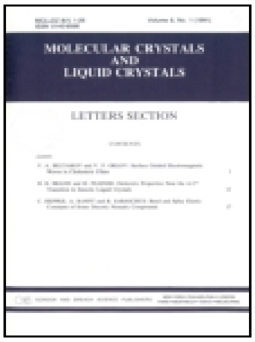

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Magnetoelectricity in polyurethanes nanocomposites

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ABSTRACT
Magnetoelectric (ME) effect, triggered much interests because of its potential of the cross correlation between the electric and magnetic properties of matter for technical applications such as magnetic field sensors, transducers, actuators. Magnetoelectric (ME) effect represents the coupling between a change in electric polarization in a solid when a magnetic field is applied. This study reports on the magnetoelectric (ME) effect observed in nanocomposite polymer consisting of polyurethane (PU) filled with 2.5wt% and 5wt% of Fe3C magnetic nanoparticles. In general, the electric response to an applied magnetic field (H) on polymer composites filled by magnetic particles is not well known. That is the reason why our study aims to show the influence of the magnetic fillers (Fe3C) in PU matrix. Our experimental findings are discussed for different situations.

KEYWORDS
Magnetoelectric effect; nanocomposite polymer; magnetic nanoparticles; magnetic field; piezomagnetic

Introduction

The ME effect is defined as the dielectric polarization induced by an applied magnetic field or an induced magnetization in an external electric field [1] (Nan et al., 2008). Here, ME effect represents the coupling between an applied magnetic field and a change in electric polarization in a solid. Intensive research have been devoted to the ME effect during the last decade because of the interesting transduction properties the magnetoelectric materials may present. The first observation of the ME effect [2] (Fiebig et al., 2004) triggered a lot of excitement because of the obvious potential of the crosscorrelation between the magnetic and electric properties of matter for technical applications [3] (Spaldin and Fiebig, 2005).

It is also interesting to note that – to the best of our knowledge – only few studies about ME effect in monolayered two-phase particulate polymer composites have been published (Nan, Li, and Huang, 2001; Nan, Li, Feng, et al., 2001)[4–6]. On a general manner, the electric response to an applied magnetic field (H) on a magnetic particles/non piezoelectric polymer composites is not well known. That is the reason why in this paper, a studies concerning the influence of magnetic fillers (Fe3C) in PU matrix was realized. Our materials are based on a simple mixture of the inorganic filler with a polyurethane matrix.

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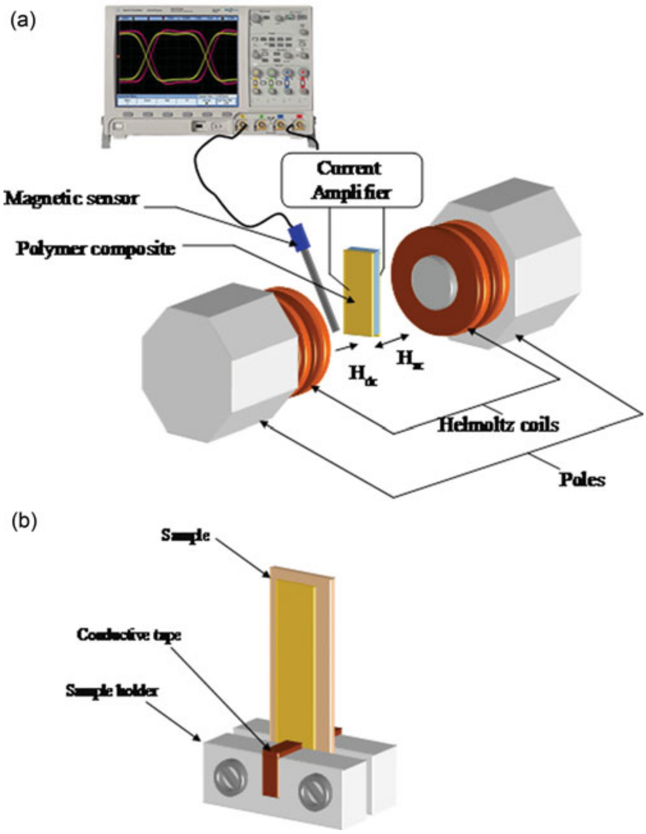

Figure 1. (a) Magnetoelectric test bench (b) Sample holder.

