

High Magnetoelectric Coupling of Metglas and P(VDF-TrFE) Laminates

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Abstract

Magnetolectric (magnetic/piezoelectric) heterostructures bring new functionalities to develop novel transducer devices such as (wireless) sensors or energy harvesters and thus have been attracting research interest in the last years. We have studied the magnetolectric coupling between Metglas films (2826MB) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) in a laminate structure. The metallic Metglas film itself served as bottom electrode and as top electrode we used an electrically conductive polymer, poly(3,4-ethylene-dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS). Besides a direct electrical wiring via a graphite ink, a novel contactless readout method is presented using a capacitive coupling between the PEDOT: PSS layer and an electrode not in contact with the PEDOT:PSS layer. From the experimental result we determined a magnetolectric coupling of $1445 \text{ V}/(\text{cm}\times\text{Oe})$ at the magnetoelastic resonance of the structure, which is among the highest reported values for laminate structures of a magnetostrictive and a piezoelectric polymer layer. With the noncontact readout method, a magnetolectric coupling of about $950 \text{ V}/(\text{cm}\times\text{Oe})$ could be achieved, which surpasses previously reported values for the case of direct sample contacting. 2D laser Doppler vibrometer measurements in combination with FE simulations were applied to reveal the complex vibration pattern resulting in the strong resonant response.

Introduction

The magnetolectric coefficient of a composite/laminate structure is the ratio between the response electric field and the applied magnetic excitation field [1]. For a laminate structure, the magnetolectric coupling mechanism is mediated via the strain induced in the magnetostrictive material by an external magnetic field, which translates into the piezoelectric layer at the laminate interface and is converted to an electric field due to the inverse piezoelectric effect [2]. With electrodes applied to the piezoelectric layer, the electric field can be measured as a voltage between the electrodes.

Among the magnetostrictive materials that can be used, Metglas is very high performing. It is an amorphous iron-nickel based material with good dynamic magnetic properties and high magnetoelastic coupling [2, 3] and has been successfully combined with the piezoelectric polymer PVDF or its copolymer P(VDF-TrFE) as laminate [3, 4]. Previous studies on these or related materials show a maximum magnetolectric coupling coefficient of $7 \text{ V}/(\text{cm}\cdot\text{Oe})$ in the non-resonant mode and $370 \text{ V}/(\text{cm}\cdot\text{Oe})$ in a resonant mode [4]. Other magnetolectric coupling on composite structures has been performed earlier on different material combinations [5–7].

In a magnetostrictive film it is possible to obtain a magnetoelastic resonance where an elastic standing wave is built up in the film [2, 3, 8, 9]. The resonance frequency is dependent on elastic modulus, shape and dimension of the film as wells as on the clamping conditions.

In this study, we use a Metglas 2826MB film as the magnetoelastic layer in combination with screen-printed P(VDF-TrFE) on top as piezoelectric. We measured the magnetic coupling coefficient both in non-

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resonant and resonant mode with physical contact to the laminate sample as well in a non-contact capacitive mode that has previously been used in other piezoelectric sensor applications [10]. The film of length 20 mm was clamped in the middle of the film. 2D scanning laser Doppler vibrometer measurements were applied to obtain the full vibration pattern. Measurements were also compared with FEM simulations. To the best of our knowledge, the obtained magnetoelastic coupling coefficients at magnetoelastic resonance are the highest reported so far.

Experimental And Methods

The Metglas 2826MB films (with chemical structure $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$) were purchased from Metglas Incorporated with a ca. 30 μm thickness. The films were further etch-processed to a structure consisting of two areas/parts: the measuring part of 20 mm length and 5 mm width and the clamping part, which are connected via a narrow bridge section (Fig. 1). The piezoelectric layers were manufactured by depositing a layer of P(VDF-TrFE) on the measuring part of the Metglas structure by means of screen printing. Piezotech FC 20 (purchased from Piezotech Arkema) was used as the piezoelectric ink in the screen printing process, which has a VDF/TrFE molar ratio of 80/20 mol%. The whole area of the Metglas film was deposited with P(VDF-TrFE). On top of the P(VDF-TrFE) layer PEDOT:PSS (Clevios™ S V3) was deposited, leaving about 1 mm margins with respect to the P(VDF-TrFE) edges. The PEDOT:PSS layer made up the top electrode, whereas the conductive Metglas itself formed the bottom electrode. A thin Au wire was connected to the PEDOT:PSS layer with a graphite ink. After the P(VDF-TrFE) and PEDOT:PSS/graphite deposition, the piezoelectric layer was electrically poled by applying a high voltage between the two electrodes. The thickness of the P(VDF-TrFE) laminate was measured by a calliper with micrometre resolution and the reading agreed well with the value obtained from the polarization curve when comparing the coercive field strength of P(VDF-TrFE) with the corresponding voltage in the poling process [11]. The P(VDF-TrFE) thickness was determined to be 4 μm . The Metglas/P(VDF-TrFE)/PEDOT:PSS laminate structure was fixed to the sample holder (a PMMA structure) with the clamping part and aligned laterally so that the symmetry axis of the Metglas film, corresponding to the node of the first magnetoelastic resonance mode, was in the centre. A photo with associated schematic picture of the sample setup is presented in Fig. 1.

