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Comparative Electromagnetic Properties of Polypropylene Composites Loaded with Cobalt Ferrites by Melt Mixing

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Abstract

Polypropylene (PP) is investigated as a polymeric matrix of functional composites by melt mixing in the compression mould. The 15 wt.% loading of cobalt ferrite ($CoFe_2O_4$) increases the electrical permittivity as a result of Maxwell-Wagner effect and induces ferrimagnetic properties in PP composites. By increasing the $CoFe_2O_4$ loading to 55 wt.%, the magnetization and relative permittivity are substantially raised. Interestingly, this high loading comparable to the percolation threshold does not affect the coercivity. Both low and high $CoFe_2O_4$ loadings have insignificant effect on magnetic permeability spectra. The results suggest that the melt mixing is a facile route to incorporate a high loading of magnetic powder into plastics, leading to composites of enhanced electromagnetic properties.

Keywords: cobalt ferrite; polypropylene; hysteresis loops; permeability; permittivity.

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Introduction

Polypropylene (PP) is a thermoplastic commonly found in everyday uses. Interestingly, it is also under development for functional composites. In addition to the magnetic polymers in forms of ferrite rubber composites [1, 2], the incorporation of a variety of magnetic powders into PP matrix has been an active topic in the past decade because of the applications as sensors [3], electromagnetic wave absorbers [4] and wastewater treatment agents [5,6]. The dynamic mechanical behaviors of PP loaded with ferrites also received attentions [7,8]

The dispersion of fillers in polymer matrices strongly influence the properties of the composites [9]. To obtain magnetic polymers with desirable properties, a variety of fabrication methods have been investigated in relation to the dispersion and agglomeration of magnetic clusters [3, 10, 11]. The melt mixing is a facile method to incorporate fillers into PP and was recently employed for PP nanocomposites with reduced graphene oxide and carbon nanotube with iron [12]. In this report, PP was loaded with cobalt ferrite ($CoFe_2O_4$) by the melt mixing in the compression mould and electromagnetic properties were compared between composites with 15 and 55 wt.% loadings. This higher loading is beyond the range previously applied and reported.

Materials and Methods

Preparation of composites: Like other ferrites [13], $CoFe_2O_4$ nanoparticles can be synthesized by the sol-gel method. $CoFe_2O_4$ in this work were obtained from a chemical reaction between iron nitrate (Sigma Aldrich, 99.95%) and cobalt nitrate (Sigma Aldrich, 99.90%) in polyvinyl alcohol gel. After the heat treatment at 800 °C, the cubic spinel $CoFe_2O_4$ phase was confirmed by X-ray diffraction without any impurity phase [14]. The particle size estimated by both Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) is of order of 100 nm and the average coercivity derived from vibrating sample magnetometry (VSM) is around 400 Oe [8]. $CoFe_2O_4$ powders of 15 and 55% by weight were mixed and pressed with PP in a compression mould at 240 °C.

Characterizations of composites: Hysteresis loops of $CoFe_2O_4$-PP composites were obtained at room temperature by a VSM in sweeping magnetic fields between ± 6 and 6 kOe. The coercivity was the x-intercept of hysteresis loops and the magnetic squareness was estimated from the ratio of magnetization in zero field (remanence) to the maximum in 6 kOe field. Relative magnetic permeability and electrical permittivity were measured as a function of frequency from 1 MHz to 1 GHz by an RF impedance/material analyzer (Agilent 4291B) equipped with a dielectric test fixture.

Results and Discussion

The variation in $CoFe_2O_4$ loadings in PP composites gives rise to marked difference in hysteresis loops in Figure 1. The magnetization in the case of 15 wt.% (PP15CF) is modest and approaches the saturation within 1 kOe field. When the loading is raised to 55 wt.% (PP55CF), the magnetization is increased by about 5 times and not saturated even in the maximum 6 kOe used. Corresponding to changing magnetization, the values of magnetic squareness is slightly decreased from 0.41 to 0.38. In contrast to the magnetizations, the coercivity is not sensitive to the $CoFe_2O_4$ loading. Both PP composites with 15 and 55 wt.% $CoFe_2O_4$ exhibit the coercivity of approximately 560 Oe.

