LIGHTWEIGHT, FLEXIBLE AND HIGH-PERFORMANCE NANOCOMPOSITES BASED ON REDUCED GRAPHENE OXIDE AND SPINEL FERRITE ($ZnFe_2O_4$ / $CoFe_2O_4$) NANOPARTICLES IN THERMOPLASTIC POLYURETHANE MATRIX FOR ELECTROMAGNETIC INTERFERENCE SHIELDING APPLICATIONS

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Abstract

Lightweight and flexible material with enhanced electromagnetic interference shielding effectiveness is highly in demand in the electronics and communication industry. Herein, we synthesized $CoFe_2O_4$ and $ZnFe_2O_4$ nanoparticles using the sonochemical method, and further, these nanoparticles were embedded inside thermoplastic polyurethane (TPU) along with reduced graphene oxide (rGO) by a melt-mixing approach using a microcompounder. $CoFe_2O_4$ or $ZnFe_2O_4$ nanocomposites in the TPU matrix with rGO showed outstanding electromagnetic shielding performance having a constant thickness of 0.80 mm, only. The maximum total shielding effectiveness (SE_T) was 48.3 dB for $ZnFe_2O_4$ nanocomposite and 50.76 dB for $CoFe_2O_4$ nanocomposite. These results indicate that the developed nanocomposite can be potentially utilized for electromagnetic shielding applications.

Keywords: Nanocomposites, Electromagnetic Interference Shielding, Graphene, Spinel ferrites, Thermoplastic Polyurethane

1. INTRODUCTION

Owing to the demand for electronic devices and telecommunication technology, electromagnetic interference (EMI) has become a serious and severe concern in various areas such as aerospace, defense, intelligence, and electronic appliances [1]. Electromagnetic interference shielding is a mechanism of reflection and absorption of electromagnetic radiation by a material that prevents the penetration of harmful electromagnetic waves into electronic devices. For commercial applications, an EMI shielding value greater than 20 dB corresponding to 99.9% of the attenuation of the electromagnetic radiation power is suitable [2].

With the broad investigation in the many previous years, polymer nanocomposites have gained a lot of attention due to their lightweight, corrosion resistance, flexibility, high conductivity, and ease of processability [3]. A homogeneous dispersion of fillers in the polymer matrix is required to determine the final properties of fabricated nanocomposites [4]. Thermoplastic polyurethane (TPU) has been broadly used in electronic applications due to its outstanding high extensibility, flexibility, low glass transition temperature, good mechanical properties, and chemical resistance [5]. Therefore, TPU can be considered as an ideal choice as a polymer matrix for fillers. However, the EMI shielding performance of a polymer nanocomposite is based on the electrical and magnetic properties of the fillers. Ferrites have been extensively utilized as magnetic material because of their low cost, ease of preparation, and large magnetic momentum. A combination of polymer–magnetic ferrite composites is a potential candidate as shielding material due to a hybrid structural and functional combination between the organic and inorganic materials [6]. Despite several attempts to design a highly conductive network in a polymer matrix, there are still gaps in utilizing spinel ferrite nanoparticles with reduced graphene oxide in the TPU matrix for EMI shielding in the literature. From this standpoint, we have utilized cobalt ferrite and zinc ferrite nanoparticles along with reduced graphene oxide as a filler in the TPU polymer matrix for electromagnetic interference shielding applications in the X-band frequency region.

2. MATERIALS AND METHODS

2.1. Materials

Cobalt nitrate $Co(NO_3).6H_2O$, zinc nitrate hexahydrate $Zn(NO_3).6H_2O$, and iron nitrate $Fe(NO_3)_3.9H_2O$ were procured from AlfaAesar GmbH & Co. KG (Germany). Sodium nitrate ($NaNO_3$) was purchased from Lach-Ner, Czech Republic. Potassium permanganate ($KMnO_4$) powder and graphite flakes were purchased from Sigma-Aldrich, Germany. Vitamin C (Livsane) was sourced from Dr. Kleine Pharma GmbH, Germany.