In order to magnetically excite and measure the dynamic magnetic response from the laminate structure, we used a magnetic AC susceptibility (ACS) measurement system built in our lab specially designed for magnetic films. It is based on two 2D in-plane coils for magnetic field excitation (the AC magnetic field) and detection, where the detection coil is rotated by 90 degrees with respect to the excitation coil to cancel excitation field and thus only measures the response from the magnetic film. We placed a magnet sheet beneath the excitation and detection coils that field biased the Metglas film (applying the DC magnetic field). The bias magnet was tuned to give an optimum magnetic response from the Metglas film with the length (20 mm) that we are using in this study. The static bias field at the Metglas film was 0.68 mT. The DC magnetic field pointed in the same direction as the AC magnetic field. We also used dedicated electronics that excited the excitation coils and collected the induced voltage, which is

dependent on the amplitude and phase of the AC susceptibility of the sample, from the detection coil. The whole measurement setup is software controlled. The DC and AC fields at the sample position were measured with calibrated commercial magnetic sensors (Lakeshore F71 Teslameter).

During the measurements we measure and control the current that enters the excitation coil. For the used current settings in the experiment, we have an AC magnetic field amplitude of 0.0035 mT (0.035 Oe) at the sample position.

The clamping part of the Metglas film and the thin Au-wire form the two electrodes to the P(VDF-TrFE) layer (Fig. 1, schematic). Both electrodes were connected differentially to a high impedance amplifier (Stanford Research Systems, model SR560, input impedance 100 MΩ) and from the amplifier output to the data collection device (Agilent Infinium 1 Gs/s oscilloscope), using the excitation current as a reference signal. From the measured piezoelectric voltage we determined both the amplitude and the phase relative to the applied magnetic field. The magnetoelectric coupling, α_{ME} is calculated according to [2, 5, 7]

$$\alpha_{ME} = \frac{dE}{dH} = \frac{V_{piezo}}{tH_{ac}} \quad (1)$$

where E is the electric field in the P(VDF-TrFE) layer, V_{piezo} is the measured piezoelectric voltage, t is the thickness of the P(VDF-TrFE) layer and H, H_{ac} is the magnetic AC field and magnetic field amplitude, respectively, applied to the sample. The measured capacitance of the P(VDF-TrFE) layer, $C = 970$ pF, together with the amplifier input impedance, $R = 100$ MΩ, gives a piezoelectric cut-off frequency at 100 kHz of $1 / (2\pi RC) \approx 1.5$ Hz. This is well below the excitation frequencies, meaning that we measure the maximum piezoelectric signal, V_{piezo} , without any phase changes of the piezoelectric signal.

We also used laser Doppler vibrometry (LDV) measurements (Polytec OFV-056) during excitation of the Metglas/P(VDF-TrFE) laminate structure in order to study any bending modes of the film. Since the laser beam was oriented perpendicular to the surface of the Metglas/P(VDF-TrFE) film, we only measured the vibrations normal to the film surface.

Results And Discussion

In Fig. 2 the magnetic signal and piezoelectric voltage are shown versus the excitation frequency when connecting the electrodes directly to the Metglas/P(VDF-TrFE) laminate.

