6. Application PVDF and its nanocomposites as piezoelectric nanogenerator in different modes

6.1. Mechanical energy harvesting from PVDF composite polymers

For mechanical energy harvesting different modes of periodic force like repetitive finger tapping, periodic bending and mechanical stretching has been adapted to harvest electric energy from mechanical force without any external polling process. Effect of various nanofiller inclusion on energy output has also been studied. Some custom built set ups have been utilized to produce mechanical force to apply on those synthesized membrane films. Output voltage in open circuit condition and current in short circuit condition has been recorded by digital oscilloscope (Tektronix-TBS 1072B) and a sourcemeter (Keithley-2450) respectively. Application of mechanical stress in different modes is schematically presented in fig. 6.1. In tapping mode, repetitive finger tapping on those synthesized films is applied and obtained voltages and currents are measured. Pressure applied on them is measured by a piezoelectric sensor placed under those sample membranes. To measure the energy output in bending mode, synthesized film on flexible PET substrate is repetitively hit by a rod attached to a rotating dc motor and output voltages in open circuit condition and currents in short circuit condition are measured (schematically shown in fig. 6.1(b)). Frequency of bending and bending angle depends on the voltage applied on the dc motor. To stretch those films repetitively films were connected to two stages connected by spring as shown in fig. 6.1(c). Average stress applied on those films was estimated by the percentage of elongation ($\Delta l/l$) from the images of those films recorded by a microscope in normal and stressed condition. From those images we found the average amount stretch of those films is ~ 1.10 ± 0.01%. Basic reason behind this generation of electric energy is that external mechanical stress applied on them dislocates ions from their equilibrium position results in generation of electric dipole. When these dipoles align in a particular direction forms an electric potential for a short period of time. But after removal of external force, dislocated ions tend to return back to their initial positions because of their inertia results in formation of potential in the opposite direction for a brief period of time due to charge separation. Thus application of repetitive mechanical force yields generation of ac signal to the output. Different methods are adapted for generation of mechanical force applied on pristine and filler induced PVDF for comparative study.

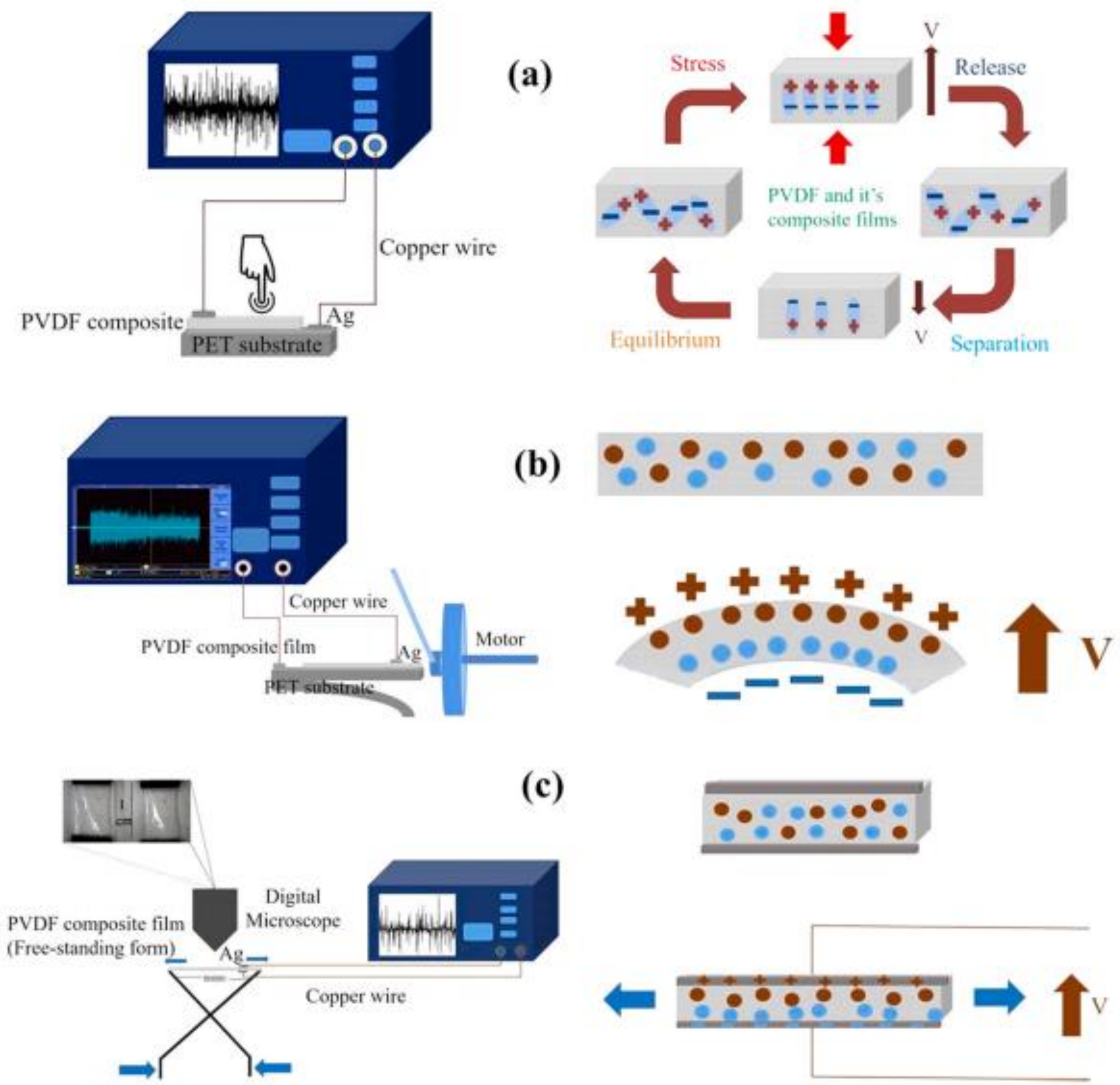

Fig. 6.1 Schematic diagram of generation of electrical energy from (a) finger tapping, (b) repetitive bending and (c) repetitive stretching mode