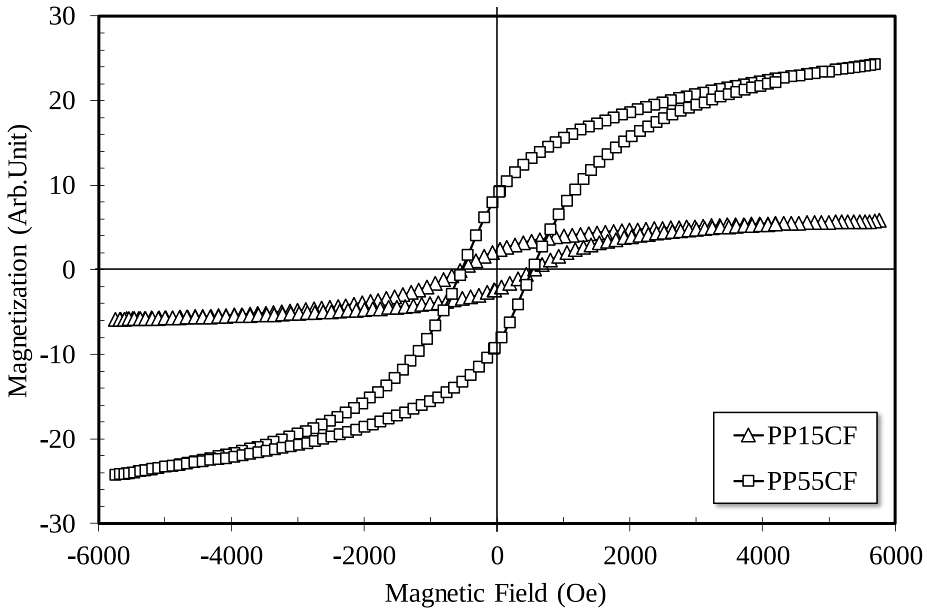
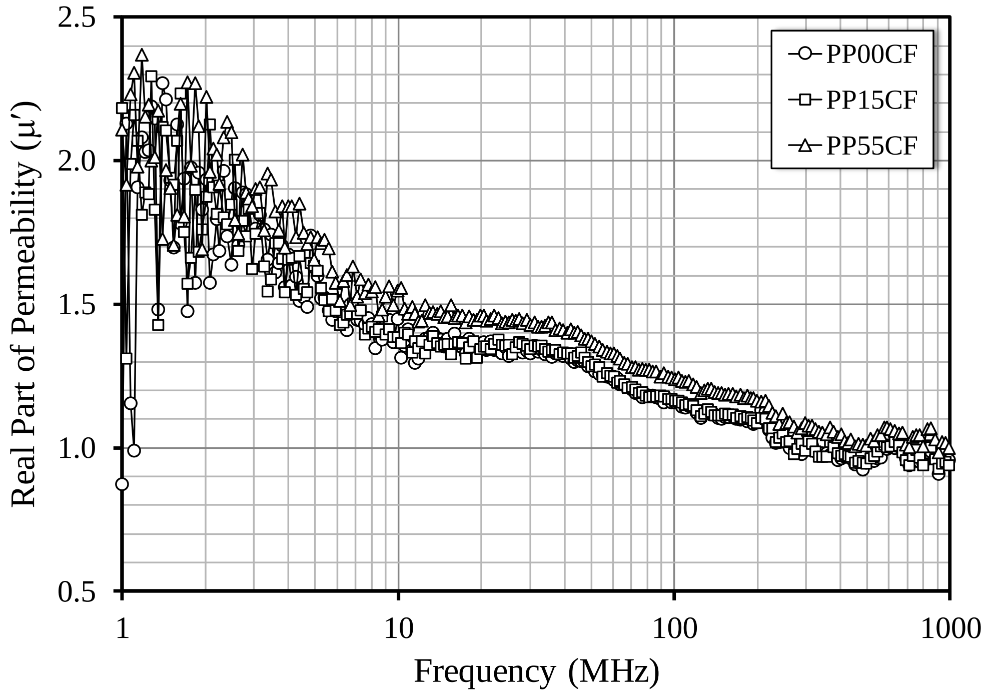


Figure 1. Comparison of hysteresis loops of $CoFe_2O_4$-PP composites with 15 and 55 wt.% loadings.

