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# Ferroelectric, Piezoelectric and Dielectric Properties of Novel Polymer Nanocomposites

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## Abstract

In this chapter, the Ferroelectric, Piezoelectric and Dielectric behavior of novel polymer/ceramic nano-composite (PCC) based on ferroelectric polymer [polyvinylidene fluoride (PVDF)] & nano Barium Titanate ( $n$ -BaTiO<sub>3</sub>) with different volume fractions of  $n$ -BaTiO<sub>3</sub> ( $f_{\text{BaTiO}_3}$ ), prepared through the novel cold pressing method has been discussed. The ferroelectric parameters of PCC are attributed to spherulites of PVDF, the increase of  $n$ -BaTiO<sub>3</sub> and the ordered homogenous structure due to the novel cold pressing. The clustering of ceramic fillers is responsible for randomization of the structures of these composite ferroelectrics for some samples, leading to decrease of electrical polarisations. The piezoelectricity and piezoelectric coefficients of these composites ferroelectrics, increases with increase of ceramic filler content and remains constant beyond a certain ratio. However, the dielectric properties increase linearly as a function of ceramic content due to increase of interfaces/interfacial polarisations. The enhancement of effective dielectric constant ( $\epsilon_{\text{eff}}$ ) is attributed to the large interfacial polarization arising due to the charge storage at the spherulites of PVDF and at the polymer/filler interfaces of PCC and have been explained on the basis of sum effect with the help of the standard models. The achieved lower loss tangent ( $\tan \delta$ ) for the PCC as compared to the polymer/metal composites (PMC) is attributed to the highly insulating nature of PVDF & semiconducting  $n$ -BaTiO<sub>3</sub>. The thermal stability of the composites is also maintained due to the higher melting temperature (170°C) of PVDF. The cold pressed PCC based on PVDF are going to act as better polymer ferroelectric/dielectrics for memory and electrical energy storage applications.

**Keywords:** Polymer ferroelectrics/dielectrics, spherulites, Ferroelectric polymers, Barium titanate, Dielectric constant, Loss Tangent, Polymer nanocomposites

## 1. Introduction

Polymer ferroelectrics (PF) and polymer dielectrics (PD) are considered recently to be the fascinating materials for their large inherent benefits of non-volatile memory/sensor/piezoelectric/dielectric/pyroelectric/magneto-electric applications [1–17]. The conventional ferroelectric ceramic materials, e.g. BaTiO<sub>3</sub>, PZT, PbTiO<sub>3</sub>, etc. being used as memory elements/piezoelectric sensors/actuators/transducers, etc. are suffering from a large number of disadvantages, such as; brittleness, high cost and consume higher energy/longer time for their preparation.

To overcome these problems, PF are undergoing development based on ferroelectric polymer as well as ferroelectric ceramics. Among the ceramic fillers, BaTiO<sub>3</sub> is a very good ferroelectric material and comparably better as others have harmful lead content [16, 17]. Among the various polymers, very few polymers, such as polyvinylidene fluoride (PVDF), polyvinylidene fluoride trifluoroethylene [PVDF Tr(FE)] and Teflon show ferroelectric/piezoelectric behavior and have high dielectric constants [18, 19]. They are also of high breakdown strength, light-weight, flexible and having permanent dipolar polarization. Among the ferroelectric polymers, PVDF shows high piezo-electric coefficients, good ferroelectric behavior. Due to these advantages, PVDF is used as piezo-electric sensors/actuators/memory devices. But the major problem with PVDF is that, the magnitudes of ferroelectric parameters aren't as good as the parameters, obtained from the conventional ceramics, which limit them from direct applications. Similarly the PD are having higher flexibility, non-toxicity, bio-compatibility, low cost, higher visco-elastic properties, etc. [20–31]. Due to their higher energy density/lower loss tangent ( $\tan \delta$ ) with higher breakdown field strength, they are going to be the emerging materials of future for electrostatic energy storage applications. The PD composed of polymers with conductor/ceramic nanoparticles are considered recently to be the demanded materials for electrical energy storage applications [20–36]. For energy storage applications, the maximum stored energy per unit volume is  $U = \frac{1}{2} K \epsilon_0 E_{\max}^2$ , where  $K$  is the relative dielectric constant and  $E_{\max}$  is the maximum electric field, which can be applied to the material (proportional to the breakdown field of the material). Over the last 20 years of research, the ferroelectric polymers e.g PVDF matrix also have been preferred due to its high static dielectric constant (~15)/higher visco-elastic properties/higher insulating nature as compared to other non-polar polymers. The preferred fillers are high dielectric constant ferroelectric ceramics in development of these PD. However, the development of the polymer-ceramic composites (PCC) have been slowed down, as the effective dielectric constant ( $\epsilon_{\text{eff}}$ ) for these composites were found to be very low i.e.  $\epsilon_{\text{eff}} \sim 100$  at low frequencies due to the low dielectric constant of the polymers as well as due to the conventional hot molding process conditions. In preparing these PCC, ferroelectric ceramic, such as, PMN-PT, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, etc. with varying particle size are introduced into the PVDF matrix through hot molding and partially the approach becomes effective in order to get better PD [5–10]. For preparing PCC based on PVDF, the traditional mixed technique (solution casting followed by hot molding) is used, during which the spherulites of PVDF get lost [2, 33, 34], which lowers the value of  $\epsilon_{\text{eff}}$ . Recently Panda et al. [23–30, 32, 33] has shown the importance of spherulites by following the cold pressing technique in preparing the PD based on PVDF, due to which the spherulites of PVDF are retained. The spherulites are responsible in the additional storage of electrical charge due to their additional interfaces, resulting higher interfacial polarization/higher value of  $\epsilon_{\text{eff}}$  [2, 33, 34].

