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

Anuchit Hunyek[1,2], Chitnarong Sirisathitkul[2*] and Pongsakorn Jantaratana[3]

[1]*Faculty of Liberal Arts, Rajamangala University of Technology Rattanakosin, Wangklaikangwon Campus, Prachuap Khiri Khan, Thailand.*
[2] *Functional Materials and Nanotechnology Center of Excellence, School of Science, Walailak University, Nakhon Si Thammarat, Thailand.*
[3]*Electrical and Magnetic Properties Laboratory, Department of Physics, Faculty of Science, Kasetsart University, Bangkok, Thailand.*

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ABSTRACT

Polypropylene (PP) was investigated as a polymeric matrix of functional composites by melt mixing in a compression mould. The sample with 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 were substantially raised. Interestingly, this high loading which was comparable to the percolation threshold, did not affect the coercivity. Both low and high $CoFe_2O_4$ loadings have insignificant effects on magnetic permeability spectra. The results suggest that the melt mixing is a facile route to incorporate high loading of magnetic powder into plastics, leading to composites of enhanced electromagnetic properties.

Keywords: Cobalt Ferrite, Polypropylene, Hysteresis Loops, Permeability, Permittivity.

1. INTRODUCTION

Polypropylene (PP) is a thermoplastic commonly found in everyday usages. 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 variety of magnetic powders into PP matrix has been an active topic in the past decade for sensor application [3], electromagnetic wave absorbers [4] and wastewater treatment agents [5,6]. The dynamic mechanical behaviors of PP loaded with ferrites also has received attentions [7,8]

The dispersion of fillers in polymer matrices strongly influences 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 paper, PP was loaded with cobalt ferrite ($CoFe_2O_4$) by the melt mixing method using the compression mould. Electromagnetic properties were compared between composites with 15 wt.% and 55 wt.% loadings. This higher loading is beyond the range previously applied and reported.

*Corresponding Author: *chitnarong.siri@gmail.com*

2. MATERIALS AND METHODS

2.1 Preparation of Composites

Similar to other ferrites [13], $CoFe_2O_4$ nanoparticles can be synthesized by the sol-gel method. $CoFe_2O_4$ in this study was 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) was in order of 100 nm and the average coercivity derived from vibrating sample magnetometry (VSM) was 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.

2.2 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. The magnetic squareness was estimated from the ratio of magnetization in zero field (remanence) to the maximum in the 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.

3. RESULTS AND DISCUSSION

The variation in $CoFe_2O_4$ loadings in PP composites shows difference trends 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 was raised to 55 wt.% (PP55CF), the magnetization increased by about 5 times and not saturated even in the maximum 6 kOe was used. Corresponding to the changing magnetization, the values of magnetic squareness was 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 wt.% and 55 wt.% $CoFe_2O_4$ exhibit the coercivity of approximately 560 Oe.

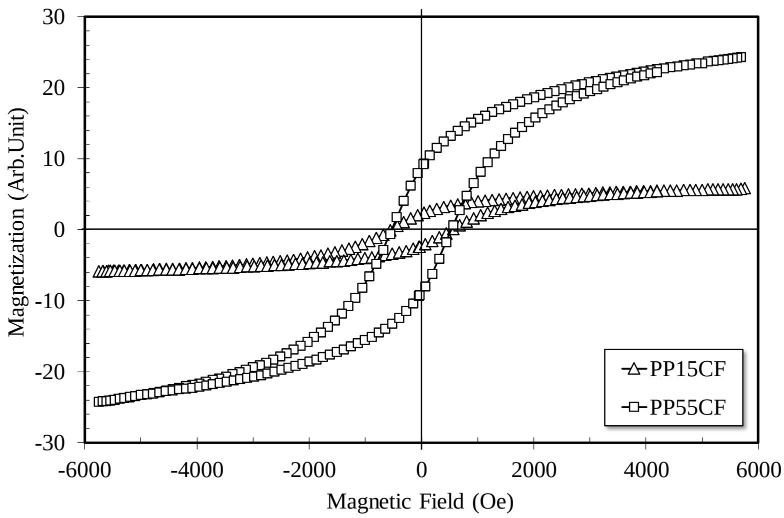
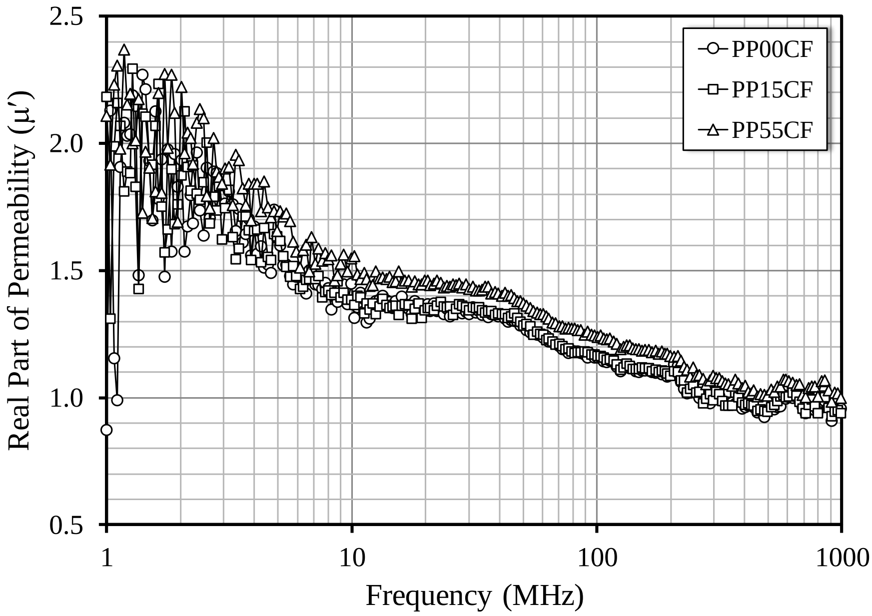


