5. Improvement of ferroelectric and dielectric properties of PVDF by nanomaterial incorporation

5.1. Polarization – electric field (P – E) loop of PVDF composites

The polarization - electric field (P–E) loop of PVDF and its composites are measured by a custom built Sawyer – Tower circuit where input signal is provided by a function generator (Tektronix AFG1022) and the output signal was measured by digital storage oscillator (Tektronix TBS1072) at room temperature and are shown in fig. 5.1. P-E loop area of PVDF/ZnO composite appears to be enhanced after introduction of ZnO nanoparticles into it. This is due to formation of F - C - Zn bonds which is also established from XPS analysis. Furthermore, polar nature of ZnO induces extra polarization in the composite. In contrary, addition of GO into the host affects ferroelectric polarization of the PVDF film greatly. The P – E loop almost vanishes by GO inclusion into the composite due to formation of F – C bonds which facilitates better transportation of charges. This easy transportation of charges prevents accumulation of charges at the interfaces which is the reason for fall of polarization. Since very little amount of GO is included in fabrication of the composite, formation of heterogeneous interfaces are less likely to happen. In PVDF/ZnO/GO tri-phase composite, polarization almost comparable to that of PVDF/ZnO but with higher fraction of β – phase content as F – C bonds dominate over vanishingly small F – C – Zn bonds. Therefore, we conclude that PVDF/ZnO/GO composite possess moderately high polarization along with transport capabilities making the composite suitable for flexible ferroelectric applications.

Ferroelectric polarizations for all of those composites at an applied electric field of 15 kV/cm are represented in Table – 5.1. ZnO containing composite polymers i.e. PVDF/ZnO and PVDF/ZnO/GO show ferroelectric polarizations of 15.98 and 14.14 $\mu C/cm^2$ respectively at an applied electric field of 15 kV/cm which is far superior compared to other PVDF and its copolymer

(PVDF-TrFE) based composites reported recently [183]. This tremendous polarization in ZnO containing composites is due to formation of defect rich and porous interfaces in the composite in addition to polar nature of ZnO itself. Energy density stored in such materials are estimated using the relation

$$\mathbf{E_d} = \oint \mathbf{PdE} \qquad \ldots\ldots\ldots \qquad 5.1$$

Estimated energy values are shown in Table – 5.1 and it can be seen that PVDF/ZnO composite has the highest capability to store energy among its other counterparts. On the other hand, energy storing ability of PVDF/GO composite is least. Therefore PVDF/ZnO is the best suited composite for energy storing application.
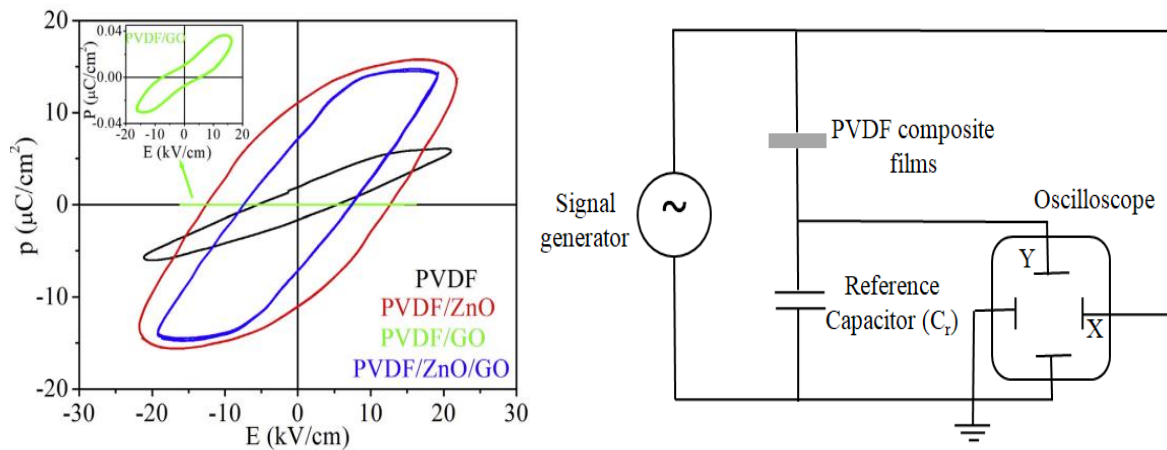