2.2. Methods

$CoFe_2O_4$ and $ZnFe_2O_4$ nanoparticles were synthesized using the sonochemical method reported in the previous literature [7] using an ultrasonic homogenizer (UZ SONOPULS HD 2070) with a frequency of 20 kHz and power of 70 W for 60 min. Graphene oxide (GO) was synthesized by the modified hummer's method [8]. Reduced graphene oxide (rGO) was obtained by chemical reduction of synthesized graphene oxide (GO) using vitamin C as a reducing agent. For the preparation of TPU based nanocomposites, 20 wt% nanofillers (spinel ferrites nanoparticles and RGO in 9:1 ratio) were mixed with TPU (C80A10) in A DSM MICRO 5 micro-compounder (Research B.V., The Netherlands) with a capacity of 5 cm^3. TPU based nanocomposites were prepared by melt-mixing method at 200 ºC for 7 min at 150 rpm, and further, these were hot-pressed to create a rectangular-shaped sheet of a 22.86 × 10.16 × 0.8 mm^3 dimension. The developed nanocomposites with 0.80 mm thickness were designated as $ZnFe_2O_4$-rGO-TPU and $CoFe_2O_4$ -rGO-TPU nanocomposites.

2.3. Characterization

X-ray diffraction pattern of nanoparticles and nanocomposites was recorded on RigakuMiniFlex 600 X-ray Spectrometer. The microstructures study was done by using a scanning electron microscope Nova NanoSEM450 (FEI company). An Agilent N5230A vector network analyzer in the frequency range 8.2 -12.4 GHz was utilized to evaluate the electromagnetic interference shielding efficiency of prepared nanocomposites. Magnetic characteristics were assessed using a vibrating sample magnetometer (VSM 7407, Lake Shore).

3. RESULTS AND DISCUSSION

3.1. Structural study

Figure 1 (a) depicts the XRD pattern of $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles. The distinctive XRD peaks assigned to crystalline planes (220), (311), (400), (422), (511), (440), and (533) which confirmed the cubic spinel structure with the Fd3m space group symmetry for both $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles [9]. Moreover, the crystallite size was calculated by debye Scherrer's formula [7], which was found to be 3.45 nm and 11.13 nm for $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles, respectively. Further, The XRD investigation of $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ -rGO–TPU nanocomposites displayed in **Figure 1 (b),** which reveals the presence of the diffraction planes (220), (311), (400), (422), (511), and (440) associated with the face-centered cubic structure of spinel ferrites. It signifies the presence of the spinel ferrite nanoparticles inside the TPU matrix. Moreover, TPU exhibits broad diffraction peaks ranging from 10º to 28º associated with an ordered structure of the hard phase and disordered structure of the amorphous phase [10], which were present in the XRD pattern of the nanocomposites as well (see **Figure 1 (b)**) and thus remarked the existence of TPU in nanocomposites.

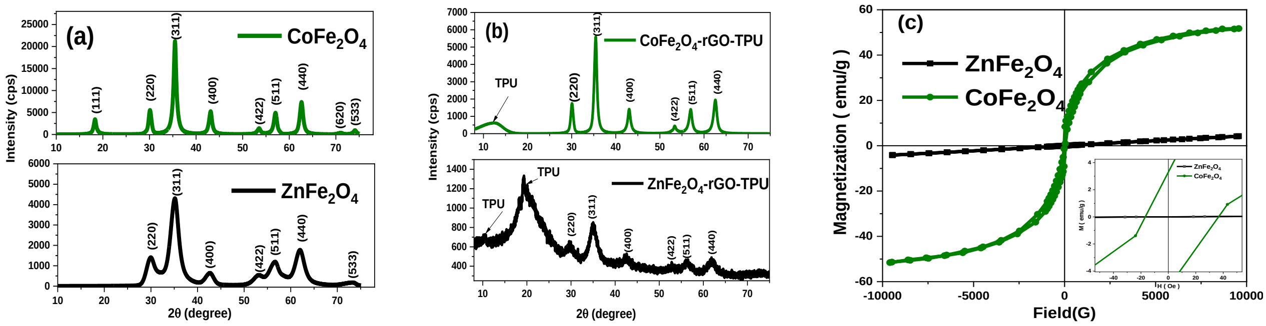

Figure 1 (a) XRD of $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles, **(b)** XRD of $ZnFe_2O_4$–rGO-TPU and $CoFe_2O_4$–rGO-TPU nanocomposites, **(c)** Magnetic hysteresis curves of $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles

3.2. Magnetic Study

The magnetic properties of synthesized $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles were investigated using a vibrating sample magnetometer (VSM) at room temperature with an applied magnetic field up to 10 kOe, as displayed in **Figure 1(c).** The saturation magnetization value is 4.07 emu/g and 51.98 emu/g for $ZnFe_2O_4$ and $CoFe_2O_4$ nanoparticles, respectively. The low value of saturation magnetization of spinel ferrite nanoparticles compared with bulk is due to its small particle size [11]. Further, the value of coercivity $H_c \approx 36.17$ Oe and remanent magnetization M_r 3.37emu/g, for $CoFe_2O_4$ nanoparticles revealing its ferromagnetic behavior. However, the value of coercivity $H_c \approx 0$ Oe and remanent magnetization $M_r \approx 0$ emu/g for $ZnFe_2O_4$ nanoparticles, proves superparamagnetic characteristics [7].

3.3. TEM and SEM study

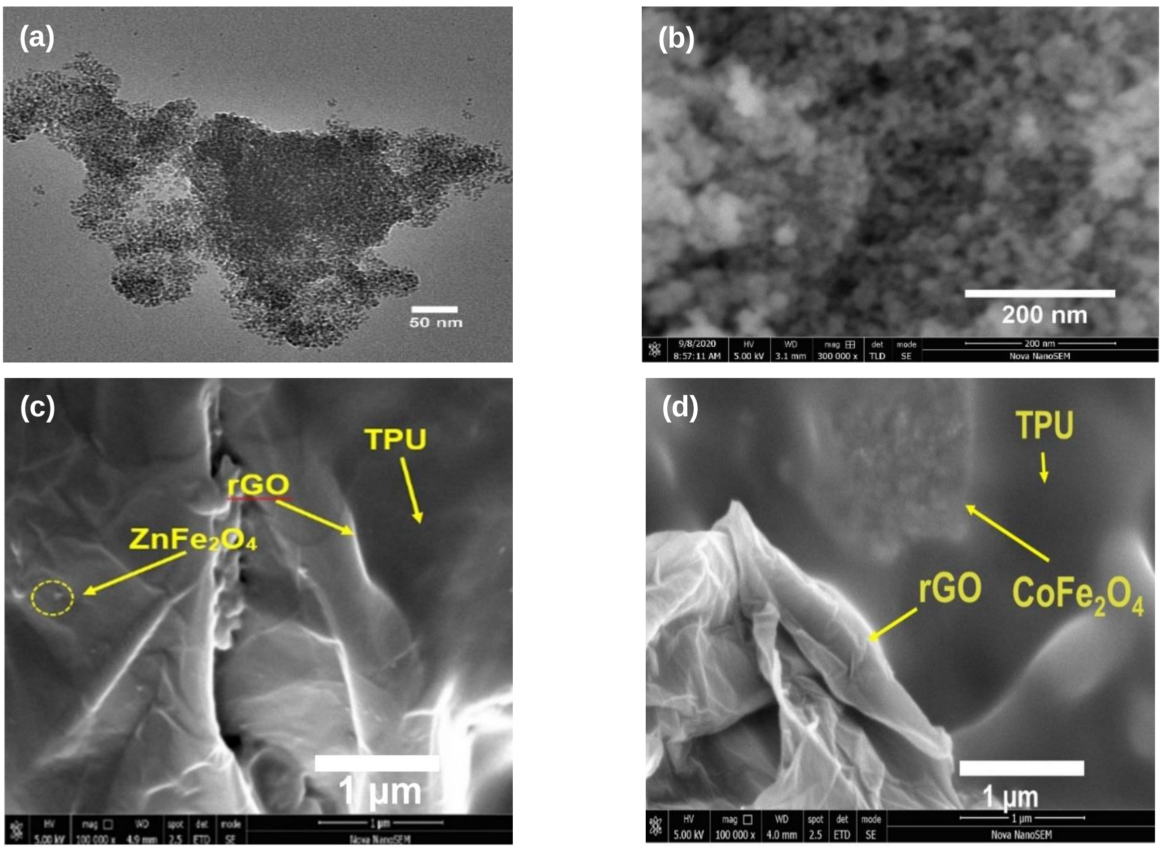

Figure 2 (a) TEM image of the $ZnFe_2O_4$ nanoparticles **(b)** FE-SEM image of $CoFe_2O_4$ nanoparticles, **(c)** FE-SEM image of the $ZnFe_2O_4$ -rGO-TPU, **(d)** FE-SEM image of $CoFe_2O_4$ -rGO-TPU

Figure 2(a) displays the TEM image of the $ZnFe_2O_4$ nanoparticles revealing the spherical particle of size 3-5 nm. A typical FE-SEM image of $CoFe_2O_4$ nanoparticles is shown in **Figure 2(b),** which shows spherical particles of the size 9-15 nm. **Figures 2(c-d)** depicts the FE-SEM image showing the cross-sectional view of the developed $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ -rGO-TPU nanocomposites, which confirm the presence of nanoparticles, rGO embedded in the TPU matrix.

