Wearable Electronic Textiles from Nanostructured Piezoelectric Fibers

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Abstract
© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim Wearable energy harvesting is of practical interest for many years and for diverse applications, including development of self-powered wireless sensors within garments for human health monitoring. Herein, a novel approach is reported to create wearable energy generators and sensors using nanostructured hybrid piezoelectric fibers and exploiting the enormous variety of textile architectures. It is found that high performance hybrid piezofiber is obtained using a barium titanate (BT) nanoparticle and poly(vinylidene fluoride) (PVDF) with a mass ratio of 1:10. These fibers are knitted to form a wearable energy generator that produced a maximum voltage output of 4 V and a power density 87 μW cm\(^{-3}\) which is 45 times higher than earlier reported for piezoelectric textiles. The wearable energy generator charged a 10 μF capacitor in 20 s which is four and six times faster than previously reported for PVDF/BT and PVDF energy generators, respectively. It also emerges that the established knitted energy harvester exhibits sensitivity of 6.3 times higher in compare with the piezofibers energy generator. A knee sleeve prototype based on a PVDF/BT wearable device for monitoring real-time precise healthcare is demonstrated. The developed processing method is scalable for the fabrication of industrial quantities of smart textiles.

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Wearable Electronic Textiles from Nanostructured Piezoelectric Fibers

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Abstract: Wearable energy harvesting has been of practical interest for many years and for diverse applications, including development of self-powered wireless sensors within garments for human health monitoring. No commercially available systems currently exist with typical problems including low energy efficiency; short cycle life; slow and expensive manufacturing; and stiff, heavy or bulky componentry that reduce wearer comfort and aesthetic appeal. Herein, a novel approach is reported to create wearable energy generators and sensors using nanostructured hybrid piezoelectric fibers and exploiting the enormous variety of textile architectures (knitting, braiding and weaving). It is found that high performance hybrid piezofiber was obtained using a barium titanate nanoparticle and poly (vinylidene fluoride) with a mass ratio of 1:10. These fibers were knitted to form a wearable energy generator that produced a maximum voltage output of 4 V and a power density 87µW/cm³ which is 45 times higher than earlier report for piezoelectric textiles. The wearable energy generator charged a 10 µF capacitor in 20 sec which is 4 and 6 times faster than previously reported for PVDF/BT and PVDF energy generators, respectively. It also emerged that the established knitted energy harvester exhibits sensitivity of 6.3 times higher in compare with the piezofibers energy generator. A knee sleeve prototype based on a PVDF/BT wearable device for monitoring real-
time precise healthcare was demonstrated. The developed processing method is scalable for the fabrication of industrial quantities of strain sensing and energy generation smart textiles.

1. Introduction

Garments traditionally perform social and protective functions, but the addition of wearable electronics provides the means to produce a new generation of smart garments. Such affordable smart garments could fulfil diverse applications, ranging from work wear in specific industries to the almost infinite scenarios of personal use including energy harvesting/ storage, force/pressure measurement, porosity or color variation and sensors (movement, temperature, chemicals).[1],[2],[3],[4],[5],[6],[7] However, performance, scalability, and cost problems have restricted the deployment of currently-available smart textiles. To build smart textiles on an industrial scale, method of manufacturing and material selection are two important requirements. The approach of new energy materials and novel fabrication methods are essential to develop wearable technologies. Wearable energy generating devices that can be seamlessly integrated into garments are a critical component of the wearable electronics genre. Currently flexible fibre energy harvesters have attracted significant attention due to their ability to be integrated into fabrics, or stitched into existing textiles. Large-scale production of energy harvester fibers using conventional manufacturing processes, however, is still a challenge.
Energy harvesting from environmental mechanical sources such as body movements including finger imparting, pushing, stretching, bending, twisting, air flow, transportation movement, and sound waves has attracted widespread attention to promote flexible self-powered devices. The best common mechanical energy harvesting methods are based on piezoelectric materials. Piezoelectric materials can be classified in three categories: piezoelectric ceramics, piezoelectric polymers, and piezoelectric composites. Unlike the energy harvesters utilizing solar or thermal energy, performance of piezoelectric generators is generally not limited by environmental factors. Piezoelectric generators have received massive interest in energy harvesting technology due to their unique ability to capture the ambient vibrations to generate electric signals. The unique energy transduction of piezoelectric materials enables their applications in fields of energy harvesting, actuators, sensors, structural health monitoring and use in biomedical devices. Numerous
approaches have been used to fabricate piezoelectric generators, such as coating \cite{24}, spinning \cite{25}, depositing \cite{26}, and printing \cite{27}.

Energy harvesting technology from human body movement is desirable due to new direction in power up portable electronic devices.\cite{28}