Fig. 5.1 P-E hysteresis loops of PVDF and its composite films and the diagram of custom built Sawyer – Tower circuit through which it is measured

Table – 5.1 Ferroelectric polarization and energy density of PVDF and its composite films

Film	P (μC/cm^2) at 15 kV/cm	E_d($\times 10^4$ J/m^3)
PVDF	5.94	11.30
PVDF/ZnO	15.98	65.50
PVDF/GO	0.03	0.06
PVDF/ZnO/GO	14.14	61.73

5.2 DC bias dependent impedance spectroscopic analysis of PVDF composite films

Impedance spectroscopic analysis is a very convenient tool to explore insight of conduction, transport, dielectric and microstructural properties of any practical substance [184]. In this method, we can deconvolute different responses arising from separate segments like core grains, boundaries, polymer – filler interfaces, inhomogeneous distributions or defect sites of any sample. Impedance spectroscopic measurement of PVDF composites are carried out at room temperature by HIOKI IM 3570 impedance analyzer in the frequency range of 100 Hz – 5 MHz. A very small sinusoidal voltage of 200 mV is applied through it when placed between conducting Ag electrodes. An additional dc bias with variation is applied for better understanding of polarization phenomenon while performing this experiment. Complex impedance of any sample can be presented as [185]

$$\mathbf{Z} = \mathbf{Z}^{/} - \mathbf{j}\mathbf{Z}^{//} \qquad \text{…..……..} \qquad 5.2$$

Where $Z^{/}$ and $Z^{//}$ represent real and imaginary part of complex impedance respectively. From the measured impedance data $Z^{/}$ and $Z^{//}$ for different films are calculated. Variation of $Z^{//}$ with $Z^{/}$ often known as Nyquist plots are drawn for all of those composites and are presented in fig. 5.2 (a-d). Nyquist plots of all of the composites are semi-circular nature which is a sign of capacitive behavior [186]. With increasing bias voltages, arcs of those semicircles also tend to rise due to increment in dipolar polarization resulting generation of potential in the composite.

Responses extracted from impedance spectroscopy can be compared to model electric circuit for estimation of different parameters such as capacitances and reaction resistances of charge transfer mechanism arising from different sections of those films. We have chosen the model circuit comprised of a series resistance with two parallel R-C circuits in series as shown in the insets of fig. 5.3 (a-b). Choice of such R- C model circuit is to take effects of grains and boundaries into account due to possibility of clogging of charges there. Although there will be

