

Dielectric Properties of Ni_{0.2}Zn_{0.8}Fe₂O₄-Polypropylene Composites

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Abstract: Problem statement: In the last decade, the studies and investigation on polymer-based composites have drawn significant attention owing to improvement in their mechanical, thermal, electrical, optical and pharmaceutical properties as compared with pure polymer. **Approach:** Different compositions of Ni_{0.2}Zn_{0.8}Fe₂O₄ (NZF) and Polypropylene (PP) can alter the useful properties of polymer-based composites. Hence, the determination toward significant percentage of NZF added into PP can improve the dielectric properties of the composites. NZF was prepared using conventional solid-state method and composites of isotactic PP filled with NZF were fabricated. The dielectric properties of the composite were investigated using Agilent 4284A Precision LCR meter. **Results:** The results indicated that with increasing ratio of wt% NZF, the dielectric constant and dielectric loss of the composite increases. The composition of 30 wt% NZF gave the highest value of the dielectric constant in the frequency range of 100 Hz-10 kHz at room temperature. **Conclusion:** The incorporation of ceramic filler improved the dielectric constant and increase the dielectric loss of the composite correspondingly increases its potential use as an absorbing material for electromagnetic waves.

Key words: Dielectric properties, composites, filled polymer, nickel-zinc ferrite, polypropylene

INTRODUCTION

Ferrites which have many applications at microwave frequencies are very good dielectric material. Ferrites have high electrical resistivity (Mohan *et al.*, 1999), low dielectric loss and chemical stability. However, the shrinkage mismatch after solid-state sintering or brittle properties may seriously influence the performance and durability of the final product. On the other hand, polymer-based composites with high permittivity were proposed due to their flexibility and ability to be easily fabricated into various shapes (Yang *et al.*, 2008; Khor *et al.*, 2009; Rittidech and Khotsongkram, 2006; Gasaymeh *et al.*, 2010).

In this study, PP was chosen as the matrix due to its very attractive solid-state properties such as high modulus and tensile strength, rigidity and excellent heat resistance (He *et al.*, 2003). The development of composites combining mineral and polymer material characteristics is definitely one of the most interesting

perspectives for isotactic polypropylene (Kotek *et al.*, 2005).

With the vision to understand the dielectric phenomena in ferrites-polypropylene composite, a study on the dielectric properties of NZF, pure PP and different compositions of NZF-PP composites were undertaken. The relative complex permittivity is defined as:

$$\epsilon_r^* = \epsilon_r' - j \epsilon_r'' \quad (1)$$

Where:

ϵ_r' = The dielectric constant

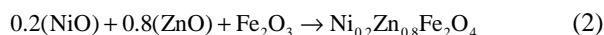
ϵ_r'' = The dielectric loss

MATERIALS AND METHODS

The filler of the composite, NZF was prepared using conventional solid-state reaction method. The starting materials, NiO (99.7%), ZnO (99.9%) and

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Fe₂O₃ (99.7%) with high purity were weighed according to the stoichiometric equation below:



These powders were dry milled and precalcined in air at 1100°C for 10 h. The powders were grinded and sieved with 45 micron siever to ensure homogeneity of particle size of the powders. Part of the precalcined powder were mixed with the binder Polyvinyl Alcohol (PVA) and pressed at 5 tonnes for 10 min to produce NZF pellets. The pellets were finally sintered at 1250°C for 10 h and ready for characterization.

The rest of the powders were also finally sintered in air at 1250°C for 10 h and the grinding and sieving process repeated to ensure homogeneous particle size of the powders when mixing with polypropylene. PP and NZF were weighed according to the ratio of 0-30 wt% of NZF. The polypropylene was heated and melted to a molten state at 160°C and blended for 10 min at different ratios of NZF-PP. The composite was removed from the Brabender Plastograph EC and hot pressed to approximately 1 mm thickness.

All the samples were examined by XRD to determine the microstructure of the samples. The dielectric properties of the samples were determined using the Agilent 4284A Precision LCR Meter at room temperature.