From Fig. 2 we can see the effect of the magnetoelastic resonance in the frequency range of 105 kHz and 120 kHz. The magnetoelastic resonance effect in magnetostrictive films and its applications have been studied and reported earlier [2, 3, 8, 9]. There is a large increase in the magnetic response at about 109 kHz where the magnetoelastic resonance is located, and it drops down to almost zero at 115 kHz where

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the antiresonance is located and then the magnetic response signal increase again with increasing frequencies. At the magnetoelastic peak resonance frequency of 109 kHz we have the first mode of an elastic standing wave with a node in the middle of the film. This mode gives maximum lateral displacements at the ends of the film as well as the largest magnetic response. At the resonance peak frequency, lateral strain amplitudes in the laminate structure are at maximum, which translates into the P(VDF-TrFE) layer and results in a maximum voltage amplitude from the piezoelectric layer, as we can see in Fig. 2. From the maximum piezoelectric voltage we can determine the magnetoelectric coupling coefficient at resonance using Eq. 1. The non-resonant magnetoelectric coupling can also be determined by using the piezoelectric voltage outside the resonance range in the range of 90 kHz, since the Metglas material have magnetostrictive properties even when the film is not in resonance. We also measured on a P(VDF-TrFE) layer that was unpoled (non-piezoelectric active) and obtained piezoelectric voltages in the range of 1.5 mV peak-to-peak voltage which is the background signal due to induced voltages in electrodes and cables close to the detection zone. The background signal was subtracted from the measured piezoelectric response. From this result we obtain a measured magnetoelectric coupling at resonance of the structure of about 1445 V/(cm·Oe) and about 100 V/(cm·Oe) at non-resonance (90 kHz). The coupling value at resonance is more than 4 times higher than previously reported values for magnetostrictive and PVDF layers in a laminate structure [2, 4]. Further, from Fig. 2 the piezoelectric voltage peak (the elastic part) is somewhat broader than the magnetoelastic resonance response peak. This is probably due to mechanical losses in the P(VDF-TrFE) and PEDOT:PSS layer. The measured phase for the magnetic response (relative to the applied magnetic field) is about 165 degrees, which is in good agreement with the theoretical phase shift of 170 degrees that returns to zero phase above the resonance. The phase of the piezoelectric response (the elastic part) changes also its phase at the resonance by about 180 degrees, according to theory [12, 13]. This shows that the piezoelectric voltage below and above the resonance is not only a background signal but instead also originates from the magnetoelectric coupling.

The result and measurement setup when using the non-contact capacitive coupling electrode above the PEDOT:PSS layer can be seen in Fig. 3.

In the experiment with non-contact measurements, we were careful that the Au-wire (that was connected to the graphite dot) did not touch the reading electrode above the PEDOT:PSS layer and not build up a close approach to the reading electrode. As can be seen in Fig. 3b even when we have a non-contact reading electrode above the PEDOT:PSS (not in physical contact with the sample), we have a piezoelectric peak voltage of about 28 mV (peak-to-peak). The peak of the piezoelectric voltage is somewhat broader in frequency than compared with the case of direct contacting the PEDOT layer (see Fig. 2), indicating a higher damping of the system. For the non-contact readout case we obtain a magnetoelectric coupling of about 950 V/(cm·Oe) at resonance, which is also higher than previously reported values using contact measurements of the sample.

As previously shown in the literature, the magnetoelectric coupling coefficient can be compensated for Loading [MathJax]/jax/output/CommonHTML/jax.js as film when excited with a magnetic field [2]. In this case the

internal AC magnetic field amplitude is calculated by considering the demagnetization field in the Metglas film and the determined magnetoelectric coupling coefficient will be an intrinsic value. When using data of measured magnetic properties of the used Metglas film [13] and demagnetization factors for thin magnetic films [14] together with the Metglas dimensions, we get a compensation of 0.23, which gives an intrinsic magnetoelectric coupling coefficient of 6200 V/(cm·Oe) at resonance for the measurements with physical contact to the laminate sample.

Through LDV (laser Doppler vibrometry) we examined the vibrations in the laminated sample when it is excited by an AC magnetic field at the magnetoelastic resonance frequency of 109 kHz (Fig. 4). We also swept the frequency over the resonance frequency and measured the LDV response. We used exactly the same set up as in the previous magnetic/piezoelectric measurements for applying AC field and DC bias. The measurements were performed with the PEDOT:PSS side facing the LDV. During excitation, the LDV measured 18090 points spread over a rectangular matrix on the laminate sample presented in Fig. 4a and measured 3810 points presented in Fig. 4b and Fig. 4c.