some minor effects due to imperfections, defect sites and sample - electrode interfaces which have been overlooked. Now these proposed parameters are estimated by using electrochemical
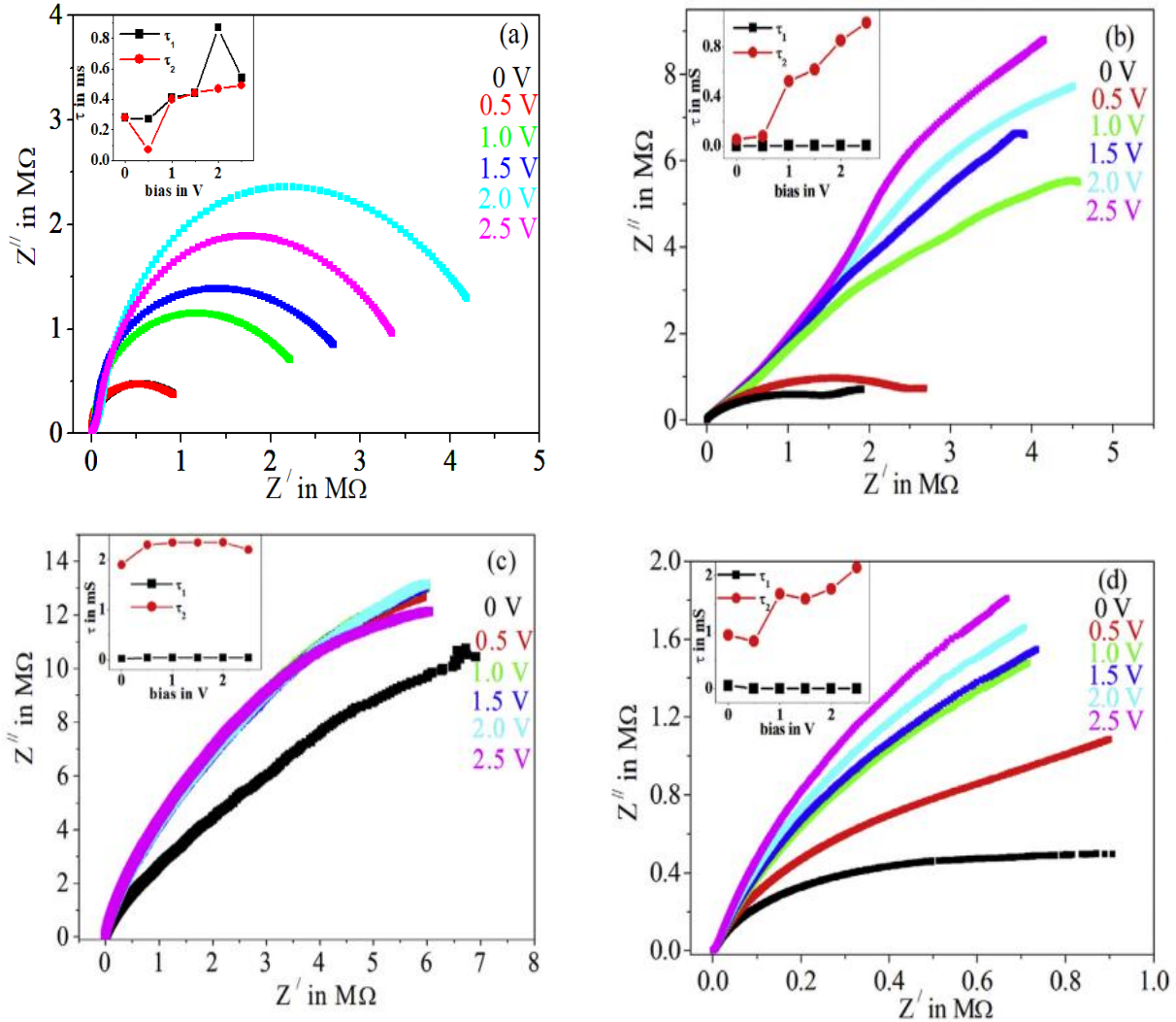

Fig. 5.2 DC bias dependent Nyquist plots for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films and variation of relaxation times with external bias in their corresponding insets

impedance spectroscopic (EIS) analyzing software [187]. Different obtained parameters are listed in Table – 5.2. Two separate relaxation times (τ_1 and τ_2) corresponding to core grains and boundaries or interfaces are calculated from these parameters. In this method obtained impedance spectroscopic data is transformed from frequency domain to time constant domain.