Among all of fiber generators or sensors, piezoelectric fibers that operate based on the piezoelectric effect as a response to applied strain are especially attractive, due to ubiquitous mechanical vibrations occurring in our daily life that can be harvested into electrical signals.\cite{19} Among the variety of materials exhibiting piezoelectricity, polymers are of interest due to several enhanced properties desirable in flexible piezoelectric generators. Recently, much attention has been paid to poly(vinylidene fluoride)\cite{29,30} (PVDF). This nontoxic material is a semi-crystalline polymer that exists in four different crystalline forms (α, β, γ, and δ) \cite{31} depending on the preparation conditions.\cite{32} The β-phase is the desirable phase owing to its ferroelectric nature.\cite{33} Spinning process such as wet spinning \cite{19}, dry spinning \cite{34}, melt spinning \cite{35}, gel spinning \cite{36}, and electrospinning \cite{37} are the most primitive process for producing flexible piezoelectric generator with the ability for mass production. Three dimensional fabric structure has been designed into fabric-based piezoelectric generator as the 3D spacer knitted fabric with ability to provide power of 1.10–5.10 \text{µW/cm}^2 under the impact pressures of 0.02–0.10 \text{MPa} at a frequency of 1 Hz.\cite{38} Another study showed simple melt-spun bicomponent filaments was developed by using PVDF and carbon black/polyethylene to supply power of 1 \text{µW/cm}^2 at an impact pressure of 20 kPa.\cite{39} While these piezoelectric textiles presented flexibility and energy harvesting performances, their piezoelectric performance (i.e. power output, sensitivity, durability) is still not satisfied because of the poor electrical connection between the piezoelectric fibers and electrodes. Furthermore PVDF showed limited piezoelectricity and power output because their active material was based on ferroelectric polymers with high piezoelectric voltage constant but a
low dielectric constant ($\varepsilon \sim 30$). One potential method to increase the dielectric constant of the PVDF polymers is to introduce high dielectric constant materials such as inorganic piezoelectric materials (i.e. barium titanate nanoparticles) into the PVDF matrix [14] [40] [41]. However, inorganic piezoelectric materials, such as, lead zirconate titanate (PZT) [42], barium titanate (BT) [43], sodium niobate [44], lead magnesium niobate lead titanate [45] and zinc stannate (Zn2SnO4) [46] have high significant piezoelectric performance but their rigid nature limit their application in flexible self-powered devices [41]. Hybrid piezoelectric composites for energy harvesting based on barium titanate (BT) is attractive because of its high-dielectric-constant ($\varepsilon \sim 2000$), low cost, natural abundance, and environmental friendliness. However, overcoming the limited flexibility and durability of the BT still remains an unavoidable challenge to be addressed for optimization of its energy harvesting performance. Consequently, several research groups have introduced some structural strategies for piezoelectric polymer design to enhance the piezoelectric efficiency by incorporating inorganic piezoelectric nanostructures as an effective piezo electron pathway [47]. Using this strategy the voltage and current outputs of the P(VDF-TrFE) nanofibers could be enhanced up to 200% by adding BT nanoparticles into the polymer matrix [25]. It was also reported that flexible piezoelectric energy generators based on PVDF-HFP/ BT composite film exhibited high electrical output up to $\sim 75$ V and $\sim 15$ $\mu$A [47]. Furthermore, a novel strategy was developed to improve the interface effect of PVDF/ BT nanocomposites to enhance energy density from 6.5 to 9.01 J cm$^{-3}$ [48]. Nevertheless, such polymer based energy harvesters still has limitation of complex fabrication methods and low flexibility which could be problems to expand their applications in wearable electronics. To solve these problems, we explore a novel approach to develop high performance textiles-based energy harvesting devices as next generation wearable energy generators and sensors. Here, different variation of textile designs from melt-spinning, knitting, weaving and braiding with the capability of low-cost, high production speed and high performance are developed.
The high-performance PVDF piezoelectric nanocomposites fibers with and without BT nanoparticles were produced through a melt-spinning process. The effect of BT nanoparticles additions on the piezoelectric properties of hybrid PVDF/BT fibers with different ratio of the BT nanoparticles was investigated by fabricated these fibers into triaxial braided energy harvester, as previously reported[^49]. The optimised PVDF/BT nanocomposite fibers were then used to create wearable woven and knitted energy harvester and strain sensors.

The wearable energy harvesting textile fabrics were made from developed piezoelectric fibers (Figure 1). A seamless feed-in process for integrating conductive fibers as electrodes with piezoelectric fibers was established to allow continuous fabrication of the energy harvesting textiles. As-fabricated knitted, triaxial braided and woven energy harvesting devices provide better mechanical properties (i.e. durability, flexibility and comfort) and piezoelectric performance in compare with PVDF fibers. The developed textile energy harvesting devices are durable, light and flexible and it is expected to be practical for wearable devices with high performance in the near future.

2. Results and Discussion

2.1. Morphology and characterization of PVDF and PVDF/BT nanocomposite

Scanning Electron Microscopy (SEM) was applied to reveal the morphological variations of PVDF/ BT films and fibers prepared with different ratios of BT to PVDF. As can be seen from Figure S1 (See supporting information for more details), an agglomerated structure occurred in the PVDF/BT nanocomposite film that were cast from solution and when the amount of BT nanoparticles was more than 10 wt% in the polymer matrix.

Both neat PVDF and hybrid PVDF/BT were prepared in a two stage process involving film casting followed by melt spinning. Films were cast containing 0, 5, 10 and 20 wt% of the BT nanoparticles. The as-prepared ground PVDF/BT nanocomposite film was fed into an extruder to aid homogenisation by shear forces and flow pressure. It was found that preparing nanocomposites with more than 10 wt% of BT was difficult due to the limited mobility of the
polymer chains even at the molten state and this method was not able to disperse the aggregated BT particles within the polymer properly.\cite{50} SEM micrographs of the as-spun PVDF and PVDF/BT nanocomposite fibers are shown in Figure 2. As can be seen from the surface morphology and cross-section (Figure 2 a-d), both melt-spun PVDF and hybrid PVDF/BT fibers are very smooth and without any observable porosity or voids. SEM images of the cross-section of PVDF/BT nanocomposite fiber shows a very dense structure with the uniform distribution of nanoparticles throughout the fiber (Figure 2 b, c). The BT nanoparticles in the polymer matrix can be seen clearly in the fiber cross-section at the higher resolution (Figure 2e). Figure 2f shows nanostructured BT nanoparticles. As is shown from elemental mapping analysis in Figure 2g (i, ii, iii), the hybrid nanoscopic structure of the melt-spun PVDF/BT was confirmed through the overlapped Ti, Ba, F mapping images (Figure 2g).