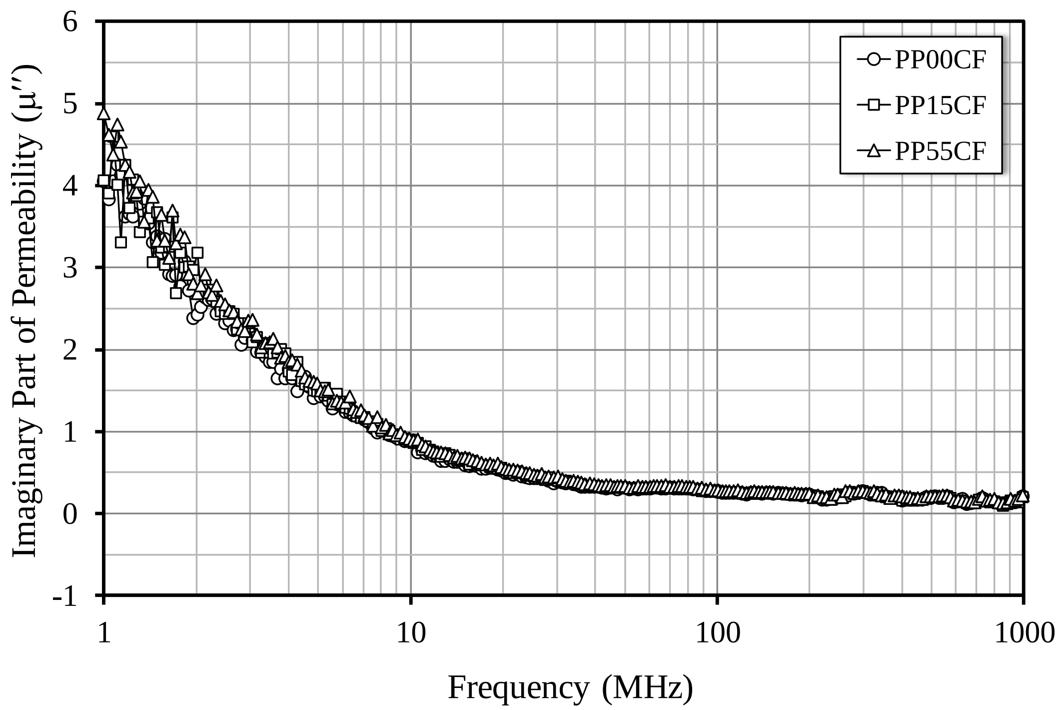
In the early works on magnetic polymer composites, Anantharaman et al. and Makled et al. showed that the changing magnetization could be described by using the rule of mixture, commonly used for mechanical properties [1, 15]. The magnetization in Figure 1 tends to follow the rule of mixture. The magnetic properties from this work are also consistent with those in extruded $CoFe_2O_4$-PP composites [8]. By mixing $CoFe_2O_4$ with PP by the extrusion, the magnetization is proportional to the magnetic loading from 0 to

45 wt.%. The measured magnetization is solely contributed by $CoFe_2O_4$ and increased with the loading of these weakly interacted magnetic particles. At high loadings, $CoFe_2O_4$ particles much smaller than 100 nm are also likely included and hence require large magnetic field to saturate. The independence of the coercivity on the ferrite loading up to 45 wt.% is previously reported in polymer composites [1,8]. Due to the mechanical stress during the process and resulting magnetic particle distribution, the coercivity values are higher than those in magnetic powder form. The increased interaction between closely distributed magnetic particles tends to reduce the coercivity. Interestingly, the coercivity is rather insensitive to the $CoFe_2O_4$ loading up to 55 wt% suggesting that the interactions among $CoFe_2O_4$ particles in PP matrix are not dominant. On the other hand, the coercivity of rubber composites significantly change with the loadings of barium ferrite [1] and NdFeB [16, 17]. The difference is attributed to higher interactions between hard magnetic particles. The percolation threshold of $CoFe_2O_4$ particles largely differs from those of hard ferrite and NdFeB and the magnetic poling during the melt mixing is unlikely to affect magnetic properties of the resulting composites.

In Figure 2, both real (μ’) and imaginary (μ”) parts of the relative magnetic permeability of the PP and $CoFe_2O_4$-PP composites exhibit fluctuation and large reduction with increasing frequency in the 1– 10 MHz range. Above 10 MHz, the complex permeabilities are less sensitive to the variation in frequency as they tend to reach minimal values around 1 GHz. The inclusion of 15 wt% $CoFe_2O_4$ (PP15CF) does not significantly affect the comlex permeability of PP. The relative permeability is only slightly increased in the case of PP composite loaded with 55 wt% $CoFe_2O_4$ (PP55CF). These modest values at high frequencies, related to the coercivity, limit the use of composites as electromagnetic wave absorbers.

