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Magnetic and dielectric properties of a double-percolating $Ni_{0.3}Zn_{0.7}Fe_{1.95}O_4$-Ni-polymer composite

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Abstract A novel three-phase, double-percolating composite with a ferromagnetic phase (NiZn ferrite) and metallic inclusion (nickel) embedded in the polyvinylidene fluoride matrix is prepared by a simple hot-molding method. The large ferrite particles in the composite not only act as magnetic phase, endowing the composite with high initial permeability, but also present as a high-volume fraction discrete (nonpercolating) phase, confining polymer and metallic particles into a continuous double-percolating structure of low volume fractions. The increase in the content of the magnetic nickel particles compensates the decrease in the content of the NiZn ferrite, hence a stable initial permeability with an enhanced dielectric constant has been observed. The dielectric losses of the composites were reduced compared with the previous works.

Keywords Composite · Dielectric constant · Initial permeability · Percolation

1 Introduction

Recently, multi-phase composites have attracted much interest, because the combination of two or more materials can not only lead to an enhanced performance but also endow the composites with new properties which are generated by the coupling between the different components [1, 2]. Polymer-based composites with high dielectric constants [3–6] or high initial permeability [7–9] have attracted much attention due to their flexibility, compatibility with print-wiring-board and ability to be easily fabricated into various shapes. The high dielectric constant could be enhanced greatly over the polymer matrix based on the percolation transition at the critical metallic concentration in the polymer matrix [10], while the high initial permeability is mainly obtained by dispersing ferrite particles with large initial permeability into the polymer matrix. These two kinds of polymer-based composites are being investigated separately. Merging the characteristics of these two kinds of composites could be attractive in that a novel polymer-based composite with both high dielectric constant and high initial permeability could be developed to work as multi-function devices.

The incessant demand for higher density circuits in electronics has greatly accelerated the miniaturization and integration of multilayer chip electronic components with high performance and multi-function, smaller size, high efficiency and low cost. This requires the multi-function component to work both as capacitance and inductance. Much work has been done to synthesize ferrite-ferroelectric ceramic composite materials to meet the requirements for multi-function component [11–14]. However, the ferrite phase and ferroelectric phase must be co-fired and sintered at high temperature. These processes are always time-consuming and waste much energy; moreover the mismatch between the two ceramic phases could cause other problems, such as warps and cracks in final products. These disadvantages could be overcome by the polymer-based composites.

In the previous works, we have proposed a three-phase system consisting of polyvinylidene fluoride (PVDF), metallic-magnetic particles (nickel) and ferrite particles (Ni0.3Zn0.7Fe1.95O4, hereafter NiZn). Obvious enhancements both in the initial permeability and the dielectric

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constant have been observed in the three-phase composites. However, the dielectric loss of such composites is high due to the insulator–conductor transition in the composites and the comparatively high conductivity of the NiZn ferrite. In order to reduce the dielectric loss, the three-phase composites with fixed volume fraction of PVDF have been fabricated. The increase in the content of the magnetic nickel particles compensates the decrease in the content of the NiZn ferrite, hence a stable initial permeability with an enhanced dielectric constant has been observed. More importantly, the dielectric loss of the three-phase composites has been reduced.

2 Experimental Procedure

The $Ni_{0.3}Zn_{0.7}Fe_{1.95}O_4$ (NiZn) ferrite powder was synthesized by solid state ceramic process. A certain amount of NiO, ZnO, and Fe_2O_3 were weighed and mixed by ball mining for 6 h. The resultant powders were pressed into disk shape and sintered at 1250 °C for 4 h and then the sintered ferrites were ground into powder with the average particle size of 75–100 μm. The nickel powder with the average particle size of 2–3 μm was used without purification. The polymer matrix used here was PVDF with a dielectric constant of about 10. The samples were fabricated by a simple hot-pressing method. The PVDF powder was firstly grinded thoroughly with the nickel powder and then the NiZn-ferrite powder was added and blended with the PVDF and nickel powders. The mixture was poured into a toroidal mold, for permeability test, or into a disk mold, for dielectric test, and hot pressed at 200 °C for 15 min. The final toroidal samples are about 3 mm in thickness, 5 mm in inner radius and 10 mm in outer radius. The disk samples are 12 mm in diameter and about 2 mm in thickness. Silver electrodes were painted on both sides of the disk samples for dielectric test. One series of the samples has a fixed PVDF volume fraction of 50 vol%. The sum of the volume fractions of nickel and ferrite is 50 vol%, wherein the volume fraction of nickel ranges from 1–10 vol%. Another series of the samples with a fixed Ni/NiZn volume ratio of 1:5 and a varying volume fraction of PVDF is also fabricated, wherein the volume fraction of PVDF varies from 20–80 vol%. The magnetic and electrical properties of the composites were tested by HP 4194A impedance analyzer in the frequency range of 1 kHz–40 MHz at room temperature. The composite microstructure was characterized with scanning electronic microscope.

