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Direct piezoelectric responses of soft composite fiber mats

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Recently soft fiber mats electrospun from solutions of Barium Titanate (BT) ferroelectric ceramics particles and polylactic acid (PLA) were found to have large ($d_{33} \sim 1$ nm/V) converse piezoelectric signals offering a myriad of applications ranging from active implants to smart textiles. Here, we report direct piezoelectric measurements (electric signals due to mechanical stress) of the BT/PLA composite fiber mats at several BT concentrations. A homemade testing apparatus provided AC stresses in the 50 Hz-1.5 kHz-frequency range. The piezoelectric constant $d_{33} \sim 0.5$ nC/N and the compression modulus $Y \sim 10^4$–10^5 Pa found are in agreement with the prior converse piezoelectric and compressibility measurements. Importantly, the direct piezoelectric signal is large enough to power a small LCD by simple finger tapping of a 0.15 mm thick 2-cm^2 area mat. We propose using these mats in active Braille cells and in liquid crystal writing tablets. © *2013 AIP Publishing LLC*
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The phenomenon of piezoelectricity in non-centrosymmetric crystals was discovered in 1880 by the Curie brothers.[1] Piezoelectric properties were also found in amorphous and polycrystalline materials, such as in ferroelectric ceramics,[2–4] liquid crystals,[5,6] and in certain synthetic and biological polymers,[7] for example, bone and tendon.[8,9] Piezoelectric effects in polymers are generally small, but can be enhanced with poling by strong DC electric fields at elevated temperatures.[10] As a result of their flexibility and the possibility to prepare films of large areas, these materials (especially polyvinylidenefluoride, PVDF) have been utilized as an active component in many applications ranging from infrared detectors to loudspeakers, as summarized in several monographs.[11,12] The search for more adaptable, stronger and softer piezoelectric materials has led to the development of the cellular polymers (ferroelectrets).[13–15] Recently, an even softer and lighter piezoelectric material has been produced[16] that unlike ferroelectrets, does not require a corona discharge. This material is produced by dispersing ferroelectric $BaTiO_3$ (BT) particles into polylactic acid (PLA) fibers by utilizing the well-known electrospinning process.[17,18] The PLA was chosen for the polymer matrix, because it has been used extensively for electrospun fibers, it is plant-based and biocompatible. The converse piezoelectric measurements (thickness change proportional to the applied voltage) have shown that the soft and lightweight ($\rho < 0.3$ g/cm^3) electrospun fiber mat has an effective piezoelectric charge constant of $d_{33} \sim 1$ nm/V. These features are attractive for applications ranging from active implants to smart textiles. Since the piezoelectric effect is reversible, one can also expect a large direct piezoelectric signal (stress induced electric polarization) that can lead to an electric current generation by applying a periodic mechanical stress.

In this paper we not only report on measurements of the direct piezoelectric effect on BT/PLA fiber mats with several BT concentrations, but also demonstrate that the effect is strong enough to switch liquid crystal pixels with simple finger taps.

The fiber mats were fabricated using an electrospinning method, as described by Morvan *et al.* in connection with the converse piezoelectric measurements.[16] In this study, the fiber mats were produced with constant (~0.15 mm) thicknesses at 0, 15, and 42 wt. % BT concentrations. Representative Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) images of 15% *BT* in PLA fiber mats are shown in Figure 1. The SEM image reveals that the fibers have pores with size comparable with that of the $BaTiO_3$ particles. The pore formation is usually attributed to rapid solvent evaporation,[19,20] thus indicating faster evaporation of the chloroform/acetone (3:1 volume ratio) around the BT particles. The OM image shows the largest fibers with some dark dots of various sizes corresponding to aggregated BT particles. The size of the BT particles ranges from 0.1 to 0.2 μm. The fibers with less than 1 μm diameters are not visible by OM. Images of other concentrations show that the diameter of the average polymer fiber increases with increasing BT concentration (roughly doubles from 0 to 42 wt. %).