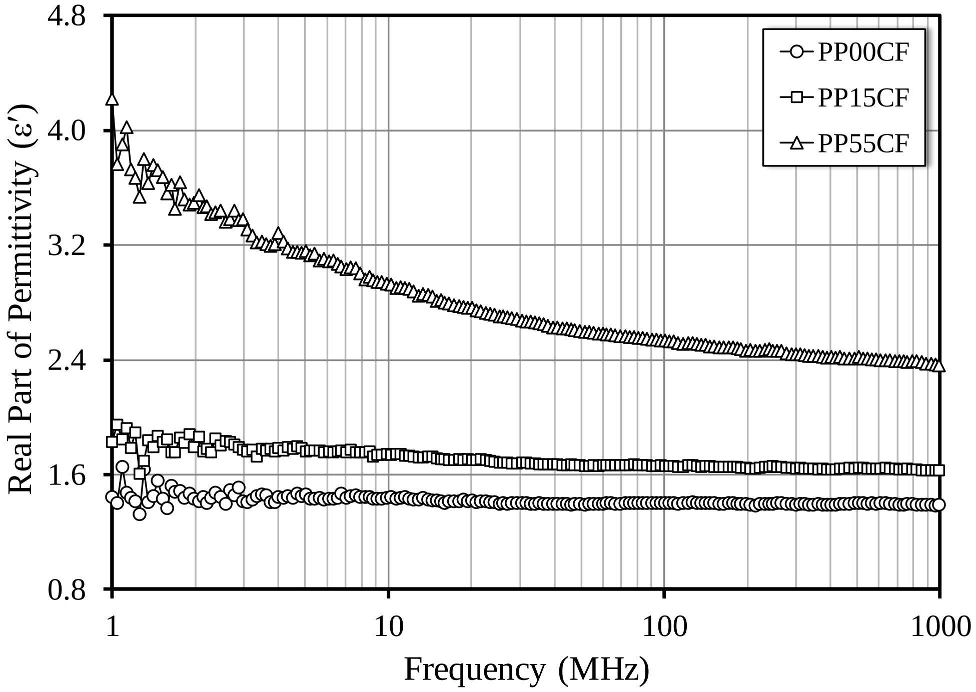


(a)

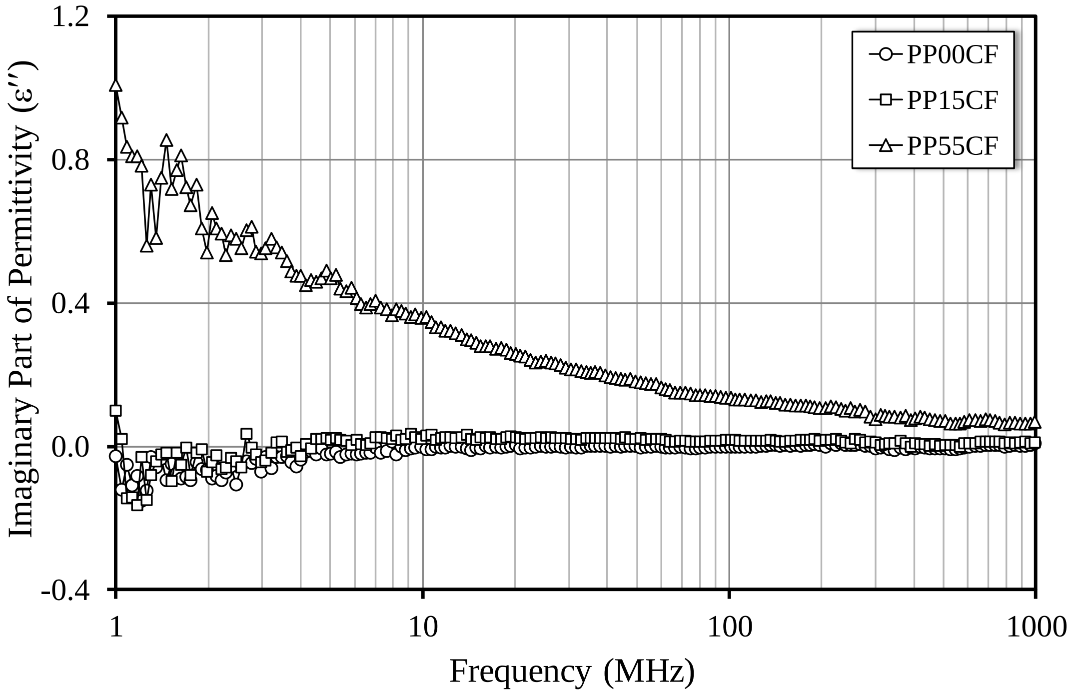


(b)

Figure 2. Relative magnetic permeability of PP and $CoFe_2O_4$-PP composites as a function of the frequency; (a) real and (b) imaginary part.