In Fig. 4a there are multiple small vertical displacement amplitudes between 0 and 8 nm (red is 0 and yellow is 8 nm) in a 2D lattice structure resulting from a complex bending mode in the film when the film is excited at the magnetoelastic resonance (109 kHz). Since the vertical displacements shown in Fig. 4a give both positive and negative vertical strains, the resulting piezoelectric voltage from these modes will be zero. The horizontal lateral strains originating from the magnetoelastic resonance cannot be visualized in this LDV analysis since the setup is only sensitive to vertical displacements. The vertical displacement pattern shows that the laminate sample does not bend during excitation, as the vertical displacement does not gradually increase from the middle of the film towards the outer free ends of the film.

The first magnetic resonance mode in the film when clamping the film in the middle is a lateral node in the middle with largest lateral displacements at the ends of the film. Instead, from Fig. 4a, we can see a small vertical displacement pattern in the laminate sample with maximum vertical displacement amplitudes of about 8 nm. This pattern can be due to higher order mechanical surface vibrational modes [15, 16]. Since we get a more or less zero vertical displacement without excitation, see Fig. 4c, it is not a surface roughness.

To get a better view of the longitudinal motion on the laminated sample, a wedge was placed below one side, giving the laminated sample a tilt angle of 2.3°. In Fig. 4b the vertical displacement pattern becomes clearer and the mode shapes on the surface from higher order surface modes is highly visible as green islands. FE simulations (using COMSOL Multiphysics®) at an excitation frequency equal to the measured magnetoelastic resonance frequency, as presented in Fig. 4d, verify that the magnetic longitudinal mode couples to a higher order of mechanical resonance frequency.

When we swept the frequency of the magnetic AC field we could see a vertical displacement amplitude (from frequency analysis of the LDV signal) and large magnetic response when we entered the resonance (from frequency analysis of the LDV signal) kHz), correlating to the frequency of the magnetic excitation

field where we have the piezoelectric response as seen in Fig. 2 and Fig. 3. Thus, no vertical displacements were measured when exciting the Metglas/P(VDF-TrFE) composite at frequencies below or above this resonance frequency range. It is also interesting that we can see the graphite dot even in the background signal from the LDV image, see Fig. 4c.

Conclusion

By magnetic and piezoelectric measurements we have obtained very high values of measured magnetoelectric coupling (1445 V/(cm·Oe) at resonance) between Metglas and P(VDF-TrFE) laminates when we use PEDOT:PSS (and graphite) as the top electrode. We believe that the PEDOT:PSS layer is more elastically compatible with the P(VDF-TrFE) laminate and enhances the strain in the P(VDF-TrFE) laminate as induced from the Metglas film, and thereby increases the magnetoelectric coupling. We have also shown that the measurements can be performed with a non-contact reading electrode by utilizing the capacitive coupling between the PEDOT:PSS layer and the reading electrode. By using laser Doppler vibrometry (LDV) measurements we have also observed a complex 2D vibration pattern of vertical displacements (at the resonance) related to higher order modes, which was confirmed both in literature as well by performed FE simulations using the actual film dimensions and properties of the laminate structure.

