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Magnetic properties of composites of $Tb_{0.28}Dy_{0.72}Fe_2$ and polyvinylidene fluoride*

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Bi-ferroic particulate composites with $Tb_{0.28}Dy_{0.72}Fe_2$ (Terfenol-D) particles randomly dispersed in ferroelectric polyvinylidene fluoride matrix prepared by a simple hot-pressing procedure were investigated. With increasing concentration of Terfenol-D, the magnetic susceptibility, saturation magnetization and initial permeability of the composites increases. The dependence of the effective magnetostriction on applied bias for the composites is similar to that for bulk Terfenol-D, but the effective magnetostriction strongly depends on the volume fraction of Terfenol-D. The observed behaviour of the composite is reasonably described by using effective medium theories.

Keywords: magnetostriction, Terfenol-D, composites, effective medium theories
PACC: 7580, 7280T

1. Introduction

It has been known that rare-earth-iron alloys, such as $Tb_xDy_{1-x}Fe_2$ (commonly known as Terfenol-D), are giant magnetostrictive materials.[1,2] Compared to piezoelectric ceramics such as lead zirconate titanate, Terfenol-D has higher force, higher energy density, lower sound velocity and lower Young modulus, and thus can be used at low bias field. Terfenol-D is very useful in the manufacture of low-frequency high power underwater acoustic transducers and actuators, as well as other magneto-acoustic devices. Magnetostrictive and piezoelectric composite materials are proposed for coil-less magnetic force control to diminish energy consumption and heat generation due to the resistance of the coils.[3]

In the polycrystalline state, maximum magnetostriction is possible when Terfenol-D grains are aligned in the easy magnetization direction $< 111 >$ because the magnetostriction is largely anisotropic as $\lambda_{111} \gg \lambda_{100}$.[1] Grain-aligned Terfenol-D is mainly produced by free stand zone melting (FSZM), modified Bridgman (MB) method, and sintering Terfenol-D powder compact. The directional solidification techniques of FSZM and MB involve controlling very accurately various process parameters for the realization of good grain alignment. Therefore, the production of grain-aligned Terfenol-D rods is considered to be inherently difficult and thus expensive. Furthermore, at high frequencies large eddy current losses in Terfenol-D limits its applications.

To solve this problem, polymer matrix composites have been developed by dispersing Terfenol-D particles into the polymers (see, for example, Refs.[4–10]). This composite method has distinct advantages over the others in being simple and cost-effective, although the effective magnetostriction of the composites is reduced due to the dilution effect for the presence of a non-magnetic polymer binder. The insulating layer of the polymer binder between the Terfenol-D particles increases the resistivity, and thus reduces the eddy current losses at high frequencies. The polymer matrix composites extend the frequency limit from about 1kHz to several tens or hundreds of kHz. This class of composites also has good mechanical properties. Thus such magnetostrictive composites have attracted considerable attention in recent years.[4−10]

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In this paper, polyvinylidene fluoride (PVDF), a ferroelectric polymer, was used as the polymer binder, and the Terfenol-D/ PVDF particulate composites were prepared using a very simple procedure. This polymer–matrix composite can be mechanically flexible. Most importantly, the combination of Terfenol-D and ferroelectric PVDF produces a bi-ferroic composite with simultaneous ferroelectricity and ferromagnetism. In addition, in the Terfenol-D/PVDF composite, the coupling interaction between magnetostriction of Terfenol-D particles and piezoelectricity of PVDF can result in a large magnetoelectric effect[11,12] characterized by the appearance of an electric polarization on applying a magnetic field. That is, when a magnetic field is applied to the composite, Terfenol-D particles change their shape magnetostrictively, and strain is passed along to the PVDF, resulting in an electric polarization. Such bi-ferroic materials provide opportunities for potential applications as transducers, actuators, and sensors. Due to the limitation to our existing experimental condition, we cannot presently make measurement on the ferroelectric and magnetoelectric behaviour of the bi-ferroic composites. Thus we focus upon magnetic and magnetostrictive properties of the Terfenol-D/PVDF magnetic/ferroelectric composites in the present work.