ME effect has been defined using the Gibbs free energy [7–8] (Kumar, et al., 1999). Kumar et al. (Kumar, et al., 1999) [8] show that the basic equation of ME can be express as

$$P_i = \alpha_{ij} H_i + \frac{1}{2} \beta_{ijk} H_j H_k \tag{1}$$

where P is the polarization developed at the electrodes of the sample, H is the external ac magnetic field amplitude and α_{ij} is the linear ME coefficient and β_{ijk} is the quadratic ME coefficient.

The more pertinent parameter to quantify the ME effect and thus to compare the ability of ME compounds is the *linear* ME voltage coefficient $\alpha_E = dE/dH$ with E is the induced electric field or linear ME polarization coefficient $\alpha_P = dP/dH$. It may be noted that α_E and α_P coefficients are related to each other by $\alpha_P = \varepsilon_r \varepsilon_0 \alpha_E$ where ε_r and ε_0 are the relative permittivity of the material and free-space permittivity, respectively [9–10] (Guyomar et al., 2008).

Experimental procedure

The test bench for measuring the direct magnetoelectric effect is shown schematically, in Figure 1(a). This consisted of an electromagnet providing DC magnetic bias field in a 0 - 1000 Oe range and a pair of Helmholtz coils powered by a linear power amplifier (ING stage linear STA-700), providing AC magnetic field in a 0–10 Oe range. Data was monitoring with an oscilloscope (Agilent DSO 7034A). The Helmholtz coil pair field output was calibrated

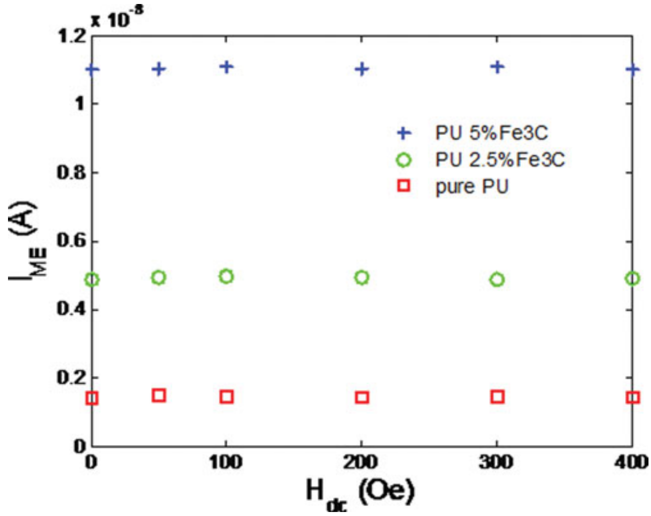

Figure 2. ME current function of H_{dc} for $H_{ac} = 1$Oe at 1kHz.

both in AC and DC mode, by direct measurement by a Linear Output Hall Effect Transducer probe (Gauss/Teslameter, F.W. Bell Model 5080).

The electromagnet poles and the coils were arranged so that the AC and DC magnetic fields were in the same axis. The composite under test was mounted in a holder as shown in Figure 1(b), and was positioned centrally between the DC electromagnet poles on the Helmholtz coils axis. The magnetoelectric sample was exposed to DC magnetic bias field strengths in a 0–400 Oe range and the superimposed AC magnetic field was varied between 1 and 3 Oe rms.

