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Article

Linearity of piezoelectric response of electrospun polymer-based (PVDF) fibers with barium titanate nanoparticles

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SUMMARY

Piezoelectric sensors respond to applied force by generating voltage between their surfaces, measurable with contact electrodes. Flexible piezoelectric polymers with nanoparticles are novel materials allowing building wearable-textile sensors with applications including helping people better adapt to prosthetic devices or providing extra sensorial input. These materials can also be embedded into constructions, such as bridges or buildings, to continuously monitor their structural health. Moreover, when the sensors' response varies linearly with their input, they can be mathematically modeled with linear systems of equations. These are much easier to solve or further adjust, as opposed to quadratic or higher degrees, exponential, or other functions. Here, we investigated whether flexible, polymer-based piezoelectric materials produced through electro-spinning a Polyvinyledene Fluoride (PVDF) solution containing a specific amount of $BaTiO_3$ nanoparticles respond linearly to applied force by producing a corresponding voltage. We applied forces up to 3.4N on electrospun fibers and on the sides of electrospun meshes and measured the voltage along them. Our results revealed that the generated voltage depends piecewise-linearly with applied force. We carried out these measurements at 20 ºC, 5 ºC and 40 ºC, and the resulting slope dependency demonstrated that the overall piecewise linear behavior was conserved. These results greatly increase the practical interest of such materials. They can be produced relatively easily, appear to be usable outdoors in a variety of climates and can be modeled with linear systems of equations, simplifying integration in complex devices. Our results show that more in-depth studies remain of interest.

INTRODUCTION

Electro-mechanical sensors have been in continuous development for almost two centuries, since the beginnings of the telegraph (1). They have been used to sense contact, position, or pressure in a wide range of domains (2). In particular, pressure sensors are used in computer interface devices, vehicle engines or subsystems, aircraft, automobiles, ships, industrial machines, biomedical applications, and automated systems, to name only a few (2). Among the large array of possible designs, thin flexible sensors with high sensitivity to pressure and accurate measurement of input force are still an active area of research (2). These sensors could be used in prosthetics, where they can help to alleviate discomfort, provide better feedback, and further enhance sensory possibilities (3). The sensors can be used as an interface between the limb parts and the prosthetic device to measure and communicate pressure buildup in various areas (3). They could also be used on the exterior part of the prosthetic to provide tactile feed-back, especially for wearable hand prosthetics (4, 5). Other application domains for such smart flexible materials include the real-time monitoring of structural deformations inside large components, such as building or bridge support beams, where they can provide early warnings and help prevent catastrophic failure (6). These materials should be able to sense the amount of pressure or deformation, and ideally, also be able to communicate the local area coordinates on their surface where the pressure is sensed.

Among the electro-mechanical properties helping to build such sensors, piezoelectricity – also studied for over a century – is one of the most promising to use (6, 7). Piezoelectricity is the property of certain materials to react to deformations from an externally-applied force by creating voltage between some of their surfaces (6, 7). These materials are typically ceramics or polymers. Ceramics are hard and can break easily, but have high sensitivity (6, 7). Piezo-polymers in turn are flexible and resilient to deformations (6, 7). They are therefore suitable for different applications. Among the more recent such polymers, polyvinylidenefluoride (PVDF) is one of the ideal candidates for smart, flexible materials (6-8). However, as piezo-polymers are less sensitive than ceramic ones, producing slower varying voltages for a given input force, nanoparticles of hard piezoelectric materials such as lead zirconate titanate (PZT), zinc oxide (ZnO) or barium titanate ($BaTiO_3$) can be mixed in the solutions used to create the polymer, enhancing the overall piezoelectric sensitivity (6-9). Considerable advances have been made in the research of flexible piezoelectric thin films, while with thin fibers or textile meshes researchers have had less success (7). Nevertheless, the latter have better spatial resolution, allowing for more precise input localization (6, 7). Active research is thus ongoing regarding piezoelectric thin fibers and meshes (6, 7). In general, the PVDF polymer can exhibit several types of internal structures and phases (7, 8). Among these, the so-called beta-phase is particularly important **(Figure 1)**. The beta-phase is the one presenting piezo-electric properties, due to the arrangement of the atoms (7). One of the more efficient ways to create PVDF fibers with naturally high content of the beta-phase is through electrospinning (10, 11). Electrospinning is a process by which a solution is injected from a syringe through a metallic needle and allowed to be pulled in thin fibers through the air using strong electrostatic fields of 10 kV or more across a gap