3.4. Electromagnetic Interference Shielding Effectiveness

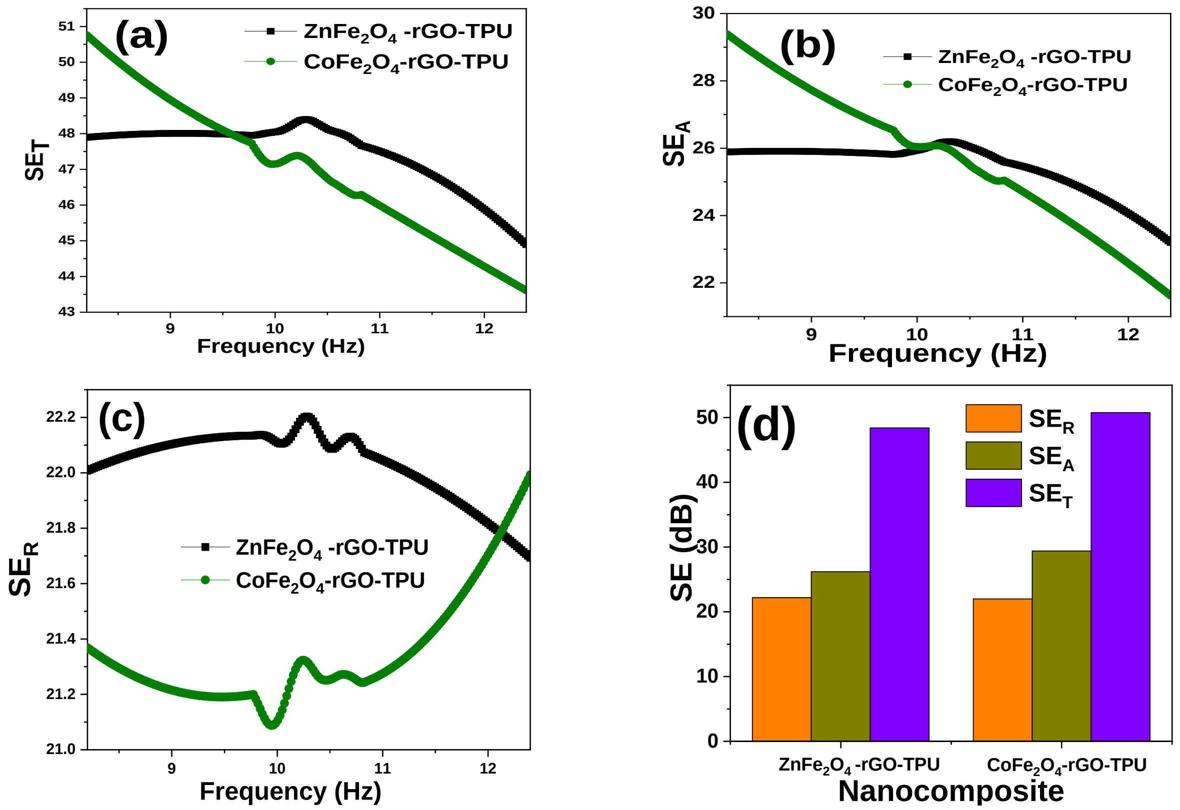

Figure 3 Frequency response of $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ -rGO-TPU nanocomposites with **(a)** SE_T, **(b)** SE_A , **(c)** SE_R **(d)** comparison chart

