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Multifunctional $SrTiO_3$/NiZn ferrite/POE composites with eletromagnetic and flexible properties for RF applications

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Abstract Multifunctional dielectric composites with electromagnetic and flexible properties for RF applications were investigated. A kind of low loss flexible dielectric and magnetic composite with $SrTiO_3$ (STO) ultrafine particles and NiZn ferrite (NZO) ultrafine particles embedded in a Thermoplastic Polyolefin Elastomer (POE) matrix was fabricated using the extrusion technology. The dielectric and magnetic properties of the as-prepared composites with different volume fraction of ceramic fillers were studied. The results indicate that when the volume of the ceramic fillers is fixed, the permittivity of the composites increase while the dielectric loss, permeability and magnetic loss decrease with the increasing of the ratio of STO to NZO. The cut-off frequencies of the composites are all above 1 GHz. The good frequency stability of the electromagnetic properties within a wide frequency range was observed. All the composites show very good flexibilities. With the increasing of the volume fraction of ceramic fillers, the tensile strength and elongation decrease. The obtained multifunctional flexible magnetic-dielectric composites are good candidates for the applications of the capacitor-inductor integrating devices in RF communications such as electromagnetic interference filters and antennas.

Keywords Multifunctional composites · Dielectric properties · Magnetic properties · Flexibility · Low loss

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1 Introduction

In recent years, with the rapid development of electronics industry, electronic components are required to have smaller size and higher performance. It is desired that the materials for the electronic components exhibit multifunctional properties, such as magnetic-electric [1, 2], magnetic-optical [3], flexibility [4], etc. The dielectric-magnetic composites have recently received much more attention. A lot of work has been carried out on synthesizing dielectric-magnetic composite materials to meet the requirement for multifunctional components [5–9]. These composite materials show both inductive and capacitive properties, which have been regarded to be an effective solution to fabricate miniature filters and antenna, electro-magnetic interference (EMI) devices and so on. For the ceramic-based composites, however, the magnetic phase and the dielectric phase need to be cofired at high temperatures; moreover, the shrinkage mismatch or diffusion between the two ceramic phases may seriously influence the performance of the final products. Alternatively, polymer-based composites with high permittivity [10–15] or high permeability [16–19] have been proposed due to their flexibility, compatibility with printed wiring board (PWB), and ability to be easily fabricated into various shapes.

According to the effective medium theory, the high permittivity of the polymer-based composites can be obtained by putting the high permittivity ceramic particles into the polymer matrices, while the high initial permeability can be obtained by dispersing ferrite particles into the polymer matrices. Some previous studies [20–23] have been carried out on this kind of composites. However, the composites obtained have a common deficiency of possessing very high loss and low cut-off frequency below 1GHz, which limits their practical high-frequency application.

Also the flexibilities of the above mentioned composites are very limited.

In this paper, a kind of high-frequency electromagnetic flexible composite has been obtained by introducing the $SrTiO_3$ (STO) and NiZn ferrite (NZO) fillers into the thermoplastic Polyolefin Elastomer (POE) matrix. The electromagnetic and mechanical properties of the composites were investigated in detail. To our best knowledge, this is the first report on the composites which possess the integration of electromagnetic properties and flexibility. Such flexible magnetic-dielectric multifunctional composites with very low dielectric and magnetic loss would be good candidates for the capacitor-inductor integrating devices such as electromagnetic interference filters and antennas in high-frequency communications.

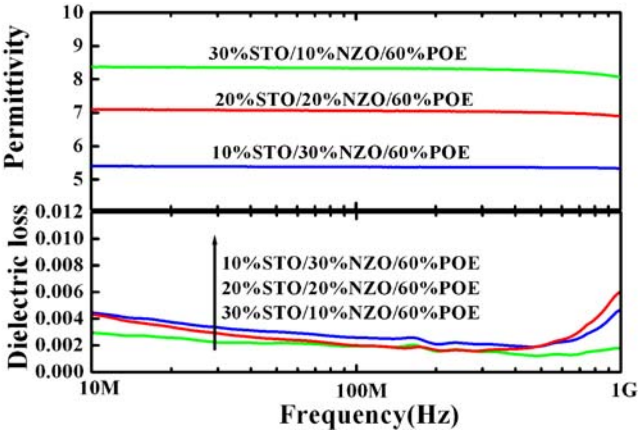


Fig. 1 Frequency dependence of the dielectric properties of the STO/NZO/POE composites with different volume ratio of NZO to STO