Being polymer kind of substance, it cannot have a sharp single relaxation time but possess distribution of relaxation times effective at different ranges frequencies [188]. According to Koop's Phenomenological theory polycrystalline materials are composed of relatively high conducting grains separated by low conducting boundaries [189]. Interfacial polarization which is prominent at boundaries or interfaces is effective at low frequency while dipolar polarization which is a feature of core grains is effective at higher frequencies [190]. Such selective frequency responses are reason for emergence relaxation time distribution. One of those relaxation times τ_1 does not change much after inclusion of fillers suggests that it must be contribution of core grains. On the other hand, the other relaxation time τ_2 shows significant change after filler incorporation implies modification of boundaries (Table – 5.2). This fact clearly indicates modification of boundaries or interfaces of host materials by nanomaterial incorporation. Moreover, a small tail in Nyquist plot for only PVDF/ZnO composite is observed implies formation of strong interfaces may be due to polar nature of ZnO.
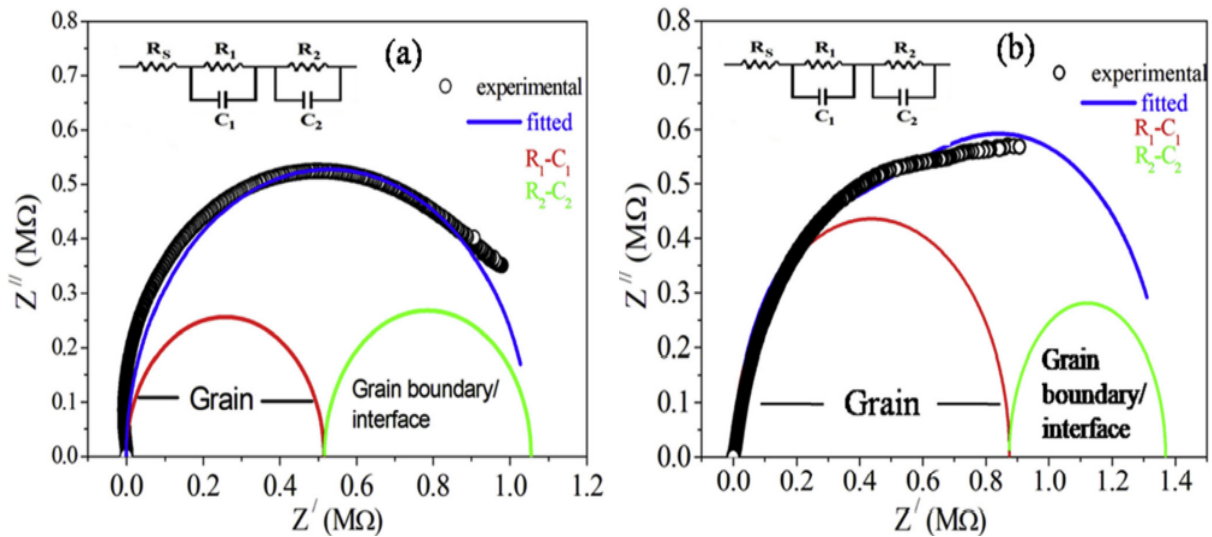
Fig. 5.3 Fitting of Nyquist plots by model electric circuit (in the insets) for (a) PVDF and (b) PVDF/ZnO/GO film

Values and rate of variation for τ_1 and τ_2 are almost similar in PVDF polymer. For composite PVDF films with ZnO and/or GO fillers the variation of τ_1 and τ_2 with external bias

(insets of fig. 5.2 (b-d)) clearly indicates the filler induced modification of the polymer interface. After filler inclusion, there is almost no variation in τ_1 value indicating that core is unaffected after nanomaterial addition. On the other hand τ_2 shows significant variation with bias after filler inclusion indicates filler induced modification of those boundaries. Variation in τ_2 with bias voltage is prominent for ZnO containing composites i.e. PVDF/ZnO and PVDF/ZnO/GO because of polar nature of ZnO. In GO containing composite PVDF/GO, there is almost no variation in τ_2 with external bias ensuring lesser interfacial polarization due to transfer of charges through conducting GO network. Although in PVDF/ZnO/GO rate of change in τ_2 is less than that of PVDF/ZnO but much higher compared to that of PVDF/GO ensuring better dielectric polarization along with some conducting feature.

Table – 5.2 Different obtained fitting parameters from EIS software 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	70.1	5.40×10^5	5.44×10^5	4.99×10^{-10}	4.96×10^{-10}	2.6×10^{-4}	2.7×10^{-4}
PVDF/ZnO	3977.1	1.80×10^5	1.33×10^6	1.03×10^{-11}	3.99×10^{-11}	1.8×10^{-6}	5.3×10^{-5}
PVDF/GO	443.0	1.53×10^5	3.13×10^7	1.26×10^{-10}	6.06×10^{-11}	1.9×10^{-5}	1.9×10^{-3}
PVDF/ZnO/GO	640.4	1.0×10^5	1.01×10^6	5.11×10^{-10}	9.49×10^{-10}	5.1×10^{-5}	9.5×10^{-4}

5.3 Dielectric studies of PVDF and its composites

Complex dielectric constant of any material can calculated using the relation

$$\epsilon = \epsilon' + j\epsilon'' = 1/j\omega C_c \qquad \text{……………} \qquad 5.3$$

Where ϵ' and ϵ'' are real and imaginary part of complex dielectric constant respectively and Cc is the capacitance when films in between the electrodes is replaced air medium. Dielectric loss

factor (D) and ac conductivity (σ_{AC}) of PVDF and its composites are calculated by using the relations

$$\mathbf{D = Z^{/} / Z^{//}} \qquad \text{…....………..} \qquad 5.4$$

$$\mathbf{\sigma_{AC} = \omega\epsilon_0\epsilon^{/}D} \qquad \text{……............} \qquad 5.5$$

