ACS APPLIED ELECTRONIC MATERIALS

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Polymer Biowaste Hybrid for Enhanced Piezoelectric Energy Harvesting

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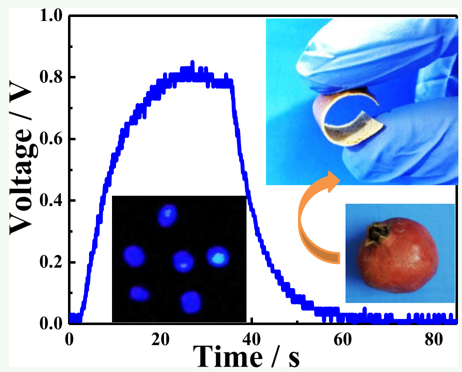
Cite This: *ACS Appl. Electron. Mater.* 2020, 2, 1426–1432 Read Online

ABSTRACT: A green composite, derived from the biowaste pomegranate peel, is used for piezoelectric energy harvesting. A hybrid of poly(vinylidene fluoride) and pomegranate peel powder is prepared through a solution route. A structural change of the polymer matrix from the nonpiezo to piezoelectric phase in the presence of a filler has been revealed through X-ray diffraction, spectroscopic, and calorimetric studies. Piezoelectric biowaste induces piezoelectricity in the polymer matrix, which is further confirmed through a range of morphological studies (optical, electronic, and atomic force microscopy). A model has been developed to focus on the synergism between two piezoelectric phases (matrix and filler), which is appropriate for energy harvesting. A device has been fabricated using the hybrid, which exhibits a high open circuit voltage and a power density of 65 V and 84 μW/cm^2. The developed device is also able to generate power under human movements such as walking, twisting, and bending, and the power is sufficient to light up LEDs and can be stored using a capacitor.



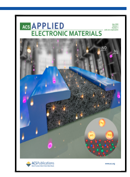
KEYWORDS: *device, energy harvesting, hybrids, biowaste pomegranate peel, nanogenerator*

1. INTRODUCTION

Energy, especially the electrical energy, is very important to endure our daily life activities and various industrial processes. The demand for energy is increasing day by day with the growing population and simultaneous industrial developments. Still now, the demand for energy is being fulfilled using fossil fuels such as petroleum, coal, and natural gases. However, with depletion of the fossil fuels and the increase of atmospheric pollution levels, there is an urgent requirement for alternative energy resources.[1] On the other hand, there are lots of biowastes, which are causing landfills and increasing the pollution level at the same time. Most of the biowastes contain natural fibers that have enormous potential for their uses in the energy sector. Therefore, utilization of the biowastes is one of the alternatives especially in the form of green composites, derived from the natural materials, or the bio-wastes and a material, which can bind in a better way. Polymeric materials are best known for their binding ability and some of them are well known to be induced in the electroactive phase by the second component. Furthermore, natural fibers have advantages over synthetic fibers for example glass fibers or carbon fibers in terms of their light weight, low cost, and eco-friendliness. Extensive work has been going on in this area to search for a possible substitute of the synthetic fibers or materials typically for energy generation. Researchers have used natural or biowaste materials for energy-harvesting purposes with and without using a polymer matrix. Ghosh et al. used fish scale[2] and fish swim bladders[3] for generating electricity under mechanical strain and meager output powers of 1.14 and 4.15 μW/cm^2, respectively, have been obtained. Tamang et al.[4] used DNA in a poly(vinylidene fluoride) (PVDF) matrix to prepare a nanogenerator for energy harvesting and a moderate power of 11.5 μW/cm^2 is obtained. Maity et al.[5] prepared a sugar-encapsulated PVDF nanofiber web that produced a power output of 33 mW/m^2 only. Kumar et al.[6] used nanohybrids of PVDF and fish scale and obtained a power of 28.5 μW/cm^2. In one of our studies, a power output of 55 μW/cm^2 using a PVDF and egg shell membrane hybrid was reported.[7]