Declarations

Acknowledgments

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Figures

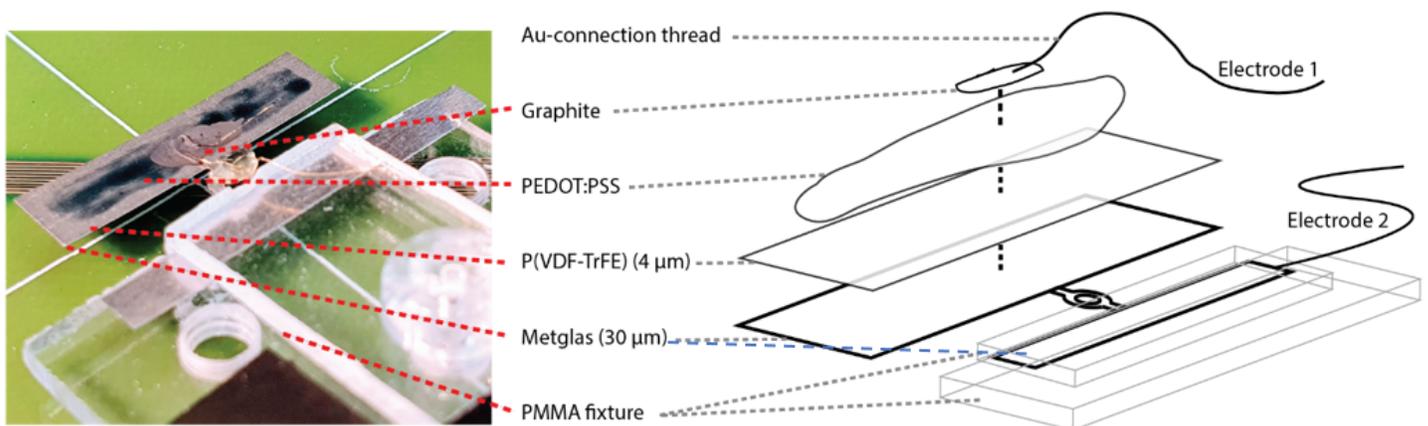


Figure 1

Sample setup showing the laminate structure comprised of Metglas film (magnetostrictive), P(VDF-TrFE) layer (piezoelectric) and PEDOT:PSS layer (conductive polymer) with a graphite dot to attach the thin Au wire (electrode 1). The second electrode (electrode 