Variation of real part of dielectric constant ($\epsilon^{/}$) with frequency at different external bias are presented in fig. 5.4 (a-d) for PVDF and its composites at room temperature. From fig. 5.4(a) it is clear that PVDF shows two different relaxation processes due crystalline motion at low frequency and non-crystalline motion due to glass transition at high frequency. With an increase in frequency, $\epsilon^{/}$ decreases rapidly due to inability of the dipoles in polymer chain to follow such high frequency alteration of field. Then $\epsilon^{/}$ value attain a peak at ~ 2.7 kHz before finally being saturated at high frequency due to β- relaxation process. This is because at so high frequency, hopping of charges between ions is unable to follow so high frequency of applied electric field [191]. With an increase in applied external bias, dielectric constant reduces in the low frequency region due to less space charge accumulation at boundary surfaces. In presence of external field, molecular dipoles orient in the direction of applied field while induced dipoles at the adjacent grain surfaces orient opposite to that of applied field. This induced dipole moment in the opposite direction decreases the dielectric constant of the film. After incorporation of ZnO in PVDF film, value of dielectric constant at low frequency region increases, because polar ZnO increases the polarization at the interfaces. However, after filler incorporation, peak implying multiple relaxations vanish (fig. 5.4(b)). $\epsilon^{/}$ value starts to fall from low frequency region before attaining saturation in the high frequencies. Also for PVDF/ZnO, decrease in $\epsilon^{/}$ value is observed with increasing bias voltage at low frequency region indicating field induced polarization at the interfaces. In contrary, for PVDF/GO membrane film significant decrease in $\epsilon^{/}$ is observed at low frequency region (fig. 5.4(c)). This must be due to modulation of interfaces of PVDF by GO conducting network. There is very slight change in $\epsilon^{/}$ value with external bias voltage is observed for PVDF/GO indicating external bias has very little effect on interfacial polarization. This is due to GO conducting network connecting adjacent grains reduces the interfacial polarization by providing conduction of charges rather than accumulation there. For PVDF/ZnO/GO composite, although $\epsilon^{/}$ value is higher than that of pristine PVDF but lower than that of PVDF/ZnO (fig. 5.4(d)). This fact clearly shows that dielectric constant of PVDF/ZnO/GO has been improved compared to that of pristine PVDF along