**Figure 2.** SEM images of the as-spun PVDF and PVDF/BT fibers a) surface of PVDF fiber, b) cross section of PVDF fiber, c) surface of PVDF/BT (10 wt%), d) cross-section of PVDF/BT at low and e) higher magnification. f) Nanostructured BT nanoparticles. (g) elemental mapping analysis performed on the hybrid PVDF/BT (10 wt%)
fiber cross-section area i) the location of titanate (Ti green dots), ii) barium (Ba red dots) and iii) Fluoride (F blue dots)

The phase transformations of the as-prepared PVDF and hybrid PVDF/BT fibers following different amounts of additive (BT) was scrutinised using FTIR, DSC, TGA and X-ray diffraction. Piezoelectric properties of PVDF fibers can be enhanced with a higher fraction of β phase. The FTIR results (Figure 3a) indicated that the ratio of the BT nanoparticles in the polymer matrix could effect β phase formation in the PVDF/BT nanocomposite fiber (Figures 3a). The vibrational bands at 764 cm$^{-1}$, 976 cm$^{-1}$ are attributed to the non-polar α phase, whereas the characteristic peaks at 841 cm$^{-1}$ and 1276 cm$^{-1}$ correspond to the electroactive β phase.$^{[51]}$ The relative fraction of the β-phase in a sample containing just α and β-PVDF can be calculated from the following formula$^{[52]}$:

$$F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta}$$

(1)

Where $A_\alpha$ and $A_\beta$ are the absorbance peaks at 766 cm$^{-1}$ (α-phase) and 840 cm$^{-1}$ (β-phase). The characteristic peaks of the α phase severely decrease in the PVDF/BT fiber in compared with the pure PVDF which signify that adding BT nanoparticles is a highly efficient method of inducing fraction of the polar β phase.
Figure 3. Characterisation of the melt-spun PVDF and PVDF/BT nanocomposite fibers with different percentage of BT nanoparticles (5%, 10%, 20% wt): a) FTIR spectra of PVDF and hybrid PVDF/BT fibers, b) The variation of the calculated β phase contents of the PVDF fiber as a function of the percentage of BT nanoparticles (%wt), c) X-ray diffraction patterns for PVDF and hybrid PVDF/BT fibers, and d) Stress–strain curves obtained from tensile tests of PVDF and PVDF/BT nanocomposite fibers.

The variation of β phase fractions for as-prepared PVDF and PVDF/BT nanocomposite fibers is shown in Figure 3b (also see Figure S2 in supporting information for the as-prepared PVDF/BT films). As can be seen from Figure 3b, the as-prepared PVDF/BT nanocomposite fibers exhibited a higher proportion of β phase compared to pure PVDF fiber. The β phase content increases from 51% for pure melt-spun PVDF fiber and reaches a maximum value of 98% for as-prepared PVDF/BT nanocomposite fiber containing 10 wt% of BT nanoparticles. The β phase content of the PVDF/BT nanocomposite fibers decreased as a result of increasing BT percentage for more than 10% wt. This phenomena could be explained through the effect of filler on the physical and mechanical properties of the polymer matrix. It was observed that
noticeable increase in β phase initiates from the interaction enhancement between the local electric field close to the nanoparticle filler and the PVDF dipoles.\textsuperscript{[53]}

However, increased defects for the case of too much BT content prevent segmental motion and asymmetrical β-phase formation which due to a decrease in $F(\beta)$ from PVDF/BT(10wt%) to PVDF/BT(20wt%).\textsuperscript{[52]}

The X-ray diffraction patterns in the 2θ range of 10-60° for PVDF and PVDF/BT nanocomposite (Figure 3c) show raising in the intensity ratio of the β to α phase for as-prepared PVDF/BT nanocomposite fiber in compar with PVDF fiber. Moreover, the peaks related to crystallization plane of the (020) and (110) reflect β phase formation at 20.6°, indicate the existence of α and β phase. Peaks at 20 ~ 22.2° which correspond to the (001) and (100) in as-prepared PVDF/BT nanocomposite fibers is an evident for tetragonal BT nanoparticles.\textsuperscript{[54]}

Due to the addition of BT modifications in the crystallinity of PVDF have been investigated on the basis of the obtained X-ray pattern. As the concentration of BT increases, the intensity of standard peaks in the X-ray pattern of PVDF decreases and slightly displaces towards shorter angle,. These peak shifts indicates the existence of specific interaction between the different phases of PVDF and BT.\textsuperscript{[55]} In addition, thermal analysis of the PVDF and hybrid PVDF/BT fibers specified that the crystalline structure formation in the as-prepared piezoelectric fibers are 41, 62, 65 and 48% for the as-prepared PVDF, PVDF/BT\textsubscript{5}, PVDF/BT\textsubscript{10} and PVDF/BT\textsubscript{20} fibers, respectively (See Figures S3, S4 and Table S1 in supporting information).

The as-prepared PVDF and PVDF/BT nanocomposite fibers have also been investigated to evaluate the effect of BT nanoparticles on the mechanical properties. During melt spinning and cold drawing process fiber are continually under tension which brings tenacity and elasticity for the final fibres.\textsuperscript{[56]} A comparison of the stress-strain curves for the various prepared fibers is given in Figure 3d. As can been seen from Figure 4 and Table S2 (See supporting information for more details), the ultimate tensile strength and elastic modulus of the prepared fibers have significantly increased for PVDF/BT\textsubscript{5} and PVDF/BT\textsubscript{10} compared to PVDF fiber. Young’s
modulus and tensile strength of the as-prepared PVDF/BT nanocomposite fiber with 10wt% BT is 130% and 170% higher than pure PVDF fiber, respectively (Figure 4a). The elongation at break of the as-prepared PVDF and PVDF/BT\textsubscript{10} nanocomposite fibers were 137% and 80%, respectively. These values are 685% and 400% higher than previously reported for melt-spun PVDF fiber \cite{49, 56}. The use of 20% wt BT nanoparticles in the polymer matrix produced PVDF/BT\textsubscript{20} fiber with significantly lower Young’s modulus and tensile strength compared with the PVDF fiber. These results confirm the reinforcing role played by BT nanoparticles in the PVDF fibers. However, the decrease in mechanical properties of the PVDF/BT\textsubscript{20} fiber with addition of more than 10% wt BT nanoparticles may be due to aggregation of nanoparticles and/or phase separation of the polymer (see Figure S1 in supporting information). This phenomena may introduce stress-concentration or low adhesion at the phase interface that would be lower the tensile strength and modulus\cite{57} \cite{58} \cite{59}.