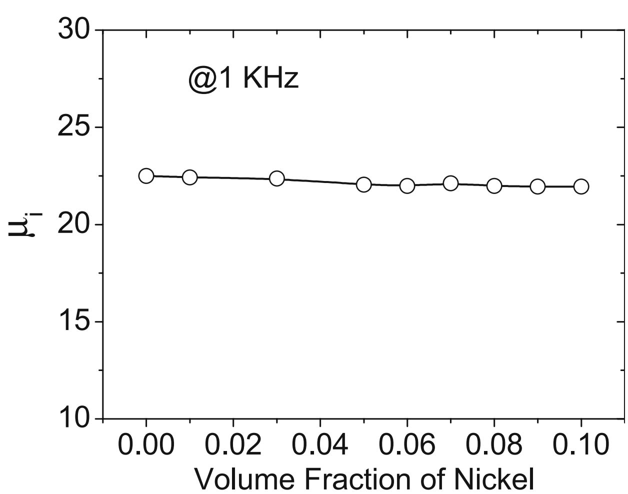
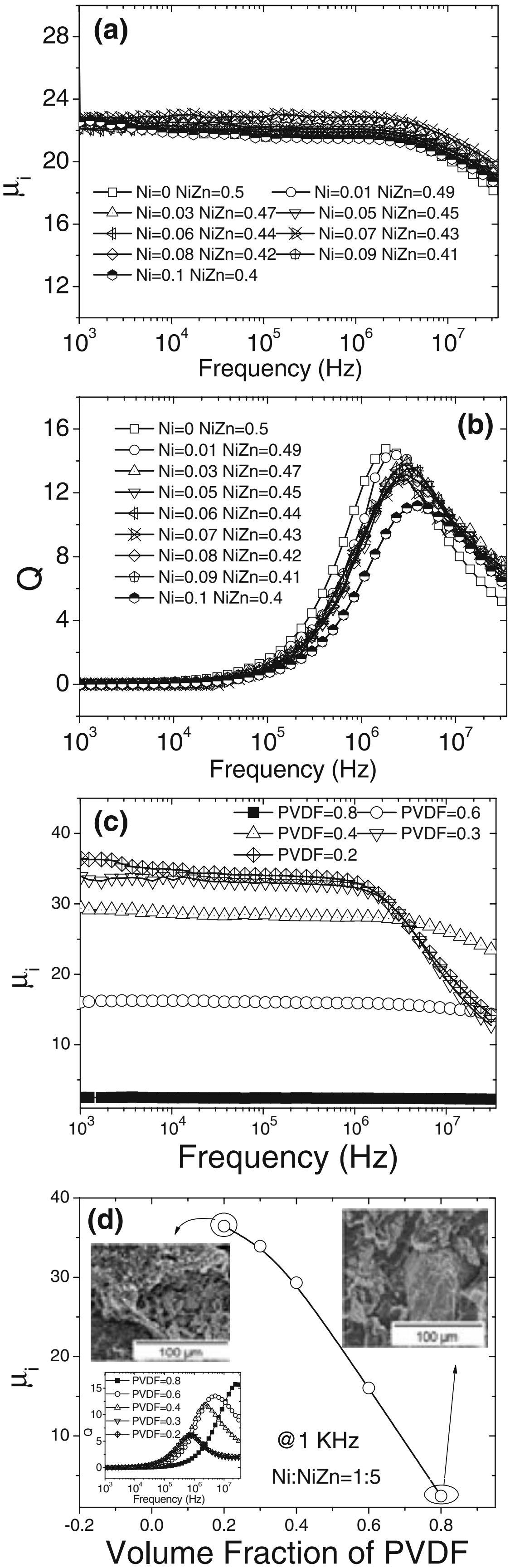