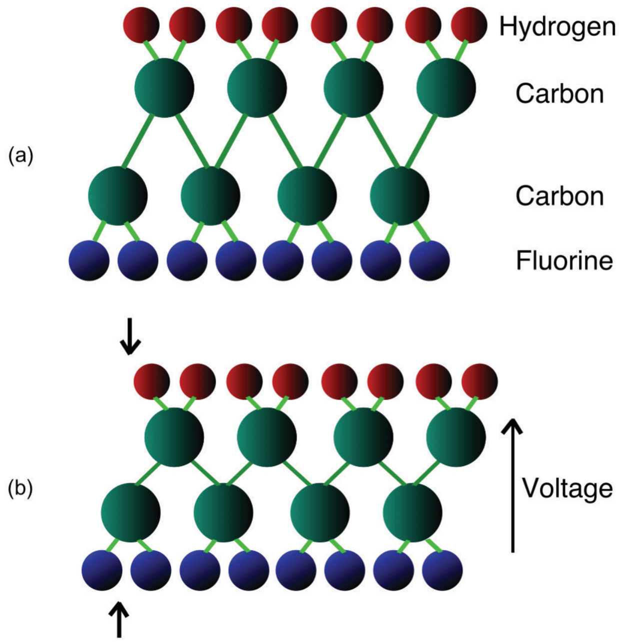

Figure 1: Beta-phase of PVDF, presenting piezoelectric properties. a) The atom arrangement structure of PDVF without applied force. **b)** The structure deformed by an external force applied to it, leading to a produced voltage.

(8). These fibers are then de-posited onto a collector, which can be fixed or rotating, and can have various shapes. As the liquid travels and deposits, it also quickly dries out, due to evaporation (12). Additionally, $BaTiO_3$, added as nanoparticles to the PVDF electrospinning solution, also promotes the beta-phase of PVDF, while being eco-friendly and lead-free (13).

However, some non-linear effects have been discovered for various PVDF-based devices (14, 15). In general, for all of these applications, a linear electrical response to mechanical input is highly desirable because it allows for more accurate modeling and processing of the signal. In particular, for piezoelectric materials, if the output voltage difference depends linearly on the applied input force, it simplifies the mathematical modeling. Of course, one could, in some situations, just use simple on-off sensors, to trigger when the deformation is above a certain threshold. However, this only offers binary responses, while a linear response can continuously vary with input within the operating range, thus allowing more precise measurement and tailored, or proportional predictions or decisions.

For this study we prepared PVDF solutions with added $BaTiO_3$ nanoparticles, and electrospun them into fibers and meshes. We hypothesized that for input forces within a range where these fibers and meshes remain elastically deformable, their voltage output should vary linearly with the input force. We also hypothesized that this type of relationship should remain relatively stable for various temperatures. Our hypotheses were confirmed by our measurements, which showed a two-slope, piecewise-linear form. The stability at

