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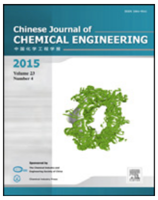

Materials and Product Engineering

A comparison of soft magnetic composites designed from different ferromagnetic powders and phenolic resins[☆]

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ABSTRACT

Soft magnetic composites (SMCs) were prepared from three different ferromagnetic powder particles: iron powder ASC 100.29, spherical FeSi particles and vitroperm ($Fe_{73}Cu_1Nb_3Si_{16}B_7$) flakes. Two types of hybrid organic–inorganic phenolic resins modified with either silica nanoparticles or boron were used to design a thin insulating layer perfectly covering the ferromagnetic particles. Fourier transform infrared (FTIR) spectrometry confirmed an incorporation of silica or boron into the polymer matrix, which manifested itself through an improved thermal stability of the hybrid resins verified by thermogravimetric-differential scanning calorimetry (TG-DSC) analysis. The core-shell particles prepared from the ferromagnetic powder particles and the modified hybrid resins were further compacted to the cylindrical and toroidal shapes for the mechanical, electrical and magnetic testing. A uniform distribution of the resin between the ferromagnetic particles was evidenced by scanning electron microscope (SEM) analysis, which was also reflected in a rather high value of the electrical resistivity. A low porosity and extraordinary high values of mechanical hardness and flexural strength were found in SMC consisting of the iron powder and phenolic resin modified with boron. The coercive fields of the prepared samples were comparable with the commercial SMCs.

1. Introduction

Soft magnetic composites (SMCs) are ferromagnetic particles coated by a thin electroinsulating layer and then pressed into the desired shape by the powder metallurgy (PM) methods. PM technology is a common economic process for a mass production of near-net-shape parts. PM techniques have been successfully used in order to prepare SMCs mostly by compaction of the pure iron powder particles, which are spatially separated from each other by insulating (dielectric) material [1–3]. The aim of PM technologies is to achieve SMCs with a high enough density and sufficiently stable mechanical properties, whereas an insulating layer between magnetic powder particles should ensure a high electrical resistivity minimizing the overall magnetic losses [4]. In comparison with laminated soft magnetic materials, SMCs prepared by PM methods have unique magnetic properties such as the three-dimensional isotropic ferromagnetic behavior, low eddy current loss, as well as relatively lower total core loss at medium and high frequencies [5,6]. The disadvantages of these materials are in a low density and high inhomogeneity, which are responsible for a lower flexural and mechanical strength. This fact represents serious problems for the handling and transport of the insulated material components and limits their application in high-speed motors [7]. The insulation coating may have organic or inorganic character [8–11]. The advantages of organic binders lie in the smart preparation of composites, high density of final green compacts and thermally undemanding curing process [12]. However, it has been demonstrated in our previous works that the thermosetting resins of hybrid organic–inorganic character are quite superior with respect to the pure organic binders because the chemical incorporation of appropriate inorganic additives into polymeric structure substantially improves mechanical properties of the final composites [13,14]. The chemical modification of phenolic resin by silica or boron generally improves the thermal stability, mechanical and flexural strength of the hybrid organic–inorganic coating [15,16]. Moreover, the dimensional and shape stability after thermal treatment of the final composite composed of ferromagnetic particles and hybrid resin is ensured by the convenient set up of productions parameters and addition of fillers [17]. Different kinds of composites with various combinations of used fillers and additives have found their application in microwave absorption due to their outstanding physicochemical properties [18–21].

The main goal of this work was to prepare SMCs with optimal mechanical and magnetic properties for technological applications at

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medium frequencies. Fe, FeSi and vitroperm ($Fe_{73}Cu_1Nb_3Si_{16}B_7$) powders were used as base ferromagnetic materials for the composite preparation. The phenol-formaldehyde resin modified with either silica or boron was synthesized through the sol–gel process, which was subsequently used as electroinsulating spacer between the ferromagnetic particles. The thermal degradation of both synthesized resins was detected by TG analysis. The chemical embedding of silica or borate esters into the polymer matrix was analyzed by FTIR spectrometry. The morphology and microstructure were observed by SEM and optical microscope (OM). In addition, the electric resistivity and coercivity field of the prepared samples were investigated in order to prove that they all belong to the family of SMCs.

2. Experimental

2.1. Material

The iron powder (ASC 100.29, Höganäs) with the size fraction in the range from 45 to 212 μm, FeSi with 3% of Si (Höganäs) and Vitroperm ($Fe_{73}Cu_1Nb_3Si_{16}B_7$) milled powder from stripe (Vacuumschmelze GmbH & Co. KG) was used as the base ferromagnetic material for the preparation of microcomposites. Phenol (P, 99%, Aldrich), formaldehyde (F, 37% aq., Aldrich), ammonia (NH_3, 26% aq., Aldrich), tetraethylorthosilicate (TEOS, 99%, Merck), 3-glycidoxypropyltrimethoxysilane (GLYMO, 98% Aldrich) and boric acid (H_3BO_3 99.5% Lachema) were used for the synthesis of pure organic and hybrid organic–inorganic resins. Tetrahydrofuran (THF, 99.9%, Aldrich) and ethanol (absolute, Fisher) were used as solvents. The base properties of three types of ferromagnetic powder particles and hybrid phenolic resins are shown in Table 1.