2. Experimental

Terfenol-D powder with an average particle size of about 20 μm was obtained by crushing bulk $Tb_{0.28}Dy_{0.72}Fe_2$ single crystal with $\lambda \sim 1600$ppm (obtained from Beijing Institute of Rare-Ferrous Metals, China) in an argon atmosphere. Initially, the Terfenol-D powder was uniformly mixed with PVDF powder (obtained from Shanghai 3F Co.). The powder mixture was then hot-pressed at a temperature of 180°C under a pressure of 10MPa for 30 minutes to obtain the sample pellets of the Terfenol-D/PVDF particulate composites.

The microstructure of the composites was examined by optical microscopy (American QUESTAR KH-1000). Magnetic hysteresis loops and initial magnetization curves were measured by VSM-7307 (American Lakeshore Co.). Magnetostriction measurements were performed by standard strain-gauge technique. Metal strain gauges with a maximum measurement up to 5% bonded with highly elastic epoxy resin were utilized to ensure measurement reliability and avoid gauge debonding.

3. Results and discussions

Figure 1 shows that the typical microstructure of the Terfenol-D/PVDF composites has Terfenol-D particles randomly distributed in the PVDF matrix. The white parts are the Terfenol-D particles, and the grey matrix is the PVDF. There are also some pores in the samples. When the volume fraction f of the Terfenol-D particles is low, i.e. f <0.2, the Terfenol-D particles are well dispersed in the PVDF matrix. When f increases, the Terfenol-D particles become aggregated to form particle clusters, and become self-connected when f >0.2. The two-point measurement of the conductivity of the composites showed that a percolation transition occurs around f=0.2.

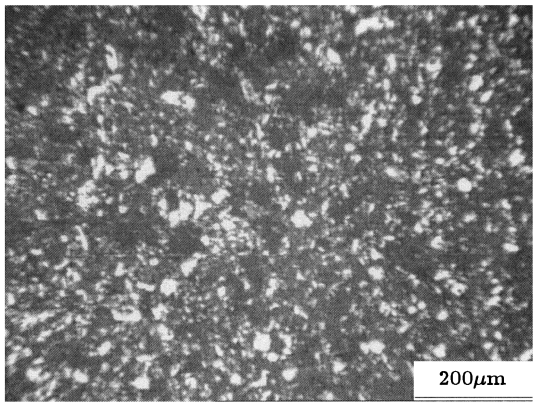


Fig.1. A typical micrograph of the Terfenol-D/PVDF composite with 50% volume fraction of Terfenol-D particles (f=0.5).

Frequency-dependent impedance of the composites with various f is shown in Fig.2. When $f \leq$ 0.2, the impedance of the composites decreases linearly with increasing frequency, which is dominated by the continuous PVDF matrix; when f >0.2, the impedance of the composites keeps constant below 100kHz, and decreases linearly with increasing frequency at high frequency, which is characteristic of a metal–insulator composite, as shown in Fig.2(a). In comparison with conductive Terfenol-D (i.e. f=1), the composites exhibit much higher impedance, even at 10^6Hz (see Fig.2(b)), which thus reduces the eddy current losses at high frequencies. The critical operating frequency f_c above which the material cannot be used due to the eddy current loss can be expressed as

$$f_c \propto \frac{\rho}{\mu_r}, \tag{1}$$

where ρ and μ_r are the resistivity and permeability, respectively. μ_r of the composites does not dramatically change with f as shown later, but ρ dramatically

changes with f, i.e. ρ increases by several orders of magnitude, such as by 10^4 times at 10^6Hz when f <0.5 (Fig.2(b)). Thus, the critical operating frequency f_c of the composites with f <0.5 can extend from the frequency limit of about 1kHz for pure Terfenol-D to high frequency range such as > 10^5Hz.