Under repetitive finger tapping with average pressure of ~ 30 ± 5 kPa, average peak value of open circuit voltage (V_{oc}) for pristine PVDF is ~ 15 V without any external polling process (fig. 6.2(a)). After introduction of small amount (10% v/v) of ZnO nanoparticle to it, V_{oc} rises to ~ 20 V under similar circumstances (fig. 6.2(b)) with short circuit current density (J_{sc}) of ~ 125 nA/cm^2 (fig. 6.3(b)).

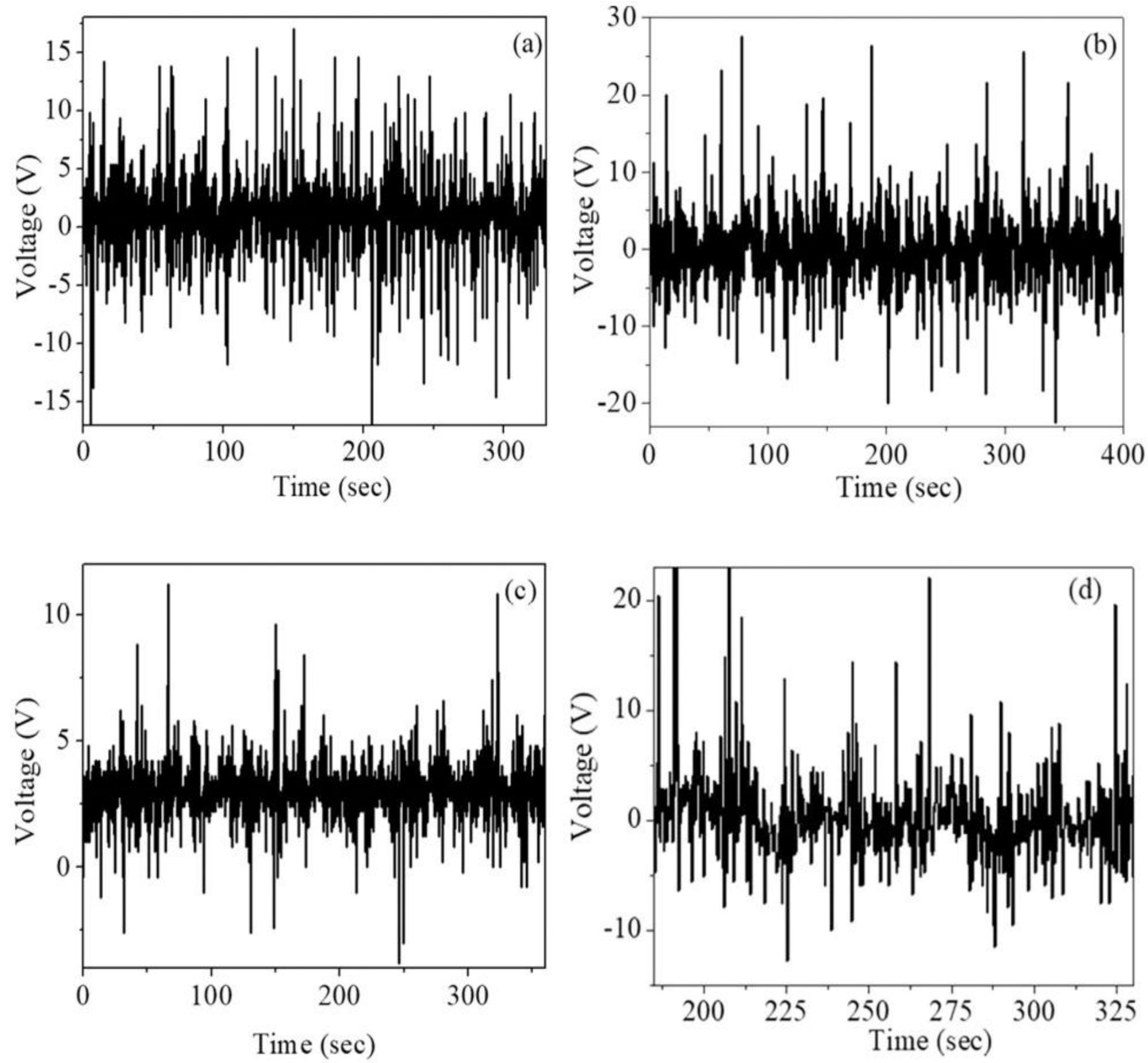

Fig. 6.2 Open circuit voltage (V_{oc}) measured in finger tapping mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

Presence of same amount of GO in PVDF membrane causes a fall in V_{oc} to ~ 6 V (fig. 6.2(c)) along with huge increment in J_{sc} to ~ 325 nA/cm^2 (fig. 6.3(c)). But for PVDF/ZnO/GO composite V_{oc} is ~ 14 V (fig. 6.2(d)) with average output J_{sc} ~ 220 nA/cm^2 (fig. 6.3(d)). Output power delivered by these nanocomposites is simply calculated by multiplying V_{oc} with J_{sc}. In finger tapping mode maximum deliverable output power is acquired from PVDF/ZnO/GO composite and is 3.1 µW/cm^2.

