Supporting Information

Flexible composite films with enhanced piezoelectric properties for energy harvesting and wireless ultrasound-powered technology

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Section 1. *Structural characterization*

Table S1. Crystallinity degree and relative content of electroactive phases in NBT-BT/PVDF composite films before and after poling.

Sample	Crystallinity degree (%)	F_{EA} (%)	F(β) (%)	F(γ) (%)	F_{EA} (%) After poling	F(β) (%) After poling	F(γ) (%) After poling
NBT-BT/PVDF 30	49	63	0	63	69.4	27.4	42
NBT-BT/PVDF 35	49	53	17	36	62.4	23.7	38.6
NBT-BT/PVDF 40	50	53	13	40	55.5	25.5	30
NBT-BT/PVDF 50	47	42	42	0	54.9	33.9	21

Table S2. Results calculated by image analysis of the PVDF-BNBT composites for the arithmetic mean of all free-path spacing values, X_m, the standard deviation of the all free-path spacing values, *s*, and the homogeneity level, *D*.

Sample	X_m (μm)	*s* (μm)	*D* index
NBT-BT/PVDF 30	8.112	2.638	0.325
NBT-BT/PVDF 35	5.6891	1.5276	0.269
NBT-BT/PVDF 40	3.6067	0.5706	0.158
NBT-BT/PVDF 50	2.3172	0.3800	0.163

Section S2. *Measurement of piezoelectric resonance*

Complex impedance response of the samples in the frequency range of radial resonance (100-200 kHz) are shown in Fig.S1 a) for composite samples with different NBT-BT content, as specified on the graphs. Thickness resonance curves (impedance modulus and phase) for the sample with 50 vol.% content of ceramic filler are shown in Fig. S1 b).
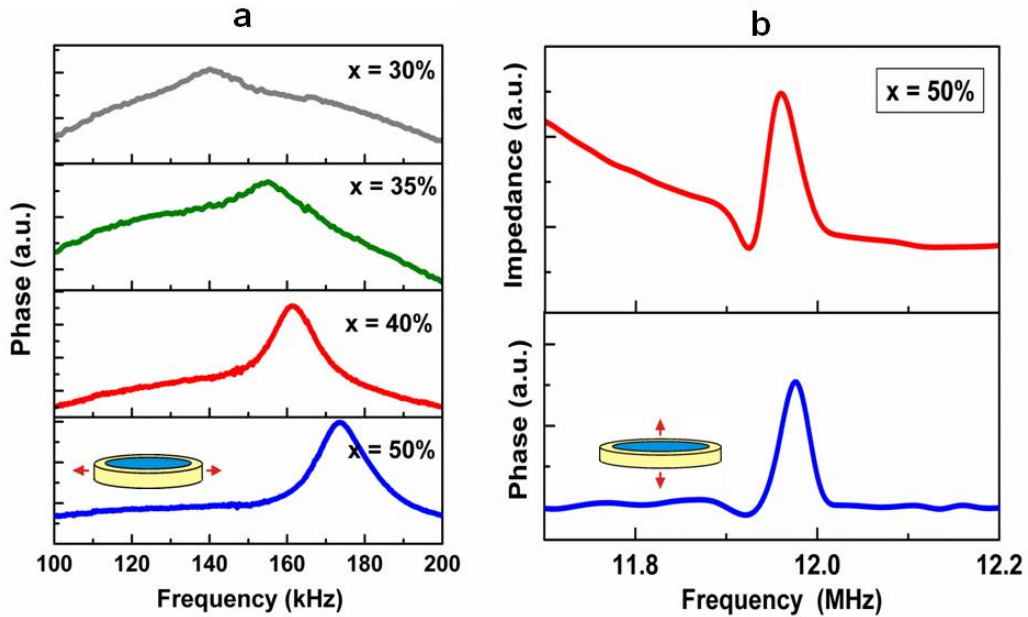

Figure S1. a) Impedance phase planar resonance spectra for composite samples with different NBT-BT content, as specified on the graphs; b) Thickness resonance (impedance modulus and phase) for the sample with 50 vol.% content of ceramic filler.

The samples have the same radial dimension (about 5 mm) and slightly different thicknesses (around 100 µm). The radial mode resonance varies between ~140 kHz (for x = 30 vol.%.) to ~175 kHz (for x = 50 vol.%.). The thickness extension (TE) mode has a resonance at a frequency of 11.86 MHz and it was evident only on the impedance spectra of the sample with x = 50 vol.%. Considering the sample thickness of about 110 µm, and by considering that the mechanically free sample has the thickness resonance at a frequency where the thickness is half of wavelength, a velocity of about 2630 m/s is found for the sample with x = 50 vol.%. For the same sample, the length extension (LE) velocity could be calculated from the radial resonance, however the procedure is much more complicated, because it requires consideration of the second harmonic of

the radial resonance, which in our case could not be determined. However, we have used the Young's modulus determined from flexural mechanical resonance measurements to calculate the length extension velocity, by using the formula $V = (Y/\rho)^{1/2}$, where $Y = 10.5$ GPa and $\rho = 3.8 \ 10^3$ kg/m^3. This gives a velocity of about 1660 m/s. The difference of the velocities for the LE and TE modes reflects the mechanical anisotropy of the films, which are much stiffer along the thickness than along the length.