With the objective of achieving flexibility with low cost/easy processing and higher value of electrical parameters, for device applications, the traditional process condition (hot molding of the thick films prepared from solution casting) is changed to cold pressing developed by our group in which the spherulites of PVDF will be retained for the case of PCC. Hence, PCC of good ferroelectric/piezoelectric/dielectric properties, are developed from good ferroelectric ceramics/good ferroelectric polymers. Since in the PZT/PVDF composites, lead is a toxic component, hence the PCC based on PVDF/*n*-BaTiO<sub>3</sub>, with different volume fraction of *n*-BaTiO<sub>3</sub> ( $f_{n\text{-BaTiO}_3}$ ), were prepared with the help of cold pressing method. The prepared composites have shown the interesting ferroelectric/piezoelectric/dielectric/conductivity properties and finds suitability for various applications.

## 2. Experimental details

Polymer composite based on PVDF/*n*-BaTiO<sub>3</sub> from 0.0 to 0.60 of volume fraction of nano filler *n*-BaTiO<sub>3</sub> ( $f_{\text{BaTiO}_3}$ ) were prepared by mechanical hand mixing with Agate mortar/Pestle for 2 hours. The final pellets under room temperature consolidation at a pressure of 30 MPa with the help of a Hydraulic press [2, 33] were prepared. The microstructure investigation on the samples was carried out with the help of FESEM. The ferroelectric hysteresis, i.e. the polarization versus electric field ( $P \sim E$ ) measurement, is done with the help of a  $P \sim E$  hysteresis loop tracer. The piezoelectric coefficient ( $d_{33}$ ) for the samples is measured with the help of Piezo-electric measurement instrument. The electrical measurements were made on all the PCC in the frequency range of 50 Hz to 5 MHz and in the temperature range of room temperature to 100°C. The dielectric results of the PCC have been understood by fitting with the help of the software Mathematica.