The schematic of the homemade experimental set-up used to measure direct piezoelectric effect is shown in Figure 2. It is based on Berlincourt's method,[21] in which an audio speaker is used to periodically stress the piezoelectric film and a lock-in amplifier measures the first harmonic of the induced current. In our device, 150 ± 20 μm thick fiber mats were sandwiched between conducting indium tin oxide (ITO) coated glass plates and the induced electric current generated by the piezoelectric sample was measured between 50 Hz and 1500 Hz by an EG&G 7265 lock-in amplifier. The membrane of the speaker was connected to the top plate of the sample via a long aluminum piston to minimize the effect of the electric signal that drives the speaker. The sample was placed on a flat heater where the sample cell position could be adjusted by a set of micro-positioners. The sample, an accelerometer (BK 4375 from Bruel & Kjaer), and a calibrated

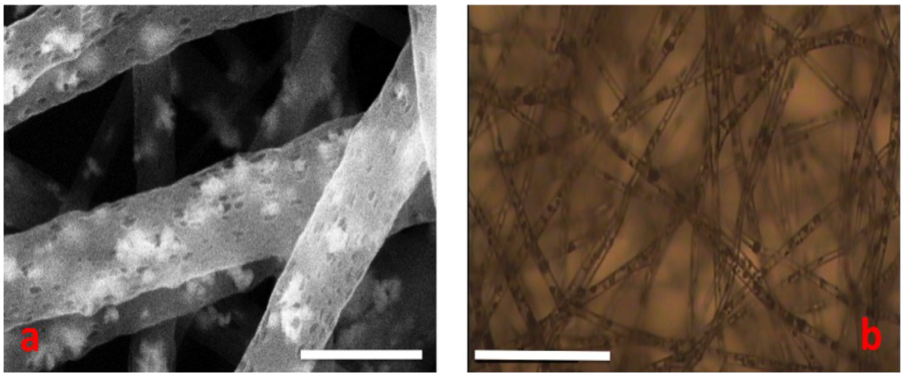

FIG. 1. SEM (a) and OM (b) images of a 15 wt. % BT in PLA fiber mat electrospun across 25 kV potential difference between the nozzle and the collecting ITO coated glass plate placed 10 cm apart from each other. The scale bars correspond to 5 μm and 50 μm in (a) and (b), respectively.

28 μm thick PVDF film sensor obtained from Images SI Inc. (Staten Island, NY), were placed on top of each other, and were sandwiched between the plate of the heater and the flat foot of the piston so that the fiber mat was slightly (<1%) compressed to ensure full contact between the speaker and the sample during the measurements.

The frequency dependence of the piezoelectric current $\tilde{I}$ of the PVDF film with known $\tilde{d}_{33} = 33pC/N$ and I_s of our samples with the unknown d_{33}, were measured as a function of frequency of the applied stress. Because the forces acting both on the sample and the piezoelectric standard are the same, the calculated d_{33} is independent of the size ratio of the sample and the PVDF sensor, and

$$d_{33} = \tilde{d}_{33} \cdot I_s/\tilde{I}. \tag{1}$$

The frequency dependences of the charge constants of 0.15 mm thick films at several BT concentrations are shown in Figure 3.

One can see that $d_{33} < 10$ pC/N of the pure PLA mat is practically negligible compared to the charge constants of the fiber mats containing BT particles. The measured d_{33} appears to be roughly proportional to the BT concentration, although they have slightly different frequency dependences. It is important to note that the measured values for the 42 wt. % composite are in good agreement with the values obtained by Morvan *et al.*[16] from the converse piezoelectric measurements.

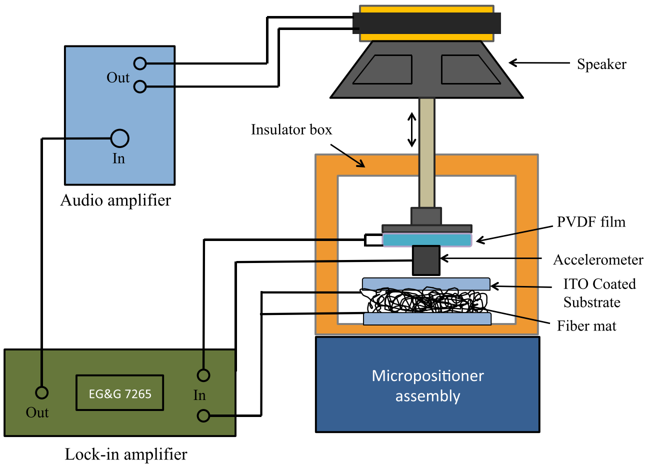

FIG. 2. Schematic of the apparatus used for applying an alternating stress to a fiber mat and measure the signal from accelerometer and samples. The testing container (orange box) was on a vertical lift assembly so that the speaker and the piston were held fixed during each sample loading. The speaker was driven by a signal coming from the output of the EG&G 7265 lock-in and amplified by an audio amplifier (Sony, HCD-RG20). The signals from fiber mat samples, the PVDF sensor, and the accelerometer were measured in the current or voltage inputs of the lock-in amplifier.