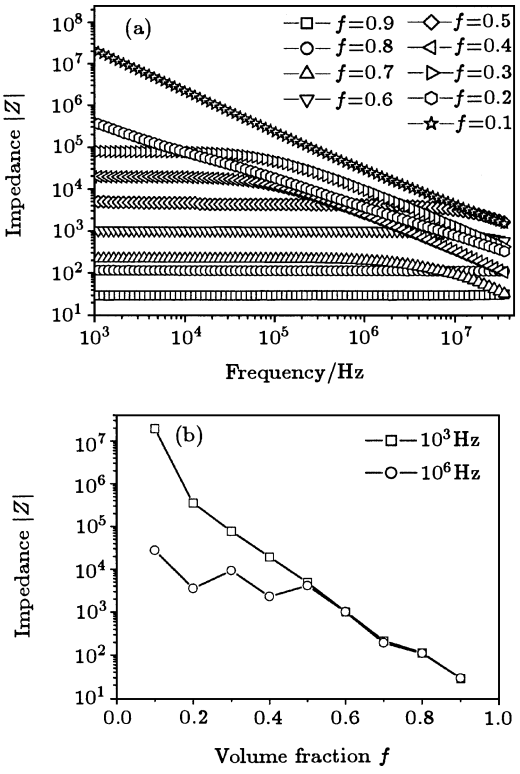


Fig.2. Dependence of impedance of the composites on (a) frequency and (b) volume fraction f of Terfenol-D.

Figure 3 shows the M–H hysteresis loops and the initial magnetization curves measured for the Terfenol-D/PVDF composites. The loops are symmetrical and display small coercivity and remanence. Similarly to Obrado *et al*'s description, [13] the magnetic moment shown in Fig.3 can be supposed to be composed of irreversible and reversible contributions, i.e.

$$M = M_{\rm rev} + M_{\rm irr}. \tag{2}$$

Only the irreversible term contributes to the hysteresis. The reversible contribution can be assumed to be linear with the magnetic field, i.e.

$$M_{\rm rev} = \chi H, \tag{3}$$

where χ is the magnetic susceptibility. From the linear fitting between $M_{\rm rev}$ and H,[13] the χ values for the Terfenol-D/PVDF composites can be obtained, as shown in Fig.4(a). Also shown in Fig.4(a) is the saturation magnetization M_s. The magnetic susceptibility and saturation magnetization of the composites increase linearly with increasing volume fraction of Terfenol-D.

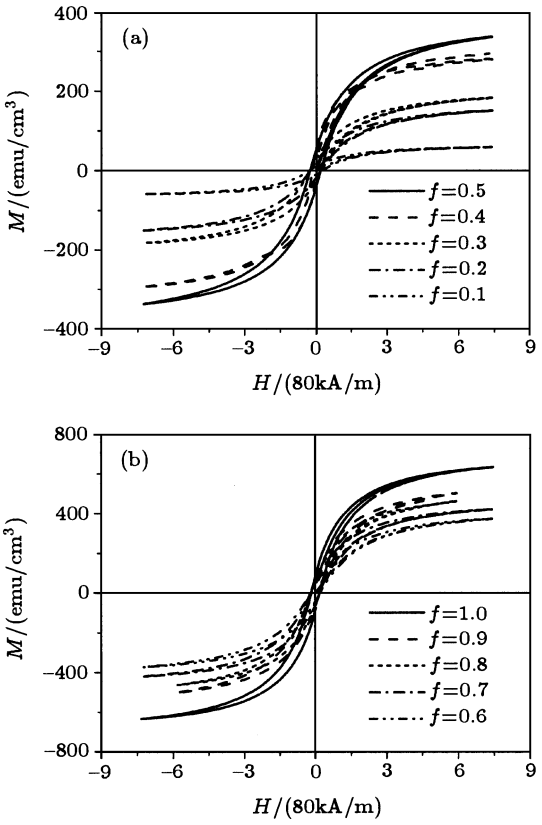


Fig.3. Magnetic hysteresis loops of the Terfenol-D/PVDF composites with various fraction f of the Terfenol-D. For clear illustration, the data are plotted as two diagrams (a) and (b). The data for f=1 were obtained by measuring Terfenol-D powder.

