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Review of the Doctoral Thesis

"Preparation and characterization of advanced spinel ferrite nanocomposites for electromagnetic applications"

by Anju

Ms. Anju has prepared the reviewed doctoral dissertation at Tomas Bata University in Zlin, under the supervision of Dr. Raghvendra Singh Yadav. The presented work covers the topics related to preparation and characterization of various cobalt ferrite nanoparticles that were synthesized using sonochemical approach and incorporated along with the conducting fillers such as graphite or reduced graphene oxide (rGO) into a thermoplastic polyurethane (TPU) matrix. Such developed polymer nanocomposites were then tested and utilized as novel materials for shielding of electromagnetic interference (EMI). The motivation of the performed studies is a growing electromagnetic pollution related to e.g. telecommunications signals that implies requirements of proper shielding of numerous devices/locations in order to limit EMI.

In my opinion, the chosen topic, presented research objectives are challenging and consistent with current trends in fabrication of light and cost-effective materials addressing the important needs related to increasing electromagnetic pollution.

The dissertation opens with a short introduction on electromagnetic pollution, its classification and quantification followed by description of traditional EMI shielding materials and novel approaches based on polymer nanocomposites with various conductive and magnetic (nano)fillers. This is a concise introduction (22 pages, 29 references) rather than a comprehensive presentation of state-of-the-art in the given topics but it is sufficient to appreciate the motivation of the undertaken research and follow the result presented in the

experimental part of the dissertation. Nevertheless, presentation of more detailed literature background would be helpful for appreciation of the novelty and importance of the presented objectives of the thesis.

Those objectives were then clearly specified and address: (1) synthesis and characterization of various cobalt ferrite nanoparticles using sonochemical approach and doped with Zn^{2+} and/or Cu^{2+} ions (magnetic fillers), (2) synthesis and characterization of rGO (conductive fillers), (3) fabrication of polymer-based nanocomposites with both conductive and magnetic fillers, (4) investigation of various parameters of the nanocomposites related to their EMI shielding efficiency.

The following chapter lists the experimental methods and characterization techniques in a clear fashion with several informative schemes and photographs. Chapter 5 presents the experimental results and their discussion divided into three general subchapters (and a final small subchapter on possible commercial application of the nanocomposites) following a given type of cobalt ferrite nanoparticles synthesized and applied in the fabrication of nanocomposites. The first subchapter focuses on zinc-doped cobalt ferrite nanoparticles that were synthesized in order to tune the magnetic and dielectric properties of the nanoparticles. The nanoparticles with various content of zinc were synthesized using a sonochemical approach and carefully characterized (e.g., XRD, FTIR and Raman spectroscopy, SEM, TEM, XPS, magnetometry) revealing e.g., their superparamagnetic properties after doping with zinc. Then, the nanocomposites based on TPU with the synthesized nanoferrite and rGO fillers were formed and studied with respect to their e.g. mechanical properties, thermal stability, and magnetic properties. The total shielding effectiveness was found to be the largest for the composites with the nanoferrite having the highest content of zinc in a broad frequency range that is related to its magnetic properties. Importantly, the correlation was also found between the zinc content and the shielding efficiencies related to both absorption and reflection of the electromagnetic waves. Especially large contribution of shielding due to absorption seems to be advantageous with respect to classical metal-based shielding as the nanocomposites may reduce the secondary reflections making shielding more environmentally-friendly. Other measurements related to e.g. electrical conductivity or dielectric loss contributed to the proposed explanation of such a good shielding performance of the nanocomposites, especially due to absorption. Overall, the obtained TPU-based nanocomposites with Zn-doped cobalt

ferrite nanoparticles and rGO as fillers were shown to exhibit a superior shielding performance combined with flexibility and small density of the material as compared to metal coatings.

The next subchapter describe analogous studies but based on Cu^{2+} -doped cobalt ferrite nanoparticles in the same polymer matrix with the same rGO fillers. The presented results revealed comparable electromagnetic shielding performance to Zn^{2+} -doped cobalt nanoferrites described in the previous subchapter. Also the general conclusion on the influence of the dopant level on the shielding performance, the role of impedance matching as well as other magnetic and dielectric properties on the shielding efficiency are in line with those formulated for the nanocomposites with the zinc-doped nanoferrites.

Chapter 5.3 describes the results of the studies on optimization of the content of the TPU-based nanocomposites with respect to the undoped cobalt ferrite nanoparticles and graphite as a conductive filler. The studies again started from detailed structural characterization of the obtained nanoparticles and composites followed by magnetic and electric characterization of the nanocomposites varying in the content of both fillers. The most efficient EMI shielding properties were found for the sample containing 15 wt% of the ferrite nanoparticles and 35 wt% of graphite. Importantly, this enhanced shielding was found to be attributed to the enhanced absorption and lesser reflection of the electromagnetic waves that seems to be beneficial for their practical applications.

Those applications were then addressed in the final subchapter (5.4). The mentioned potential applications of those light EMI shielding materials include spacecraft industry, consumer electronics, medical devices but also military applications related to electromagnetic camouflage and protection of data centers or sensitive scientific apparatus. The overall scientific achievements of the thesis are clearly collected in the concluding remarks.

The results presented in the thesis have been published in three research papers in good scientific journals and collected in a review paper. The PhD candidate is a coauthor of three other papers and coeditor of a book. This makes Anju's overall achievements well above the average for a PhD student. Due to my role as a reviewer, I would also like to add some comments and possible corrections that the candidate may address during the defense of the thesis:

(1) There was no stabilizer (neither low molecular weight nor polymeric surfactant) used in the synthesis of magnetic nanoparticles that could prevent aggregation of the nanoparticles

and eventually improve their magnetic performance and/or dispersibility in the polymer matrix. Would you consider application of any additive like this for the performed syntheses?

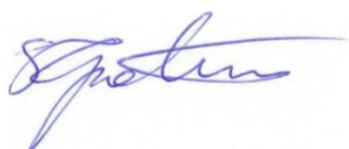
(2) What was the reason for using different contents of the fillers (20%, for composites with rGO and 50% for graphite) in the formation of the nanocomposites?

(3) Have you considered/performed any aging or accelerated aging studies on the formed nanoferrites and/or nanocomposites? One may expect e.g., some variation in Fe/Co/Zn/Cu cations distribution or partial dissolution of the nanoparticles that may affect their performance.

(4) Why the ferromagnetic undoped ferrite but not one of the synthesized dope ferrite having superparamagnetic properties was chosen for the optimizations studies (chapter 5.3)?

(5) Why shielding due to reflection (Figure 5.38 c) does not change monotonically with the content of the nanoparticles in the composites? SE_R is exceptionally small even SE_T is the largest for GF15-TPU? Would you consider this property beneficial or not?

In summary, Ms. Anju has confirmed her competency in synthesizing and characterizing both functional nanoparticles and respective polymer-based nanocomposites. Importantly, an impressive number of methods was used for determination of magnetic, electrical properties and the detailed EMI shielding performance addressing also the mechanisms of this action. The obtained materials were shown to exhibit exceptional shielding ability paving the way for their commercial applications. The research methodology was generally clearly described and the whole dissertation was clearly written. Thus, in my opinion, the reviewed thesis fulfills the criteria set for a PhD thesis and I ask for admission of Ms. Anju to the public defense of the dissertation.



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