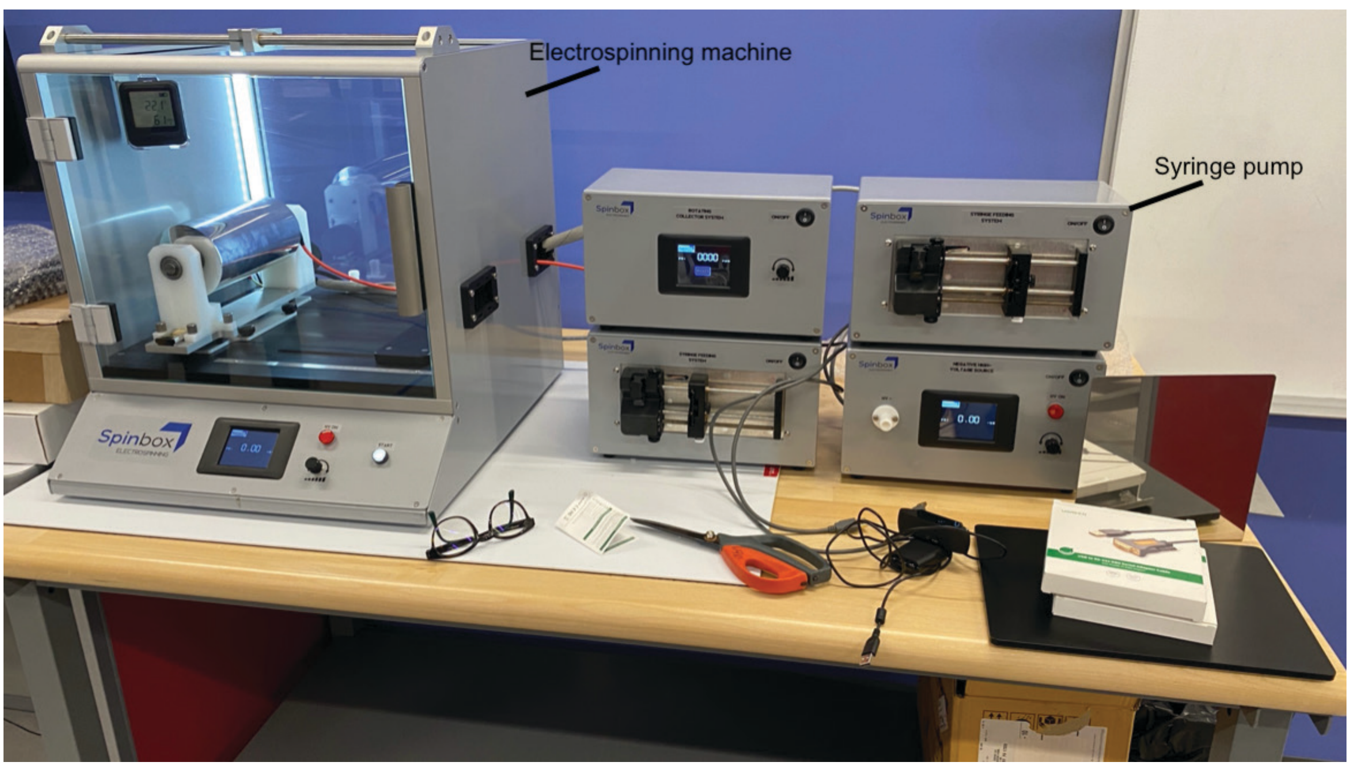

Figure 2: Spinbox Electrospinning machine with syringe pumps, which are the two boxes with metal rods and black syringe holders on their front plate. The syringe is inserted in these holders and the pump is programmed to slowly compress it, to have the fluid travel out from the syringe to the electrospinning machine on the left, where it flows out of a needle and is pulled towards the metal cylinder through a large voltage, e.g. 15 kV.

various temperatures, ranging from 5 ºC to 40 ºC, gives hope to potential applications in many climates. Indeed, bridges or buildings have many exposed parts, and also prosthetic elements can be exposed or only lightly protected. Overall, more precise and detailed studies can be motivated by these initial results.

RESULTS

To carry out the study, we prepared samples and applied force onto them. We measured the resulting voltage, plotted, and fitted the resulting data with linear functions. We then repeated the process at different temperatures.