2 Experimental

The POE (density: 0.87 g/cm^3, glass transition temperature: −55°C, elongation exceeds 800%) used was Engage™ POE 8100 (Dupont Dow Co., USA). The ceramic fillers were prepared by conventional mix-oxides method and ground into powders with the mean grain size of about 500 nm. The permittivity of STO and permeability of NZO are 250 and 35, respectively. The ceramic powders were surface modified by fully mixing with 2% oleic acid solution. Then the surface modified ceramic powders and the POE were mixed for 12 min in a Rheomix600p system (Rheomix600p, HAAKE Co., Germany) operated at 60 rpm and 180°C. The mixture was put into a disk mold and hot-pressed into a sample under 10 MPa at a temperature of 180°C for 5 min. The microstructure was analyzed using a scanning electron microscope (SEM) (JSM-6700F, JEOL Ltd., Japan). The stress–strain behaviors of the as-prepared composites were measured on a tensile test machine (PT-1036PC, Perfect Instrument Co. Ltd, China Taiwan) with a deformation speed of 5 mm/min. The dielectric and magnetic measurement in the frequency range of 100 MHz–1 GHz were carried out by a HP4291B impedance analyzer with a HP16453A dielectric material test fixture and a HP16454L magnetic material test fixture, respectively. The magnetic hysteresis loops of the composites were measured by vibrating sample magnetometer (VSM) (Lake Shore 7410, USA).

3 Results and discussion

Figure 1 shows the dielectric properties of the composites with the same matrix volume but with different volume ratio of NZO to STO. As expected, the permittivity increases and the dielectric loss decreases with the increasing of STO. The dielectric losses of all the composites are very low in the high frequency range. The permittivities show good stability within a wide range of frequency. It also can be found that the dielectric losses of the composites are relatively high in the low frequency range. The dielectric losses decrease first and then increase with the increasing of frequency. This is attributed to the low resistance of NZO and can be explained by Debye formula [24]. When an alternating electric field is applied, not only polarization loss but also leakage loss generates. The dielectric loss is divided into two parts.

$$D = D_{\mathrm{P}} + D_{\mathrm{G}} = \frac{(\varepsilon_S - \varepsilon_\infty)\omega\tau}{\varepsilon_S + \varepsilon_\infty\omega^2\tau^2} + \frac{\gamma}{\omega\varepsilon_0}\left(\frac{1}{\varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1+\omega^2\tau^2}}\right) \tag{1}$$

where D is the total dielectric loss, D_{P} is the polarization loss and D_{G} is the leakage loss. It can be deduced that at a certain temperature when frequency (ω) go to 0, i.e., static electric field, D_{P} go to 0. In such a case, the dielectric loss is almost attributed to the leakage loss. Thus when the frequency is very low, $\omega\tau << 1$, the dielectric loss can be described approximately as below.

$$D \cong \frac{\gamma}{\omega\varepsilon_0\varepsilon_S} \tag{2}$$

Hence the dielectric loss is inversely proportional to frequency in the low frequency range. As the frequency increasing, the D_{P} gradually increases and becomes predominant while the D_{G} decreases. In the higher frequency range towards the end of the measurement range of HP 4291B, a resonant peak would occur due to the LC resonance in the measurement circuit which caused the increasing of the measured dielectric loss.

Figure 2 shows the magnetic hysteresis loops of the composites with the same matrix volume but with different volume ratio of NZO to STO. The saturated magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) were determined from the hysteresis loops, as shown in Table 1. As it can be seen in Table 1, the magnetic properties of the composites clearly depend on the ferrite loading. It is obvious from the Fig. 2 that the saturated magnetization (M_s) and the remnant magnetization (M_r) decrease with the increasing of STO as expected, since the magnetic properties depend on the total content of the magnetic material. The reduction of the values may be caused by nonlinearity of the magnetic moments at the surface of the NZO particles, resulting in a decrease of the saturated magnetization (M_s) and the remnant magnetization (M_r) for a higher STO content [25]. The coercivity (H_c) keeps constant as the variation of NZO content, which means that all the samples have very similar microstructures.