Section S3. *Measurement of ferroelectric hysteresis loop*

For ferroelectric characterization a Precision Multiferroic Test System with High Voltage Interface-Radiant Technologies, Inc. was employed up to 4000 V. The polarization curves were measured on virgin samples.

P-E hysteresis loops of composites measured at room temperature, at 100 kV/cm and frequency of 100 Hz, are presented in Figure S2.
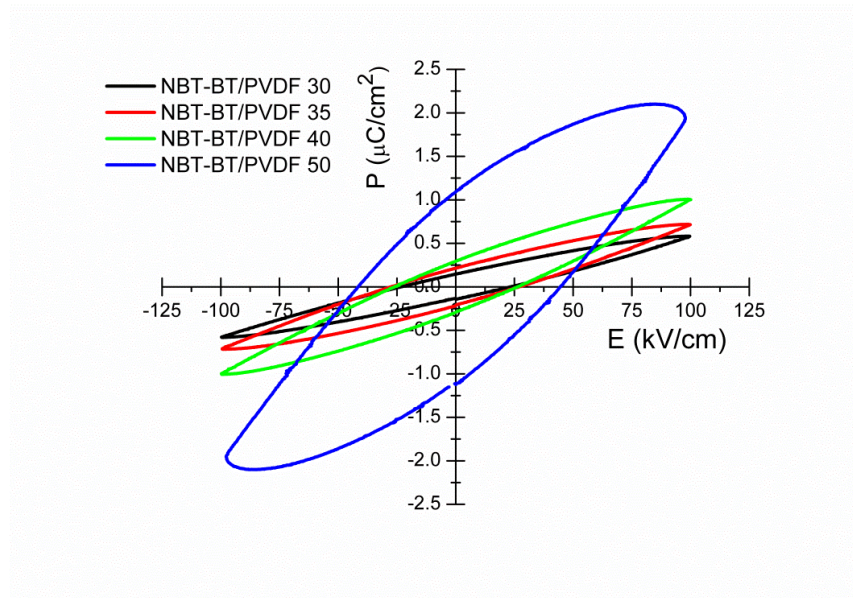

Figure S2. P-E hysteresis loops of composite NBT-BT/PVDF samples with different amount of ceramic filler.

The hysteresis loops are not saturated, due to the difficulty to apply high electric fields, which ultimately lead to breakdown. Therefore the remnant polarization values of the films cannot be

reliably obtained. However, it is evident that the increasing of the NBT-BT ferroelectric ceramic phase produces an increase of the remnant polarization.

Section S4. *Models for predicting the dielectric and piezoelectric properties of composites*

We recall here the main existent models for predicting the properties of random composites. Generally, random ceramic/PVDF composites can be approximated by an ensemble of spherical ceramic dielectric particles (with dielectric constant ε_c) which are homogeneously distributed in the PVDF polymer matrix (with dielectric constant ε_p). The volume fractions of the two components are x_c and x_p, respectively ($x_p + x_c = 1$). A model extensively used for calculating the permittivity of the mixture was proposed by Kerner [1]. In this approach the composite permittivity ε is given by the relation:

$$\varepsilon = \frac{x_p \varepsilon_p + x_c \varepsilon_c (E_c / E_p)}{x_p + x_c (E_c / E_p)} \tag{1}$$

where E_c and E_p are the average electric fields in ceramic and polymer components in the direction of the applied electric field, E_0. Furthermore, in this expression E_p is taken to be E_0 (approximation valid for $\varepsilon_c >> \varepsilon_p$). E_c, the field in a spherical ceramic particle, has been calculated to be [2] $E_c = 3\varepsilon_p /(2\varepsilon_p + \varepsilon_c)E_0$. The relation obtained by substituting this expression in Eq. (1) has been widely used to calculate the composite permittivity, however it gives underestimated values. This comes from the following reason: in the model of dielectric filler particles dispersed in a continuous medium, when an electric field is applied to the composite, the dielectric particles are polarized by the applied electric field and every single particle can be seen as a dipole moment. This dipole influences the field locally in the surrounding medium. However, this is not relevant for very small volume fraction of filler. In this case the Kerner model would give results close to the experimental values. However, as x_c is increased, interaction effects between the neighboring particles cannot be neglected. The model proposed in Ref. [3] by Jayasundere and Smith (J-S model) includes these

interacting effects as variation of the dipole moment and, ultimately, to the particle internal field. It is thus shown that the interacting field inside the ceramic particle is

$$E_c^{int} = \frac{3\varepsilon_p}{2\varepsilon_p + \varepsilon_c} \frac{\varepsilon_c - \varepsilon_p}{2\varepsilon_p + \varepsilon_c} 3x_c E_0 \qquad (2)$$

As can be seen from Eq. (2), the interacting field in a ceramic particle depends on the dielectric permittivities of the ceramic and the polymer surrounding medium, as well as on the ceramic volume fraction and the applied electric field.