To prepare the samples, we electrospun five batches of PVDF+$BaTiO_3$ powder dissolved in DMSO and acetone. We produced fibers of 0.7 mm to 1 mm thickness, and meshes of 0.2 mm thickness, to which we attached metal electrodes of copper and aluminum foil **(Figure 2)**.

To test the range, linearity, and stability of the piezoelectric response of these polymers, we applied forces onto these samples, ranging up to 300 g-equivalent-weight for fibers and 350 g-equivalent-weight for meshes, which translates to 3.4 N. To know what force we were applying, we measured these forces with a scale under a stand, in grams (equivalent of weight of the corresponding mass). To measure the voltage response while applying these forces, we used a voltmeter connected to the attached electrodes. To study the temperature dependence, we have repeated these measurements at three temperatures of the samples: 5 ºC, 20 ºC and 40 ºC, for three samples from each of the five batches, and five measurements per sample **(Figure 3)**.

Each of the six measured response sets for combinations of polymer type and temperature demonstrated well-fit piecewise-linear functions with two slopes, m_1 and m_2, with R^2 values between 0.97 and 0.99 for each of them **(Figure 4)**. The voltage range appeared consistently higher for meshes than for fibers, for the same forces.

Our results showed that the slope values increased linearly with temperature **(Figure 5a)**. We also observed that the slope-change points decreased with temperature and have attempted to fit them quadratically **(Figure 5b)**. Both dependencies could be justified by a larger deformability for the same force when the temperature increases. The second slopes (m_2) did not seem to vary substantially with temperature; they appeared to become slightly smaller, but this could also have been due to noise in the data.

DISCUSSION

Our goal was to study whether electrospun piezoelectric PVDF polymer fibers and meshes with added $BaTiO_3$ nanoparticles would produce linearly-varying voltages when forces were applied to them. We hypothesized that this would be true, provided the forces do not become so great as to deform them beyond their elasticity limits. We also hypothesized that the dependency would remain linear above and below room temperature.

We did indeed find a linear dependency, remaining so at different temperatures. However, our results show a piecewise-linear dependency, with two different slopes. The very interesting two-slope linear profile could point to the influence of a density threshold inside the polymer, reached at a specific level of compression. A further study, lowering the $BaTiO_3$ mass proportion down to zero, could show whether the slope-change force value changes accordingly, suggesting then a possible mechanical interaction due to the volume and stiffness of $BaTiO_3$ nanoparticles, which could create non-negligible resistance to further compression. If, on the contrary, this effect persists even in pure PVDF materials, then it is related to the intrinsic piezoelectric effect characteristics of the polymer itself. In our experiments we homogenized the solution by stirring for an hour followed by sonication before electrospinning. It would therefore not be counterintuitive to have similar slope-change points and voltages for both fibers and meshes.

Regarding the homogeneity, we have used lithium chloride (LiCl) in order to improve the uniformity of the fibers and avoid beading (16). We chose dimethyl sulfoxide (DMSO) to be the PVDF solvent as it has low toxicity (17). We performed initial studies varying PVDF and $BaTiO_3$ mass and solvent volume proportions, and we fixed the PVDF mass proportion at 16% of the total solution mass and the two-solvent volume proportion at 6:4 to ensure an optimal viscosity as well as material consistency when electrospinning. Indeed, the acetone helped to increase the fluidity of the solution, at the cost of less consistency of the material immediately after electrospinning. Moreover, Kalimuldina, Gulnur *et al.* extensively note that such mass proportions appear to favor smoother fibers, and that the volatility of solvents does affect the final structure of the material (11). We have also fixed the $BaTiO_3$ mass proportion at 30% of the total solid mass PVDF+$BaTiO_3$, to produce a good response over a larger range of forces. In the preliminary studies we had observed that an increased proportion of $BaTiO_3$ increases the voltage for the same range of applied forces, but it also increases the viscosity of the solution, making electrospinning more difficult.