The frequency dependence of the magnetic properties of the composites with different volume ratio of NZO to STO is shown in Fig. 3. It can be seen that with the increasing of NZO the initial permeability and magnetic loss increase. According to Rikukawa [26], for either domain wall movement or spin rotation, the initial permeability is proportional to M_s^2. As explained above, with the increasing of NZO into the composites, M_s increases. With the increasing of frequency, the permeabilities of all the composites nearly keep constant and the magnetic losses show dispersion and increase slightly only in high frequency range. It is also found that the cut-off frequencies (i.e., the frequency where the μ'' value is maximal) of all the composites are above 1 GHz. And it can be assumed that with the decreasing of NZO, the cut-off frequency increases. According to Snoek's law [27], the product of the initial susceptibility and cut-off frequency is a constant for a ferromagnetic material, i.e., $(\mu_i - 1)f_r = \gamma/2\pi M_s$, where f_r is the cut-off frequency, γ is the gyromagnetic ratio, M_s is the saturation magnetization and μ_i is the initial permeability. The decreasing of NZO may cause the decrease of M_s. Accordingly, the increase of cut-off frequency can be expected. Additionally, the magnetic losses of all the composites are all very low. This is probably due to the insulating matrix wrapping the NZO particles which drastically increases the resistance and reduces the eddy-current loss [28] of the composite.

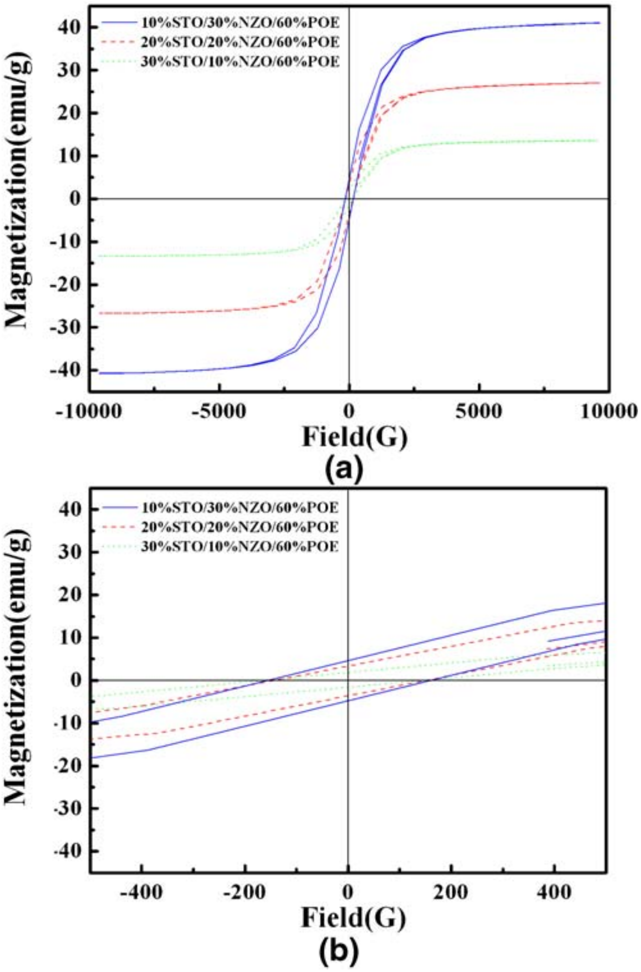


Fig. 2 Magnetic hysteresis loops of the STO/NZO/POE composites with different volume ratio of NZO to STO in the full range (**a**) and low-field range (**b**)

Figure 4 shows the frequency dependence of the magnetic properties for the bulk NZO ceramic and the 0.1STO/0.3NZO/0.6POE composite. The bulk NZO ceramic shows a resonance at about 100 MHz whereas the resonance frequency of the three-phase composite shifts to a much higher frequency beyond the HP4291B measurement range. The three-phase composite possesses an advantage of much wider working frequency range.