In the present study, biowaste pomegranate peel has been used for energy generation after molding it in a polymer template, which is very flexible but tough enough to withstand under constant load. Pomegranate peel, a biowaste, is a by-product of juice and syrup industries or obtained from its consumption as fresh fruit,[8,9] and has been used as an antibacterial agent,[10,11] an antioxidant,[12] and in different other ways.[8,13] In this study, biowaste pomegranate peel has been used as a green composite of a polymer to induce piezoelectricity in the binder polymer. PVDF is a useful

Received: March 11, 2020
Accepted: May 5, 2020
Published: May 5, 2020



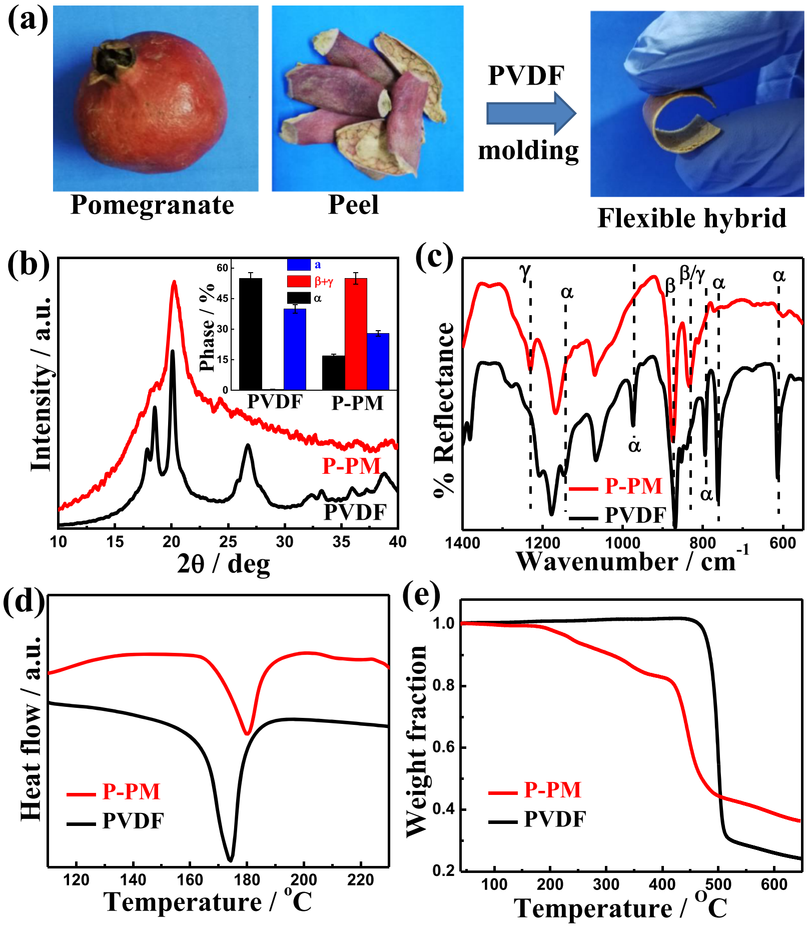


Figure 1. (a) Photographic image of pomegranate, its peel, and hybrid with PVDF, showing its flexible nature; (b) X-ray diffraction pattern of PVDF and hybrid indicating the β/γ phase in the hybrid, the inset indicates the various phase fractions in the hybrid in comparison to pure PVDF; (c) FTIR spectra of PVDF and the hybrid indicating different peaks corresponding to various phases; (d) differential scanning calorimetric patterns of PVDF and its hybrid; and (e) TGA thermograms of pure PVDF and the hybrid showing thermal stability of the hybrid.

polymer and has the capability to alter its structure in the presence of a filler in its hybrid form.[14−16] A device has been fabricated using the hybrid piezoelectric material to demonstrate its superior power generation capability using waste mechanical energy from human body movements and normal activities.

2. EXPERIMENTAL SECTION

2.1. Materials. Seasonal pomegranate was purchased from a local market, Commercial SOLEF 6008, PVDF was kindly supplied by Ausimont, Italy. The solvent, Dimethyl formamide (DMF), was purchased from Hi-media. Poly(dimethyl siloxane) (PDMS) for encapsulation of the device is purchased from Ellsworth adhesives, India.