Our results have also indicated a scale difference between

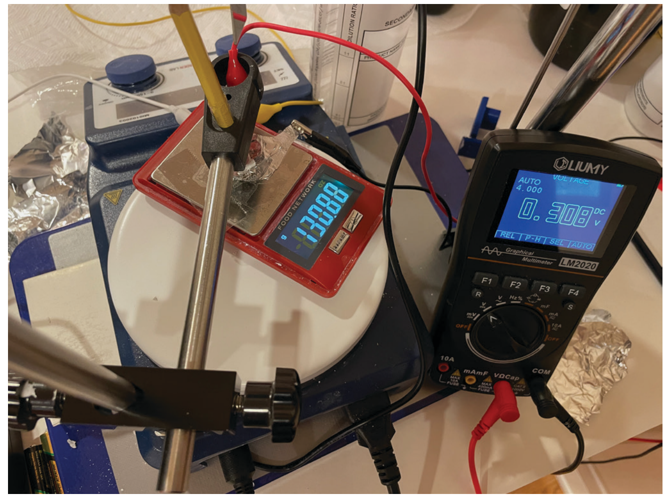

Figure 3: Voltmeter and scale for measuring voltage response to applied force to PVDF. The force is applied through the eraser end of the pencil (yellow rod in the top left), which is soft and thus does not damage the PVDF. The pencil is held in the support as shown, and the force it exerts on the sample and thus on the scale underneath is varied by adjusting its height and retightening the screws of the support, and waiting a few seconds for the numbers to stabilize, before writing them. The electrodes are above and below the sample, connected as shown to the voltmeter, with the red and black wires.

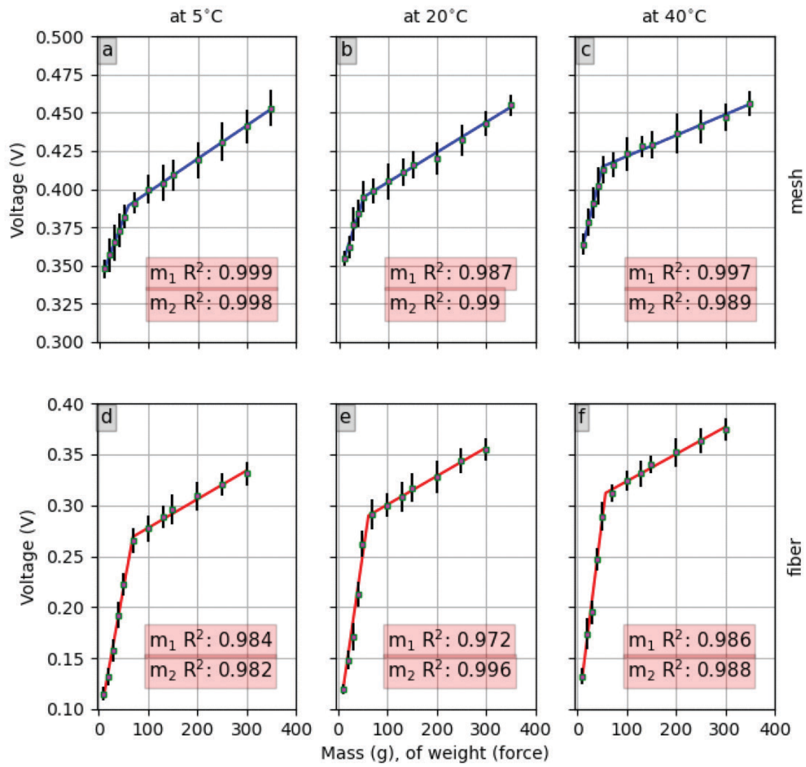

Figure 4: The empirical data points and piecewise-linear fits through them. Voltage response vs applied force (given as mass in g for the equivalent weight), for PVDF meshes and fibers, measured at temperatures of 5 ºC, 20 ºC and 40 ºC, together with piecewise two-slope linear fits. The upper row is for meshes (a, b, c) and the lower row for fibers (d, e, f), with columns corresponding to the three temperature points. The error bars represent standard deviation from the five batches with three samples per batch, and five measurements for each sample, at each temperature.

