the microcomposite sample FePFRT₂, one still may observe there, a rather rare formation of 10 µm SiO₂ clusters (figure 6a). The higher content of SiO₂ particles in the resin

Figure 5. OM image on hybride resin network in (a) sample PFRT₂ and (b) sample PFRT₃.

Figure 6. (a) SEM image of the sample FePFRT₂ with mapping technique for distribution, (b) C, (c) Si and (d) EDX analysis of Si cluster.

causes a creation of greater clusters, which consequently prevent the continuous networking. Note that any imperfections in FePFRT_{1–3} composite essentially affect electric, magnetic and mechanical properties. The morphology of fractured surface and the distribution of elements in each phase was elucidated by SEM supplemented with the mapping technique (figure 6a–c). The location of SiO₂ clusters, which are marked by place 'x' in figure 6, was identified by EDX analysis (zoom in figure 6a). The nanoscale of silica powder particles isolated from PFRT₂ prepolymer was verified by TEM (figure 7). The outcomes of our measurement indicate that each individual particle has a spherical shape, whereas they have an obvious tendency to form native SiO₂ agglomerate. The statistical analysis was evaluated using Gatan Digital Micrograph software and indicates that the average particle size was 152.77 nm. Statistical dispersion of particles around the average size was 41.73 nm, whereas the minimal size of particles was 84.99 nm and the maximal size was 263.48 nm, respectively.

3.4 Mechanical properties

The mechanical properties of prepared composites are usually the limiting factor for their perspective usage. A typical value of tensile strength for an insulated material including Fe powder isolated by 3% of Si is of the order of 50 MPa

(Bas *et al* 2003). The primary disadvantage of these materials is in their low mechanical strength and low value of flexural strength. Because they are not sintered, their mechanical strength is not comparable with that of conventional heat-treated SMCs at higher temperature. This may present a serious problem for the handling and transport of materials, and limits their application in high-speed motors.

The measured mechanical hardness and flexural strength of FePFR and FePFRT_{1–3} are summarized in table 3. The measured data for mechanical hardness and flexural strength imply that the best composition from the viewpoint of mechanical stability was achieved in the sample FePFRT₂. Although the highest mechanical hardness was detected in the sample PFRT₃, the high standard deviation suggests a considerable decrease in homogeneity of SiO₂ distribution. This effect is quite evident from SEM images depicted in figure 5(b). This insufficiency has a direct consequence on a flexural strength of the FePFRT₃ sample, which is substantially lower than the flexural strength of the sample FePFRT₂.

3.5 Magnetic properties

The inductance and the resistance of toroid-shaped samples were measured to characterize the magnetic complex permeability of final microcomposites FePFR and FePFRT_{1–3}. The

Figure 7. TEM image of SiO₂ particles.

Table 3. Mechanical, electric and magnetic properties of prepared microcomposites.

Sample	Hardness HV/10	Flexural strength (MPa)	Specific resistivity ρ ($\mu\Omega\cdot\text{m}$)	Relaxation frequency f_r (MHz)
Höganäs Fe	115 ^H	*	0,162	–
FePFR	83.63 $\pm$ 7.35	86.34 $\pm$ 5.88	45 800	3.06
FePFRT ₁	80.19 $\pm$ 4.70	68.38 $\pm$ 4.22	396 464	4.68
FePFRT ₂	90.62 $\pm$ 2.97	97.52 $\pm$ 9.66	66 036	3.09
FePFRT ₃	95 $\pm$ 19.17	87.70 $\pm$ 6.41	207 256	3.32

*Not quoted due to a high plasticity of the sintered Fe.