This interacting component adds to the field E_c to give the the total field inside the sphere

$$E_c^t = E_c + E_c^{int} = \frac{3\varepsilon_p}{2\varepsilon_p + \varepsilon_c} \Phi(\varepsilon_c, \varepsilon_p, x_c) E_0 \qquad (3)$$

where $\Phi(\varepsilon_c, \varepsilon_p, x_c) = 1 + 3x_c(\varepsilon_c - \varepsilon_p)/(2\varepsilon_p + \varepsilon_c)$ is a function of the ceramic and polymer dielectric permittivities, and of the ceramic volume fraction.

By substituting the total field E_c^t for E_c in Kerner's formula and using $E_p = E_0$ for $\varepsilon_c \gg \varepsilon_p$, Jayasundere and Smith obtain

$$\varepsilon(x_c, \varepsilon_p, \varepsilon_c) = \frac{x_p \varepsilon_p + x_c \varepsilon_c [3\varepsilon_p/(2\varepsilon_p + \varepsilon_c)]\Phi(\varepsilon_c, \varepsilon_p, x_c)}{x_p + x_c [3\varepsilon_p/(2\varepsilon_p + \varepsilon_c)]\Phi(\varepsilon_c, \varepsilon_p, x_c)} \qquad (4)$$

This equation converges to the correct values of the permittivity limits of the composite, that is $\varepsilon = \varepsilon_p$ for $x_c = 0$ and $\varepsilon = \varepsilon_c$ for $x_p = 0$.

By considering the same model as for the dielectric permittivity of a composite with 0-3 connectivity, an analytic expression has been developed in Ref. [4] for the calculation of the piezoelectric coefficient d_{33}, with the assumptions that there is no applied electric field and the piezoelectric constant of the polymer is negligible. We briefly outline here the peculiar features of this model. When a stress σ is applied to the composite film in the thickness direction (3), which is the polarization direction, the local average stress on the piezoelectric particle, σ_c, generates, by piezoelectric effect, a polarization P_c on the ceramic particle surface given by $P_c = d_{33}^c \sigma_c$, where d_{33}^c is the piezoelectric coefficient of the ceramic. This produces an electric field inside the ceramic

particle $E_c = P_c / \varepsilon_c = d_{33}^c \sigma_c / \varepsilon_c$. By using the interactive model between the polarized ceramic

particles, as previously done for evaluating the dielectric constant of the composite, it is found that

there is an interactive field inside the ceramic particle given by the expression

$$E_{ci} = \frac{3x_c d_{33}^c \sigma_c}{2\varepsilon_p + \varepsilon_c} \tag{5}$$

Thus the total field E_{ct} inside the ceramic particle (due to piezoelectric effect and interactions) is

$$E_{ct} = E_c + E_{ci} = \frac{d_{33}^c \sigma_c}{\varepsilon_c}\left(1 + \frac{3x_c \varepsilon_c}{2\varepsilon_p + \varepsilon_c}\right) \tag{6}$$

This is used to calculate the dielectric displacement D in the composite due to the applied stress σ,

in the absence of an applied electric field, $D = \varepsilon E = d_{33}\sigma$, where E is the average electric field

produced in the composite, ε is the dielectric constant and d_{33} is the piezoelectric constant of the

composite. By taking into account that there is no applied electric field, we have $E = x_c E_{ct}$, and

using the Eq. (6) for E_{ct} it is found that

$$D = \varepsilon E = d_{33}\sigma = \varepsilon x_c E_{ct} = \varepsilon x_c \frac{d_{33}^c \sigma_c}{\varepsilon_c}\left(1 + \frac{3x_c \varepsilon_c}{2\varepsilon_p + \varepsilon_c}\right) \tag{7}$$

Thus the piezoelectric constant d_{33} of the composite is found as

$$d_{33} = \frac{D}{\sigma} = x_c d_{33}^c \frac{\sigma_c}{\sigma}\frac{\varepsilon}{\varepsilon_c}\left(1 + \frac{3x_c \varepsilon_c}{2\varepsilon_p + \varepsilon_c}\right) \tag{8}$$

The local average stress σ_c on the ceramic particles has been evaluated in Ref. [5] with the

simplified assumptions on the properties of the constituent materials, which are considered isotropic

and incompressible media. With these assumptions the factor σ_c/σ has been found to be:

$$\frac{\sigma_c}{\sigma} = \frac{Y_c}{Y}\frac{1}{x_c}\frac{Y - Y_p}{Y_c - Y_p} \tag{9}$$

and by introducing it in the expression above, the dependence of piezoelectric constant of the

composite on the volume fraction of the ceramic phase is found to be

$$d_{33}(x_c, d_{33}^c, \varepsilon_c, \varepsilon_p, Y_c, Y_p) = d_{33}^c \frac{Y_c}{Y} \frac{Y - Y_p}{Y_c - Y_p} \frac{\varepsilon}{\varepsilon_c} \left(1 + \frac{3x_c \varepsilon_c}{2\varepsilon_p + \varepsilon_c} \right) \qquad (10)$$

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