Figure 5 presents the frequency dependence of the magnetic properties of the NZO/POE composites with different volume ratio of NZO. It can be easily found that with the increasing of NZO and the increasing of frequency, the magnetic behaviors of composites show the same tendency as that of the STO/NZO/POE composites with the same volume of NZO. The magnetic losses of the two kinds of composite are very similar, which implies that both STO and polymer matrix have very high resistances. The difference is that the initial permeabilities of the STO/NZO/POE composites are a little higher than those of the NZO/

Table 1 Magnetic parameters of STO/NZO/POE composites with different volume ratio of NZO to STO.

Sample	M_s (emu/g)	M_r (emu/g)	H_C (G)
30%STO/10%NZO/60%POE	37	4.8	157.72
20%STO/20%NZO/60%POE	24	3.3	157.46
10%STO/30%NZO/60%POE	12	1.8	157.88

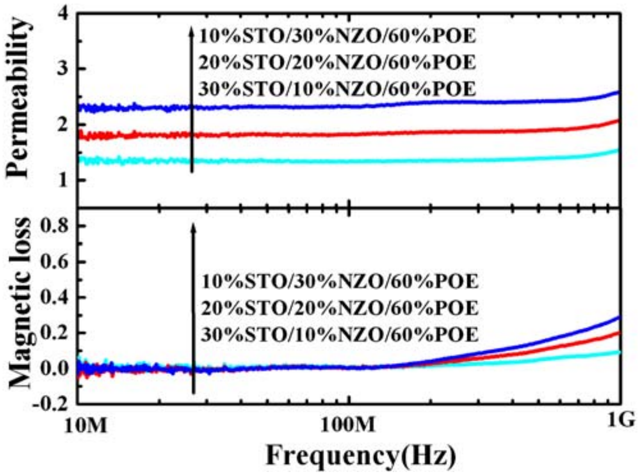


Fig. 3 Frequency dependence of the magnetic properties of the STO/NZO/POE composites with different volume ratio of NZO and STO

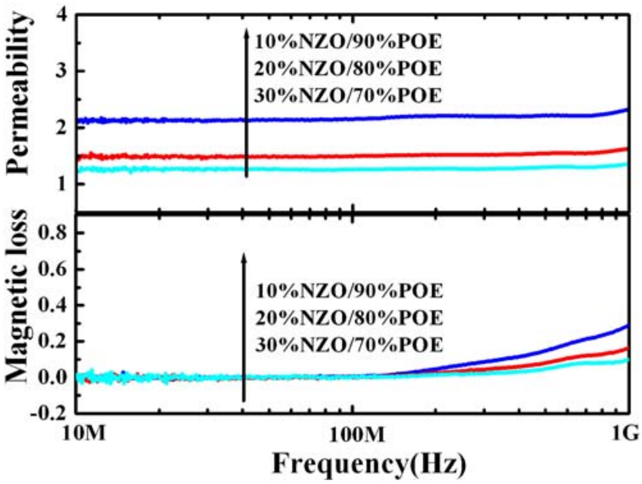


Fig. 5 Frequency dependence of the magnetic properties for the NZO/POE composites with different volume ratio of NZO

POE composites possessing the same volume of NZO. For illustration and comparison, the theoretical calculations using the well-known Maxwell–Garnett (MG) formula are also shown. For the two-phase composite of spherical ferrites and nonmagnetic host matrix, the MG formula for the effective permeability of the composite is

$$K = K_1\left(1 + \frac{3f_{\mathrm{NZO}}\beta}{1 - f_{\mathrm{NZO}}\beta}\right) \tag{3}$$

where $\beta = (K_2 - K_1)/(K_2 + 2K_1)$; K is the effective permeability of the composite; K_1=1 and K_2=35 are the initial permeabilities of the polymer matrix and NZO, respectively; f_{NZO} is the volume fraction of NZO. As shown in Fig. 6, for the NZO/POE composites, when $f_{\mathrm{NZO}}<0.40$, the experimental permeabilities are in good agreement with that calculated by MG formula. However, for the STO/NZO/POE composites, the experimental permeabilities are a little larger than that calculated by MG formula. This is due to the fact that the STO/NZO/POE composites have more ceramic fillers than the NZO/POE composites and ceramic filler clusters easily occur.