RESULTS

Figure 1 shows the XRD spectrum of nickel-zinc ferrite (Ni_{0.2}Zn_{0.8}Fe₂O₄)-polypropylene composites at different compositions. The composite matched with 00-050-2397 and 00-008-0234 of the ICDD database that showed polypropylene and nickel zinc iron oxide respectively. Ni_{0.2}Zn_{0.8}Fe₂O₄ (filler) is in crystalline structure while polypropylene is a semicrystalline structure (Busico and Cipullo, 2001). Thus, there are lots of small peaks obtained throughout the spectrum. Figure 1 also reveals that there is no unwanted reaction occurring between NZF and PP and the crystal intensities of NZF phase increase with the increase of NZF content. Meanwhile, the relative intensities of matrix PP in the low angle range (20-35°) decrease as the content of NZF increases (Wu *et al.*, 2007).

Figure 2 shows the dielectric properties of isotactic polypropylene with frequency from 20 Hz-1 MHz. It can be easily seen that the dielectric constant decrease with increasing frequency exceeding 10 kHz. The curves also showed that polypropylene is a good capacitive material at low frequency with a low loss and a stable dielectric constant from 100 Hz-10 kHz.

The dielectric constant and loss are 2.88 and 0.001 at 1 kHz, respectively.

The dielectric properties of NZF with respect to frequency from 20 Hz-1 MHz is shown in Fig. 3. NZF has a small region of uniform dielectric constant from 100-1 kHz. The dielectric constant and loss are 40.5 and 10.7 at 1 kHz, respectively.

Figure 5 exhibits the dielectric constant of NZF-PP composites changing with frequency from 20 Hz-1 MHz. Dielectric properties of pure PP are also plotted for comparison. The dielectric constant of NZF-PP composites with different wt% (5-30 wt%) of NZF content are in the range of 2.63-3.46 at 1 kHz.

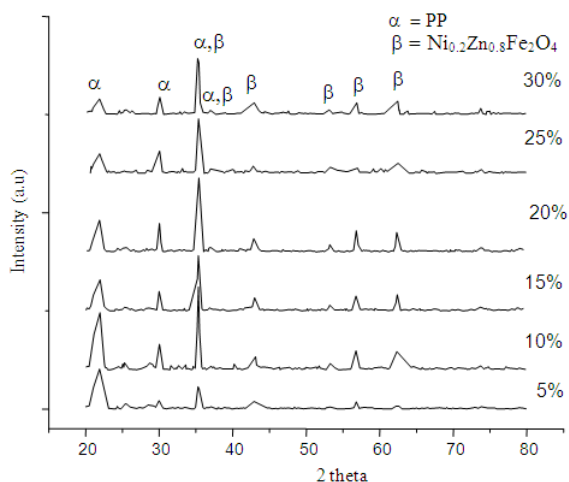


Fig. 1: XRD patterns for Ni_{0.2}Zn_{0.8}Fe₂O₄-polypropylene composites at different compositions of NZF

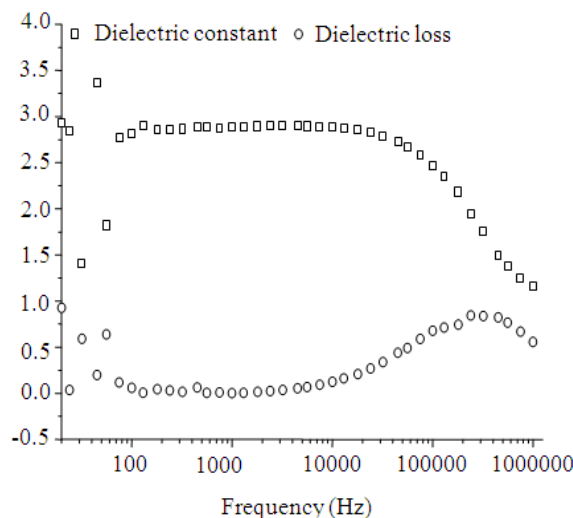


Fig. 2: Dielectric constant and dielectric loss versus frequency for polypropylene