## 3. Results and discussion

### 3.1 Microstructure

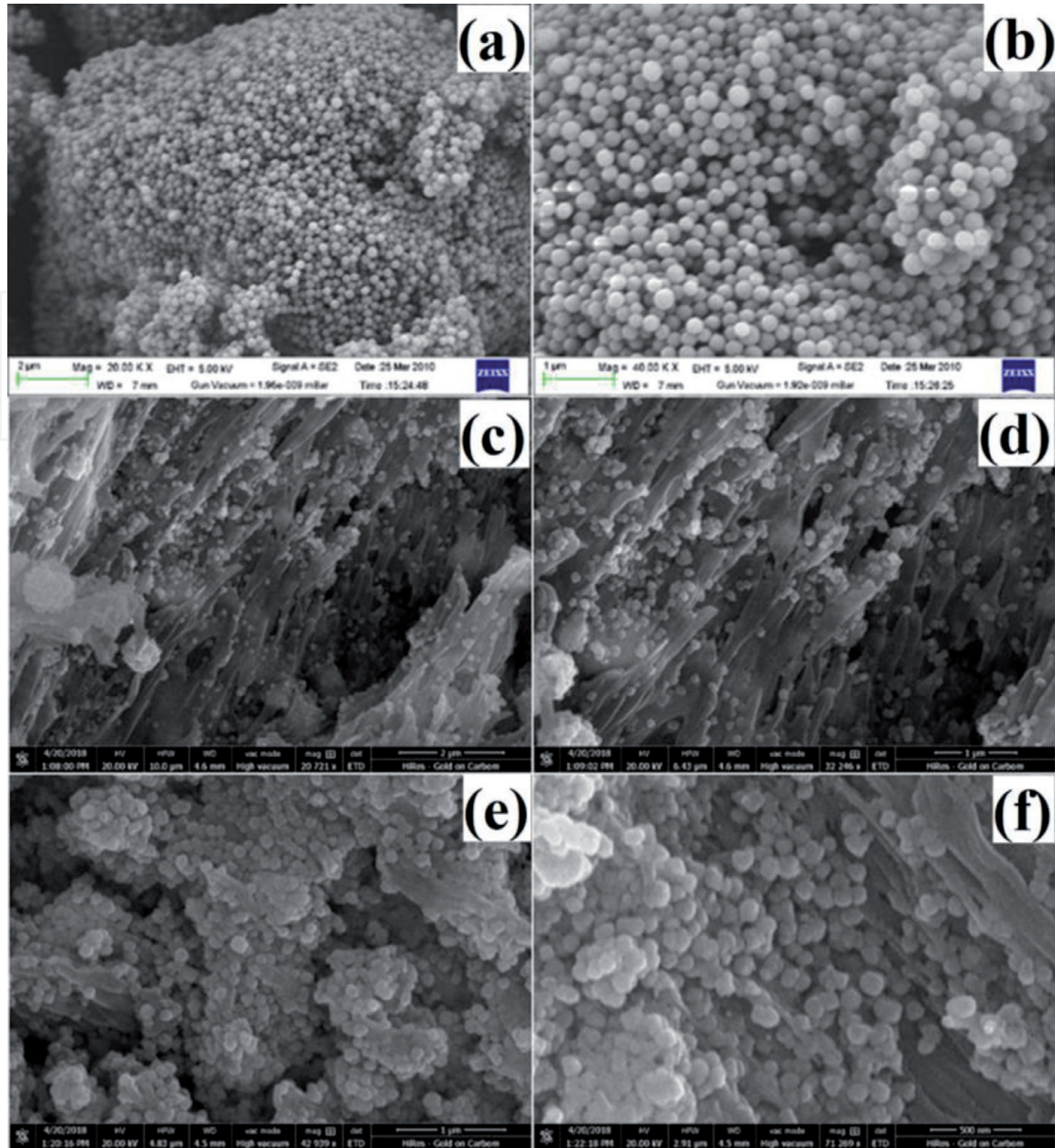
The FESEM micrographs of pure PVDF are given in **Figure 1a** and **b**. **Figure 1a** and **b** shows the presence of spherulites (the spherical semi-crystalline regions of the polymer). The micrographs of PVDF/*n*-BaTiO<sub>3</sub> composites with different  $f_{\text{BaTiO}_3} = 0.2$  and  $f_{\text{BaTiO}_3} = 0.60$  are shown (**Figure 1c–f**). The ordered homogenous structures are also observable and is attributed to the recent novel method of cold pressing as evident from the sample with  $f_{\text{BaTiO}_3} = 0.2$  (**Figure 1c** and **d**). The spherulites present in the polymer are of diameter of the order of  $\sim 0.1 \mu\text{m}$  (**Figure 1a** and **b**). The *n*-BaTiO<sub>3</sub> are also of the order of diameter of the spherulites as they are of size 100 nm, i.e.  $0.1 \mu\text{m}$ . During cold pressing, the *n*-BaTiO<sub>3</sub> clusters (**Figure 1c** and **d**) inside the polymer matrix, may have taken the typical shapes. For the sample with  $f_{\text{BaTiO}_3} = 0.6$  (**Figure 1e** and **f**), shows high level of heterogeneity, as lot of defects and dislocations has emerged in the structure and is responsible for giving a decrease in the ferroelectric & piezoelectric properties of the PF. **Figure 1** reveal slight agglomeration of BaTiO<sub>3</sub> nanoparticles in the nanocomposites. The average filler size in the nanocomposites are of  $\sim 100 \text{ nm}$ . The nano-dispersion of filler in the polymer matrix is well observed. It is also obvious that a variety of interfaces have occurred into the composites, which will be always useful in the storage of electrical charge at the interfaces. The large amount of *n*-BaTiO<sub>3</sub> into the PCC will also be responsible for giving better ferroelectric/piezoelectric/dielectric properties [2, 34–36].