The stress–strain curves of the STO/NZO/POE composites with different volume fraction of ceramic fillers are shown in Fig. 7. The results show that the mechanical properties decrease with the increasing of the volume fraction of fillers. The interface between ceramic fillers and the polymer matrix and the dispersion of the filler particles in the matrix play important roles in determining the properties of a composite [29, 30]. The SEM micrographs of STO/POE composites with different volume fraction of fillers are shown in Fig. 8. It can be seen that the ceramic fillers were uniformly distributed in the polymer matrix for all the composites and the composites are very dense. For the composites with 40 vol.% fillers, the fractures happened through the interface between ceramic fillers and the polymer matrix. With the decreasing of the

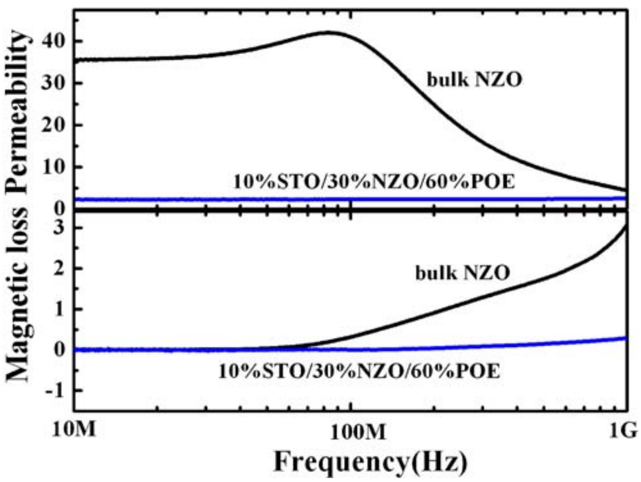


Fig. 4 Frequency dependence of the magnetic properties of the 0.1STO/0.3NZO/0.6POE composite and the bulk NZO

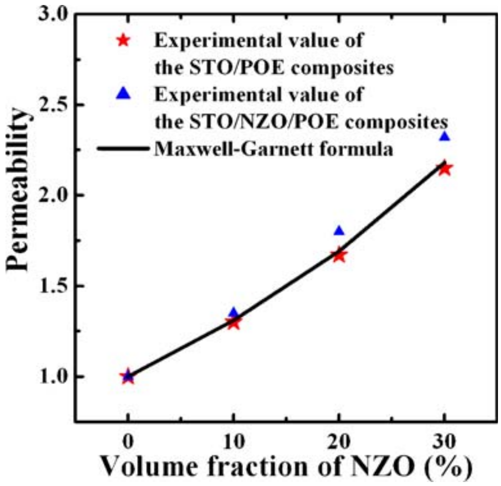


Fig. 6 Experimental and calculated permeabilities of the STO/NZO/POE composites vs. the volume fraction of NZO