Table 1
Properties of original powders and used hybrid resins

Sample	Average diameters/μm	Surface area/$m^2 \cdot g^{-1}$	Apparent density/$g \cdot cm^{-3}$	Electrical resistivity/$\mu\Omega \cdot m$
Fe ASC 100.29	98.06	0.08	2.97 ± 0.075	0.162 [22]
FeSi -355	150	0.04	4.46 ± 0.005	0.6 [23]
FeSi-150	90	0.12	4.37 ± 0.005	0.6 [23]
Vitroperm	178.3	0.04	6.42 ± 0.005	1.1–1.2
PFR	Amorphous	Amorphous	1.21 ± 0.002	Dielectric
PFRGT	Amorphous	Amorphous	1.26 ± 0.008	Dielectric
PFRB	Amorphous	Amorphous	1.14 ± 0.002	Dielectric

2.2. Composite preparation

The chemical synthesis of pure phenol-formaldehyde resin (PFR) and hybrid phenol-formaldehyde resin (PFRGT) modified with silica using GLYMO and TEOS were carried out according to the procedure thoroughly described in our previous work [12]. The new hybrid resin PFRB modified with boron was synthesized by the analogous sol–gel process with exception that H_3BO_3 was used as a source of boron additionally incorporated into the polymer matrix. The initial molar reaction ratio of $Ph/F/NH_3/H_3BO_3$ was 1/1.5/0.35/0.1. The chemical composition of resins was analyzed by FTIR spectrometry (Shimadzu, IRAffinity, KBr pellets 1 mg sample + 300 mg KBr). The comparison of thermal degradation of the prepared resins was detected by TG-DSC analysis (METTLER 2000 C).

The hybrid resins were dissolved approximately in 10 ml of solvents and the predetermined amount of soft magnetic powders was mixed in this solution after complete evaporation of solvent from the suspension. PFR and PFRB are soluble in ethanol, while PFRGT is soluble just in the THF. In this way, the core-shell powders Fe/PFRB, Fe/PFRGT, FeSi/PFRGT, vitroperm/PFRGT and vitroperm/PFRGT pre-annealed at 500 °C were prepared. The composition of the final products is given in Table 1. In order to prepare the final microcomposites, the coated powder was pressed at 800 MPa into the required shapes for mechanical, electrical and magnetic testing. The prepared samples were cured under the ambient pressure up to 200 °C.

2.3. Composite testing

The microstructure and morphology of all samples were examined by the scanning electron microscope (SEM) (JEOL JSM-7000F) and optical microscope (OM) (Olympus GX 71). The density of each prepared sample was determined by the helium pycnometer (AccuPyc II 1340, Micromeritics). The average diameters and surface area of used powder were measured by granulometer (Malvern Mastersizer 2000) equipped with statistical software 5.60. Vickers hardness test HV10 [STN-EN-ISO 6507-1 (42 0374), MPIF 43] and electrical resistivity were measured on the cylindrical shaped samples with dimensions of 10×3 mm ($d \times h$) determined by Teraohmmeter–Picoampermeter Sefelec M1501P. The flexural strength transverse rupture strength [TRS) (STN (42-0891-4), MPIF41] was detected on prism-shaped samples of dimensions $5 \times 4 \times 2$ mm ($w \times h \times l$). Magnetic measurements were recorded on the toroid-shaped samples with the outer diameter of 24 mm, the inner diameter of 17 mm and the height of 2 mm. The direct current (DC) hysteresis loops at maximum induction (B_m) of 0.1 T were measured by fluxmeter based hysteresisgraph.

3. Results and Discussion

3.1. FTIR and TG characterization of hybrid resins

The chemical structure of PFR and PFRGT as derived from FTIR and NMR analysis are illustrated in Fig. 1(a) and (b) (see Ref. [13] for more details on chemical aspects of the relevant polymeric structure). On the other hand, two typical bridging modes as shown in Fig. 1(c) and (d) could be expected in the synthesized PFRB resin according to the previously published literature [24].

FTIR spectra for the native PFR, the hybrid PFRGT and PFRB resins are depicted in Fig. 2. The recorded FTIR spectrum for PFR gives evidence of the condensation reaction between phenol and formaldehyde as it has been already discussed in detail in our previous works and work by Poljansek and Krajnc [13,25]. FTIR spectrum of PFRGT demonstrates reaction between resol-type phenolic resin and GLYMO. This spectrum displays noticeable increase of two signals 2942 and 2881 cm^{-1}, which reveals a presence of stretching vibration of $-CH_2-$ alkane arising from GLYMO. Moreover, the signal at 1458 cm^{-1} ($-CH_2-$ methylene bridge) in the PFR spectrum was divided into two peaks in the spectrum of PFRGT: 1492 cm^{-1} ($C-H$ aliphatic) and 1462 cm^{-1}, which confirm the chemical linkage between phenolic resin and silica. The chemical bonding of Si to polymer matrix is also evident from the presence of symmetric stretching peak $Si-O-Si$ and a new covalent bond $Si-O-C$, which nearly overlap and give the signal at 1112 cm^{-1}. The band at 461 cm^{-1} represents the deformation vibration of $Si-O-Si$, which is also clearly visible in the spectrum of PFRGT. The FTIR spectrum for the resole-type resin modified with boric acid was reported by Gao and co-workers [26]. According to this work, the apparent change in the PFRB spectrum in comparison with PFR spectrum is observable in the range 1180 cm^{-1}–900 cm^{-1}. This qualitative change in the FTIR spectrum can be attributed to the chemical reaction of the methylol hydroxyl group (1200 cm^{-1}) with boric acid, which yields aromatic borate esters as displayed in Fig. 1(c) and (d).

Next, TG analysis was performed in order to provide information about thermal stability of synthesized resins. It can be seen from Fig. 3 that pure PFR exhibits a sharp transition at 175 °C, which can be attributed to a rapid evolution of water and other volatile by-products (the solid-black line). Such a rapid crosslinking of polymer causes undesirable creation of cracks and foaming of PFR resin on the sample surface [13,17]. Contrary to this, a slower and more gradual release of water