(a)



(b)

Figure 3. Relative electrical permittivity of PP and $CoFe_2O_4$-PP composites as a function of the frequency; (a) real and (b) imaginary part.

Besides magnetic properties, the incorporation of $CoFe_2O_4$ enhances dielectric properties of the PP matrix. The relative electrical permittivity of the PP and $CoFe_2O_4$-PP composites as a function of frequency is composed of real (dielectric constant, ε') and imaginary (dielectric loss, ε") parts shown in Figure 3. The complex permittivities are decreased with increasing frequency as a result of Maxwell-Wagner effect. Independent surface charges in the composites are not completely polarized under electric field and the conversion of electromagnetic energy into heat by the relaxation process is also diminished at high frequencies [18, 19]. Such changes in polarization of surface charges and the relevant relaxation process reduce the permittivity of dielectric materials [2].

As compared in Figure 3, the increase in $CoFe_2O_4$ loading from 15-55 wt% enhances the complex permittivity. This is due to the Maxwell-Wagner polarization by the accumulation of surface charges in the case of high loading [20]. Since these $CoFe_2O_4$ are electrical resistive and non-interacting particles, the permittivity is dependent of its fraction in the PP matrix. The high loading of 55 wt% (PP55CF) increases the real part of relative permittivity of PP (PP00CF) from around 2 to 4 at low frequencies. The variation in complex permittivity with the frequency is pronounced in the regime between 1 and 10 MHz and becomes moderate at higher frequencies up to 1 GHz. The coercivity and permittivity spectra observed in this report are in accordance with the comparison of differential scanning calorimetry (DSC) peaks of PP loaded with 0-45 wt% $CoFe_2O_4$ [21]. The high magnetic loading, indeed decreases the degree of PP chain crystallinity, but the interactions between $CoFe_2O_4$ particles in interchain spacing remain weak.

Conclusion

Complex permittivity and permeability of PP composites loaded with 15 and 55 wt.% $CoFe_2O_4$ were measured from 1 MHz to 1 GHz. The incorporation of $CoFe_2O_4$ did not affect the magnetic permeability but substantially increased the magnetic permittivity of PP as a result of Maxwell-Wagner effect. The $CoFe_2O_4$ loading introduced the ferrimagnetic properties in PP. The highly loaded composite (55 wt.%) may possess larger magnetizations but the coercivity was independent on the magnetic loading. Magnetic properties in these composites are comparable to those prepared by the extrusion. The melt mixing in in the compression mould is therefore a useful alternative particularly when the batch is too small for the extruder.

Acknowledgements

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References

[1] M.H. Makled, T. Matsui, H. Tsuda, M. Mabuchi, M. K. El-Mansy, K. Morii, "Magnetic and dynamic mechanical properties of barium ferrite-natural rubber composites," J. Mater. Process. Technol., **160**, 2 (2005) 229-233.

[2] H. S. Gokturk, T. J. Fiske, D. M. Kalyon, "Electric and magnetic properties of a thermoplastic elastomer incorporated with ferromagnetic powders," IEEE Trans. Magn., **29**, 6 (1993) 4170-4176.

[3] M. A. Ramazanov, A. M. Maharramov, J. R. Sultanova, F. V. Hajiyeva, U. A. Hasanova, "The magnetic polymer nanocomposite materials based on polypropylene and iron nanoparticles: Synthesis and structure," J. Ovanic Res., **12**, 4 (2016) 193-200.

[4] M. A. Ramazanov, F. V. Hajiyeva, A. M. Maharramov, L. Di Palma, D. Sannino, M. Takafuji, H. M. Mammadov, U. A. Hasanova, H. A. Shirinova, Z. A. Bayramova, "New

magnetic polymer nanocomposites on the basis of isotactic polypropylene and magnetite nanoparticles for adsorption of ultrahigh frequency electromagnetic waves," Polym.-Plast. Technol. Eng., **57**, 5 (2018) 449-458.

[5] Y. L. Zhu, "Preparation and characterization of a new hydrophilic and biocompatible magnetic polypropylene carrier used in wastewater treatment," Environ. Technol., **39**, 21 (2018) 2736-2746.