![Figure 4](image.png)

**Figure 4.** Young’s modulus and tensile strength of PVDF and PVDF/BT nanocomposite fibers at different BT concentration.

### 2.2. Wearable energy generator and sensor performance

Initial evaluation of piezoelectric energy harvesting performance of the hybrid fibers used the triaxial braided textile structure described in our previously reported results.\cite{49} The dielectric
constant ($\varepsilon_r$) and dielectric loss ($\tan \delta$) of the as-prepared braided wearable energy generators were measured at room temperature in a frequency range up to $10^6$ Hz as shown in Figure 5a-b. It was reported $^{30, 52, 60}$ that piezoelectric properties of PVDF nanocomposite polymer could be significantly improved for the piezoelectric polymer with high dielectric constant and low dielectric loss due to enhancing its electroactive $\beta$ phase. The dielectric constant influences the performance of a piezoelectric power generator. Higher dielectric constants in harvester systems lead to larger power output.$^{[60]}$ It should be also noted that the piezoelectric coefficient is linearly proportional to the dielectric constant ($\varepsilon$) of the piezoelectric materials, i.e., $d_{33} \sim \varepsilon \Pr$, where $\Pr$ is the remnant polarization.$^{[61]}$ The dielectric constant of the braids prepared with the hybrid fibers was decreased with increasing frequency for all samples. However, the dielectric constant values were higher in braids made with higher BT content fibers due to the large dielectric constant of BT (Figure 5a). The gradual decrease in dielectric constant when measured at higher frequencies can be attributed to the reduction in dipole mobility where the dipoles are not sufficiently mobile to displace to the same extent when the frequency of the applied electric field exceeds the relaxation frequency.$^{[62]}$ On the other hand, the dielectric loss increased only slightly with increasing BT contents.

The dispersion of the BT nanoparticles into the polymer matrix increases the filler/polymer interfacial area and formation of the $\beta$ phase fraction and consequently increase dielectric properties and decrease loss tangent (Figure 5a-b). Electroactive $\beta$ phase formation can be explained by the surface charge/dipole interaction occurring between the BT nanoparticles and PVDF chains.$^{[63]}$ The BT nanoparticles surface charge contribute significantly in the electroactive $\beta$ phase nucleation procedure.$^{[64]}$

This step-like decrease in dielectric constant with frequency may be explained by the Maxwell–Wagner–Sillars interfacial polarization mechanism.$^{[65]}$
Figure 5. The dielectric properties of the as-prepared textile energy generator as a function of frequency: a) dielectric constant of the braided energy generator; b) loss tangent of the braided energy generator; c-d) dielectric constant and dielectric loss as a function of frequency for woven and knitted wearable energy generators based on PVDF/BT\textsubscript{10} nanocomposite fiber, respectively.

The voltage output of the braided PVDF and PVDF/BT nanocomposite fibers occurring as a result of mechanical deformation caused by repeated impact is shown in Figure 6 and Figure S7. Mechanical stimulation of the braid occurred by compressing the braid between a solid flat surface and platen that was driven vertically by an oscillating cam attached to a reciprocating motor. The amplitude and frequency of the cyclic compression were initially kept constant to investigate the effect of fiber composition on the piezoelectric output of the braided energy generator. An example of the developed braided energy generator device is shown in Figure 6a. As can be seen from Figure 6c, the voltage output of the triaxial braided energy generator was significantly improved due to synergistic effects of piezoelectric BT nanoparticles incorporated into the PVDF piezoelectric polymer. As-spun PVDF fiber generated a maximum
voltage output of 480 mV, while the voltage output of the braided PVDF/BT\textsubscript{10} fiber was found to be 1100 mV. This value is 229% and 250% higher, respectively, than PVDF fiber or previously reported for melt-spun hybrid PVDF/BT fiber with the same 10 wt% content of BT nanoparticles.\cite{49} \cite{19} The voltage output of the braided PVDF/BT\textsubscript{20} with more than 10 wt% BT nanoparticles generated a maximum voltage output of 895 mV which is much lower compared to the braided PVDF/BT\textsubscript{10} fiber. The voltage output can be estimated using the following expression:

\[
V = g_{33} \varepsilon Y D
\]

Which voltage output (V), strain (\varepsilon), Young's modulus (Y), piezoelectric voltage constant (\(g_{33}\)) and the fiber diameter (D) have the above relation. The D and \varepsilon are similar in all of the as-prepared hybrid PVDF/BT fibers, and the Y is higher in PVDF/BT\textsubscript{10} than that in PVDF/BT\textsubscript{20} nanocomposite fibers (~891 and 412 MPa, respectively). The measured V is higher in the as-prepared PVDF/BT\textsubscript{10} fiber than that in PVDF/BT\textsubscript{20} fiber, but the combined analysis indicates the \(g_{33}\) is much larger in PVDF/BT\textsubscript{20} than in PVDF/BT\textsubscript{10} meaning the piezoresponse in PVDF/BT\textsubscript{20} fibers is more sensitive to external stress.\cite{52}

Adding piezoelectric nanoparticles to the polymer matrix can negatively affect the piezoelectric performance of the composite because of the positive and negative piezoelectric co-efficient of BT nanoparticle and PVDF polymer and canceling their effect.\cite{30, 60, 66}

The voltage output of the braided PVDF/BT\textsubscript{10} energy generator device under cyclic impact was further investigated. The generated positive and negative pulse signals corresponding to the pressing and releasing process during a cyclic impact is shown in Figure 6b which was selected and magnified from Figure 6c in the colored background region.
Figure 6. a) Digital photograph of triaxial braided piezo fibers: i) illustration of energy harvesting mechanism, ii) a bobbin of flexible triaxial braided energy harvester, b) effect of BT nanoparticle content (wt%) on open circuit voltage of the as-prepared triaxial braided piezo fiber energy generators, c) the magnified image of the open circuit voltage in the region of 101–106 s for the braided PVDF/BT\textsubscript{10} nanocomposite fiber, d) the voltage output and power dependence on the load resistance of the braided PVDF/BT\textsubscript{10} which was obtained at an impact pressure of 0.0031 MPa.