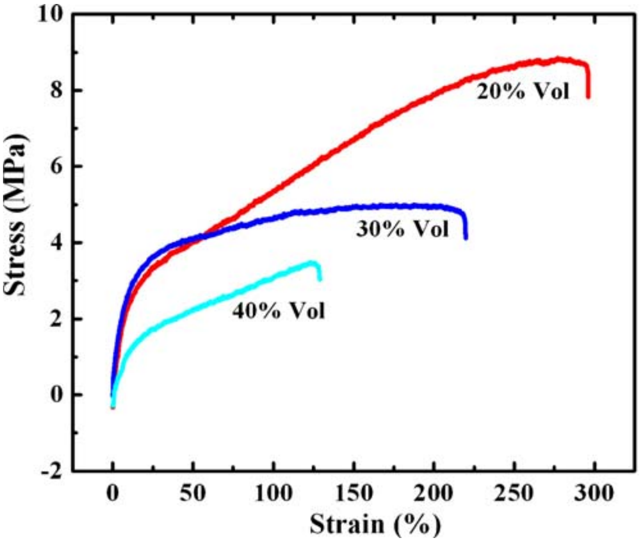


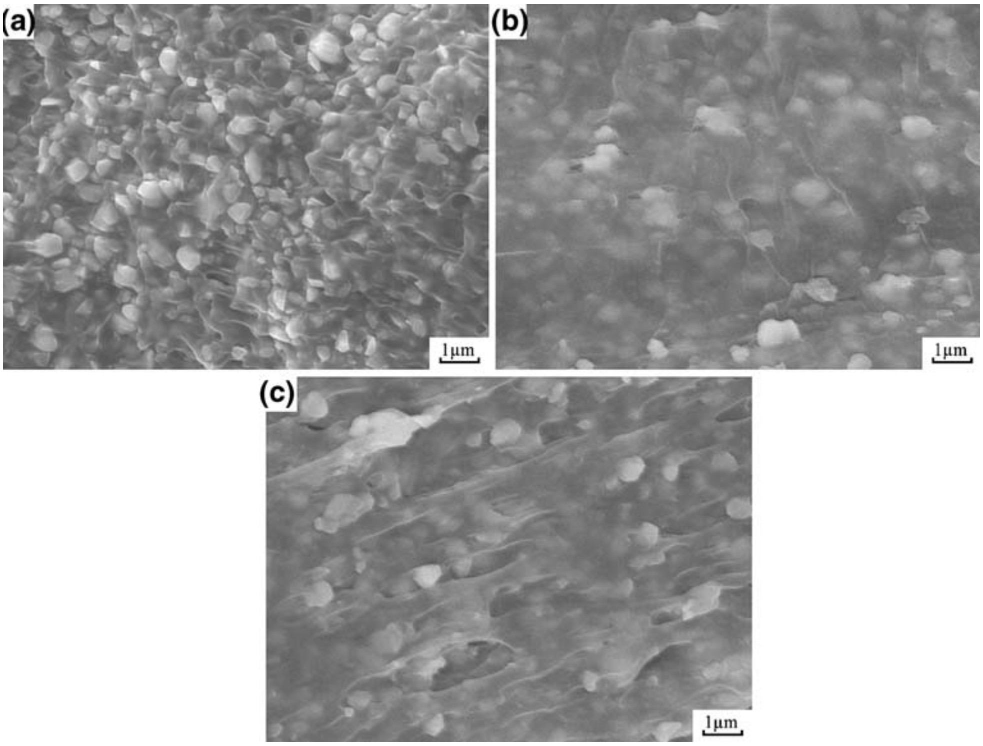
Fig. 7 Stress–strain curve of the STO/NZO/POE composites with different volume fraction of ceramic fillers

volume of ceramic fillers, more and more fractures happened through the polymer matrix. It is known that the interface is the vulnerable area of the composite. So with the increase of the volume of fillers, the tensile strength of the composites decreases. Because the elongation of the composite is responsible by the flexible polymer matrix, the elongation of the composite decreases with the increasing of the volume of fillers. The composite containing 40 vol.% fillers has a tensile strength of 3.5 MPa with an elongation at the break value of about 126%.

4 Conclusions

Multifunctional STO/NZO/POE flexible electromagnetic composites with various volume fractions of ceramic fillers were prepared by using the extrusion technology. As the volume of the ceramic fillers was fixed, the permittivities of the composites increase while the dielectric losses, permeabilities and magnetic losses decrease with the increasing of the ratio of STO to NZO. The cut-off frequencies of the composites are all above 1 GHz. The permittivities and permeabilities of all the composites have shown good frequency stability and low dielectric and magnetic losses have been obtained within the measurement range from 10 MHz to 1 GHz. For the 0.1STO/0.3NZO/0.6POE composite, the permittivity, dielectric loss, permeability and magnetic loss are 5.4, 0.0018, 2.3 and 0.002 at 100 MHz, respectively. The mechanical properties of composites decrease with the increasing volume fraction of the ceramic fillers. All the composites have very good flexibilities. The composite with 40 vol.% fillers has a tensile strength of 3.5 MPa with an elongation at the break value of about 126%. Such multifunctional flexible magnetic-dielectric composites are candidates for the capacitor-

Fig. 8 SEM micrographs of STO/NZO/POE composites with different volume fraction of ceramic fillers. (**a**) 40 vol.%, (**b**) 30 vol.%, (**c**) 20 vol.%



inductor integrating devices such as electromagnetic interference filters in RF communications.

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