According to recent publications about ME materials, the ME voltage coefficient may be determined using two distinct methods. The first one consists in the measurement of the output electric charge Q_{ME} with a charge amplifier in short-circuit condition [11] (Cai et al., 2003) and the ME voltage V_{ME} is obtained using $V_{ME} = Q_{ME}/C$ where C is the static capacitance of the ME sample. The second method consists of directly measuring the output voltage V_{OC} generated between the electrodes of the material under an open circuit condition using a differential amplifier [12] (Lin et al., 2005). However, a perfect open circuit may be difficult to realize; in fact it is strongly dependent upon the impedance of the sample. In our case, these are quite high values (~200 MΩ), so it implies to connect in series with the sample a very high impedance component - generally an operational amplifier with a very high input resistance- leading to severe disturbances in the direct ME voltage measurement. Besides, ME effect induced by a magnetic field yields by definition electric charge generation, so ME films may be considered as current generator and current amplifier is well suitable to measure this direct effect [13] (Belouadah et al., 2011). For these reasons, it was chosen to acquire the total output current *i* under short-circuit condition using a current amplifier (Keithley 617).

Results and discussion

Figure 2 shows the amplitude of the magnetoelectric current I_{ME} at 1kHz for Hac = 1 Oe and 1 kHz as a function of bias magnetic field (H_{dc}) for the different composition. Using equation (1) and data of the literature, the data should be found an optimal value H_{dc} bias magnetic field yielding an optimal piezomagnetic coefficient and consequently a peak of I_{ME} value [14] (Jiles

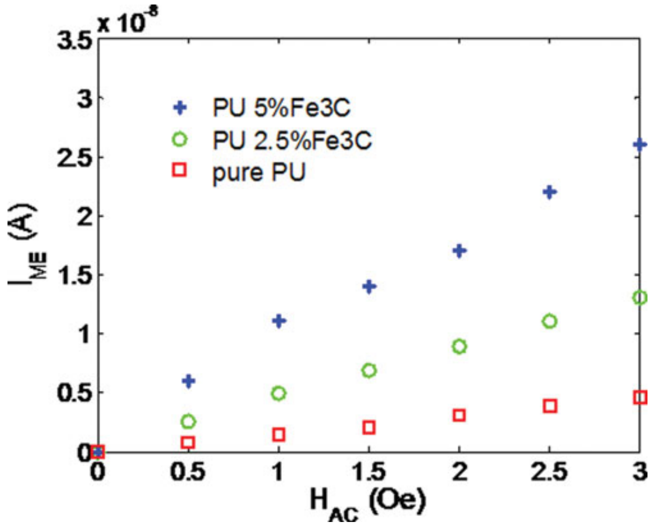

Figure 3. Magnetoelectric current function of dynamic magnetic field at 1kHz.

et al., 1988), it can be clearly observed that with increasing the bias magnetic field, I_{ME} remains roughly constant (Fig. 2). This strongly suggests that the magnetic properties of the material do not influence the magnetoelectric effect. In fact, ME coupling does not originate from magnetostriction but rather linear elastic interaction between the particles aggregates and/or agglomerates and the highly polar microdomains of semi-crystalline polymer PU [15–17] (Li et al., 1992)(Guiffard et al., 2006)(Guyomar et al., 2009). This results show that the quadratic ME coefficient β can be neglected for the different composite.

Figure 3 shows the variation of the output current magnitude I_{ME} delivered at the electrodes of the two types of nanocomposite film PU filled with 2 wt%, 5 wt% Fe3C magnetic particles and the pure PU sample, as a function of the ac magnetic bias field (H_{ac}) at 1kHz. It can be clearly seen that both 2%C Fe3C and 5%Fe3C exhibit higher current amplitudes than the pure – unfilled- PU film in the whole H_{ac} range.