A graph of instantaneous power at different load resistances is shown in Figure 6d. The power generated by the as-prepared PVDF and PVDF/BT nanocomposites fibers was calculated through:

$$P = \frac{1}{T} \int \frac{U^2(t)}{R} \, dt$$ \hspace{1cm} (3)

where $U(t)$ is the real-time voltage integrated over time $t$, $R$ is the external load resistance, and $T$ is the period of load application.\textsuperscript{[67]}

With further increasing load resistance, the voltage starts to increase up to 3V at the load resistance of 1000 kΩ. As a power source, the developed triaxial braided PVDF/BT\textsubscript{10} piezo fibers reaches the maximum power output of $\sim 0.21 \mu$W when the load resistance equals to 400
kΩ. Although fibers output impedance based on the measured voltage and current output is ~1MΩ but it is covered with internal resistance of the Keithley which was used for measuring these data. The amount for the load resistance is in the range according to the latest researches [68] [69] [70] which depends on the filler type and sample thickness.

To demonstrate the feasibility of harvesting energy using the flexible triaxial braided piezo nanocomposite fibers a bridge rectifier (4 diodes of 1N5817) was placed in the circuit to feed a different capacitor under mechanical pressures (Figure 7a). While this was the more conventional approach adopted for this development stage, one can find a higher efficient circuit by Mirvakili et al.[71] Harvesting energy has a close relationship with the diode characteristics, and a diode with low reverse leakage current is favourable so that the Schottky diode 1N5817 is one the best options at this stage of development. For future, and more extreme target conditions, other more suitable options for higher frequency rates and lower drop voltages are recommended, e.g. Avago HSMS-285C or SDM03U40.

**Figure 7.** a) Equivalent of the full wave rectifier circuit for charging a capacitor with resistance 430 kΩ, b) Charging of the different capacitors by the power generated from the four parallel connections of the braided
PVDF/BT₁₀ under periodic impact pressure, c) Charging–discharging (V–t) graph of one triaxial braided piezo PVDF/BT₁₀ structure across capacitor 10 μF and d) Resistor-capacitor (RC) graph for charging capacitor in experimental and simulated fit for magnified part of charging graph C.

different capacitors (0.68, 2.2, 10 and 22 μF) charging performances were carried out upon mechanical force on the triaxial braided piezo nanocomposite fibers (PVDF/BT₁₀) in a RC circuit (Figure 7b) and it is observed that the build up voltage increases exponentially and reaches a steady state as shown in Figure 7b. In order to calculate the voltage across the capacitor (as shown in Figure 7d) during charging capacitor, Equation 4 was used which related to RC circuit charging:

\[ V_c(t) = V(1 - e^{-\frac{t}{RC}}) \]  \hspace{1cm} (4)

Where \( C \) is the capacitance of the capacitor, \( R \) is the resistance in RC circuit. The time constant (\( \tau = RC \)) in experimental and theoretical, have a good correlation with each other as shown in Figure 7d. A slight difference may be due to the power consumption by the measuring unit present in the device during the measurements.
The voltage output performance and the voltage profile of the charged capacitor (10 µF) using as-prepared wearable energy harvester based on PVDF/BT$_{10}$ fibers a); woven energy generator, (a$_1$) voltage output vs time for woven generator (a$_2$) charging voltage vs time for woven generator, b); triaxial braided energy generator (b$_1$) voltage output vs time for braided generator, (b$_2$) charging voltage vs time for braided generator c); circular knitted energy generator, (c$_1$) voltage output vs time for knitted generator, (c$_2$) charging voltage vs time for knitted generator.

The comparison of braided energy generators prepared with different hybrid fibers indicated that the PVDF/BT$_{10}$ composition provided optimal performance and these fibers were then used to prepare knitted and woven textiles, as shown in Figure 8. The storage energy calculated for different as-developed energy harvesters in the capacitor was determined using capacitor potential energy formula:

$$E = \frac{1}{2} CV^2$$  \hspace{1cm} (5)

Where $C$ is the capacitor capacitance, $V$ is the charging voltage across the capacitor under steady state condition at a definite time ($t$).\textsuperscript{[72]} The energy storage based on the as-fabricated
textiles energy harvesters (woven, triaxial braided and circular knitted structures in Figure 8) in 10 μF capacitor were found to be 61.25, 2.81 and 36.45 μJ, respectively. The energy conversion efficiency of the as-developed triaxial braided PVDF/BT_{10} energy generator can be estimated as,

$$\eta = \frac{E_s}{E_x \times n_{cy}} \times 100$$  \hspace{1cm} (6)

Where $E_s$ is the total energy stored in capacitor (Equation 6), $E_x$ is the input mechanical strain energy during a single cycle and $n_{cy}$ is number of impact cycles to charge the capacitor. \[^{[73]}\] Based on the equations and the charging process of the 10 μF capacitor, the energy conversion efficiency of the as-developed triaxial braided, circular knitted and woven energy generators are calculated as 27%, 29% and 40%, respectively (see Discussion S1 of the Supporting Information for more details). The obtained results suggested that the developed textiles energy harvester would establish the viability of such wearable piezoelectric energy generators in real life applications. The knitted PVDF/BT_{10} energy generator was able to charge a 10 μF capacitor in just 400s under periodic impact and relaxation (Figure 8c2). The obtained results are very promising compared to previous reported systems (See Table S3 in the supporting information). The circular knitted structure enables the ready integration of electrodes into the triaxial structure (inner and outer electrodes) which could enhance the collection of charge and energy conversion.