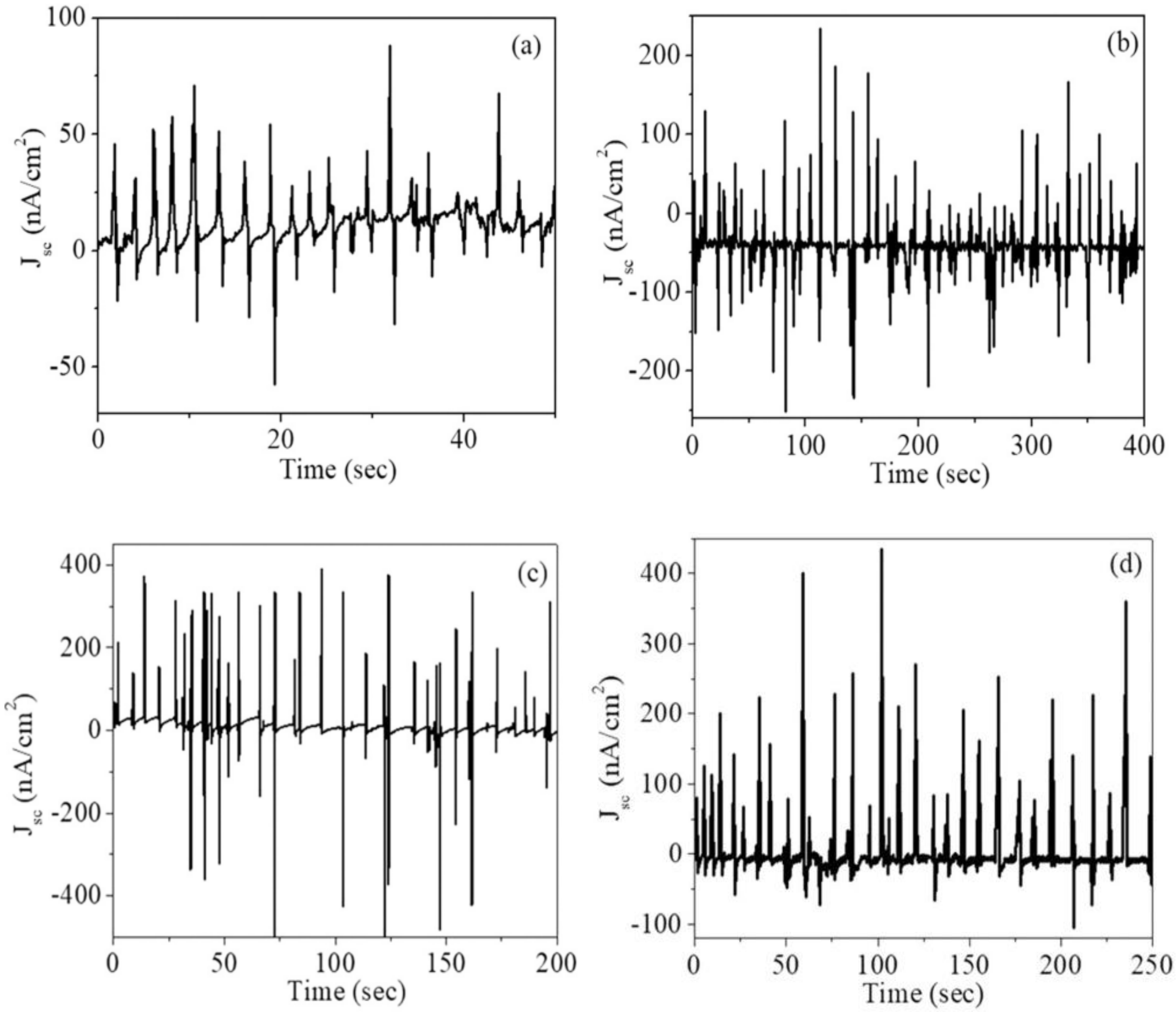

Fig. 6.3 Short circuit current density (J_{sc}) measured in tapping mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

Open circuit voltages (V_{oc}) in periodic bending mode for different composites are obtained and are presented in fig. 6.4(a-d). In this mode, obtained V_{oc} for PVDF film is ~ 0.5 V which shows a huge rise to ~ 6.5 V for PVDF/ZnO composite. However, a little drop in short circuit current density (J_{sc}) is observed from 0.6 μA/cm^2 for PVDF (fig. 6.5(a)) to 0.5 μA/cm^2 for PVDF/ZnO (fig. 6.5(b)). In presence of GO, output current density in the composite increases considerably to 1.1 μA/cm^2 (fig. 6.5 (c)). Finally, for PVDF/ZnO/GO nanocomposite both V_{oc} and J_{sc} increases in such a way that makes output power ~ 5.4 μW/cm^2 which is maximum when compared to that for other composite membranes.