In Figure 4 we plot the strain dependence of the measured short circuit currents at a constant frequency (1 kHz). The strain was determined by the voltage signal V_a of the accelerometer fixed to the sample. Knowing the sensitivity $b = 6.08 \times 10^{-4} \frac{V}{ms^{-2}}$ of the accelerometer, the displacement Δs of the top substrate could be obtained as $\Delta s = V_a/[b \cdot \omega^2]$, where ω is the angular frequency of the vibration. We see that even as small as 0.04% strain of 0.15 mm thick and 2 cm^2 area fiber mat with 42 wt. % BT concentration is able to generate 2 nA of electric current. Similar current levels were obtained recently on a M13 phage-based piezoelectric generator, but with 6% of strain.[22]

Calculating the induced polarization from the short circuit current I_s measured in the samples of area A as $P = I_s/(\omega \cdot A)$, and the stress T from Δs as $T = Y \cdot \left(\frac{\Delta s}{l}\right)$, where Y is the compression modulus of the sample with thickness l, d_{33} can be related to Y as $d_{33} = \frac{P}{T} = \frac{I_S}{\omega A} \cdot \frac{l}{Y \cdot \Delta S} = \frac{I_s \cdot b \cdot l \cdot \omega}{V_a \cdot Y \cdot A}$. With these the compression modulus can be calculated from the measured I_s, V_a, and d_{33} values, as

$$Y = \frac{I_s}{V_a} \cdot \frac{b \cdot l \cdot \omega}{d_{33} \cdot A}. \tag{2}$$

Combining Eqs. (1) and (2), we see that Y can be obtained also from $\tilde{I}$ of the PVDF sensor and its known charge constant $\tilde{d}_{33}$, as

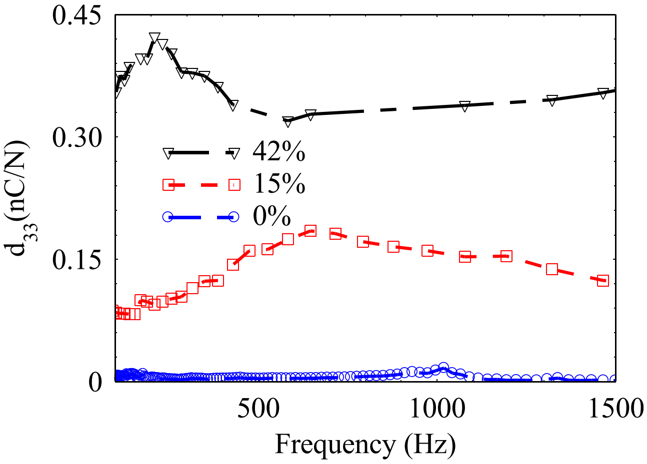

FIG. 3. The frequency dependence of the piezoelectric charge constant d_{33} for 0.15 mm thick PLA fiber mats containing 0, 15, and 42 wt. % of $BaTiO_3$ particles.

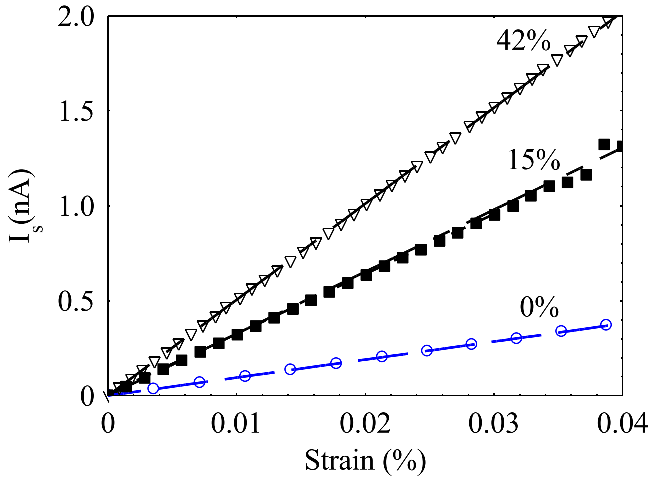

FIG. 4. The strain dependence of the induced short circuit electric current measured at 1 kHz for samples with different BT concentrations.

$$Y = \frac{\tilde{I} \cdot b \cdot l \cdot \omega}{V_a \cdot \tilde{d}_{33} \cdot A}. \qquad (3)$$

Using this equation, the compression moduli Y of the mats were obtained from the measured frequency dependence of $\tilde{I}$, and plotted in Figure 5.