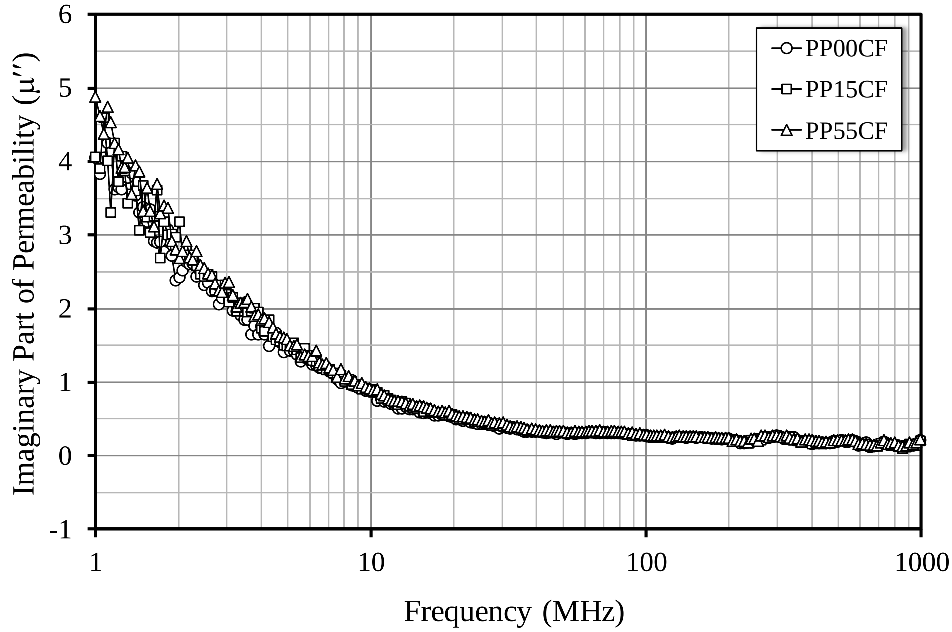
Figure 1. Comparison of hysteresis loops of $CoFe_2O_4$-PP composites with 15 wt.% and 55 wt.% loadings.

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 wt.%. to 45 wt.%. The measured magnetization was 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 were also included and hence require large magnetic field to saturate. The independence of the coercivity on the ferrite loading up to 45 wt.% was previously reported in polymer composites [1,8]. Due to the mechanical stress during the process and resulting magnetic particle distribution, the coercivity values were higher than those in magnetic powder form. The increased interaction between closely distributed magnetic particles tends to reduce the coercivity. Interestingly, the coercivity was rather insensitive to the $CoFe_2O_4$ loading up to 55 wt% suggesting that the interactions among $CoFe_2O_4$ particles in PP matrix were not dominant. On the other hand, the coercivity of rubber composites significantly changed 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 complex 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.