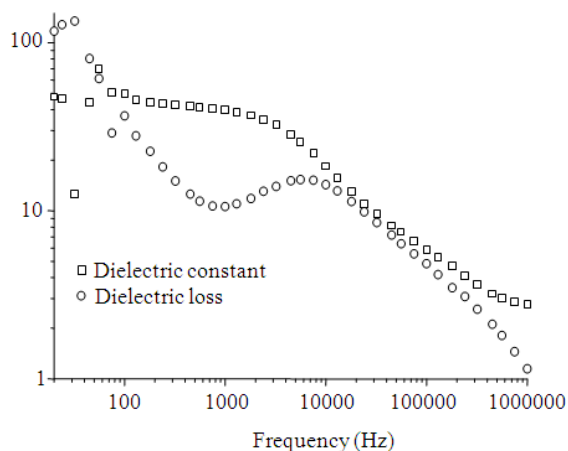


Fig. 3: Dielectric constant and Dielectric loss versus frequency for $Ni_{0.2}Zn_{0.8}Fe_2O_4$

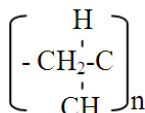


Fig. 4: Structural formula of polypropylene

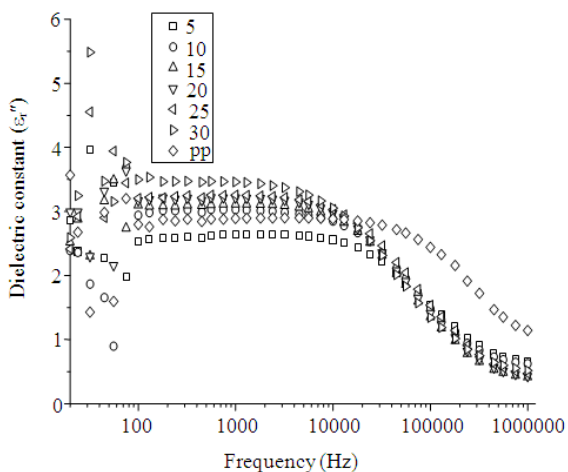


Fig. 5: Variation of the dielectric constant with respect to frequency for $Ni_{0.2}Zn_{0.8}Fe_2O_4$ -polypropylene composites

Figure 6 shows the frequency dependence of the dielectric loss of the composites at different weight ratios of NZF and PP. It is found that the loss peak shifted to the lower frequency with increasing weight ratio of NZF.

The composition dependence of the dielectric loss peak of NZF-PP composites can be seen in Fig. 7.

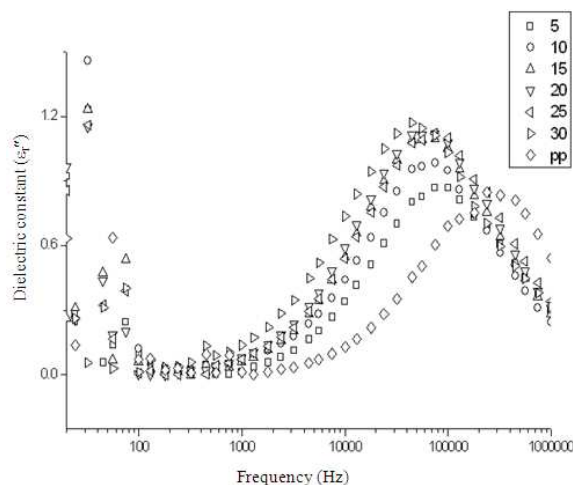


Fig. 6: Variation of the dielectric loss with respect to frequency for $Ni_{0.2}Zn_{0.8}Fe_2O_4$ -Polypropylene composites

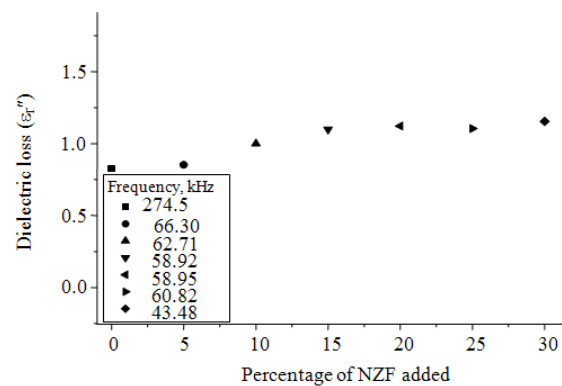


Fig. 7: Variation of the dielectric loss of loss peak with respect to weight ratio for $Ni_{0.2}Zn_{0.8}Fe_2O_4$ -Polypropylene composites

The dielectric loss increases with the weight ratio of NZF. The loss peak of the composites is in the range of 0.83-1.15.