Fig. 1 Variation of the initial permeability with the volume fraction of Ni for the Ni–NiZn–PVDF composites

3 Results and discussion

The variation of initial permeability with the volume fraction of nickel is shown in Fig. 1. Though the volume fraction of the ferrite decreases from 49 to 40 vol%, the initial permeability of the composites do not greatly decrease. Instead, almost stable initial permeability is observed in the composites when the content of the ferrite decreases. This phenomenon can be understood if one takes into account the nickel particles existing in the gaps between the ferrite particles. Hence, the increase in the content of the magnetic nickel particles compensates the decrease in the content of the NiZn ferrite. Moreover, the magnetic nickel particles existing between the ferrite particles can reduce the demagnetizing field around the ferrite particles. The magnetic spectra of the three-phase composites are shown in Fig. 2(a). As the content of the NiZn ferrite is over 40 vol%, the magnetic behavior of the NiZn ferrite is dominant in the three-phase composites; hence the initial permeability shows little frequency dependence in the frequency range lower than the cut-off frequency of the NiZn ferrite, as verified in other works [7–10]. The Q factors of the three-phase composites all reach a peak at about 1.5 MHz, as shown in Fig. 2(b). Slightly decrease in the Q factor with the volume fraction of nickel is also observed.According to the results mentioned above, the optimized volume ratio of Ni to NiZn is set to be 1:5. The samples with a fixed Ni/NiZn volume ratio of 1:5 and a varying volume fraction of PVDF are also investigated. The

Fig. 2 Frequency dependence of (**a**) initial permeability and (**b**) quality factor for the Ni/NiZn/PVDF composites; (**c**) frequency dependence of initial permeability for the samples with a fixed Ni/NiZn volume ratio and a varying PVDF volume fraction; (**d**) variation of initial permeability on the volume fraction of PVDF for the samples with a fixed Ni/NiZn volume ratio and a varying PVDF volume fraction, the insets are the dependence of Q factor on frequency and the micrographs of two samples with different content of PVDF respectively ▶



magnetic spectra of such samples are shown in Fig. 2(c). The initial permeability of the sample with smaller PVDF volume fraction is large but their cut-off frequency shifts to a lower frequency compared with samples with larger