2.2. Hybrid Preparation. Firstly, the pomegranate is peeled and its edible part and peels are separated. The peels are then dried and crushed to a fine powder, which is used as a filler for hybrid preparation. PVDF and pomegranate peel powder are weighed to desired concentrations for preparing a hybrid. Hybrids having 10, 20, and 40 wt % of the pomegranate peel powder (PM) content were prepared. For hybrid preparation, first PVDF was dissolved in DMF and in a separate beaker, the PM was dispersed in DMF. When the PVDF is completely dissolved in DMF, both the solutions were mixed and stirred for 4 h for complete mixing. The solution was then sonicated and poured into a Petri dish for drying and a trace amount of solvent was removed by further keeping it in a vacuum oven overnight at 50 °C. The hybrids with 10, 20, and 40 wt % of the PM content are labeled as P-PM-10, P-PM-20, and P-PM-40, respectively. This is to mention that the hybrid having more than 40 wt % PM is very brittle and, therefore, is avoided to use further.

2.3. Device Preparation. A smooth rectangular sample (1×1 cm^2) is cut from the film prepared and is coated with conducting silver paste on both the sides. Then copper electrodes are attached on both the sides for measurements. The assembly is then covered with polypropylene tape. The prepared device is then encapsulated with PDMS to protect it from external damage. The impedance of the probe is the same as of an oscilloscope, which is 1 MΩ. The impedance of the probe and the oscilloscope should be properly matched to prevent the signal loss.

2.4. Characterization. *2.4.1. X-ray Diffraction.* A Rigaku Miniflex 600 X-ray diffractometer is used to obtain the diffraction pattern at a voltage of 40 kV and a current of 15 mA using Cu Kα radiation (λ = 1.54 Å) at a scan rate of 3°/min. Three to five samples are used for the measurement for good error estimation.

2.4.2. Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) is performed at room temperature from 650 to 4000 cm^{-1} using a Nicolet 5700 instrument with a resolution of 4 cm^{-1} in ATR mode.

2.4.3. Scanning Electron Microscopy. Surface morphology of the sample is obtained by using a scanning electron microscope (SEM; SUPRA 40, Zeiss). The sample was gold coated before observation using a SEM. Polarized optical microscopy: A Leica polarized optical microscope is used to obtain the optical images. Thin film samples (~40 μm) are prepared for imaging.

2.4.4. Atomic Force Microscopy. Atomic force microscopy (AFM) is performed to investigate the changes in the surface morphology using NTEGRA Prima, NT-MDT.