Figures 3(a-c) displays the SE_T, SE_A, and SE_R of $ZnFe_2O_4$ –rGO-TPU and $CoFe_2O_4$ –rGO-TPU nanocomposites with a thickness of 0.80 mm in the frequency range of 8.2 to 12.4 GHz. The value of SE_T, which is a sum of the magnitude of SE_A and SE_R, is found to be 48.39 dB for $ZnFe_2O_4$ -rGO-TPU and 50.76 dB for $CoFe_2O_4$ -rGO-TPU nanocomposites [7]. It can be noticed from **Figure 3(b)** that the maximum value of SE_A for $ZnFe_2O_4$ -rGO-TPU is 26.19 dB. On the other hand, the maximum value of SE_A for $CoFe_2O_4$ –rGO-TPU is 29.39 dB. However, the value of SE_R is 22.20 dB for $ZnFe_2O_4$ -rGO-TPU and 21.99 dB for $CoFe_2O_4$ -rGO-TPU, as shown in **Figure 3(c)**. It signifies that absorption is the major contributor to the shielding performance of $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ –rGO-TPU nanocomposites [11]. The high shielding effectiveness due to absorption is attributed to the interaction of electric and magnetic dipoles. Moreover, the conducting network of the rGO sheet with nanoparticles enhanced interfacial polarization, which might have created a good balance between impedance matching and attenuation constant [7,12]. A comparison chart displayed in **Figure 3(d)** reveals the better performance of $CoFe_2O_4$ -rGO-TPU nanocomposite compared with $ZnFe_2O_4$ -rGO-TPU nanocomposite. Since lightweight is a crucial factor for choosing a shielding material, especially in the aircraft industry, on taking this into account, the specific shielding effectiveness (SSE), which is the ratio of SE_T and density of the material, was calculated [13]. The density of the nanocomposites is in the range of 0.93 to 1.06 cm^3/g, and the thickness of the nanocomposites is 0.80 mm. The calculated value of SSE is found to be in the range of 47 dB cm^2/g to 51 dB cm^2/g [13]. However, for practical application, the SSE alone is not sufficient for analyzing the lightweight shielding performance of a material. Considering this, the absolute shielding efficiency (SSE/t), defined as the ratio of specific shielding efficiency to the thickness of the material, is also evaluated. The magnitude of SSE/t is in the range of 597 dB cm^3/g to 648 dB cm^3/g for developed nanocomposites [13].

4. CONCLUSION

Herein, we developed lightweight and flexible nanocomposites based on TPU as matrix and spinel ferrite nanoparticles ($CoFe_2O_4$ and $ZnFe_2O_4$) and rGO as nano-fillers. The developed nanocomposites exhibit total shielding effectiveness of 48.39 dB and 50.76 dB for $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ -rGO-TPU nanocomposites, respectively, in the X-band frequency range with a thickness of only 0.80 mm. Also, both the nanocomposites are suitable for commercial applications as they possess a shielding effectiveness value greater than 20 dB. Therefore, lightweight and flexible $ZnFe_2O_4$ -rGO-TPU and $CoFe_2O_4$ -rGO-TPU nanocomposites can be a promising candidates for electromagnetic interference shielding applications.

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REFERENCES

[1] MA, Z., KANG, S., MA, J., SHAO, L., ZHANG, Y., LIU, C., WEI, A., XIANG, X., WEI, L., And GU. J., Ultraflexible and Mechanically Strong Double-Layered Aramid Nanofiber–Ti3C2Tx MXene/Silver Nanowire Nanocomposite Papers for High-Performance Electromagnetic Interference Shielding. *ACS Nano 2020,* vol. 14, pp. 8368−8382.

[2] SONG, W.-L., GONG, C., LI, H., CHENG, X.-D., CHEN, M., YUAN, X., CHEN, H., YANG, Y., FANG, D. Graphene-Based Sandwich Structures for Frequency Selectable Electromagnetic Shielding. *ACS Appl. Mater. Interfaces* 2017, vol. 9, no. 41, pp. 36119–36129. Available from: https://doi.org/10.1021/acsami.7b08229.

[3] JIANG, D., MURUGADOSS, V., WANG, Y., LIN, J., DING, T., WANG, Z., SHAO, Q., WANG, C., LIU, H., LU, N., WEI, R., SUBRAMANIA, A., GUO, Z. Electromagnetic Interference Shielding Polymers and Nanocomposites - A Review. *Polymer Reviews* 2019, vol. 59, no. 2, pp. 280-337. Available from: https://doi.org/10.1080/15583724.2018.1546737.

[4] SONG, P., QIU, H., WANG, L., LIU, X., ZHANG, Y., ZHANG, J., KONG, J., GU, J. Honeycomb Structural RGO-MXene/Epoxy Nanocomposites for Superior Electromagnetic Interference Shielding Performance. *Sustainable Materials and Technologies.* 2020, vol. 24, p. e00153. Available from: https://doi.org/10.1016/j.susmat.2020.e00153.