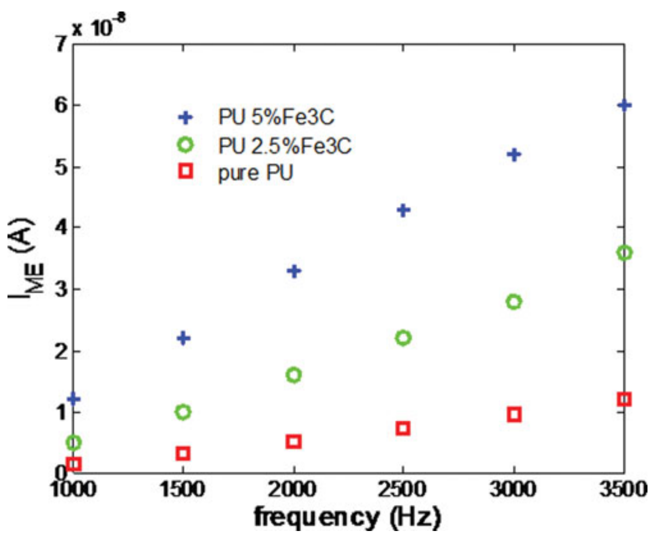

Figure 4. Magnetoelectric current I_{ME} versus frequency for $H_{ac} = 1Oe$.

Table 1. Magnetoelectric coefficient values of pure and filled films at 1kHz.

Type	α_P (C/(m².Oe))	ε_r at 1kHz	α_E (V/(m.Oe))
Pure PU	$0.8.10^{-9}$	4.8	18
PU 2.5%Fe3C	$6.9.10^{-9}$	6.6	118
PU 5%Fe3C	14.10^{-9}	6.7	240

Figure 4 represents the ME current versus current for a constant $H_{ac} = 1$ Oe, the data shows that the current amplitude roughly exhibits a linear variation as a function of the frequency, in the absence of DC bias field. It is possible to demonstrate this theoretical dependence of the current versus frequency using equ. 1 and equ. 2.

$$I_{ME} = A\frac{\partial P_i}{\partial t} = A\left[\alpha_{ij}\frac{\partial H_i}{\partial t} + \frac{1}{2}\beta_{ijk}\frac{\partial H_j H_k}{\partial t}\right] \tag{2}$$

where A is the electrodes surface of the sample.

Sample has been exited by sinusoidal wave form (H_{ac}) and $\beta = 0$ equ. 2 become:

$$I_{ME} \approx A.\alpha_P\omega.H_{ac} \tag{3}$$

With ω the pulsation of the magnetic excitation.

Table 1 gives the values of magnetoelectric coefficient for the different materials. It is clearly observed that the pure PU have a lower ME coefficient than filled polymer (2,5 wt%, 5wt% of Fe3C) with an enhancement of the coupling by 5.7 in case of PU 5wt%Fe3C. Moreover the magnitude of ME coefficient is independent of the applied dc bias magnetic field and is a linear in function of the ac alternative field or applied frequency.

Recently, different studies have been dedicated ME properties [1] (Nan et al., 2008). Compared with Guzdek et al. [18] (Guzdek et al., 2012) and Bi et al. [19] (Bi et al., 2011), this study proposes a new easier method for manufacturing high-performance sensors using simple polymer matrix PU and magnetic particules (Fe3C), which improves upon the ability to achieve affordably scaling-up fabrication. More importantly, the results show the possibility of create ME coupling with monolayered particulate composite—with nonpiezoelectric but partly polar PU matrix—which is different than classical approach[1] (Nan et al., 2008). Moreover the ME coupling obtain in this study are the same order than classical data, with $\alpha_E = 30$ mV/(cm.Oe)). All the results show the potential of the proposed concept for real-world engineering applications.

Conclusion

In this paper, ME effect has been studied in PU-based nanocomposites filled with Fe3C nanoparticles. It is clearly observed that the pure PU shows lower current values than filled polymer which allows to conclude that the monolayered PU 2.5wt%Fe3C and PU 5wt%Fe3C composites show a ME effect. The magnitude of magnetoelectric current is independent of the applied dc bias magnetic field and is a linear in function of the ac alternative field or applied frequency. Voltage ME coefficients are of the same order of magnitude than those of Cr_2O_3 single crystals. Besides, the studied nanocomposites present multiple interesting characteristics: they are very simple to prepare, flexible.

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