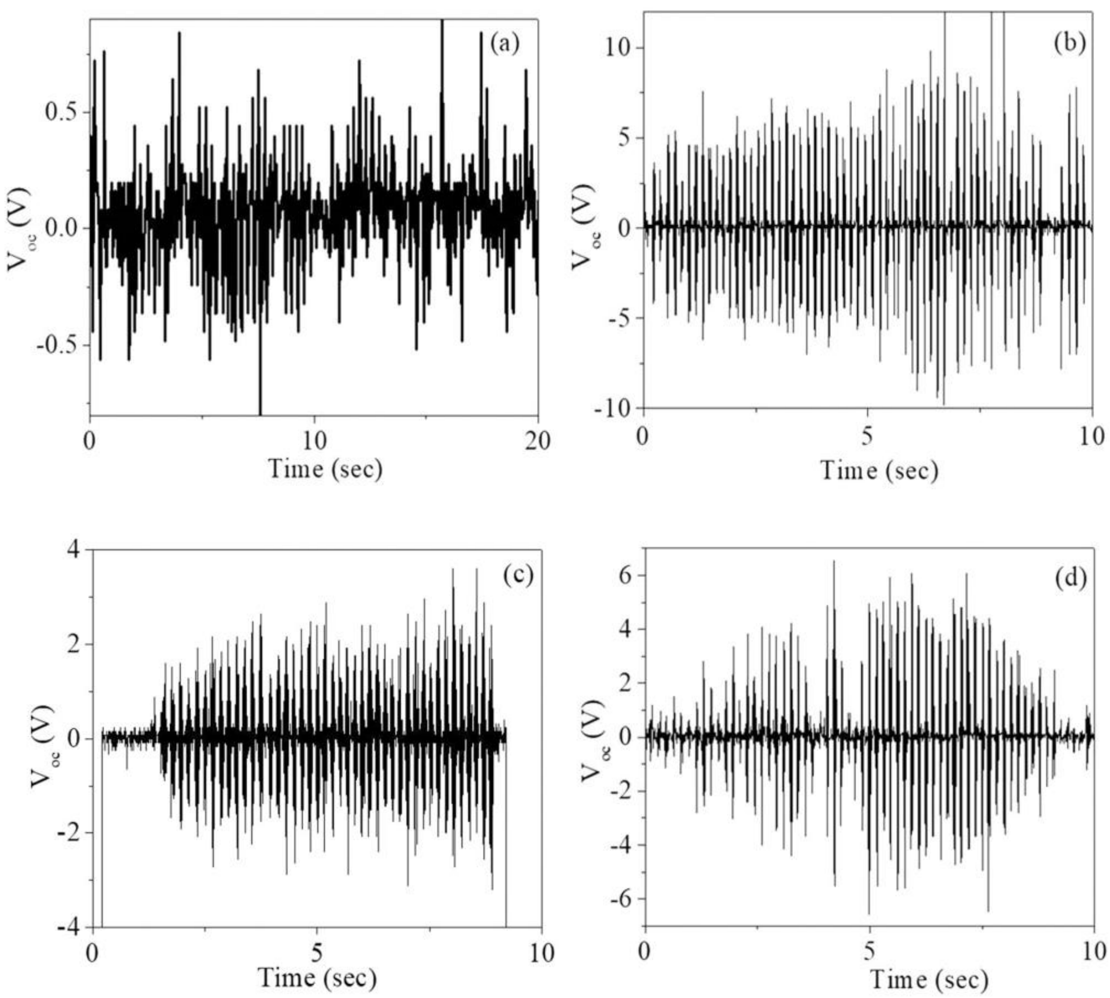

Fig. 6.4 Open circuit voltage (V_{oc}) measured by periodic bending mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