### 3.2 Ferroelectric properties

#### 3.2.1 Ferroelectric hysteresis

The ferroelectric properties of the PF, prepared from PVDF/*n*-BaTiO<sub>3</sub>, the polarization versus electric field ( $P \sim E$ ) of both the pure materials are given (**Figure 2**) at different voltages. **Figure 2a** shows narrow hysteresis loops for pure PVDF due the mixed phases [ $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  &  $\epsilon$ ] as well as the electrical non-poling of the polymer PVDF.

The polarization versus electric field ( $P$ - $E$  hysteresis loop) of the PF under different voltages for various  $f_{\text{BaTiO}_3} = 0.2$  (**Figure 3a**),  $f_{\text{BaTiO}_3} = 0.3$  (**Figure 3b**)  $f_{\text{BaTiO}_3} = 0.4$  (**Figure 3c**) and  $f_{\text{BaTiO}_3} = 0.5$  (**Figure 3d**) are shown. All the samples show symmetrical  $P$ - $E$  hysteresis loops. The loop area increases of with increasing

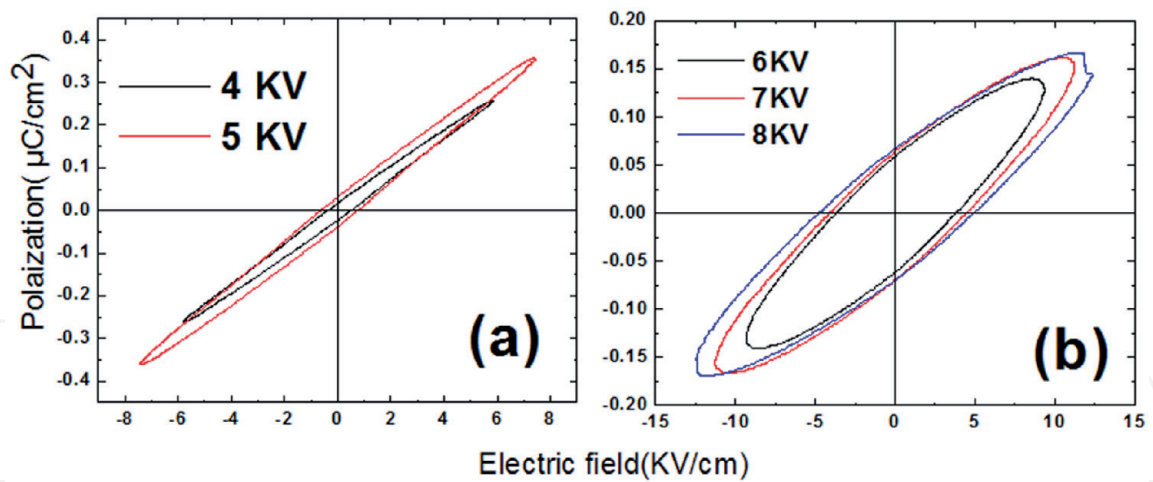


**Figure 1.**

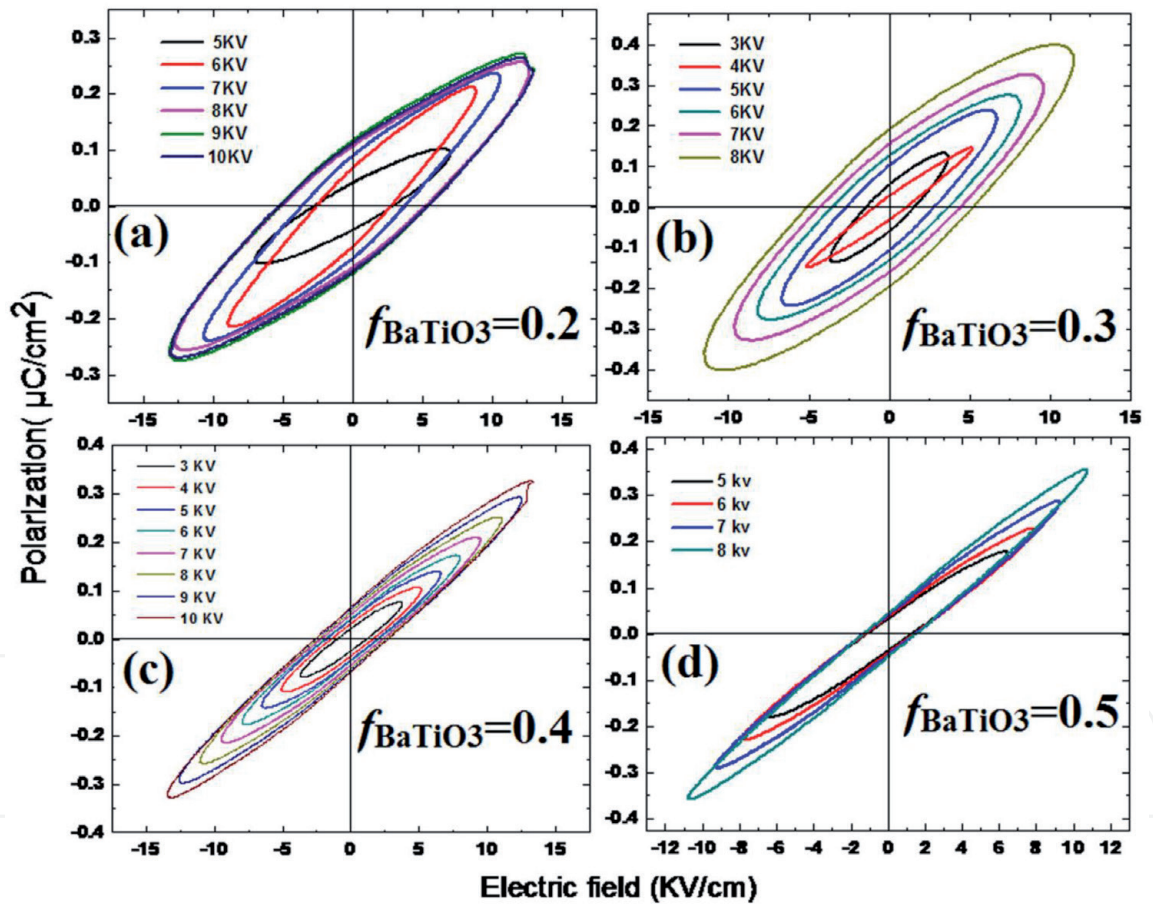
FESEM micrographs of cold pressed PF (a) pure PVDF (lower resolution) (b) pure PVDF (higher resolution) (c)  $f_{\text{BaTiO}_3} = 0.2$  (lower resolution) (d)  $f_{\text{BaTiO}_3} = 0.2$  (higher resolution) (e)  $f_{\text{BaTiO}_3} = 0.6$  (lower resolution) (f)  $f_{\text{BaTiO}_3} = 0.6$  (higher resolution).