From the initial magnetization slopes in Fig.4(a), the initial permeability of the Terfenol-D/PVDF composites are obtained, and shown in Fig.4(b). The initial permeability μ_i of the composites also increases approximately linearly with increasing the volume fraction of Terfenol-D. Actually, this dependence of μ_i on f can be described by using simple effective-medium theory for random composites,[14] i.e.

$$(1-f)\frac{1-\mu_i}{1+2\mu_i} + f\frac{\mu_T-\mu_i}{\mu_T+2\mu_i} = 0, \tag{4}$$

where μ_T is the initial permeability of the Terfenol-D.[1] As shown in Fig.4(b), the calculations by this simple effective-medium equation are in reasonably good agreement with the measured initial permeability of the composites.

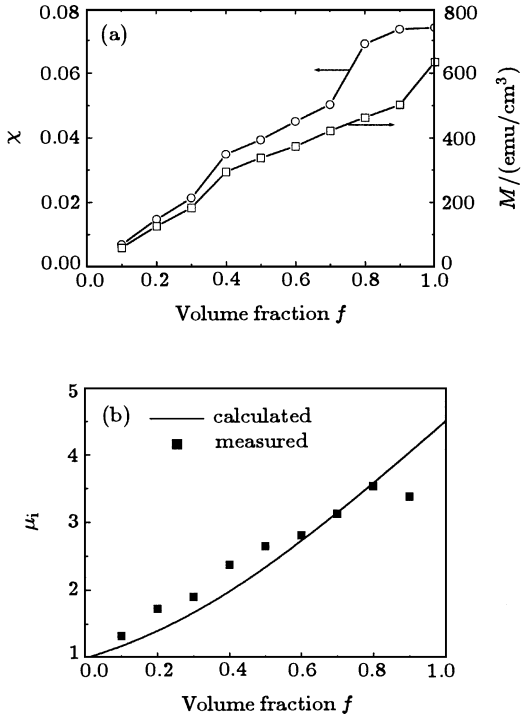


Fig.4. (a) The magnetic susceptibility χ and saturation magnetization M_s, (b) initial permeability of the Terfenol-D/PVDF composites as a function of the volume fraction f of the Terfenol-D particles. For comparison, the calculated initial permeability by the effective-medium equation is also shown in (b).

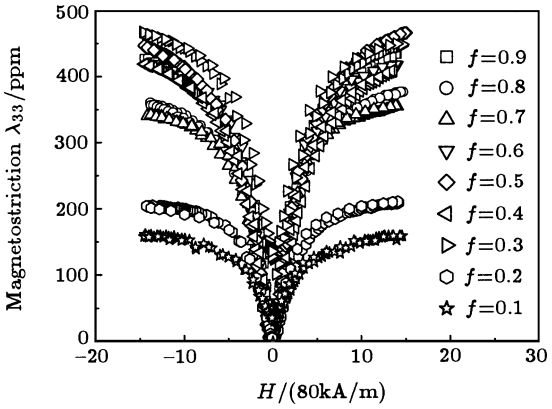


Fig.5. Longitudinal magnetostriction vs applied field for the Terfenol-D/PVDF composites.

Figure 5 shows the longitudinal magnetostriction λ_{33} (along the direction of the magnetic field) of the Terfenol-D/PVDF composites. As expected, with increasing applied field, the magnetostriction increases sharply in the low field range of $< 4 \times 10^5$A/m. In the high magnetic field range of $> 4 \times 10^5$A/m, λ_{33} goes up steadily to approach its saturation, especially for f <0.2. The longitudinal maximum magnetostriction value of the composites is about 470ppm at 12×10^5A/m. Due to the dilution effect of the nonmagnetic phase PVDF, the magnetostriction of the composites is smaller than that of bulk Terfenol-D.