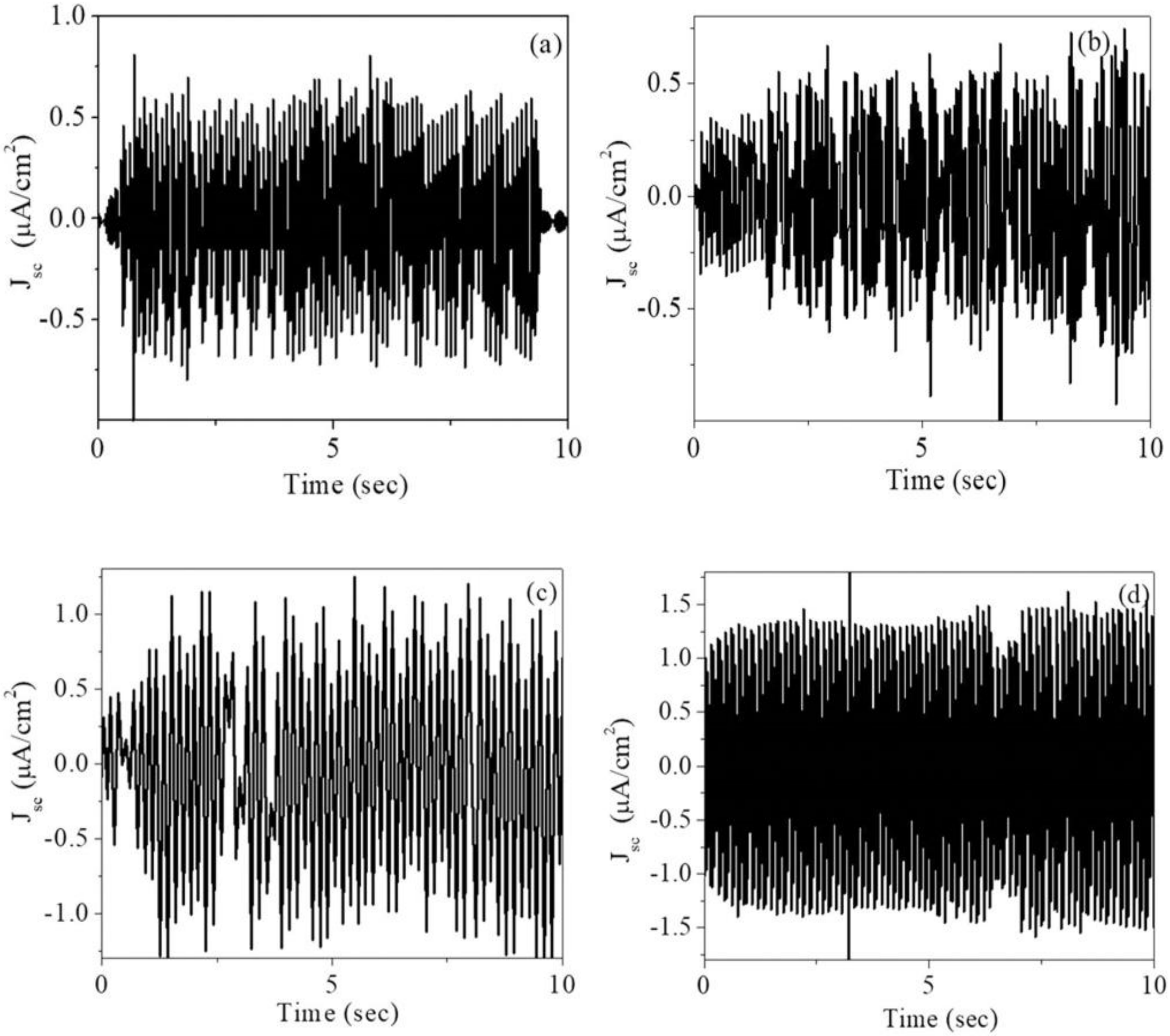

Fig. 6.5 Short circuit current density (J_{sc}) measured by periodic bending mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

Mechanical energy harvesting from those films under repetitive stretching and compressing are also performed and shown in fig. 6.6(a-d) and fig. 6.7(a-d). For pristine PVDF average open circuit voltage (V_{oc}) in stretching mode is ~ 8 V (fig. 6.6(a)) along with short circuit current density of ~ 255 nA/cm^2 making output power ~ 2.0 μW/cm^2. In this mode, after ZnO incorporation, there is no change in V_{oc} is observed but increment in J_{sc} rises to ~ 323 nA/cm^2. On the other hand, small amount of GO in the PVDF membrane increases V_{oc} to ~ 14 V with drop in J_{sc} to ~ 172 nA/cm^2. The tri-phase PVDF/ZnO/GO exhibits increment in both V_{oc} to ~ 10 V and J_{sc} to ~ 304 nA/cm^2. In this mode also PVDF/ZnO/GO composite arises out to be the best suited composite for energy harvesting with output power delivery of ~ 3.0 µW/cm^2. V_{oc}, J_{sc} and output powers obtained from different nanocomposites in different modes are presented in Table – 6.1.