2) is connected to the metallic Metglas film that is clamped by the PMMA structure. For the non-contact measurements (capacitive coupling) an electrode was placed at various distances above the PEDOT:PSS layer, and electrode 2 was connected with contact to the clamped Metglas film to the electronics (see Figure 3).

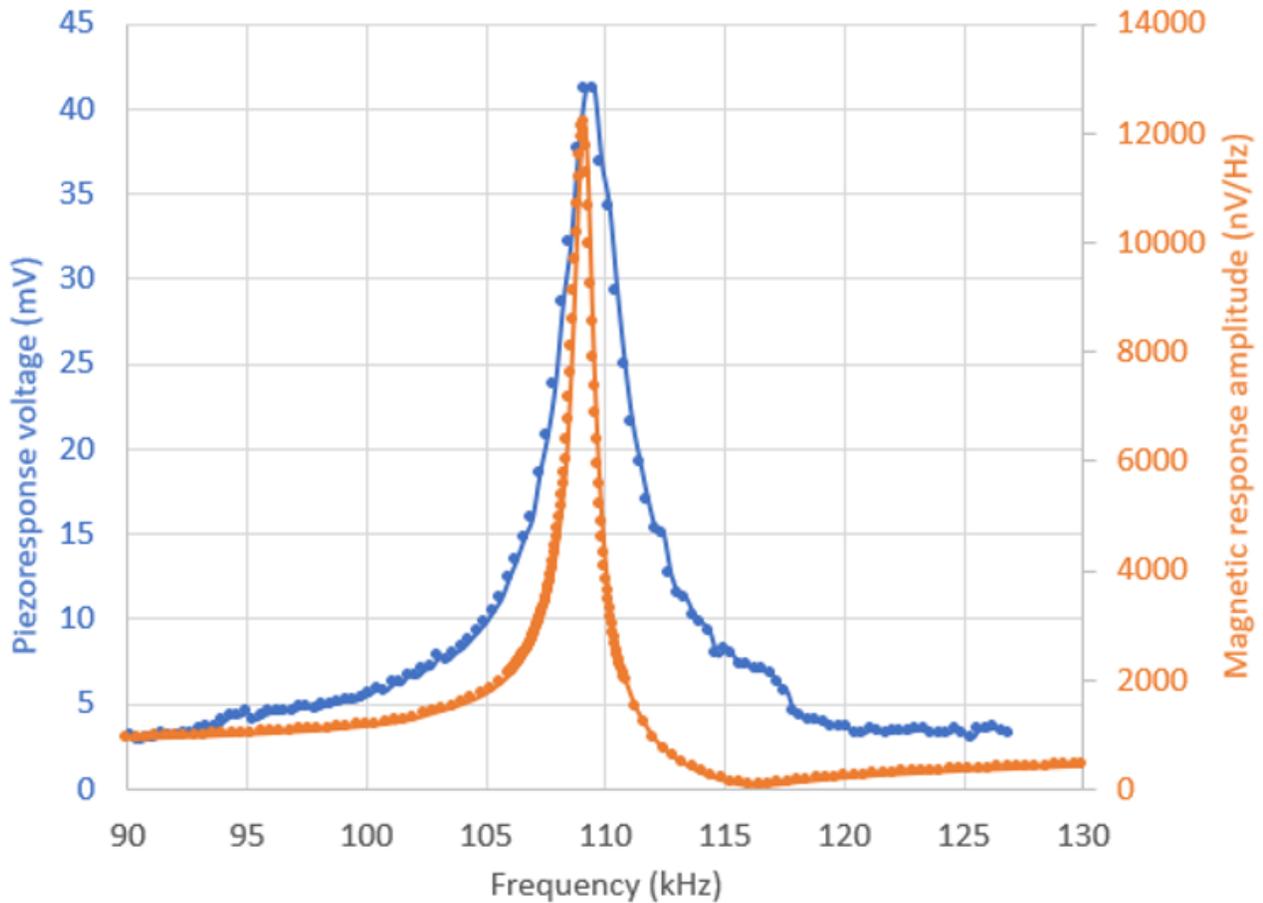
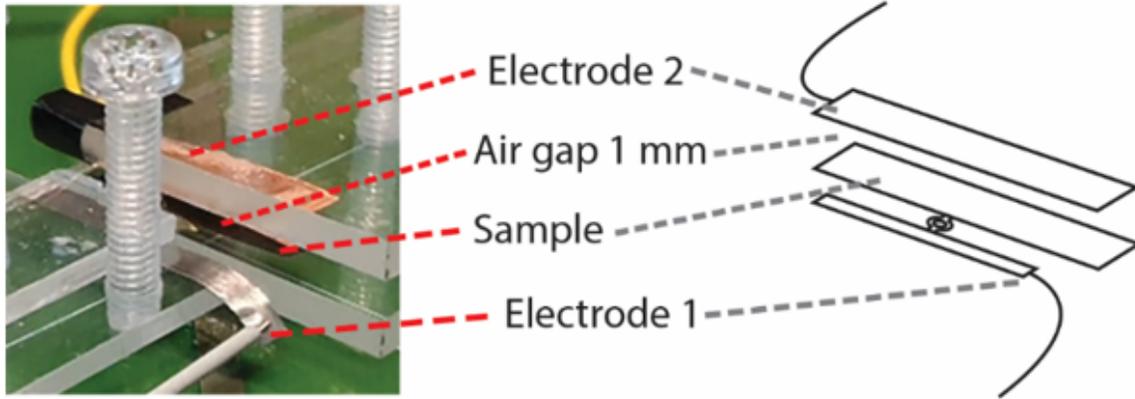