The force sensitivity and power output of the wearable energy harvesters based on PVDF/BT_{10} textile structure were compared, as shown in Figure 9a. The sensitivity of the wearable energy generators were assessed by a ratio of voltage output to the applied force when the textiles were subjected to compress using repeated impact as shown in Figure S7.\[^{[49]}\] The voltage output of the piezoelectric textiles were proportional to the applied force. It was found that the force sensitivity of the textile energy harvesters were 3, 4, and 10 V/N for woven, braided and knitted
energy generators, respectively. The results revealed that the knitted energy generators exhibited an almost 6.3-fold increase in the value (10 V/N) compared to the recent reporte\textsuperscript{[49]}. The power output of the wearable energy harvesters were found to be 36.2, 38.8 and 87 µW/cm\textsuperscript{3} under a periodic compression for woven, braided and knitted energy generators, respectively. The power output density of the woven wearable energy generator was significantly enhanced and it was 294\% and 4578\% higher than previous reporte for braided and woven piezoelectric energy generators, respectively.\textsuperscript{[49,56]} (See Table S4 in the supporting information). The novelty of circular knitting and braiding techniques for piezoelectric fibers is their packaging structures which interwinded fibers to each other and due to more durability and flexibility. The experimental results in our previous work \textsuperscript{[49]} confirmed the stability performance of the triaxial braided piezoelectric fibers in the bending test during 1000 cycles to a maximum strain of 50\% at 0.6 Hz with no change in its performance.

The obtained results suggested that developed wearable energy generators would be able to charge the capacitors to a certain voltage under a specific time for the self-powered electronic devices. Consequently the integration of the developed wearable energy generator with energy storage device (i.e. rechargeable battery or capacitors) can be of great potential for practical applications, including development of self-powered wireless sensors within garments and monitor the status of human health.
In addition, developed wearable energy generator prototype device was used as the integration of garment for self-charging power a rechargeable battery or capacitors. Figure 10 shows the performance of the developed energy generator when integrated into garments for biomechanical energy harvesting and storage during walking and/or running. The voltage output of the wearable energy generator could be tailored in the range of 300 (Walking) to 1000 mV (Running) as shown in Figure 10b. As can be seen from Figure 10c, the wearable energy generator could increase the voltage of the storage capacitor from 0 to 25 mV in 20 sec so that the 10 µF capacitor was fully charged after approximately 25 steps at a running frequency of 1.2 Hz. This fast charging rate is 4 and 6 times faster compared to previously reported for the nanofiber piezoelectric PVDF/BT energy generator and hybridized energy conversion and storage based on PVDF film. The choice of 10 µF was sufficient to demonstrate full charging of a capacitor at this stage of development, with minimum input (25 steps), a higher storage (> 500 µF) is recommended for applications outside the laboratory, e.g. sports training demonstrators. In such cases, it is also recommended to increase the voltage of the output of the system through a selection of approaches, e.g. by implementing voltage multiplication, parallel charge-serial discharge techniques.
We have explored the potential applications of the developed wearable energy harvester as movement sensors. As demonstration examples, both wearable and portable textile sensors have been developed as shown in Figures 11-12. Wearable movement sensors are useful for real-time precise healthcare applications. Here a knee sleeve prototype device from a woven PVDF/BT$_{10}$ nanocomposite fibers was established to support personal recovery after an injury (Figure 11 and Movie S1). A wireless data acquisition board could be assigned to the developed knee sleeve prototype device for data transmission of knee flexion resulting from tension and bending of the woven textile sensor. As can be seen from Figure 11a and Figure 11b, the developed knee sleeve prototype device generated a voltage output that varied with knee bending angle from the initial (zero bending Figure 11a), bent (45° bending Figure 11a$_1$) and bent (90° bending Figure 11a$_2$). A voltage divider used to connect an expansion board (AnEx
board) and a portable wireless device. The AnEx board can be attached to the knee sleeve and linked to it by an external connector. The collected data can be transferred via Bluetooth to a laptop for signal analysis.

![Photograph of the developed portable knee sleeve based on wearable woven PVDF/BT<sub>10</sub> piezoelectric sensor](image)

**Figure 11.** Photograph of the developed portable knee sleeve based on wearable woven PVDF/BT<sub>10</sub> piezoelectric sensor; a) wearable strain sensor at initial zero bending, a<sub>1</sub>) bent at 45°, a<sub>2</sub>) bent at 90°, b) The generated voltage associated with repeated knee bending and unbending to the maximum angle of 0°, 45° or 90°, as indicated.