the dc voltage from 5 kV to 10 kV. A comparison of P-E hysteresis loops, demonstrate that the samples with  $f_{\text{BaTiO}_3} = 0.2$  &  $0.3$  shows better ferroelectric hysteresis (higher hysteresis loop area) as compared to  $f_{\text{BaTiO}_3} = 0.4$  &  $0.5$ . For precise assessment, the hysteresis loops at 8 kV for all the samples shows that the hysteresis loop area increases as a function of  $f_{\text{BaTiO}_3}$ , up to  $0.30$  (**Figure 1a–d**). On the other hand, beyond  $f_{\text{BaTiO}_3} = 0.30$ , the heterogeneity/disordered structure is accountable for the decrement of ferroelectric properties and that is also accredited to the clustering of n-BaTiO<sub>3</sub> into the polymer medium (**Figure 1e and f**). It is also experiential that with rising the field, the saturation polarization ( $P_s$ ), remnant polarization ( $P_r$ ) and the coercive field ( $E_c$ ) also increases as a function of  $f_{\text{BaTiO}_3}$  and the finest result is obtained for the sample with  $f_{\text{BaTiO}_3} = 0.3$ .

To have a thorough analysis and cross examination of the ferroelectric behavior of the PF, the P-E hysteresis loop of all the samples as a function of  $f_{\text{BaTiO}_3}$  for different fields from 5 kV/cm to 8 kV/cm is shown in **Figure 4**. At all the fields, the ferroelectric behavior from the P-E hysteresis loops, are characterized by the change of  $P_r$ ,  $P_s$  and  $E_c$ .