Figure 2

Piezoelectric peak-to-peak voltage (blue) and magnetic amplitude signal response (orange) versus frequency of the magnetic field excitation. Since we measure the magnetic response from the induction voltage from the detection coil, we normalize the magnetic signal with frequency in order to obtain the AC susceptibility magnitude. The contacts to the amplifier are physically connected to the sample (Metglas clamping and Au-wire).

3a)



3b)

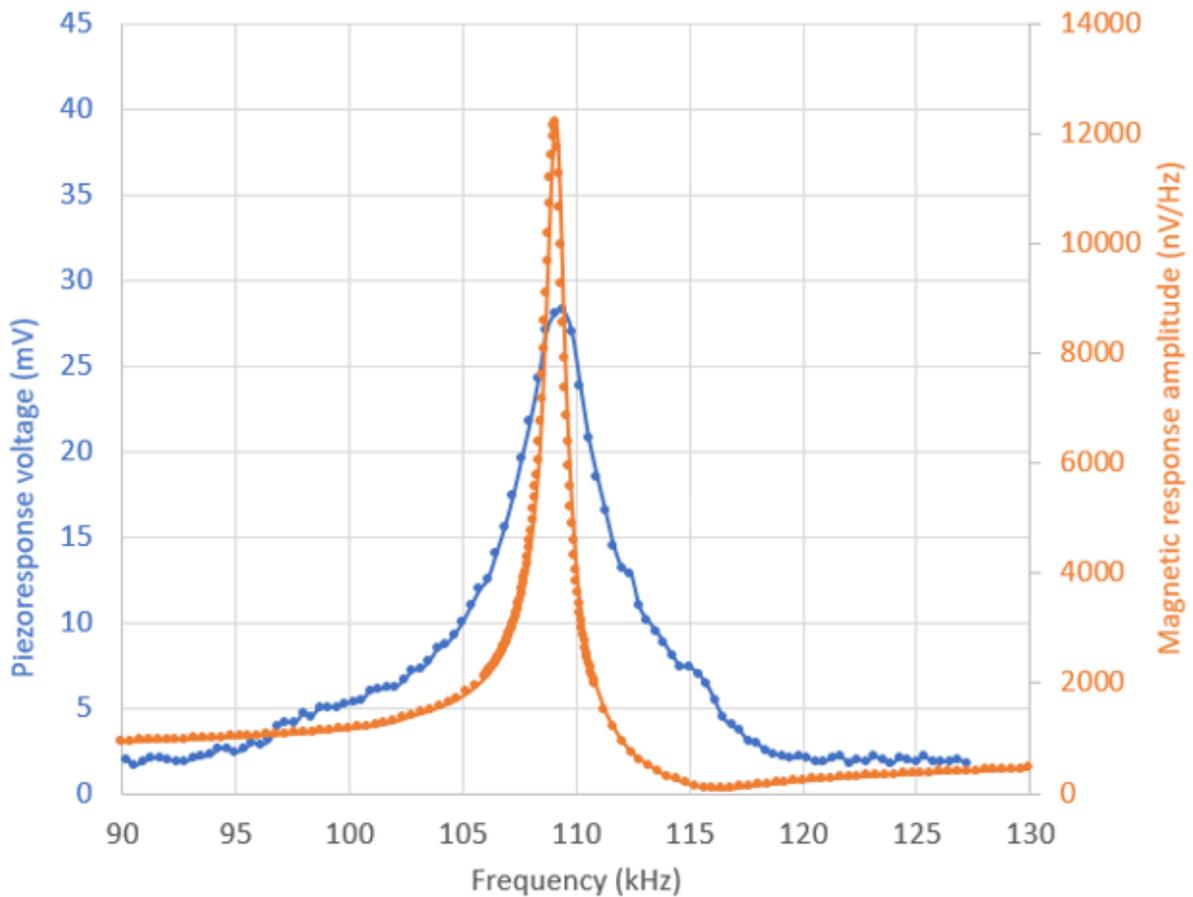
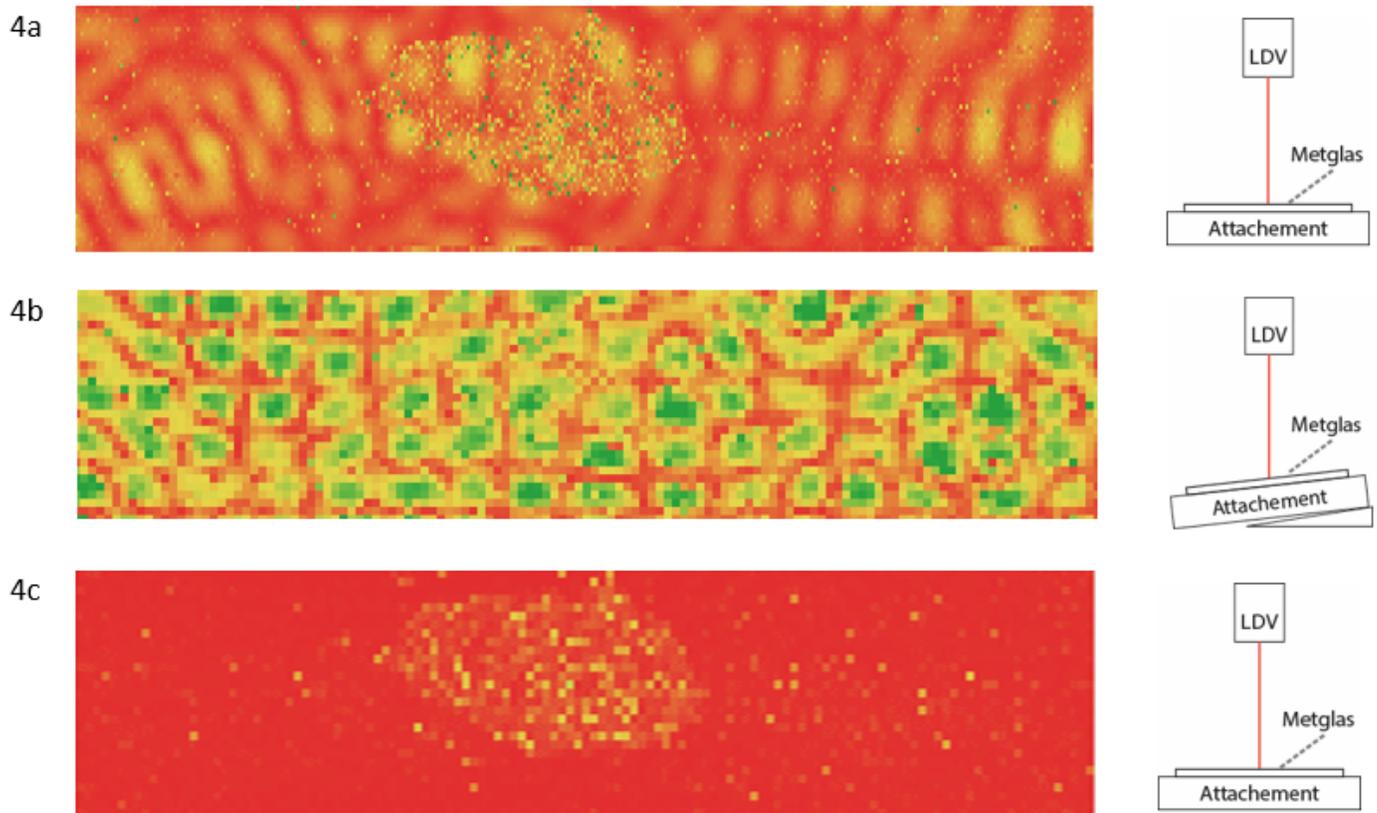


