FILLER INFLUENCE ON MICROSTRUCTURE OF Fe/RESIN COMPOSITES

M. Strečková, R. Bureš, M. Faberová, T. Sopčák

Abstract
The microcomposite material based on Fe and phenol-formaldehyde resin was prepared. The technological undesirable effect of water release was suppressed by addition of SiO₂ and ZnSO₄. These polymer additives are response for desirable effects. The suitable curing schedule was proposed to achieve a better dimensional and shape stability. Both additives were confirmed as good water absorbents using TG and DSC analysis. The addition of ZnSO₄ to pure PFR causes very unusual and unexpected polymerization of PFR. Scanning electron microscopy (SEM) was confirmed in the final cured Fe-PFR-ZnSO₄ microcomposite samples, which result in the fibrillar structure. The significant increase of its mechanical hardness was found in Fe-PFR-ZnSO₄.

Keywords: phenol-formaldehyde resin, zinc sulphate, silica, cross linking

INTRODUCTION
The phenol-formaldehyde resins (PFR) belong to the oldest thermosetting polymers with a wide range of usage, especially because of their low cost, aging endurance, undemanding preparation and grate modification with regard for further use [1,2]. Moreover, organic coatings usually represent a convenient end economical method for an effecting protection of metals against corrosion [3]. The appropriate design of composite powder materials with desirable mechanical and physical-chemical properties is a very difficult task, because their chemical modification should simultaneously improve various properties such as density, dimensional and shape stability, tensile strength, electric, magnetic and optical properties. Soft magnetic composites (SMC), which are used in electromagnetic application, can be produced from ferromagnetic powder particles coated by an electrical insulating film [4]. PFR are one of the most important insulating organic coatings for preparation of SMC, but conservation of dimensional stability after curing is a limiting factor of overall sample preparation. The evolution of water and other volatile by-product is a natural part of cross-linking process during curing. It has been found by C. Kaynak [5] that release of water molecules during polymerization reaction causes formation of micro and macro voids, as well as, foaming of resin at the surface due to the water vapour bubbles getting trapped in the specimen. For this purpose the very long heating schedule was designed for the slow enough water release that prevents bubble formation. One way to avoid the undesirable release of water gaseous products is an addition of good water adsorbent into the prepared resin.

In this work we will focus our attention on the preparation of resol type PFR and PFR modified by inorganic additives SiO₂ and ZnSO₄, which will be subsequently serve as a suitable organic coatings for Fe powder particles with the aim to prepare Fe-PFR, Fe-
PFR-SiO$_2$ and Fe-PFR-ZnSO$_4$ composites. The influence of silica and ZnSO$_4$ additives will be examined termogravimetric (TG) and differential scanning calorimetric (DSC) analysis. The change in morphology and microstructure will be related to the character of additive. The emphases are laid on mechanical properties of prepared microcomposite material whereas the hardness and flexural strength will be explored in detail.

EXPERIMENTAL

Preparation of microcomposite material

The PFR was synthesized by using phenol (99.0%, Aldrich), formaldehyde (37% aq, Aldrich) and NH$_3$ as catalyst (26% aq, Slavus). Dried SiO$_2$ and ZnSO$_4$ mean grain size around 150 nm were intercalated as inorganic additives to PFR. The reaction molar ratio of phenol/formaldehyde/ammonia (Ph/F/NH$_3$) was (1.0/1.5/0.35). The resin for this purpose was synthesized through a conventional route employed for a resol-type resin and previously reported by our research group [6]. In the final stage of preparation (after removing water under vacuum at 95°C) both additives were added to still viscous resin and consequently, two types of resins PFR-SiO$_2$ and PFR-ZnSO$_4$ were prepared.

The coated iron particles were obtained from the solution containing PFR or modified PFR and acetone after drying of solvent. The resulting coated microcomposite Fe powder was pressed at 800 MPa to required shapes due to the further samples tests. The final microcomposites were cured under proposed heating schedule (Tab.1). The composition, hardness and flexural strength of prepared microcomposites, is listed in table 2.

Characterization techniques

The influence of both additives in the pure PFR and also in microcomposites was analysed by TG and DSC analysis. Simultaneous DSC and TG analysis were performed by use of difference scanning calorimeter (METTLER 2000 C). The samples were heated up to 700°C at a heating rate of 10°C/min in an air atmosphere. The microstructure and morphology of fracture surfaces was observed by the scanning electron microscopy SEM (JEOL JSM-7000F). Vickers hardness test was measured according to STN EN ISO 6507 – 1 (42 0374), MPIF 43. For this purpose the samples were prepared in cylindrical shape 10 x 3 mm (d x h). The flexural test according to standard STN 42 0891-4, MPIF 41 was measured on samples of prism shape 5 x 4 x 20 mm (w x h x l).