with better transport property. ϵ' values for different PVDF composites at a frequency of 100 Hz without any bias voltage are listed in Table – 5.3.
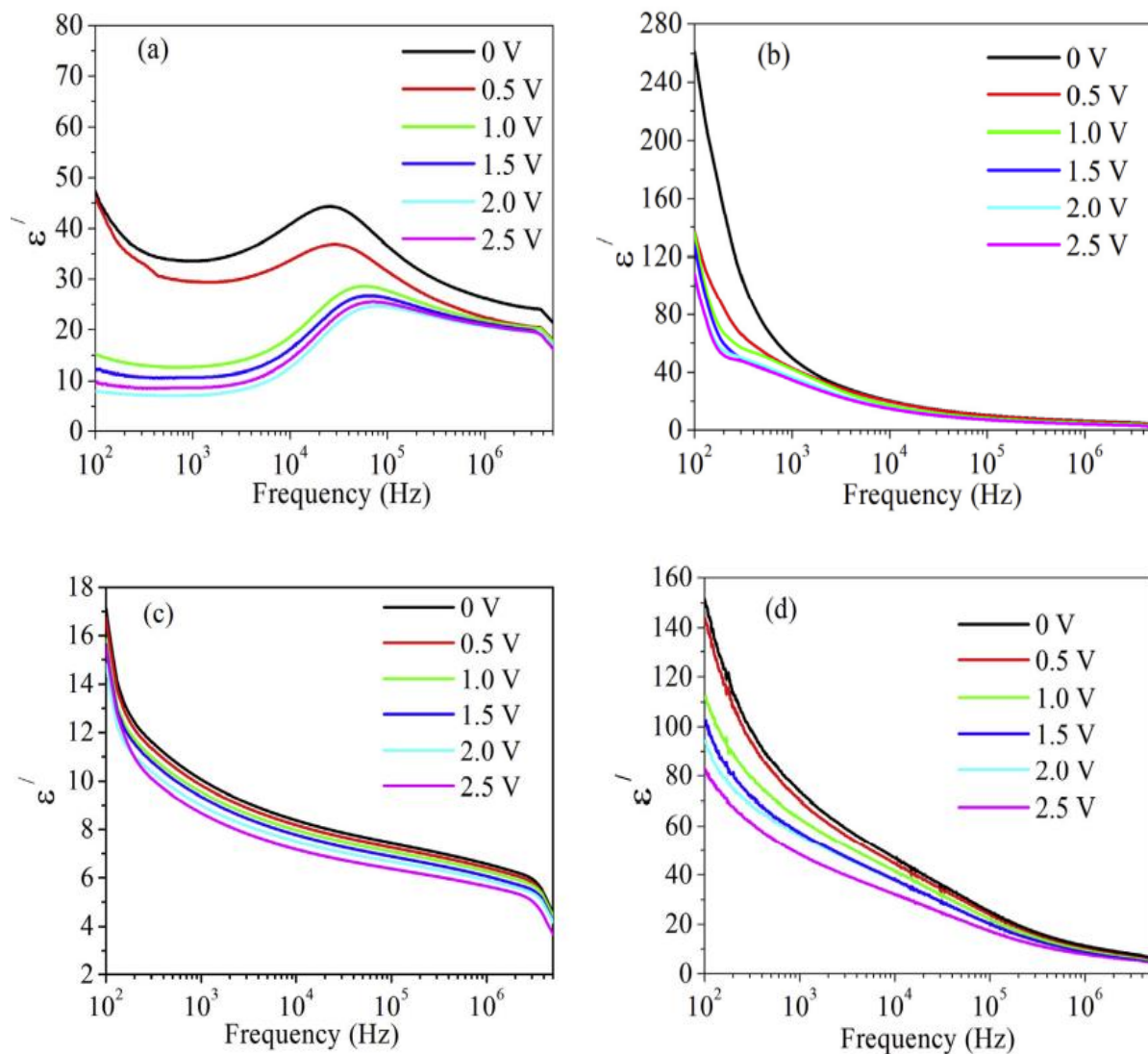

Fig. 5.4 Frequency vs. real part of dielectric constant (ϵ') for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films at different external bias voltages

Dielectric loss (D) is another important parameter used to describe performance of dielectric materials. It is defined as the amount energy dissipated in form of heat due to application of electric field. It is dependent on various factors like lattice distortions, defects, interfacial polarization etc. [192]. Dielectric loss usually appears to be higher at low frequency ranges and

falls at high frequency ranges due to enhanced conductivity by hopping of charges there. Dielectric loss factor for different PVDF composites are presented in Table – 5.3 and shows that for PVDF/GO, loss factor is minimum. This is because of conducting GO network, charges faces less obstruction there to reduce loss of energy dissipation.

Table – 5.3 Estimated values of dielectric constant, dielectric loss and ac conductivity of PVDF and its composite films

Film	$\epsilon^{/}$ (at 100 Hz)	D (at 100 Hz)	σ_{AC}(S/m) (at 1 MHz)
PVDF	47	2.31	3.04×10^{-4}
PVDF/ZnO	261	2.69	1.14×10^{-4}
PVDF/GO	17	0.46	8.75×10^{-5}
PVDF/ZnO/GO	151	1.15	2.52×10^{-4}