It can be seen that the compression moduli are on the order of 10-100 kPa, which are much smaller than the compression modulus of the PVDF standard of $\tilde{Y} \approx 3$ GPa, therefore the displacement Δs deduced from the accelerometer signal corresponds to the thickness variation of the our fiber mats. The observed compression moduli are largest for the pure PLA (300–500 kPa), and smallest (15–30 kPa) for the mat containing 42 wt. % BT particles. This probably is related to the increased width of the fiber when the BT particles inserted, which results in a decrease of the number of nodes of the fiber mesh. We note that the Young modulus of the 42 wt. % BT mat obtained from these direct piezoelectric measurements are in good agreement with Y ~ 16 kPa reported based on DC compression measurements (measuring variation of the film thickness as a function of weights added on the top of the mat). The significance of these compression modulus values is that they are on the order of the Young moduli of biological tissues, such as muscle, brain, etc.[23] This mechanical impedance matching thus maximizes the energy conversion between the fiber mat and the soft load, and make them ideal in applications, such as in active Braille, noise insulators, energy harvesters and in liquid crystal writing tablets.

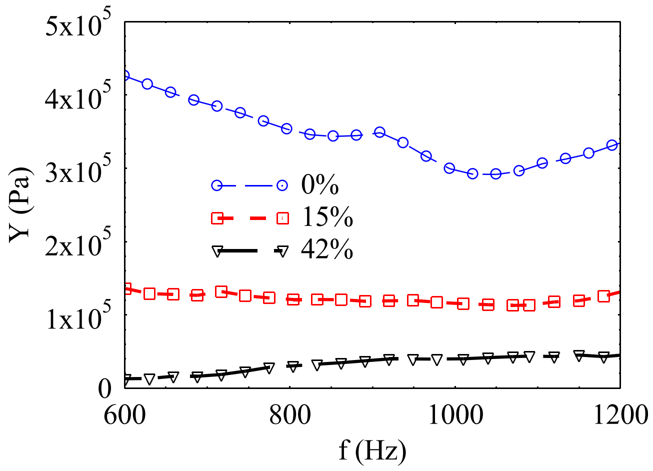

FIG. 5. Frequency dependence of the compression moduli as calculated from Eq. (3).

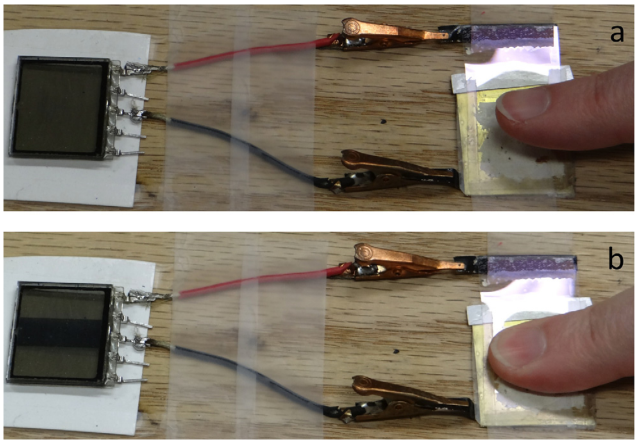

FIG. 6. Illustration of the electric power generation by a 0.15 mm electrospun PLA fiber mat containing 42 wt. % $BaTiO_3$ particles: powering a liquid crystal pixel by a finger tap.

In order to illustrate this latter possibility, we made a simple prototype where a single pixel LCD panel was connected to the electrodes of a 0.15 mm thick and 2-cm^2 area fiber mat sandwiched between two ITO glasses. When a finger taps the mat, the LCD pixel switches to a black (homeotropic) state (Figure 6). This shows that the generated voltage on the liquid crystal pixel is over 3 V. From this prototype, it was estimated that a 1 mm-thick fiber mat would provide enough voltage to switch a cholesteric liquid crystal writing tablet (Boogieboard®) commercialized by Kent Displays, Inc, thus making it completely power-free.

To summarize, we have measured the effective piezoelectric charge constant of electrospun fiber mats consisting of $BaTiO_3$ nanoparticles. We found good agreement with the recent converse piezoelectric measurements and demonstrated that thin (0.15 mm) mats can switch a liquid crystal (LC) display by a finger tap, making them promising for powering some liquid crystal displays and other applications.

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