<table>
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<tr>
<th>Samples notation</th>
<th>PFR [wt %]</th>
<th>Fe [wt %]</th>
<th>SiO$_2$ [wt %]</th>
<th>ZnSO$_4$ [wt %]</th>
<th>HV10</th>
<th>TRS [MPa]</th>
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</table>
RESULTS AND DISCUSSION

Thermal analysis

Figure 1a shows the TG traces of the pure phenolic resin (sample A) and PFR with both mentioned additives (samples D, E), which were heated within the temperature rate 20-700 °C in air atmosphere. The two transition states are clearly seen in each sample. In the case of pure PFR, the first is around 175 °C, which represents the loss of the absorbed water. Fast evaporation of gaseous products causes the formation of micro- and macro voids in prepared resin and foaming of resin at the surface of the Fe-PFR composites. This of technologically unwanted process was suppressed by two inorganic additives with good water absorption ability. More slow evolution of gasses was observed in the case of sample D and E. The second transition state around 650 °C corresponds to a thermal degradation of resins. Two exothermic peaks are evident from DSC traces (Fig.1b), which can be attributed to the described transition states. Figure 1c displays the traces of Fe powder coated by pure and modified PFR: samples C, F and G. A small mass loss can be observed around 50 °C, which corresponds to a release of chemically weakly bonded water. Note furthermore that the highest mass loss up to 200°C occurs in the iron powder coated with the modified resin PFR-ZnSO₄ because of different interaction between PFR-ZnSO₄ with Fe in comparison with PFR-SiO₂ with Fe. It is quite evident that, Fe substantially affects the cross linking temperature of resin in sample C where this temperature shifts to lower values (around 100°C) in comparison with the sample of pure resin (170°C). It also turns out that the addition of SiO₂ or ZnSO₄ significantly influences the stability of modified resins in the samples F and G above the temperature 400°C.
SEM characterization of microcomposites materials

The effects of addition of afore-mentioned additives are clearly seen from displayed macrostructure in Fig.2. Unwanted foaming of PFR on the surface (Fig.2a) was sufficiently suppressed by SiO\textsubscript{2} addition (Fig.2b). The similar effect was also observed in the case of Fe-PFR-ZnSO\textsubscript{4}. This implies that both additives act against surface deformation and PFR separation from the composite. However, slow release of water or other gaseous products still caused very fine cracks under surface. This technological undesirable effect will by subject of further research.

![Image of macrostructure](image_a.png)

![Image of macrostructure](image_b.png)

**Fig.2.** SEM image on macrostructure of a) Fe-PFR without additives (effect of foaming) b) Fe-PFR-SiO\textsubscript{2} microcomposite.

Figure 3 shows different morphologies of modified PFR uncured coating on Fe powder particles. A very smooth and uniform coating was observed in the case of Fe-PFR-SiO\textsubscript{2} microcomposite powder. On the other side, the addition of ZnSO\textsubscript{4} provokes the polymerization of resin in the form of fibres (Fig.3b), which are spatially spread to all sides around Fe particles. PFR fibres are approximately 10 µm long with thickness about 100 nm.

![Image of microcomposite](image_a.png)

![Image of microcomposite](image_b.png)

**Fig.3.** SEM micrographs of microcomposite powder before curing a) Fe-PFR-SiO\textsubscript{2} b) Fe-PFR-ZnSO\textsubscript{4}, (zoom on the polymer fibers).

The different microstructures of Fe-PFR-SiO\textsubscript{2} (Fig.4a) and Fe-PFR-ZnSO\textsubscript{4} (Fig.4b) became evident also after curing of final microcomposite samples. A very fine
SiO$_2$ agglomerates were found in the PFR coating (zoom in fig.4a). It can be assumed than the fibrillar microstructure of PFR-ZnSO$_4$ coating could cause significant changes in mechanical properties of composite.

![Fig.4](image)

It can be seen, that PRF is uniformly distributed around each Fe particle and creates homogenous network (Fig.5). Continuous, uniform and adhesive coating without any exfoliation is evident from fig.5 b, which shows a detail of PFR coating on Fe particle. Note furthermore that just insignificant porosity was observed in the samples.

![Fig.5](image)

**CONCLUSION**

The iron powder coated by PFR as a thin electrical insulating layer was prepared with aim to design a new class of prospective soft magnetic composite. Resol type prepolymer was synthesized with NH$_3$ catalyst and modified with two inorganic additives SiO$_2$ and ZnSO$_4$. The elimination of undesirable foaming of PFR on the surface was achieved by proposed curing schedule. The results of TG and DSC analysis showed that both additives are suitable water absorbents. Higher water absorption was found in the case of PFR-SiO$_2$, which can be attributed to larger specific surface of SiO$_2$ additive.
Nevertheless, the addition of ZnSO$_4$ caused a significant change in the polymer structure, which consist of nano-fibers linking Fe particle in final composite. The fibrillar structure was studied by SEM in detail. The mechanical hardness test has confirmed that the fibrillar structure of Fe-PFR-ZnSO$_4$ microcomposite powder results in mechanically more stable material with a significantly higher hardness.

**Acknowledgement**

This work was financially supported by Slovak Research and Development Agency under the contract no APVV 0222/10.

**REFERENCES**