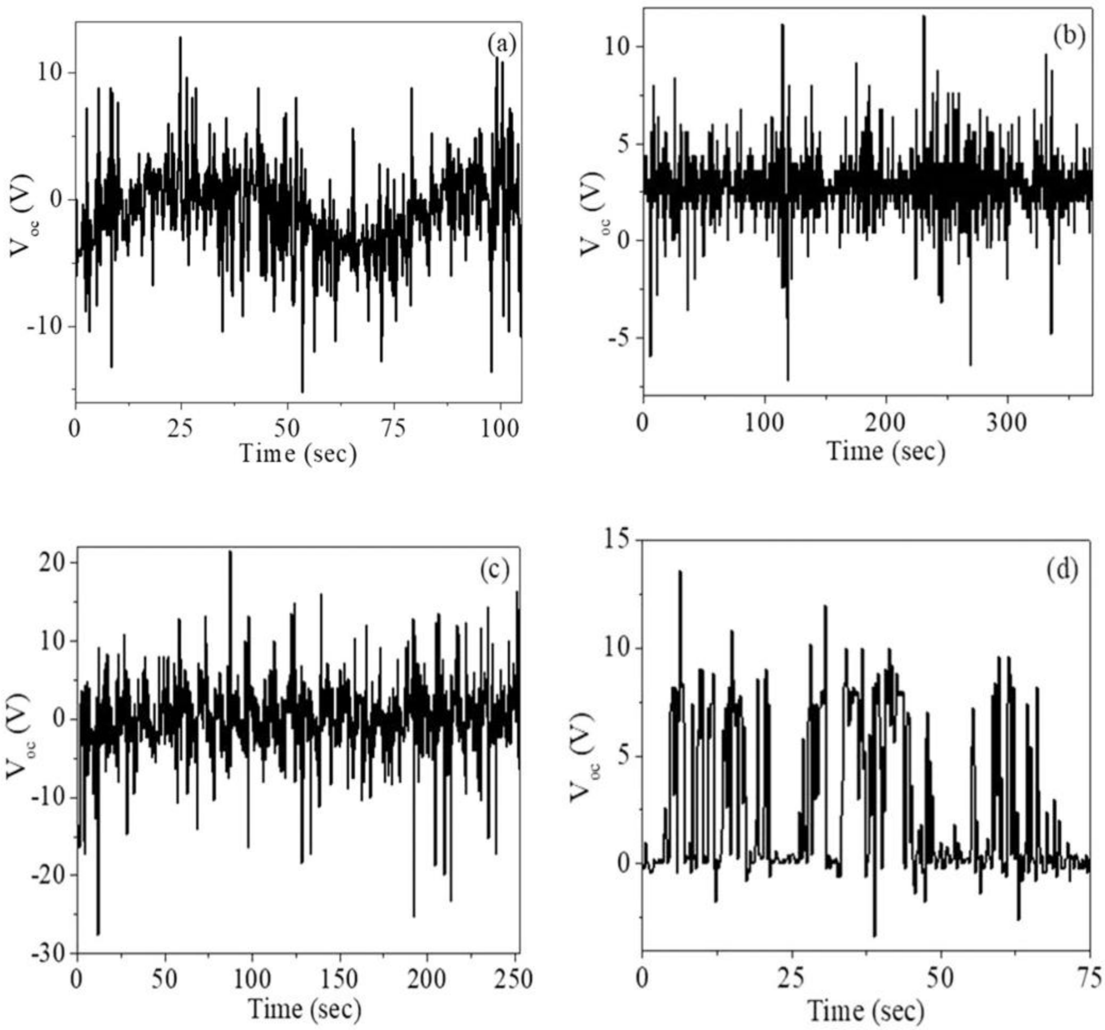

Fig. 6.6 Open circuit voltage measured in repetitive stretching mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

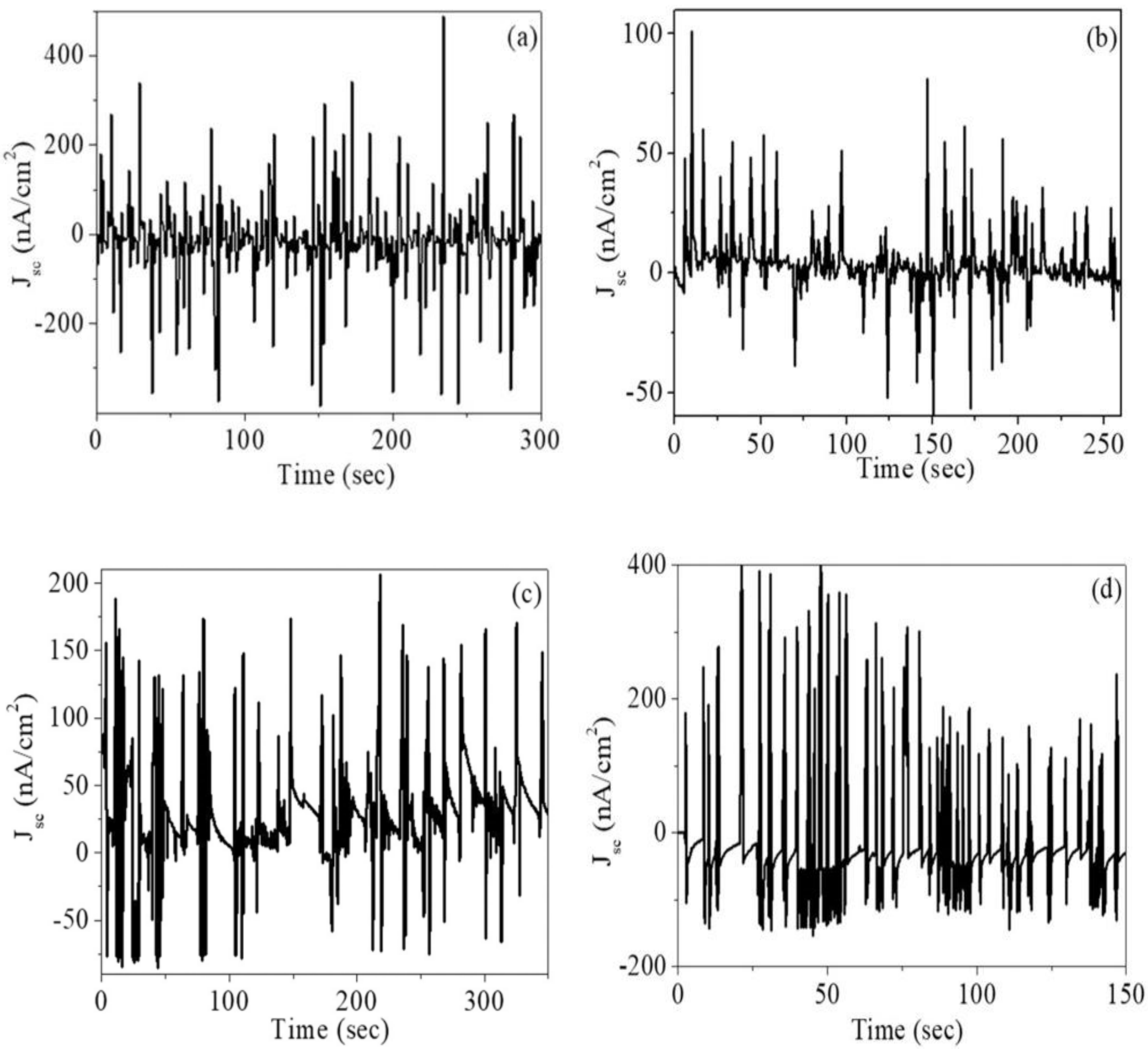

Fig. 6.7 short circuit current density (J_{sc}) measured in repetitive stretching mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films