fiber and mesh response. This may come from the different degree of poling during electrospinning, due to a large difference in thickness between the fiber and the mesh, with fibers being potentially more anisotropic. This is to say that the PVDF material might be distributed with different densities throughout the fibers. Another possibility could be that the $BaTiO_3$ particles might be unevenly distributed. The $BaTiO_3$ particles have 0.1 μm diameters, and further spectroscopic analysis could characterize more precisely their localization inside the electrospun material, to compare with the extensive analysis performed by Sharma *et al.* on the non-electrospun solution otherwise very similarly prepared, which appeared to have a fairly homogeneous dispersion of $BaTiO_3$ (13).

The upper limit of the force currently observed may come from the relative ease with which the mesh and fiber polymer materials can be deformed; beyond a certain applied force, their remaining thickness is too small to prevent our electrodes from touching. Further studies with better shaped electrodes could further extend the accessible range of force, and thus clarify if the response remains piecewise linear or starts to contain higher-order terms or other functions.

Currently, our data support a quadratic fit for our slope-changing point dependence on temperature. However, a larger number of replicates and data points would be desirable, to provide more empirical evidence. This would then help determining with more confidence whether that is indeed the correct mathematical model for this relationship. It is possible that the correct form is instead given by an exponential decay. Similarly, the apparent linear form of the m_1 slope dependence on temperature could also be part of a rising higher degree curve or even an exponential. Future studies with a more precise temperature-controlled environment, more temperature points, and better shaped electrodes would be able to provide data for more accurate modeling and further study of the m_2 dependence on temperature.

For more precise studies, the detection circuitry can also be easily programmed to obtain both localization information as well as magnitude of pressure information from a detector made from PVDF and $BaTiO_3$ nanoparticles, for instance using a matrix of electrodes on the mesh. For potential applications, from a technical standpoint, methods to properly embed flexible electrodes along with the fibers or meshes would need to be decided. Afterwards, a new set of measures and calibrations would be necessary. For a final product, the sensing material would need to be encased in an outer layer of neutral flexible material. This would ensure both the necessary mechanical and electrical connection, as well as protection against damage, external interference, or excessive wear and tear. The results we are presenting here show that, since electrospun PVDF with 30% $BaTiO_3$ appears to behave piezoelectrically linearly in a large range of temperatures, it is a promising material, warranting further study. Thus, refining the model and expectations could help advance towards feasibility assessments for novel sensing applications. Among these, we suggest hand prosthetics or structural monitoring from inside construction elements.