To demonstrate potential applications of the developed circular knitted piezoelectric strain sensor for the detection of human and/or industrial activities, knitted wearable piezoelectric fibers were assembled into two wearable sensors with the required structures to track these activities as shown in Figure 12. The sensing performance of the developed knitted piezoelectric PVDF/BT<sub>10</sub> fibers based on assembling core-sheath structure has been evaluated as shown in Figure 12a. The performance of the potential real life applications of the developed wearable sensor under biomechanical pressure of periodic finger pressure and relaxation was demonstrated in Figure 12a<sub>1</sub>-a<sub>2</sub>.
Furthermore, the versatility of circular knitted piezoelectric PVDF/BT10 sensors was demonstrated by knitting the textile with seamlessly integrated electrodes (Figures 9 b and 12 b). Sequentially feeding silver coated nylon, followed by PVDF/BT\textsubscript{10} fibers and then again silver coated nylon into the knitting machine produced the textile structure shown in Figure 12 b. This textile was coated with silicon resin to enhance its durability as well as creating new applications such as hydraulic and/or pneumatic pressure sensors. The performance of the silicon coated knitted piezoelectric sensor under biomechanical pressure of periodic finger pressure and relaxation was shown in Figure 12 (b\textsubscript{1}-b\textsubscript{2}). The response time of the silicone coated knitted sensor (Figure 12 b\textsubscript{2}) was significantly improved (2.5 sec) as compared to core-sheath knitted structure (5 sec) in Figure 12 a\textsubscript{2}. In addition, the capability of the silicone coated knitted piezoelectric structure as hydraulic and/or pneumatic pressure sensors was demonstrated in Figure 12 c,d and Movie S2. As can be seen from Figure 12 (c-c\textsubscript{1}), the developed knitted sensor was subjected under hydraulic pressure where 2 ml water was pumped into the developed hollow structure (5 mm diameter and length of 20 mm) and it exhibited very fast response time (~ 2 sec) with higher voltage output compared to other (Figure 12 a\textsubscript{2} and b\textsubscript{2}). Figure 12 (d-d\textsubscript{2}) show knitted sensor under pneumatic pressure of 20 kPa. The development of silicon coated circular knitted piezoelectric structure capable of sensing pressure these stimuli is of great importance for various application such as heart rate detection, pressure monitoring, strain gauges, robots, etc due to its ability to response to bending, twisting, and compression motion. More importantly, developed processing method is scalable for the fabrication of industrial quantities of strain sensing and smart textiles.
3. Conclusion

In summary, smart textiles based on wearable knitted, braided and woven energy generators and sensors were developed from nanostructured piezoelectric nanocomposite fibers. Hybrid piezoelectric PVDF fiber with and without barium titanate nanoparticles were developed.
through a melt-spinning process. It was found that high-performance hybrid PVDF/BT\textsubscript{10} piezofiber with 98% of the electroactive β-phase generated a maximum output open circuit voltage of 4V and a power density 87µW/cm\textsuperscript{3} during cyclic compression. These energy generator could charge a capacitor (10 µF) 6 times faster than previously reported. In addition, the wearable textile-based piezo sensors were utilized and designed for various sensing response including hydraulic and/or pneumatic pressure sensors with tunable sensitivity.

The demonstrated processing method is scalable for the fabrication of industrial quantities of strain sensing and energy harvesting smart textiles.

4. Experimental Section

Materials

The piezoelectric polymer powder provided by brand name Solef 6010 was from Solvay Soleris (Milan, Italy). Barium titanate piezoelectric nanoparticles with the mean diameter of 50 nm and with 99.9% trace metals basis were purchased from Sigma Aldrich Company (China). N,N-dimethylformamide (DMF, >99.8%, Merck) as the solvent was used. Silver plated polyamide yarn (235/36dtex 4 ply) supplied from Shieldex USA. Woven and knitted conductive fabric, which are silver plated nylon with weight 80 gr/m\textsuperscript{2} purchased from core electronics Australia.

Nanostructured Hybrid PVDF/BT films

To optimise ratio of BT nanoparticle into PVDF polymer matrix for enhancing piezoelectric and mechanical properties of the hybrid PVDF/BT fibers, we have prepared PVDF/BT nanocomposite films with different amount of BT nanoparticle. To prepare PVDF/ BT nanocomposite, first 30 g of PVDF powder was dissolved into DMF (200 ml). A clear and transparent solution was obtained upon continuous stirring on heater in water bath at 70 °C during overnight. To prepare PVDF/BT nanocomposites solution with different amount of BT nanoparticle wt% (i.e 5, 10, 15, 20 and 25), the BT nanoparticles were dispersed into DMF (50 ml) using a probe sonicator for 60 min under nitrogen flow at 0°C then dispersed BT was added to the as-prepared PVDF (15 wt%) solution and to form a stable suspension, sonicated for
30 min under nitrogen flow at 0°C then stirred for 2 h. The suspensions were casted onto a clean glass plate and after evaporation of the solvent, the film was peeled off from the dish. The resultant composite was chopped into small pieces finally to have homogenous mixing, then the chopped film was ground finely and used for further characterizations. Hybrid PVDF/BT nanocomposites films with different percentage of BT nanoparticles were obtained using film casting method with the thickness of 440 µm and dimensional of 4 × 2 cm. (see Fig.S1 in the Supporting Information). All as-prepared sample were subjected to cold drawing process as post treatment at 80°C which did increase the sample length by 13%.

*Melt-spinning of PVDF and PVDF/BT nanocomposites fibers*

The PVDF and PVDF/BT nanocomposites fibers were produced through melt-spinning process. As-prepared PVDF/BT nanocomposite films which were prepared through film casting were used to produce the met-spun fibers. The met-spinning of PVDF with and without BT were performed with a twin screw extruder (Barrel Scientific Ltd.) and a spinneret with a hole diameter of 3 mm as illustrated in Figure S5 and Movie S3 (Supporting Information). The grounded nanocomposite powder was at the temperature of 70ºC overnight and then fed into the extruder. In order to achieve uniform fiber feeding powder to the spinneret was controlled. The temperature for the nine sequential zones of extruder set from 180 to 220°C. Melt-spun PVDF/BT nanocomposite fibers containing 5, 10 and 20 wt% of the BT were prepared (labelled PVDF/BT_x, where x = 5, 10, 20 is the wt% of BT into the PVDF polymer, (PVDF/BT_5, PVDF/BT_10 and PVDF/BT_20)). The final diameter of the stretched PVDF and PVDF/BT nanocomposite fibers was ~170 µm.

*Fabrication of Wearable Energy Harvester*

We demonstrate the scalability and tuneability of the textile fabrication approach for generating wearable energy harvesters that offer an extra design dimension in constructing and optimising piezoelectric modules, yet this is a totally unexplored area. The textile structure determines the
mode of deformation at the individual fibre level (bending, twisting and/or stretching), allowing the tuning of fibre properties to maximise both mechanical and power-generating performance. Consequently manufacturing of the wearable energy generator and sensors were carried out using conventional textiles production including knitting, breading and weaving techniques.