https://dx.doi.org/10.1021/acsaelm.0c00197
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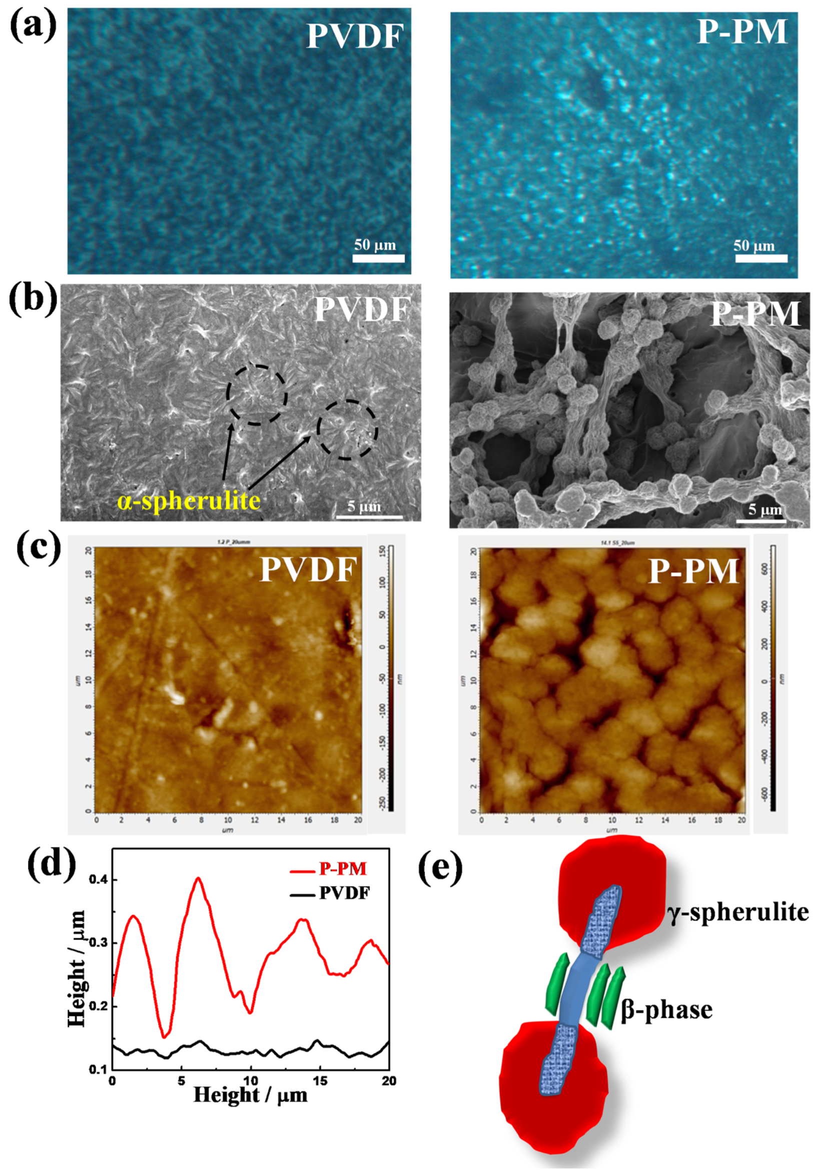

Figure 2. (a) Polarized optical microscopic images of PVDF and the hybrid (as cast film), the bright fringes in the hybrid indicate greater birefringence arising from the γ-phase; (b) scanning electron microscopic images of PVDF and the hybrid, α-spherulite of pure PVDF is encircled while the fibrous and globular morphology is observed in the hybrid; (c) AFM images of PVDF and the hybrid showing the globular morphology of the hybrid; (d) average height profile of pure PVDF and the hybrid surface indicating the rough surface in the hybrid; and (e) schematic diagram of crystallization of PVDF on the peel fibers along with different electroactive phases (induced crystallization) as observed in the SEM and AFM images.

2.4.5. Power Measurement. The output voltage from the devices under mechanical load is measured under different resistances for power calculation and the power is calculated using the relation $P = V^2/R$. A digital storage oscilloscope (TBS-1072B) is used for voltage measurement.

3. RESULTS AND DISCUSSION

The pomegranate peels, a major biowaste, are transformed into the powder form and a hybrid with PVDF has been prepared through the solution route. Figure 1a shows the flexible and tough hybrid film, which can sustain the high impact load. The X-ray diffraction (XRD) pattern of the pomegranate peel powder is shown in Figure S1, showing its crystalline nature. Figure 1b shows the XRD patterns of pure PVDF and its hybrid (P-PM). Pure PVDF has its characteristic peaks at 17.6, 18.3, and 19.9° because of the presence of the α-phase,[17,18] while the hybrid shows 18.6 and 20.2° peaks because of the phase changeover from α to β and γ, respectively, in the presence of pomegranate peel.[19,20] Both β and γ-phases are polar and piezoelectric in nature and the filler (PM) induces the β and γ-phase in the PVDF molecules through epitaxial crystallization. The total piezoelectric phase fraction in the hybrid is calculated from the deconvolution of XRD peaks and is found to be ~55%. Multiple measurements are done to estimate the actual electroactive phase content. For example, five samples are tested for the P-PM sample and the electroactive phase fractions are calculated to be 55, 57, 53, 55, and 54%. Hence, the average value of 55% is reported and the error limit is shown in the inset of Figure 1b. The appearance of both the piezoelectric phases (β- and γ-phase) and the decrease in the α-phase in the hybrid (P-PM) are evident from the FTIR spectra (Figure 1c). Pure PVDF in its