^HHöganäs Corporation 1998 Höganäs eisen-und stahlpulver für sinterformteile. p. 79–83.

real (μ') and imaginary (μ'') parts of the initial complex permeability were determined from the inductance L_s and resistance R_s of the coil wound on the ring samples using the following relations:

$$\mu' = \frac{L_s}{L_0} = \frac{L_s l_e}{\mu_0 N^2 A_e}, \quad (1)$$

and

$$\mu'' = \frac{R_s}{\omega L_0} = \frac{R_s l_e}{\omega \mu_0 N^2 A_e}, \quad (2)$$

where L_s is the self-inductance of the sample core, L_0 derived from geometrical relations showing the inductance of the winding of the coil without the sample core, N the total number of turns of the coil, μ_0 permeability of free space, ω the angular frequency, A_e and l_e are the area of cross-section and the mean flux density path of the ring sample, respectively. Two main types of magnetization processes may basically influence the magnetic behaviour of solid-state materials. In general, the dispersions caused by domain wall displacements occur in radiofrequency range (below 10 MHz), and those caused by domain rotations often appear in the

microwave range (100 MHz–10 GHz). The measured spectra in our composite samples were closely associated with the relaxation process of the domain wall motion (Valenzuela 2001).

It is quite obvious from figure 8 that the real part, μ' of complex permeability at 1 kHz ranges in between 39 and 51 for all composite samples, whereas its size basically depends on the density of the sample, the arrangement and homogeneity of the PFR matrix influenced by the content of inorganic silica particles embedded in the PFR matrix. The best magnetic response was found in the sample FePFRT₂ with the highest real part of complex permeability at 1 kHz, but the real part of complex permeability of FePFRT₁ sample becomes the highest one beyond the frequency of 10 MHz. This finding could be related to a higher volume of pores and/or structural defects in the sample FePFRT₁, which can reduce the eddy current between Fe powder particles. It is well established that the real part of complex permeability, μ' strongly depends on the density, number of pores, non-magnetic phase, crystal anisotropy and magnetic anisotropy (Taghvaei et al 2010b), because all these factors suppress domain wall displacement. For example, the presence of a

non-magnetic material between the magnetic powder particles acts as a source of demagnetizing field quite similarly as an air gap. Consequently, the domain wall movement is more restricted and this limits an increase in the real part of complex permeability. The effect of SiO₂ content on the imaginary part, μ'' of the complex permeability can also be understood from the frequency dependence shown in figure 8. The imaginary part of the complex permeability reflects the power losses due to eddy currents and hysteretic behaviour. The imaginary part of the complex permeability exhibits a pronounced round peak at a frequency that slightly depends on the content of silica particles inside the insulating layer, at which the real part of complex permeability simultaneously displays a rapid decrease. The higher the electric resistivity of the sample is, the higher is the relaxation frequency, f_r corresponding to a maximum of the imaginary part of complex permeability (table 3). The damping of domain wall displacement could be mainly attributed to the eddy current and hysteresis effects. The coercivity of the samples is higher than a weak alternating field during the inductance, L_s and resistance, R_s measurements of the coil, which indicates that the hysteresis effects may be neglected. The damping associated with domain wall motion contributes to the eddy currents, while the relaxation frequency is the most closely related to the resistivity of the samples.

The d.c. magnetic properties of all prepared samples are represented by the hysteresis loops measured for maximum induction, $B_m = 0.2$ T, figure 9. Since all samples consist of the same ferromagnetic material, the slope of the hysteresis loops reflects the way how the non-ferromagnetic material (resin, pores) is distributed in the composite material. In the sample FePFRT₂, the ferromagnetic particles produce

the weakest demagnetizing field, H_d oriented in opposite to the external magnetic field, H and the hysteresis loop is simultaneously the steepest (Anhalt *et al* 2008).

It is worthwhile to remark that the coercive field of all samples is very similar (approx. 210 A/m). Owing to this fact, one may suppose that the ferromagnetic particles are relatively well insulated from each other and the magnetization reversal occurs independently for individual Fe powder particles. The most important magnetization process is with a high probability domain wall displacement inside the Fe powder particles due to a small maximum induction. It could be concluded that the sample FePFRT₂ exhibits the best d.c. magnetic properties. The area of the hysteresis loops is equal to the value of hysteresis loss, P_h , which represents a part of core losses in a.c. magnetic fields.