This output electrical power generated from external mechanical force in form of periodic bending is then utilized to charge a 1 μF capacitor (fig. 6.8). The ac output signal is at first rectified by a bridge rectifier shown in the inset of fig. 6.8. This converted electric signal is then allowed to charge the capacitor and its output is measured by a sourcemeter. Among those composites, PVDF/ZnO/GO tri-phase composite charges the composite at fastest rate ensuring it is capable of generating highest output power as compared to other composite membranes.

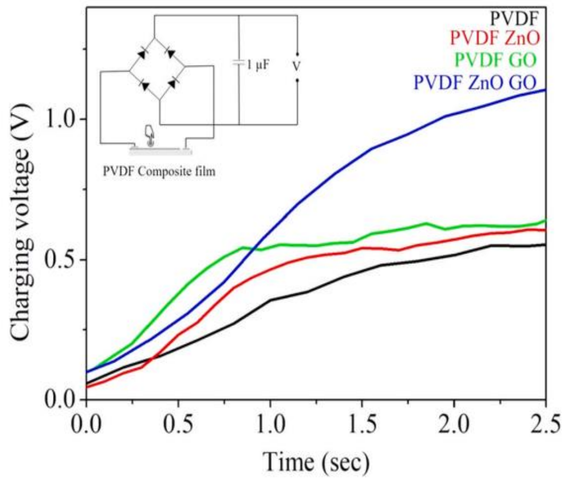

Fig. 6.8 Rate of charging a 1 μF capacitor by output power of obtained from PVDF and its composite films from periodic bending

Table – 6.1 Average peak values (amplitude) of V_{oc}, J_{sc} and maximum deliverable output power density for PVDF and its composites in different modes

Film	Tapping			Bending			Stretching		
	V_{oc} (V)	J_{sc} (nA/cm^2)	P (μW/cm^2)	V_{oc} (V)	J_{sc} (μA/cm^2)	P (μW/cm^2)	V_{oc} (V)	J_{sc} (nA/cm^2)	P (μW/cm^2)
PVDF	15	50	0.8	0.5	0.6	0.3	8	255	2.0
PVDF/ZnO	20	125	2.5	6.5	0.5	3.3	8	323	2.6
PVDF/GO	6	325	1.8	2.3	1.1	2.4	14	172	2.3
PVDF/ZnO/GO	14	220	3.1	4.0	1.3	5.4	10	304	3.0

6.2. Impedance spectroscopic analysis

From the obtained results, we see that presence of little amount of ZnO or GO has great influence on performance of PVDF as nanogenerator. This mechanism of improvement in performance of PVDF as nanogenerator by introduction of ZnO and/or GO can be studied in detail by complex ac impedance spectroscopic analysis. This allows us to get a detailed insight and role of ZnO nanoparticle and GO nanosheets in energy harvesting process in those nanocomposites. Also role of different components like grains and interfaces can be deconvoluted by such analysis. AC impedance spectroscopic study has been performed for such composites in the frequency range of 50 Hz – 5 MHz in ordinary temperature. From those obtained data, imaginary part of complex impedance ($Z^{//}$) is plotted with real part of it ($Z^{/}$) known as Nyquist plots are drawn for those composites. Nyquist plots for all of those composites appear to be semi – circular in nature and are shown in fig. 6.9(a-d). Now, materials can be thought composed of relatively high conducting array of grains separated by low conducting boundaries [189]. These boundaries behave as an effective potential barrier to the charge particles causing an obstruction to their path. It results congestion of charges at those barriers and gives rise to emergence of capacitance there. So we try to fit the experimentally obtained data with a model circuit consist of a series resistance along two R-C parallel circuits. The reason behind choosing such circuit is to consider the capacitive effects arising from core grains and the boundaries separating them. Different parameters of the model electric circuit are estimated by EIS spectrum analyzing software with ± 2% error [187]. Obtained circuit parameters for different composites are presented in Table – 6.2. From these obtained parameters different relaxation times (τ) are calculated. One of those time constants τ_1 is ~ 10^{-4} sec does not change much after various filler inclusion must be the effect arising from grains. On the other hand τ_2 shows a huge increment from 10^{-6} sec for PVDF to 10^{-3} sec after incorporation of ZnO and/or GO. Therefore, this relaxation time must be effect arising from boundaries or interfaces which got modified after filler incorporation. Addition of ZnO in PVDF introduces additional interfaces which enhances interfacial polarization as well as dielectric constant reflected from the modulation of relaxation time. Thus, application of external mechanical force produces high open circuit voltage compared to pristine PVDF. Additionally being polar nature itself, ZnO helps producing extra output voltage. So compositing ZnO through flexible PVDF enables it to undergo sufficient mechanical stress and produce higher output. Introduction of GO introduces lot of free charges through its conducting network. Accumulation of free charges at host – filler interfaces increase the polarization and hence rise in relaxation time τ_2 is observed. So inclusion of GO in the composite actually helps in separation of charges produced in form of piezo-potential and increases the short circuit current. Therefore, combination of these advantages in PVDF/ZnO/GO makes it best suited nanogenerator for piezoelectric energy harvesting.