https://dx.doi.org/10.1021/acsaelm.0c00197
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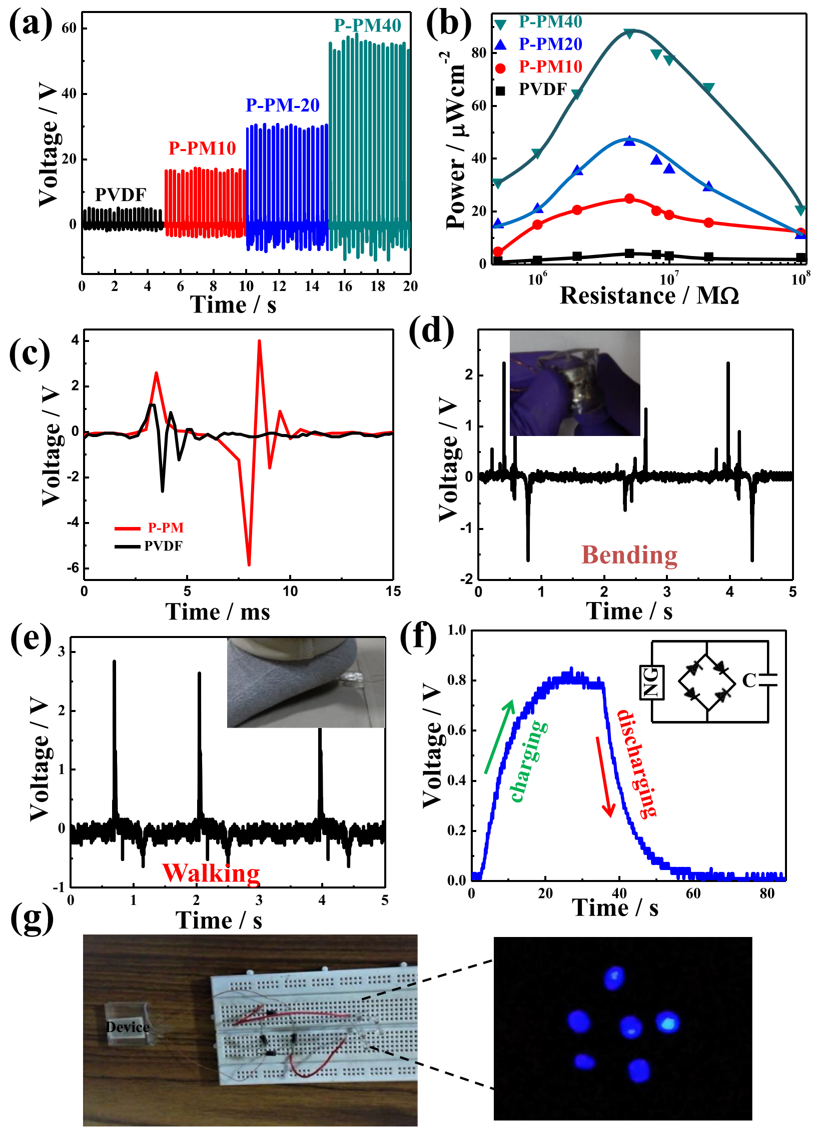

Figure 3. (a) Open circuit voltage of the devices made of PVDF and its hybrids with various compositions (filler content); (b) corresponding power density from the devices made of pure PVDF and hybrids with different filler contents as a function of applied resistance/load. (c) Voltage response from the device by using it as a cantilever. Voltage generation from the device made of the hybrid under human body movement *e.g.* (d) bending and (e) walking. Inset images show the application of load on the devices; (f) capacitor charging and discharging out of the electricity generated from the device under finger tapping mode of load; and (g) LED lightning and the corresponding circuit demonstrating the efficiency of power generation from the device.