Knitted wearable energy harvesters

Knitted wearable sensors and energy generator based on as-prepared nanostructured PVDF and hybrid PVDF/BT fibers have been developed using a Harry Lucas circular knitting machine with the head size of 1/12 in, gauge, 28 and 20 needles. A feeding tension setting of 10 and pickup tension of 32 was applied to fibers and knitted structures respectively. The linear density of the as-prepared knitted structure was 0.034 gr/cm. As can be seen from Figure 13 and Movies S4 (see supporting information), as-prepared melt-spun piezoelectric fibers shown superior mechanical properties and comparable with commercially available fibers which enables to be utilized in knitting machine with the requirement of the applied mechanical stress and strain during the knitting process. To assembly of the knitted wearable energy harvester device, the commercially available woven conductive fabric as inner and outer electrodes with thickness of 80 µm was embedded inside and outside of the knitted structure. The use of the circular knitting would be able to provide more protection (i.e short circuit) for the knitted wearable devices due to surrounding inner electrode by knitted structure. In addition stripes electrodes could be fabricated into knitted structure as needed and for example a wearable knitted device with two knitted electrodes into the structure has been developed (see Figure 9b).
Figure 13. a) The process for producing a knitted structure by circular knitting machine, b) Circular knitted structure of PVDF/BT fiber, c) magnified image of loops formation in knitted structure, d) optical photograph of the circular knitted piezo generator (i) conductive woven fabric as electrodes and (ii) knitted PVDF/BT fiber as the middle layer.

Braided wearable energy harvester

Wearable energy generator and sensors based on as-prepared PVDF and hybrid PVDF/BT fibers have been developed using a braiding technic. Manufacturing of the triaxial braided energy harvester was accomplished using a Trenz-Export braiding machine in a multi-step process. The fabricated triaxial braided structure is illustrated in Figures 14. A silver coated Nylon (235/36 dtex 4 ply thread) was used as the core electrode along the length of 12 braided PVDF fibers. Finally to provide outer electrode, the whole structure covered with 12 silver coated nylon fibers using braiding machine. As we previously reported[49], the developed triaxial piezoelectric energy generator has the ability for mass production to supply required
power. Moreover, novel packaging of the triaxial braided structure to protect PVDF fibers and electrodes provides more durability for the piezoelectric energy generator device.

![Figure 14](image)

**Figure 14.** Micrograph of the as-developed triaxial braided piezo generator; (i) silver coated nylon as electrodes and (ii) PVDF fibers in braided structure as the middle layer.

**Woven wearable energy harvester**

Wearable energy generator and sensors based on as-prepared PVDF and PVDF/BT nanocomposites fibers were developed through weaving process. The preparation was based on plain weave structure which is each weft yarn passes above and below (riser and sinker) the warp yarns repetitively so formed a simple cross pattern (Figure 15).

In the plain weave the short length of yarn intertwined between warp and weft yarn which leads to have fabric with high density and consequently prevent short circuits between two electrodes. Moreover, the plain weave structure has homogeneous surface to provide moderately constant electrical properties.[75]

The thickness of developed PVDF and PVDF/BT woven structure was 260 µm. The linear density of as-prepared PVDF and PVDF/BT woven structure were 0.057 and 0.029 gr/cm² respectively.

To assembly of the woven wearable energy harvester device, the commercially available woven conductive fabric as electrodes with thickness of 80 µm was attached to the top and bottom of
as-prepared fabric using sewing machine. (Figure S6) (See supporting information for more details.)

![Figure 15. Woven structure of: a) pure PVDF fiber, b) PVDF/BT fiber and c) magnified image of PVDF/BT woven structure](image)

**Poling Process**

To enhance piezoelectric performance of the developed wearable energy harvesters, the electric poling procedure for both PVDF and PVDF/BT structures was carried out. For the wearable triaxial braided structures, the poling has done in radial direction (inner and outer electrode) for 25kV DC at 80°C, which is equal to the 37 Mv/m of the electric field as previously reported [49]. The poling process for the knitted and weaved structure also carried out by applying voltage on conductive fabric as top and bottom of the as-prepared structure at the above conditions.

**Sample Excitation Method**

An in-house setup was made to performance assessment of all three piezoelectric textile structures which could apply periodic impact force. An illustrative graph of the measurement system and assembly details is shown in Figure S7. In order to reduce the interference of triboelectric charges, the samples and impact head were covered with tape. Continues force applied in frequency of 1 Hz. A Nema stepper motor run by Ultimate board was used as the impact power source, and the generated open-circuit voltage and short-circuit current were collected with a Keithley (2612B, USA) system simultaneously.
Characterizations
Differential scanning calorimeter (DSC) (TA Instrument) at a heating rate of 10 °C/min used to measure melting temperature ($T_m$) and melting enthalpy ($\Delta H_m$) of the fibers. The characteristics crystalline phases of PVDF fibers was examined through Fourier transform infrared spectroscopy (FTIR, Shimadzu IR, ATR mode) study over a range of (400–4000) cm$^{-1}$. X-ray diffraction (XRD GBC, MtriX SSD,) was carried out to identify the crystal phase of materials. Surface morphology of the fibres were examined with the field emission scanning electron microscopy (SEM, JEOL 7500). Leica M205A stereo microscope used to measure fibers diameters. The mechanical properties of the fibers were measured using a Shimadzu tensile tester (EZ-S). The samples were mounted between two grips and were subjected to tensile test with the strain rate of 10 mm/min.

The electrical response of piezoelectric sample was measured by a Picoscope 4424 digital oscilloscope (Pico Technology) and 2612B Source Measure Unit (Keithley, USA). Dielectric loss and impedance properties were measured with a precision impedance analyzer (4294A, Agilent Technologies, Inc.) at room temperature with a frequency range from $10^2$ to $10^5$ Hz.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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