DISCUSSION

From Fig. 2, the decrease of the dielectric constant is due to the transition from interfacial polarization to dipolar polarization. Interfacial polarization generally takes a longer time to form completely than other polarizations. Hence, PP failed to accumulate charges at structure interfaces at high frequencies.

From Fig. 3, The Ni^{3+} and Fe^{2+} of NZF are active ions which promote hybrid bonds and ferroelectricity

(Mohan *et al.*, 1999). The asymmetry produces a high dipole moment which interacts strongly with the applied field, resulting in high relative dielectric constant (Newnham and Troler-McKinstry, 1993).

PP is a slightly polar polycrystalline polymer with the main chain represented in Fig. 4 (Bur, 1985). The permanent dipole moments of PP are mainly dependent on the arrangement of the side chain, -CH₃- group. The resulting moment of PP will depend on whether the moment of the individual segment reinforce or compensate each other (Blythe and Bloor, 2008). In this case, the side chains of PP are randomly arrange and some of the dipoles moments of alternate-CH₃-groups balance each other and decrease the dielectric constant of PP. Thus, dielectric constant of NZF is much higher than PP.

According to the effective medium theory, a higher dielectric constant of the polymer-based composite can be obtained by adding high dielectric constant filler into the low dielectric constant polymer matrices as shown in Fig. 4 (Yang *et al.*, 2008; Wu *et al.*, 2007; Giordano, 2003).

From Fig. 5, it can be concluded that with increasing NZF content, the dielectric constant increases. However, the existence of NZF may take part in compensating the dipole moment of PP. Hence, the dielectric constant of 5 wt% of NZF composite is lower than pure PP due to the small amount of NZF (moderate dielectric properties) added which do not give a significant contribution toward PP-based composite, resulting in a much lower dielectric constant.

From Fig. 2 and 3, the loss peak of PP is at 200 kHz while the loss peak of NZF is at 10 kHz. The addition of NZF into PP shifted the loss peak of the matrix to the lower frequencies. Hence, the small shift of the loss peak of the composites followed the trend of NZF with increasing wt% NZF as shown in Fig. 6. It also showed that the dielectric loss are observed to correspondingly increase with the percentage of NZF added. This is probably due to NZF having higher dielectric loss added to PP increased the dielectric loss of the composites.

Table 1: Composition dependence of dielectric loss for loss peak of NZF-PP composites

Composition (%)	Frequency (Hz)	ϵ_r''
0 (PP)	2.75×10^5	0.83
5	6.63×10^4	0.85
10	6.27×10^4	1.00
15	5.80×10^4	1.10
20	5.90×10^4	1.12
25	6.08×10^4	1.10
30	4.35×10^4	1.15

The obvious increase in the dielectric loss of the loss peaks are probably due to the increase in the ratio of the high dielectric loss material NZF into PP. On the other hand, the increase ratio of NZF also affected the loss peak of composites shifting it to the lower frequency which is shown in Fig. 6 and the value tabulated in Table 1. The addition of NZF caused the dispersion of the composite to occur earlier compared to pure PP. The loss peaks of 15-25 wt% are approximately equivalent probably due to the ratio of NZF almost reaching the limit of peak shifting, thus the small change in weight ratio does not shift the peak significantly.

CONCLUSION

The NZF-PP composites with high purity were successfully prepared, which is confirmed with X-ray diffraction. From the present investigation, it shows the composite containing 30 wt% NZF gives the highest dielectric constant of 3.46 and dielectric loss of 0.14 at 1 kHz. A significant improvement on the dielectric constant of the composites is obtained with the addition of NZF with more than 10 wt%. The incorporation of NZF filler increase the dielectric loss of the composite correspondingly increases the potential to absorb electromagnetic wave at low radio frequency.

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