α-phase shows the peaks at 610, 760, 795, 972, and 1144 cm^{-1}[17,18] while the hybrid shows the peaks at 840, 878, and 1232 cm^{-1}, out of which the peak at 840 cm^{-1} is a combined peak of the β and γ-phases.[19,21] The peak at 878 cm^{-1} is the distinctive peak for the β-phase, and similarly the peak at 1232 cm^{-1} is the exclusive peak for the γ-phase.[19,22] The FTIR spectrum of pure pomegranate (PM) is shown in Figure S2, which indicates the presence of alcohols, alkenes, ethers, and amides. The melting behavior of both pure PVDF and the hybrid is also studied using differential scanning calorimetry (Figure 1d). Pure PVDF has a melting temperature of 177 °C, which increases in the hybrid to 182 °C because of the presence of the γ-phase. The order of melting temperature of different phases of PVDF is $\gamma > \alpha > \beta$.[19,20] This is to mention that the extent of the γ-phase is very prominent from the FTIR pattern (high-intense peak), which is also reflected in the melting behavior of the hybrid (showing predominant γ-phase melting). The thermal degradation behaviors of pure PVDF and the hybrid are shown in Figure 1e, indicating the safe use of the hybrid up to 200 °C. The early degradation of the hybrid is associated with the thermal decomposition of the organic peel as clear from the thermogravimetric analysis (TGA) plot of the pomegranate peel powder presented in Figure S3.

The changes in the structure are usually associated with the alteration in the surface morphology. Figure 2a shows the polarized optical microscopic images of pure PVDF and its hybrid. Pure PVDF has the α-phase as clear from the low-intense (low birefringence) tiny spherulite while the γ-phase in the hybrid is evident from the presence of higher birefringence (bright) and even smaller spherulites. Figure 2b shows the scanning electron microscopic images indicating the spherulite pattern of pure PVDF (encircled)[17,19] while a globule-like morphology at the end of the fibrous pattern of pomegranate

(PM) (SEM of PM is shown in Figure S4), which might be formed because of the crystallization of PVDF in the γ-phase at the end part of the fiber. The β-phase is crystallized presumably in the vicinity of the stretched fiber. The atomic force microscopic images of pure PVDF and its hybrid are shown in Figure 2c, endorsing the globular morphology of the hybrid, similar to the SEM micrograph. The average height profiles of PVDF and its hybrid are shown in Figure 2d indicating the rough surface of the hybrid because of the globular morphology. Now, the induced crystallization of PVDF in the hybrid is visualized on the fibrous pattern of pomegranate and a schematic is presented in Figure 2e where PVDF is crystallized in the all trans β-phase over the extended part of the fiber while the thermodynamically more stable γ-phase is induced at the edge part of the fiber leading to a "dumb-bell"-like morphology, which is observed through SEM and AFM micrographs. However, it is quite evident that electroactive phases are induced in the presence of pomegranate peel as the filler and the hybrid is expected to behave like a good piezoelectric material.

The energy-harvesting capability of the piezoelectric material is evaluated by fabricating the device as explained in the Experimental Section. The prepared piezoelectric device is able to generate voltage on application of mechanical stress. Devices have been fabricated using pure PVDF or its hybrids with different filler contents. The open circuit voltages from different devices are shown in Figure 3a. The output voltage gradually increases with the filler content in the hybrid indicating the superior effect of the filler in the piezoelectric hybrid. The device with highest filler percentage (40%) produces 65 V as open circuit voltage as compared to meager 6 V from pure PVDF. The corresponding power density (P) is calculated by measuring the output voltage across external resistances using the formula

$$P = \frac{V^2}{R \times A}$$

where V is the output voltage, R is the external resistance, and A is the area of the device.