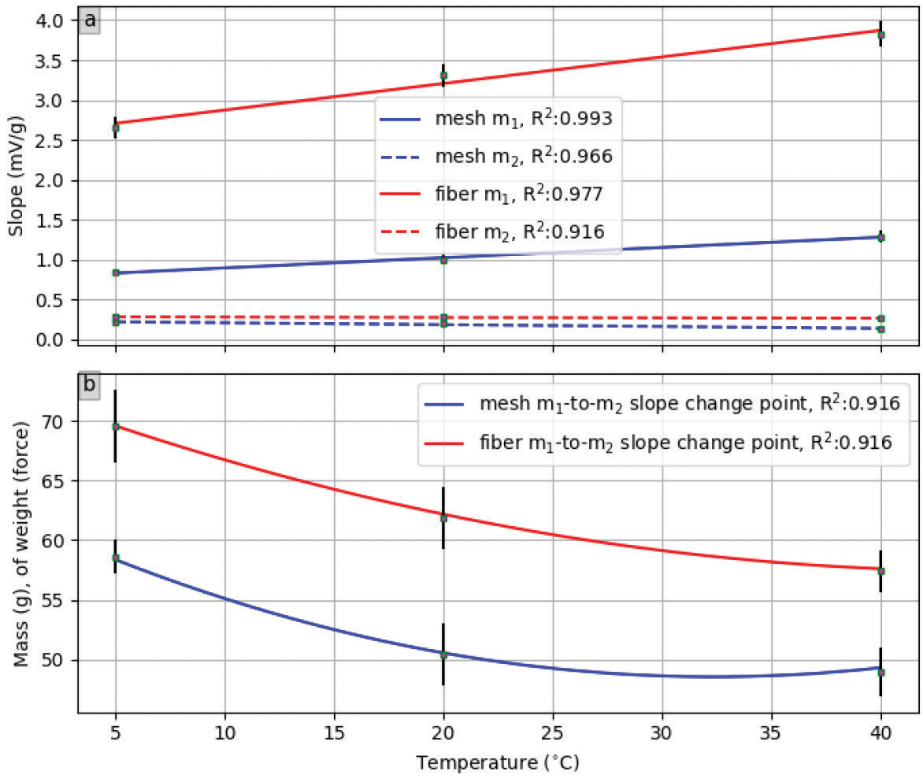

Figure 5: Temperature dependence of slopes and slope-change points for meshes and fibers. For each of fiber and meshes we plot the two slopes for each of the measured temperatures. For graph (a), from our empirical data we seem to be able to linearly fit the first slope m_1 increase with temperature. We show the linear fit for each of the slopes, for fibers and meshes. For graph (b), from our empirical data, we seem to be able to quadratically fit the slope-changing point of force (mass) dependency on temperature.

MATERIALS AND METHODS

Materials and Solvents

Our supplies to prepare the solution to electrospin were all purchased from Sigma Aldrich Millipore Sigma USA, Milwaukee WI and Allentown PA. We used 20 g of PVDF powder catalog # 182702-250G lot # MKCP9819, 8.57 g of $BaTiO_3$ catalog # 467634-100G lot # MKCN7725, 0.09 g of LiCl powder catalog # L9650-100G lot #BCCF9622, 60 mL of DMSO catalog # 276855-12X100ML lot # SHBN5918, and 40 ml of acetone catalog # 179973-1L lot # SHBN3660. This amounted to a 7:3 mass ratio of PVDF+BaTiO3 and a 6:4 volume ratio of DMSO and acetone.

Solution Preparation

The PVDF and LiCl powders were dissolved by stirring with an overhead mechanical stirrer manufactured by JoanLab, Model # OS-10L at 50 ºC on a hot plate manufactured by Four E's Scientific, Fristanden Lab Model # MI0102003 for 30 minutes until homogenized. Then the BaTiO3 powder was added while stirring, until again homogenized. Afterwards, the solution was sonicated for 10 minutes with an ultrasonic homogenizer manufactured by CGoldenwall, China, Part # CNA-996F, and then degassed at room temperature for two hours.

Electrospinning

The electrospinning was performed on a modular bench-top system manufactured by Bionicia, Model Name Spinbox System, comprising an electrospinning chamber, high voltage source, and syringe pump. The system was set at 15 kV, with the tip-to-collector distance of 17cm. The needle had 20 gauge, and the syringe pump speed was 20 micro-liters per minute. We have collected the mesh samples on a rotating drum collector. The fibers were collected inside a guiding tube.

Force Measurements

The force measurements were made using an electronic scale on which the samples were sandwiched between electrodes and an increased force was applied through a rod fixed on a stand controlled with a screw knob **(Figure 3)**. The voltage was measured using a voltmeter with leads attached to the electrodes. The force and voltage readings were manually recorded, and the weight force was gradually increased and then released. We have also collected data with weights set in a randomized order, to avoid introducing systematic error from monotonically increasing them. The cooling of the sample was done in a freezer at -20 ºC, and the heating using a hair dryer, both periodically checked with an electronic thermometer. For the data analysis, we used a piecewise-linear form using the non-linear least-squares fitting Python SciPy *curve_fit* toolbox which we also used to estimate temperature dependencies.

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