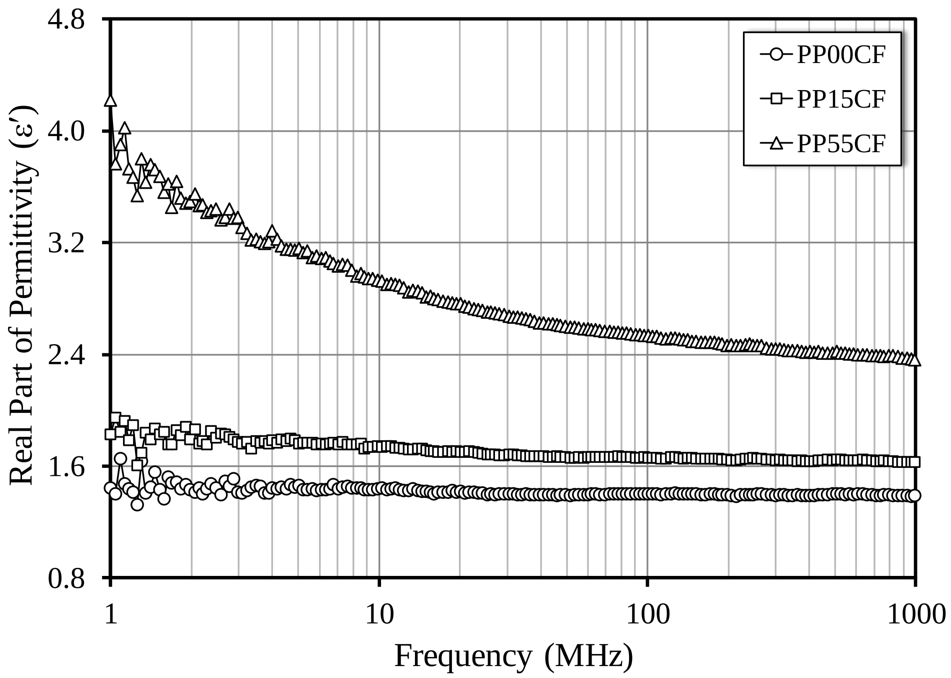
(a)



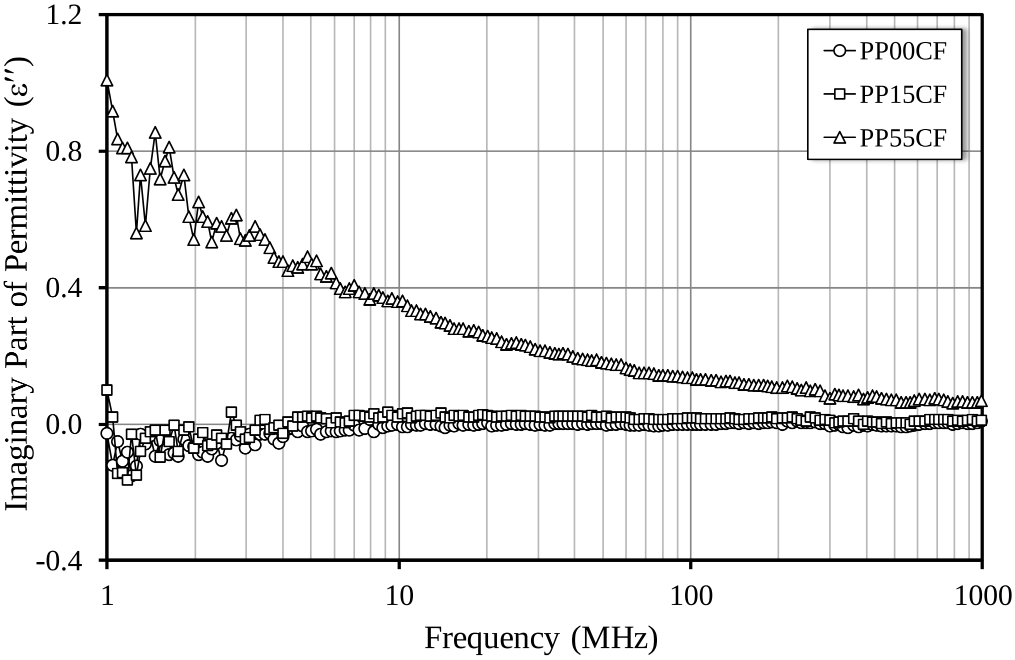
(b)

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.

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 decrease 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].



(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.

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 MHz and 10 MHz and becomes moderate at higher frequencies up to 1 GHz. The coercivity and permittivity spectra observed in this study is 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.

4. 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 method. The melt mixing in the compression mould is therefore a useful alternative particularly when the batch is too small for an extruder.

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