[5] SOBHA, A.P., SREEKALA, P.S., NARAYANANKUTTY, SUNIL. K. Electrical, Thermal, Mechanical and Electromagnetic Interference Shielding Properties of PANI/FMWCNT/TPU Composites. *Progress in Organic Coatings.* 2017, vol. 113, pp. 168–174. Available from: https://doi.org/10.1016/j.porgcoat.2017.09.001.

[6] ISMAIL, M. M., RAFEEQ, S. N., SULAIMAN, J. M. A., MANDAL, A. Electromagnetic Interference Shielding and Microwave Absorption Properties of Cobalt Ferrite CoFe2O4/Polyaniline Composite. *Appl. Phys. A* 2018, vol. 124, no. 5, p. 380. Available from: https://doi.org/10.1007/s00339-018-1808-x.

[7] YADAV, R. S., ANJU, JAMATIA, T., KUŘITKA, I., VILČÁKOVÁ, J., ŠKODA, D., URBÁNEK, P., MACHOVSKÝ, M., MASAŘ, M., URBÁNEK, M., KALINA, L., HAVLICA, J. Superparamagnetic $ZnFe_2O_4$ Nanoparticles-Reduced Graphene Oxide-Polyurethane Resin Based Nanocomposites for Electromagnetic Interference Shielding Application. *Nanomaterials* 2021, vol. 11, no. 5, p. 1112. Available from: https://doi.org/10.3390/nano11051112.

[8] BAI, Y., RAKHI, R. B., CHEN, W., ALSHAREEF, H. N. Effect of PH-Induced Chemical Modification of Hydrothermally Reduced Graphene Oxide on Supercapacitor Performance. *Journal of Power Sources.* 2013, vol. 233, pp. 313–319. Available from: https://doi.org/10.1016/j.jpowsour.2013.01.122.

[9] ATIF, M., ASGHAR, M. W., NADEEM, M., KHALID, W., ALI, Z., BADSHAH, S. Synthesis and Investigation of Structural, Magnetic and Dielectric Properties of Zinc Substituted Cobalt Ferrites. *Journal of Physics and Chemistry of Solids.* 2018, vol. 123, pp. 36–42. Available from: https://doi.org/10.1016/j.jpcs.2018.07.010.

[10] BARICK, A.K., TRIPATHY, D.K. Preparation, Characterization and Properties of Acid Functionalized Multi-Walled Carbon Nanotube Reinforced Thermoplastic Polyurethane Nanocomposites. *Materials Science and Engineering: B.* 2011, vol.176, pp. 1435–1447.

[11] YADAV, R. S., ANJU, JAMATIA, T., KUŘITKA, I., VILČÁKOVÁ, J., ŠKODA, D., URBÁNEK, P., MACHOVSKÝ, M., MASAŘ, M., URBÁNEK, M., KALINA, L., HAVLICA, J. Excellent, Lightweight and Flexible Electromagnetic Interference Shielding Nanocomposites Based on Polypropylene with $MnFe_2O_4$ Spinel Ferrite Nanoparticles and Reduced Graphene Oxide. *Nanomaterials.* 2020, vol. 10, pp. 2481.

[12] RAJU, P., SHANKAR, J., ANJAIAH, J., MURTHY, S. R. Shielding Effectiveness Studies of NiCuZn Ferrite-Polyaniline Nanocomposites for EMI Suppression Applications. In: *Proceedings of the International Conference on Advanced Materials.* Kerala: AIP 2019, p. 020027. Available from: https://doi.org/10.1063/1.5130237.

[13] YADAV, R. S., KUŘITKA, I., VILČÁKOVÁ, J., MACHOVSKÝ, M., ŠKODA, D., URBÁNEK, P., MASAŘ, M., JURCA, M., URBÁNEK, M., KALINA, L., HAVLICA, J. $NiFe_2O_4$ Nanoparticles Synthesized by Dextrin from Corn-Mediated Sol−Gel Combustion Method and Its Polypropylene Nanocomposites Engineered with Reduced Graphene Oxide for the Reduction of Electromagnetic Pollution. *ACS Omega.* 2019, vol. 4, pp. 22069−22081.