The effective magnetostriction of the composites is strongly dependent on the volume fraction f of the Terfenol-D particles in the composites (Fig.5). For further illustration, Fig.6 shows the magnetostriction measured at 12×10^5A/m for these composites. Also shown in Fig.6 is the saturation magnetostriction calculated by using the recent effective-medium approach based on the Green function technique,[15,16] i.e.

$$\lambda_s = \frac{1 - G_1/G}{1 - G_1/G_2} \frac{2\lambda_{100} + 3\lambda_{111}}{5}, \qquad (5)$$

where G_1, G_2, and G are the shear moduli of the PVDF, Terfenol-D and the composites, respectively; λ_{111} and λ_{100} are single-crystal magnetostriction constants of the Terfenol-D. The values of these properties of the two phases used for calculations have been given previously.[11] The calculated magnetostriction of the composites monotonically increases with increasing f. With increasing volume fraction f of Terfenol-D, the measured magnetostriction increases in the range of f <0.5, as expected. However, at high concentration of Terfenol-D, e.g. as $f > 0.5$, the measured magnetostriction values are lower than the calculated, and this discrepancy becomes larger with increasing f. The large discrepancy between the measured and calculated magnetostriction is attributed mainly to porosity and weak Terfenol-D particle–particle interface contact with slipping boundary due to lack of the PVDF binder between directly contacted bare particles. As the volume fraction of Terfenol-D is low, e.g. $f < 0.5$, the high concentration of PVDF ensures good quality of the composites with very low porosity with most Terfenol-D particles bound by the PVDF matrix. In this case the Terfenol-D content dominates the effective magnetostriction of the composites. As a result, the effective magnetostriction increases with the increase in f. On the other hand, with further increasing f, the content of the Terfenol-D particle–particle direct contact without binder between them and porosity increase, which have a negative effect on the magnetostriction, thus leading to far smaller measured magnetostriction than expected. The performance of the composites remains to be further improved by optimization of the composite processing techniques.

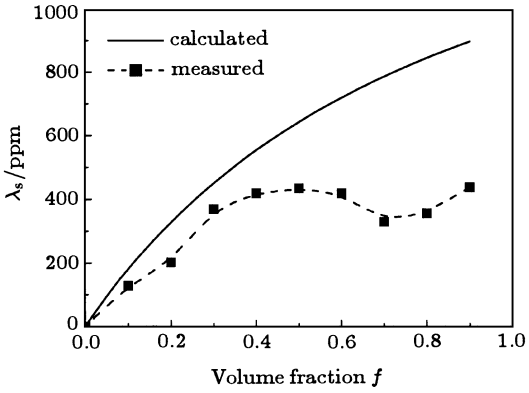


Fig.6. Dependence of the effective magnetostriction measured at 12×10^5A/m and calculated on the volume fraction f of Terfenol-D.

4. Conclusions

The Terfenol-D/PVDF particulate composites have been prepared via a very simple procedure. The micrograph of the composites shows that the Terfenol-D particles are well dispersed in the PVDF matrix. With increasing concentration of Terfenol-D, the magnetic susceptibility and saturation magnetization of the composites increases linearly, and also the initial permeability of the composites increases as described by the simple effective-medium theory. The dependence of the effective magnetostriction on applied bias for the composites is similar to that for bulk Terfenol-D, but the effective magnetostriction strongly depends on the volume fraction of Terfenol-D. The large discrepancy between the measured and calculated magnetostriction at high concentration is attributed mainly to porosity and weak Terfenol-D particle–particle interface contact with slipping boundary. The ferroelectric and magnetoelectric behaviour of the biferroic composites remains to be explored.

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