[6] J. H. Zhu, H. B. Gu, S. B. Rapole, Z. P. Luo, S. Pallavkar, N. Haldolaarachchige, T. J. Benson, T. C. Ho, J. Hopper, D. P. Young, S. Y. Wei, Z. H. Guo., "Looped carbon capturing and environmental remediation: Case study of magnetic polypropylene nanocomposites," RSC Adv., **2**, 11 (2012) 4844-4856.

[7] R. R. Mocellini, O. A. Lambri, D. Gargicevich, F. G. Bonifacich, B. Weidenfeller, M. Anhalt, W. Riehemann, "Magnetic memory effect in magnetite charged polypropylene composite," Compos. Interf., **24**, 6 (2017) 611-633.

[8] A. Hunyek, C. Sirisathitkul, "Electromagnetic and dynamic mechanical properties of extruded cobalt ferrite-polypropylene composites," Polym.-Plast. Technol. Eng., **50**, 6 (2011) 593-598.

[9] N. Nurul Reffa Azyan, M. Norkhairunnisa, C. H. Tay, M. A. Azmah Hanim, "Techniques on dispersion of nanoparticles in polymer matrices: A review," Pertanika J. Sci. Technol., **25**, 4 (2017) 1073-1084.

[10] L. Di Palma, I. Bavasso, F. Sarasini, J. Tirillo, D. Puglia, F. Dominici, L. Torre, A. Galluzzi, M. Polichetti, M. A. Ramazanov, F. V. Hajiyeva, H. A. Shirinova, "Effect of nano-magnetite particle content on mechanical, thermal and magnetic properties of polypropylene composites," Polym. Compos., **135**, 42 (2018) 46820.

[11] Q. L. He, T. T. Yuan, Z. P. Luo, N. Haldolaarachchige, D. P. Young, S. Y. Wei, Z. H. Guo, "Morphology and phase controlled cobalt nanostructures in magnetic polypropylene nanocomposites: The role of alkyl chain-length in maleic anhydride grafted polypropylene," Chem. Commun., **49**, 26 (2013) 2679-2681.

[12] M. Nisar, M. D. S. Bernd, L. C. P. da Silva, J. Geshev, N. R. D. Basso, G. B. Galland, "Polypropylene nanocomposites with electrical and magnetic properties," J. Appl. Polym.

Sci., **135**, 42 (2018) 46820.

[13] Z. I. Takai, M. K. Mustafa, S. Asman, K. A. Sekak, "Preparation and characterization of magnetite (Fe_3O_4) nanoparticles by sol-gel method," Int. J. Nanoelec. Mater., **12**, 1 (2019) 37-46.

[14] A. Hunyek, C. Sirisathitkul, "Variation in magnetic properties of sol-gel-synthesized cobalt ferrites," Mater. Tehnol., **47**, 6 (2013) 845-848.

[15] M.R. Anantharaman, K. A. Malini, S. Sindhu, E. M. Mohammed, S. K. Date, S. D. Kulkarni, P. A. Joy, P. Kurian, "Tailoring magnetic and dielectric properties of rubber ferrite composites containing mixed ferrite," Bull. Mater. Sci., **24**, (6) (2001) 623–631.

[16] P. Jantaratana, C. Sirisathitkul, A. Hunyek, S. Maensiri, "Electric and magnetic properties of recycled NdFeB-natural rubber," Adv. Compos. Lett., **20**, 2 (2011) 48-51.

[17] M. Kokabi, F. Arabgol, M. Manteghian, "$Nd_2Fe_{14}B$ permanent polymeric composite magnets," Iran. Polym. J., **14**, 1 (2005) 71-79.

[18] E. T. Thostenson, T. W. Chou, "Microwave processing: Fundamentals and applications," Compos. Part A: Appl. Sci. Manufac., **30**, 9 (1999) 1055-1071.

[19] H. A. Begum, N. Khatun, S. Islam, N. A. Ahmed, M. S. Hossain, M. A. Gafur, A. Siddika, "Synthesis and characterization of structural, magnetic and electrical properties of Ni–Mn–Zn ferrites," Int. J. Nanoelec. Mater., **11**, 1 (2018) 15-24.

[20] T. J. Fiske, H. S Gokturk, D. M. Kalyon, "Percolation in magnetic composites," J. Mater. Sci., **32**, 20 (1997) 5551-5560.

[21] S. Khongtong, A. Hunyek, C. Sirisathitkul, "Effect of cobalt ferrite loading on differential scanning calorimetry of magnetic polymer composites," Proc. Natl. Acad. Sci. India Sect. A: Phys. Sci., **85**, 2 (2015) 315-318.