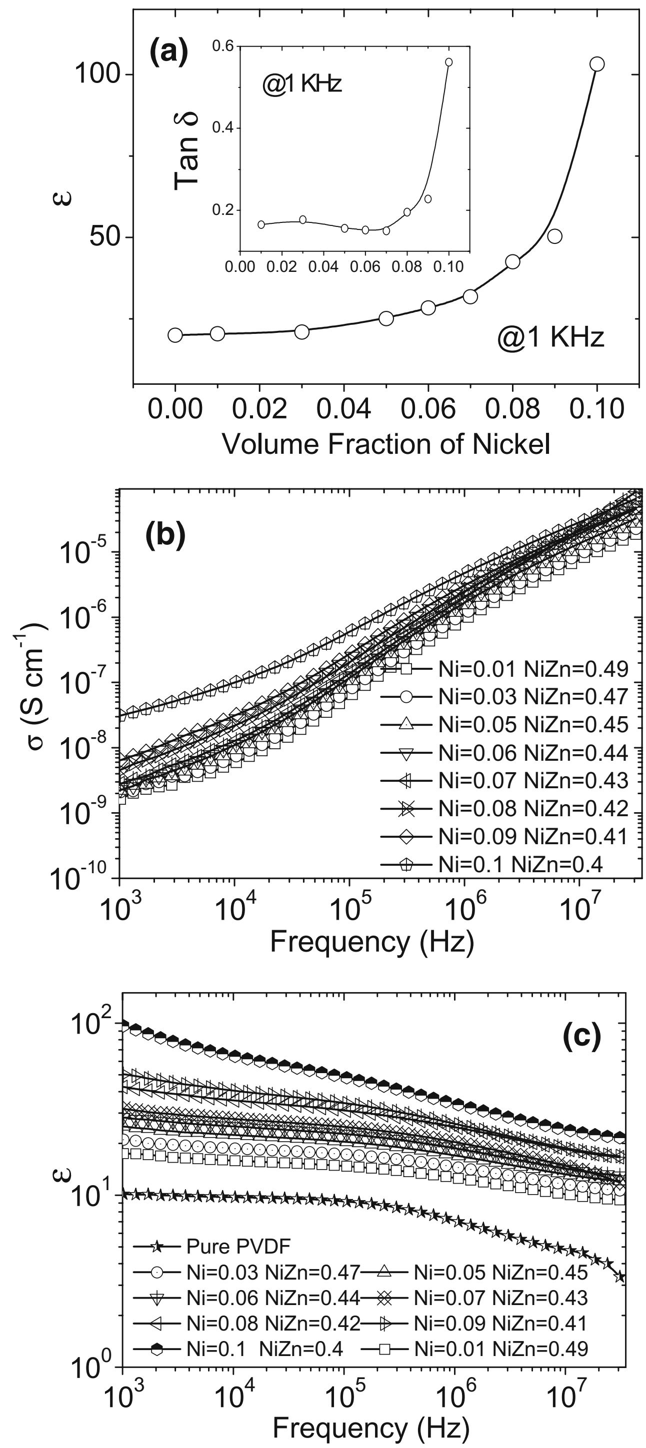


Fig. 3 Variation of (**a**) dielectric constant for the Ni/NiZn/PVDF composites at 1 kHz with the volume fraction of Ni, the inset shows the dependence of dielectric loss on the volume fraction of Ni; and the dependence of (**b**) conductivity and (**c**) dielectric constant on frequency for the Ni/NiZn/PVDF composites

PVDF volume fraction. Figure 2(d) shows the dependence of initial permeability on the volume fraction of PVDF. A rapid drop in the initial permeability is observed when the content of PVDF increases from 20 to 80 vol%. Though the initial permeability of the sample with 20 vol% PVDF loaded can reach nearly 40, the Q factor of this sample decreases to almost 5 as shown in the inset of Fig. 2(d). This decrease in the Q factor counteracts the enhancement in the initial permeability, which can be attributed to that when the content of PVDF decreases the polymer can not fill the gaps between the filler particles and thus more pores come into being, as shown in the insets of Fig. 2(d). These pores introduce much air into the composite, which greatly decreases the Q factor.

The dielectric behavior of the three-phase composites is shown in Fig. 3. The measured conductivity shows that the percolation transition occurs and the percolation threshold obtained by a linear-fit operation is f_c=0.09. This value is lower than the theoretical percolation threshold, i.e., f_c= 0.16. This phenomenon can be attributed to the double-percolating structure. When the nickel particles are forced to distribute in the gaps between the ferrite particles, they can connect with each other more easily [15]. A continuous conduction path can be established at lower concentration of metallic particle. The measured dielectric constant [Fig. 3(a)] also shows a clearly percolation transition. The divergent behavior of the effective dielectric constant in the vicinity of the percolation threshold is observed, as predicted by the power law [10]:

$$\varepsilon = \varepsilon_0 \left| \frac{f_{cd} - f}{f_{cd}} \right|^{-q} \tag{1}$$

where ε_0 is the dielectric constant of the PVDF polymer matrix loaded with NiZn, f_{cd} is the percolation threshold for the dielectric constant, and q is the critical exponent of about 1. Just below the percolation threshold, the fitting of Eq. 1 to the data gives f_{cd}≈0.09, and q≈0.7. f_{cd} is consistent with f_c. The dielectric constant of the three-phase composite can be enhanced to over 100 with 10 vol% nickel loaded. The dielectric loss of the three-phase composite is 0.6 at the percolation threshold, as shown in the inset of Fig. 3(a). This value is lower than those reported in previous works, where the dielectric loss is over 3 at the percolation threshold [16]. However, the dielectric loss of such three-phase composite is still large. The usage of the ferrite with lower conductivity and fine processing technology could probably reduce the dielectric loss to a lower level.