The maximum power density obtained from P-PM40 (40% PM in the hybrid) is 88 μW/cm^2 (Figure 3b). Power density from the device prepared from pure pomegranate peel is only 15 μW/cm^2 (Figure S5). Very high power density from the hybrid device is explained from the synergistic effect of the filler and the induced electroactive phase of PVDF over the pomegranate fibers. The output voltage and power obtained are much higher than the reported values in the literature. The maximum power of 11.5 μW/cm^2 is obtained with DNA in the PVDF matrix[4] while a power output of 55 μW/cm^2 was reported in our earlier work using the egg shell membrane-PVDF hybrid.[7] Furthermore, different forms of waste mechanical energy (bending, walking etc.) are demonstrated to generate power, which takes into account of the unique features of the developed device. The hybrid is more porous as compared to pure PVDF and this is an advantage for the hybrid as the porous structure is soft and more flexible than the normal compact structure of pure PVDF. Figure 3c shows the signals (output voltage) from the devices if the load is applied like a cantilever on them that is one end of the device is fixed and the force is applied at the other end. The pure PVDF shows a response time of ~4 ms while the nanohybrid shows ~9 ms also in the hybrid, and there is a time gap between the bending and releasing mode, which is absent in pure PVDF. The response time indicates the duration of power generation under application of stress. The working principle of the nanogenerator is explained in Figure S6, which shows the generation of positive and negative charges on the surface of the device. The biowaste (pomegranate peel composed of many proteins, sugars, fibers, and acids) exhibits piezoelectricity because of the rotation of the polar atomic groups or the formation of new dipoles upon the application of stress.[23,24] The hydroxyl (−OH) groups can interconnect the molecules through inter and intramolecular hydrogen bonding (Figure S7), which develops the electric dipoles inside the crystal and, thereby, favors the induced crystallization of the PVDF matrix in the electroactive phase at the edges of the peel fiber as shown in the scheme of Figure 2e.[25] The piezoelectric effect is because of the displacement or reorientation of the dipoles in the crystal upon the application of stress.[26,27] The long-range-ordered polymer crystals undergo stress and induce polarization causing the piezoelectricity under the mechanical stress. Although the origin of piezoelectricity in the biomaterials is not clear yet as they do not follow the classical model of piezoelectricity, based on the ideal crystalline structure,[28] the better piezoelectricity in the hybrid is because of the electromechanical coupling arising from better interaction between the two phases under the application of pressure.[29] The device is also able to produce voltage under various stresses/human activities, which demonstrates the practical applications of the device. Open circuit voltage under bending and walking is 3.8 and 4 V, respectively, as shown in Figure 3d,e. The capacitor charging from the device by finger imparting is shown in Figure 3f. The capacitor is charged in almost 35 s and discharged in another 30 s. The stored charge in the capacitor can be used to power small devices. Figure 3g shows the lightning of the LEDs by finger imparting and the corresponding circuitry. The whole process (LEDs glowing instantly on finger pressing) is captured and presented in Video VS1. However, the biowaste hybrid is demonstrated as the superior energy harvester utilizing the waste mechanical energy especially from body movement, which is able to generate enough power for lighting LEDs and this idea can be extended to power the implants in the human body utilizing its own movements.

4. CONCLUSION

The hybrids of PVDF and pomegranate peel are prepared using different peel contents through a solution route. The crystalline phase of pure PVDF (α-phase) has transformed into piezoelectric phases (β + γ-phases) in the hybrid in the presence of peel. This induction of electroactive phases is also confirmed through spectroscopic and thermal measurements. Morphological investigations indicate this transformation through both optical and electronic microscopy (bright contrast γ-phase in the hybrid and dumb-bell-shape-like β- and γ- phases through SEM and AFM studies). Devices have been fabricated using pure PVDF and hybrids and both the open circuit voltage and power density consistently increase with a higher content of pomegranate peel as the filler. A very high open circuit voltage and a power density of 65 V and 84 μW/cm^2 have been achieved using the hybrid device and are explained because of the synergistic effect of the piezoelectric peel and the induced piezo-phase of the PVDF matrix. The developed device is also able to produce power under different types of human body movements and day to day activities and

https://dx.doi.org/10.1021/acsaelm.0c00197
ACS Appl. Electron. Mater. 2020, 2, 1426−1432

glow several LEDs. The capacitor charging and LED glowing from the device clearly indicate its real-life applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.0c00197.

Chemical composition of pomegranate and its peels; XRD and FTIR of the pomegranate peel powder; major functional groups present in the peel; TGA and SEM of the pomegranate peel; OCV and power of the device made of the pomegranate peel; working principle of a nanogenerator; and possible interaction between the peel constitutes and PVDF (PDF)

Video showing LEDs glowing instantly on finger pressing (AVI)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Author acknowledges the institute for her teaching assistantship.

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