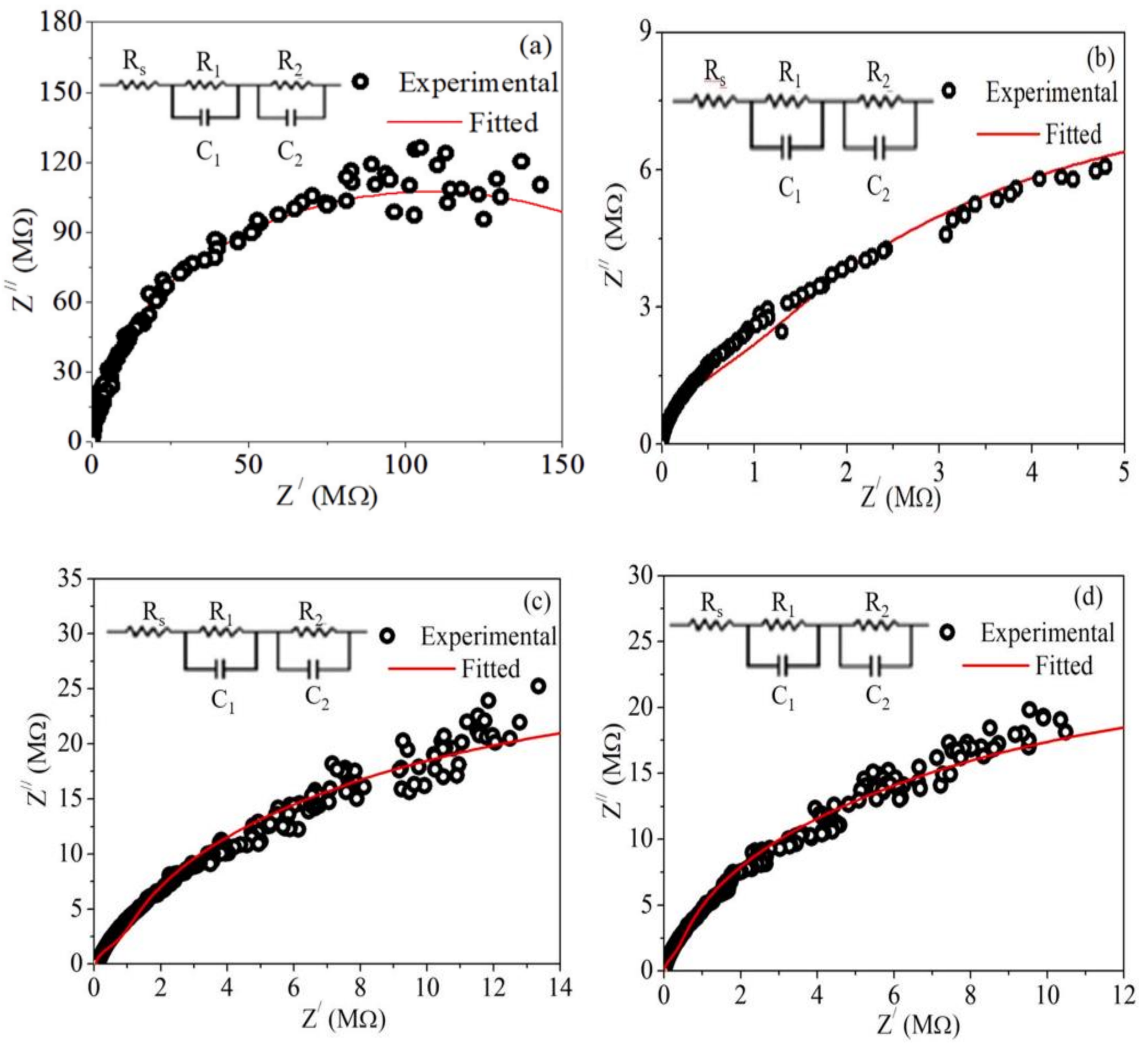

Fig. 6.9 Nyquist plots and their fittings curves for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films with model electrical circuit in their inset by which they are fitted

Table – 6.2 Different obtained parameters and relaxation times for PVDF and its composites

Film	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	C_1 (F)	C_2 (F)	$\tau_1 = (R_1C_1)$ (sec)	$\tau_2 = (R_2C_2)$ (sec)
PVDF	33238	2.14×10^{8}	5.32×10^{5}	6.6×10^{-13}	2.2×10^{-12}	1.41×10^{-4}	1.21×10^{-6}
PVDF/ZnO	609	1.17×10^{6}	1.39×10^{7}	3.4×10^{-10}	3.5×10^{-10}	3.97×10^{-4}	4.86×10^{-3}
PVDF/GO	63796	9.39×10^{5}	4.66×10^{7}	1.4×10^{-10}	1.0×10^{-10}	1.31×10^{-4}	4.66×10^{-3}
PVDF/ZnO/GO	10000	4.31×10^{5}	4.11×10^{7}	2.6×10^{-10}	1.1×10^{-10}	1.13×10^{-4}	4.52×10^{-3}