Figure 3

Non-contact measurement of the ME coupling. a) Sample with schematic showing the airgap between the sample and electrode 2. b) Piezoelectric peak-to-peak voltage (blue) and magnetic amplitude signal response (orange) versus frequency of the magnetic field excitation. The cables to the amplifier are connected to the clamped part of the Metglas film (electrode 1 in Figure 3a) and to the non-contact electrode (with an area equal to the PEDOT:PSS area), at a distance 1 mm above the PEDOT:PSS layer (utilizing the capacitive coupling between PEDOT:PSS and electrode).



Displacement colour bar for the three LDV measurements:

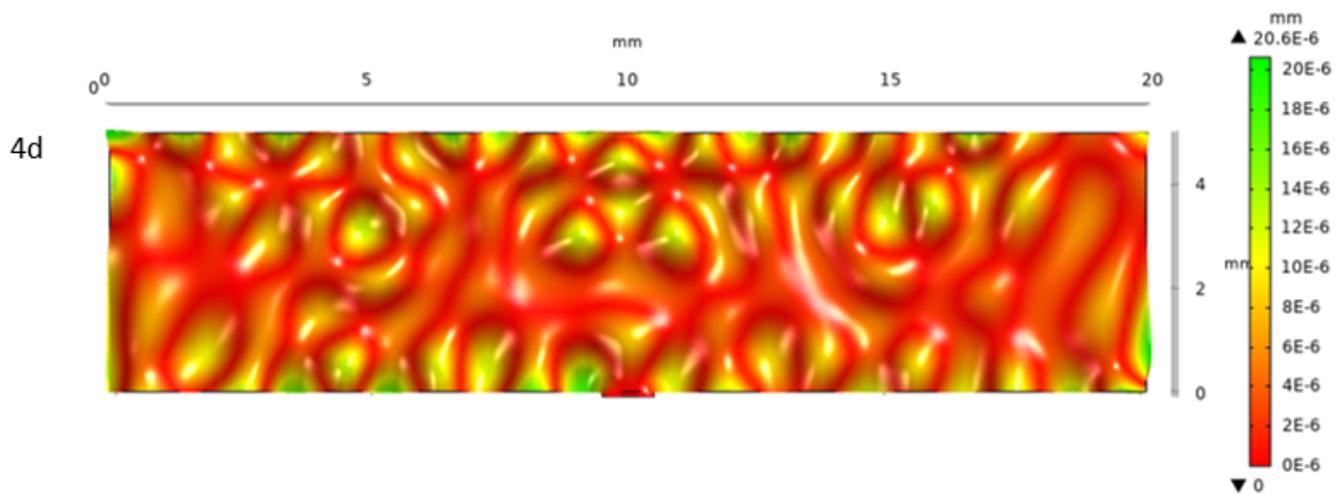


Figure 4

LDV measurements on vertical displacement on the laminate sample over the whole surface area top view followed by schematic side view. a) The vertical displacement at the P(VDF-TrFE)/PEDOT:PSS side when the laminate sample surface is excited perpendicular at the magnetoelastic resonance frequency (109 kHz). b) The vertical displacement at the P(VDF-TrFE)/PEDOT:PSS side when the laminate sample is excited at a tilted angle of 2.3° at the resonance frequency (109 kHz), to be able to get a clearer view of

the surface longitude movement. c) The background signal at the P(VDF-TrFE)/PEDOT:PSS side obtained with no excitation. d) Simulated vertical displacement amplitudes for Metglas with a layer of PVDF to verify the magnetic mode coupling to the mechanical mode and the pattern visible from LDV.