The conductivity of the three-phase composite increases with the frequency is shown in Fig. 3(b). According to the percolation theory, as $f \rightarrow f_c$

$$\sigma \propto \omega^u \tag{2}$$

where $\omega=2\pi\nu$, ν is the frequency and u is a critical exponent. Linear-fit operation for the data of the sample with f=0.09 gives u=0.86, which is lower than the normal value from the percolation theory. This discrepancy has also been observed in other works [11]. The percolation theory can describe the singular change in the conductivity near the percolation threshold exactly only when the difference between the conductivity of the matrix and that of the filler is very large. But in this three-phase composite, the conductivity of the NiZn ferrite is over 10^{-7} S/cm, and the content of the NiZn ferrite is over 40 vol%, so when the NiZn/PVDF two-phase system are treated as matrix in the Ni/NiZn/PVDF three-phase composite, the matrix is not an ideal insulator. Figure 3(c) shows a promising advantage of the three-phase composite: the weak dependence of the dielectric constant on the frequency. Of interest to note is that the characteristic relaxation drop in the dielectric constant of pure PVDF at about 10^5 Hz is eliminated in the three-phase composite. The dielectric constant of the three-phase composite decreases slightly with the frequency where f_{Ni}<0.09, and drops more rapidly with the frequency where f_{Ni}>0.09.

4 Conclusion

The $Ni_{0.3}Zn_{0.7}Fe_{1.95}O_4$-Ni-PVDF three-phase composite with a fixed PVDF volume fraction of 50 vol% and a fixed Ni/NiZn volume ratio of 1:5 has been investigated. Stable initial permeability is observed though the volume fraction of NiZn ferrite decreases from 50 to 10 vol%. At the same time, the dielectric constant of the composite is enhanced 10 times more than the PVDF matrix. Although high content of Ni and NiZn can increase the initial permeability of the composite, the reduction of PVDF in the composite causes more pores in the gaps between the filler particles, which causes the Q factor to decrease to a low value. The dielectric loss is comparatively reduced but still more works need to be done to lower the dielectric loss further.

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References

1. R.B. Thompson, V.V. Ginzburg, M.W. Matsen, A.C. Balazs, Science **292**, 2469 (2001)
2. R. Yang, S. Ogitani, P. Kohl, C.P. Wong, J. Appl. Polym. Sci. **83**, 1084 (2002)
3. Y. Bai, Z.Y. Cheng, V. Bharti, H.S. Xu, Q.M. Zhang, Appl. Phys. Lett. **76**, 3804 (2000)
4. Z.M. Dang, Y. Shen, C.W. Nan, Appl. Phys. Lett. **81**, 4814 (2002)
5. Z.M. Dang, Y.H. Lin, C.W. Nan, Adv. Mater. **15**, 1625 (2003)

6. Y. Shen, C.W. Nan, M. Li, Chem. Phys. Lett. **396**, 420 (2004)
7. J. Slama, R. Dosoudil, R. Vicern, A. Giruskova, V. Olah., I. Hudec, E. Usak, J. Magn. Magn. Mater. **195**, 254 (2003)
8. R. Lebourgeoisa, S. Berenguerb, C. Ramiarinjaonab, T. Waeckerle, J. Magn. Magn. Mater. **191–194**, 254 (2003)
9. J.H. Paterson, R. Devine, A.D.R. Phelps, J. Magn. Magn. Mater. **196–197**, 394 (1999)
10. C.W. Nan, Prog. Mater. Sci. **37**, 1 (1993)
11. J.V. Mantese, A.L. Micheli, D.F. Dungan, J. Appl. Physi. **79**, 1655 (1996)
12. T. Yamamoto, M. Chino, R. Tanaka, Ferroelectrics **95**, 175 (1989)
13. K.K. Patankar, V.L. Mathe, R.P. Mahajan, Mater. Chem. Phys. **72** (1), 23 (2003)
14. X.W. Qi, J. Zhou, Z.X. Yue, Z.L. Gui, L.T. Li, S. Buddhudu, Adv. Funct. Mater. **14**, 920 (2004)
15. R. Mezzenga, J. Ruokolainen, G.H. Fredrickson, E.J. Kramer, D. Moses, A.J. Heeger, O. Ikkala, Science **299**, 1872 (2003)
16. Y. Shen, Z.X. Yue, M. Li, C.W. Nan, Adv. Funct. Mater. **15**, 1100 (2005)