Iron loss in magnetic cores can mainly be divided into two components, i.e. the static and dynamic losses. These losses are more precisely named as hysteresis loss, classical eddy current losses and anomalous losses, which are also known as excess eddy current losses (Bozorth 1993). The total iron losses, P can be expressed by

$$P = P_h + P_e + P_a \text{ (W/kg)}, \quad (3)$$

where P_h , P_e and P_a are the hysteresis losses, eddy current losses and anomalous losses, respectively. The eddy current losses, P_e under sinusoidal excitation can be calculated from the well-known formula

$$P_e = \frac{\pi^2 B_m^2 d^2 f^2}{\beta} \sigma, \quad (4)$$

Figure 8. Real, μ' part and imaginary, μ'' part of complex permeability of FePFR and FePFRT₁₋₃.

Figure 9. DC hysteresis loops of FePFR and FePFRT₁₋₃ measured at maximum induction, $B_m = 0.2$ T.

Figure 10. Core loss of FePFR and FePFRT_{1–3} at maximum induction, $B_m = 0.1$ T.

where d is the effective diameter of eddy currents, B_m the maximum flux density, f the frequency, σ the conductivity and β the geometrical coefficient.

The eddy current losses depend on the geometry of the specimen and they arise if the insulation between particles is not perfect and currents between particles exist. The bulk resistivity of an iron powder material is related to a perfection of the insulation between particles, i.e. a high resistivity implies a good insulation, which consequently forces the eddy currents to circle mostly inside powder particles and the geometry dependence is thereby low. A decrease in the insulation between Fe powder particles lowers the bulk resistivity and increases the geometry dependence of the eddy current loss. The classical eddy current loss in an iron powder material can be separated into two parts. One part is due to eddy currents in the bulk material, i.e. currents flowing in the entire cross-section of the material, while the other part is owing to eddy currents set-up in the interior of a powder particle. The total eddy current loss is a combination of the two parts and the contribution of each part is determined by the size and shape of the specimen and powder particles, respectively, as well as by the bulk resistivity of the material. The influence of the content of nano-sized SiO₂ particles in the organic–inorganic insulating layer of the microcomposites on the total core losses, P is displayed in figure 10. Interestingly, the core losses of the prepared FePFR and FePFRT_{1–3} samples do not generally decrease with increase in the electrical resistivity of the bulk material. This is probably due to the major contribution of the interior eddy currents part and different effective diameter of eddy currents of the powder cores. The lowest values of the core losses were observed in the sample FePFRT₂ in the frequency range from 120 Hz to 40 kHz on behalf of the best uniform arrangement and homogeneity of

the insulating coating PFRT₂ compared with the insulating coating of other samples.

4. Conclusions

In the present article, we have shown one possible way for a design of new SMCs, which retain the shape and dimensional stability immediately after the sample preparation and possess a good enough magnetic properties. SMC materials based on Fe powder and PFR modified by nano-sized SiO₂ particles have been obtained by undemanding and low-cost way. Before one can give a detailed explanation of FePFRT composites, one must at first describe all chemical aspects of a preparation of the organic–inorganic coating. The hybriide PFRT polymer with three different amounts of nano-sized SiO₂ particles were synthesized by the sol–gel method under which the hydrolysis and condensation of TEOS occur in two successive steps within PFR environment. At this stage, the condensation of silica particles accompanies the polymerization of PFR in order to form the hybriide polymer PFRT, whereas the nano-sized SiO₂ particles of two different dimensions (ca. 42 and 153 nm) were detected by TEM. TG analysis has confirmed that the silica particles suppress technologically undesirable effects such as an evolution of water and other volatile by-products during crosslinking and thus, they act against the formation of any structural defects. The optimal composition of hybriide polymer and its distribution within the final samples was achieved in the sample FePFRT₂ with approximately 2% of nano-sized SiO₂ particles embedded in the insulating layer. The very uniform and homogeneous distribution of PFRT coating allows one to prepare the samples with a rather high value of the mechanical hardness and flexural strength. The ferromagnetic particles are relatively well insulated and the slope of the hysteresis loops reflects the way how the non-ferromagnetic material (resin, pores) is distributed in the composite material. The best soft magnetic properties (the highest real, μ' part of permeability and the lowest core losses) were observed in the sample FePFRT₂ due to the most uniform arrangement and homogeneity of the insulating coating PFRT₂.

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