AC conductivity (σ_{AC}) of PVDF and its composite membranes are also measured and are presented in fig. 5.5 (a-d). At low frequencies, ac conductivities for all of those films are very low and independent of frequency. But when frequency increases higher than that of electron hopping frequency, dipole formation starts and ac conductivity rises. At high frequency region, ac conductivity rises due to external field affected transport of charges and hopping of charges. AC conductivity of PVDF and its composites at a frequency of 1 MHz are presented in Table – 5.3. From fig. 5.5 (a-d), it is evident that ac conductivity does not differ much at the application of external bias at low frequency but exhibits a small variation at high frequency region. These all occurrences justify dielectric and ferroelectric modification of PVDF films by inclusion of nanofillers. Therefore fabricated PVDF/ZnO/GO demonstrates high dielectric and ferroelectric polarization compared to PVDF and its copolymer based nanocomposites [183, 193].
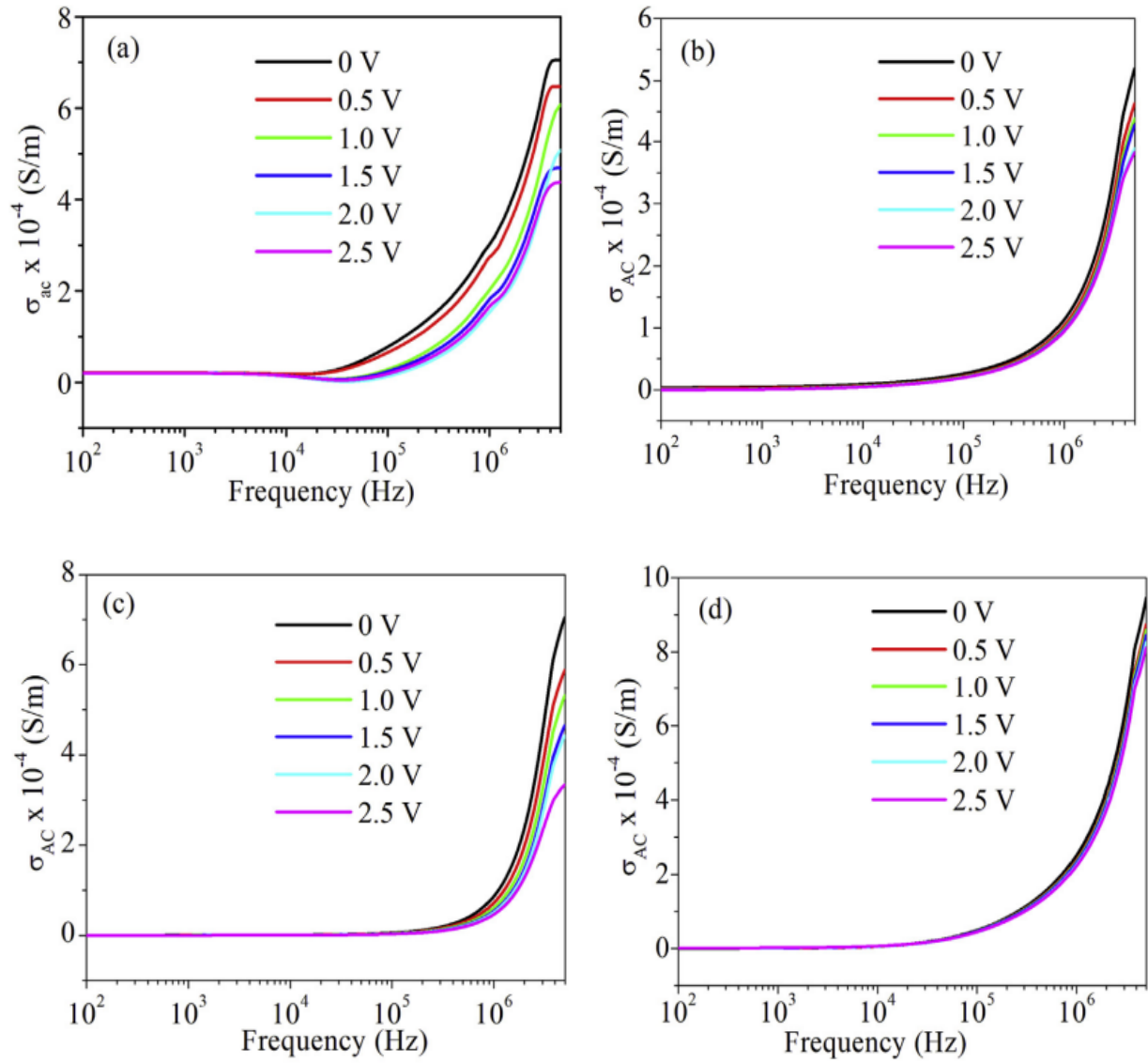
Fig. 5.5 Frequency vs. ac conductivity of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films at different external bias voltages