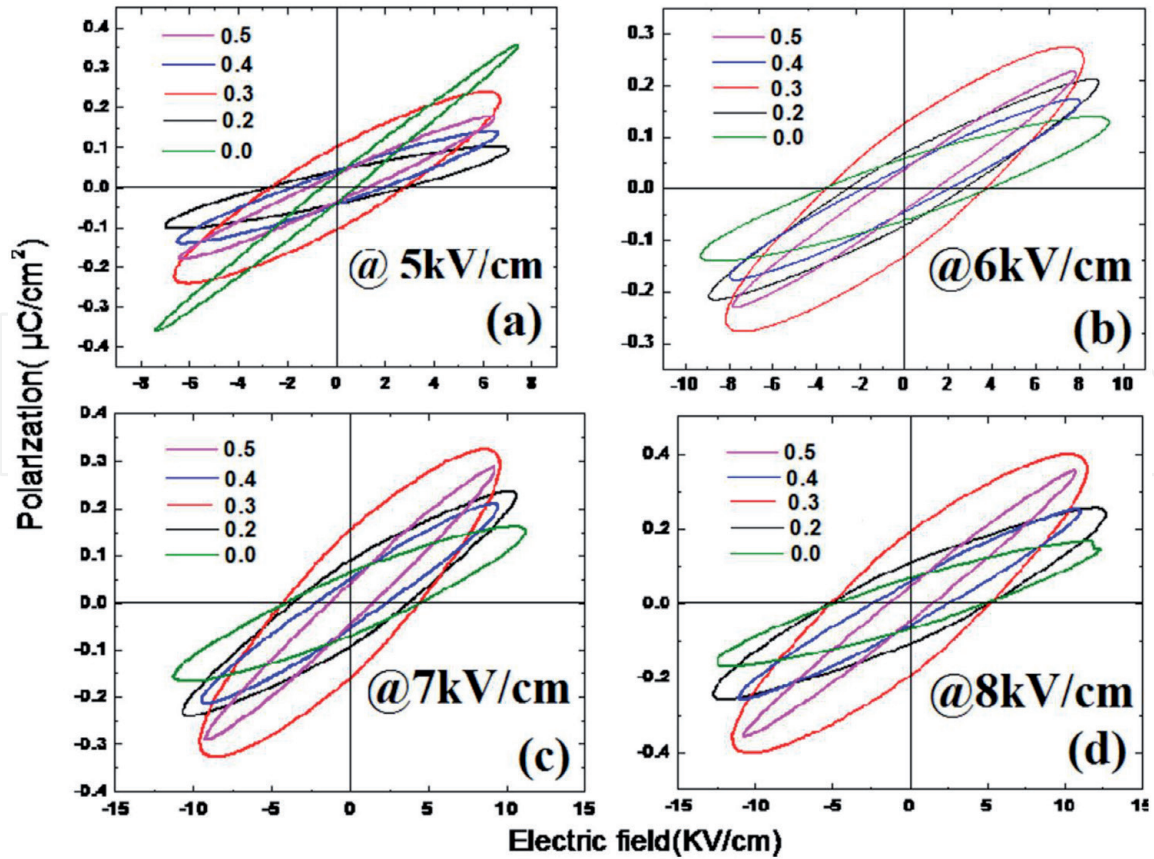


**Figure 2.**  
 (color online) polarization ( $P$ ) vs. applied electric field ( $E$ ) hysteresis loop measured at a frequency of 1 Hz with different voltages for pure (a) PVDF (b)  $n$ -BaTiO<sub>3</sub>.



**Figure 3.**  
 (color online) polarization ( $P$ ) vs. applied electric field ( $E$ ) hysteresis loop measured at a frequency of 1 Hz with different fields for different  $f_{BaTiO_3}$  (a) 0.20 (b) 0.30 (c) 0.40 (d) 0.50.

The experimental observation is that with increasing of the  $f_{BaTiO_3}$  in the PF, the  $P_r$ ,  $P_s$  and  $E_c$  also increases. This obviously indicates that the addition of  $n$ -BaTiO<sub>3</sub> enhances the ferroelectric nature of the polymer material. But when the amount of  $n$ -BaTiO<sub>3</sub> filler content improved, there is trivial agglomeration of filler in the PVDF matrix. The agglomeration of  $n$ -BaTiO<sub>3</sub> act as hindrances, which eliminate PVDF Polymer from flowing into the BaTiO<sub>3</sub> agglomerates and the aggregated filler causes poor enhancement in ferroelectric nature (decrement in



**Figure 4.** (color online) polarization ( $P$ ) vs. applied electric field ( $E$ ) hysteresis loop measured at a frequency of 1 Hz with different  $f_{\text{BaTiO}_3}$  for different fields (a) 5 kV/cm (b) 6 kV/cm (c) 7 kV/cm (d) 8 kV/cm.

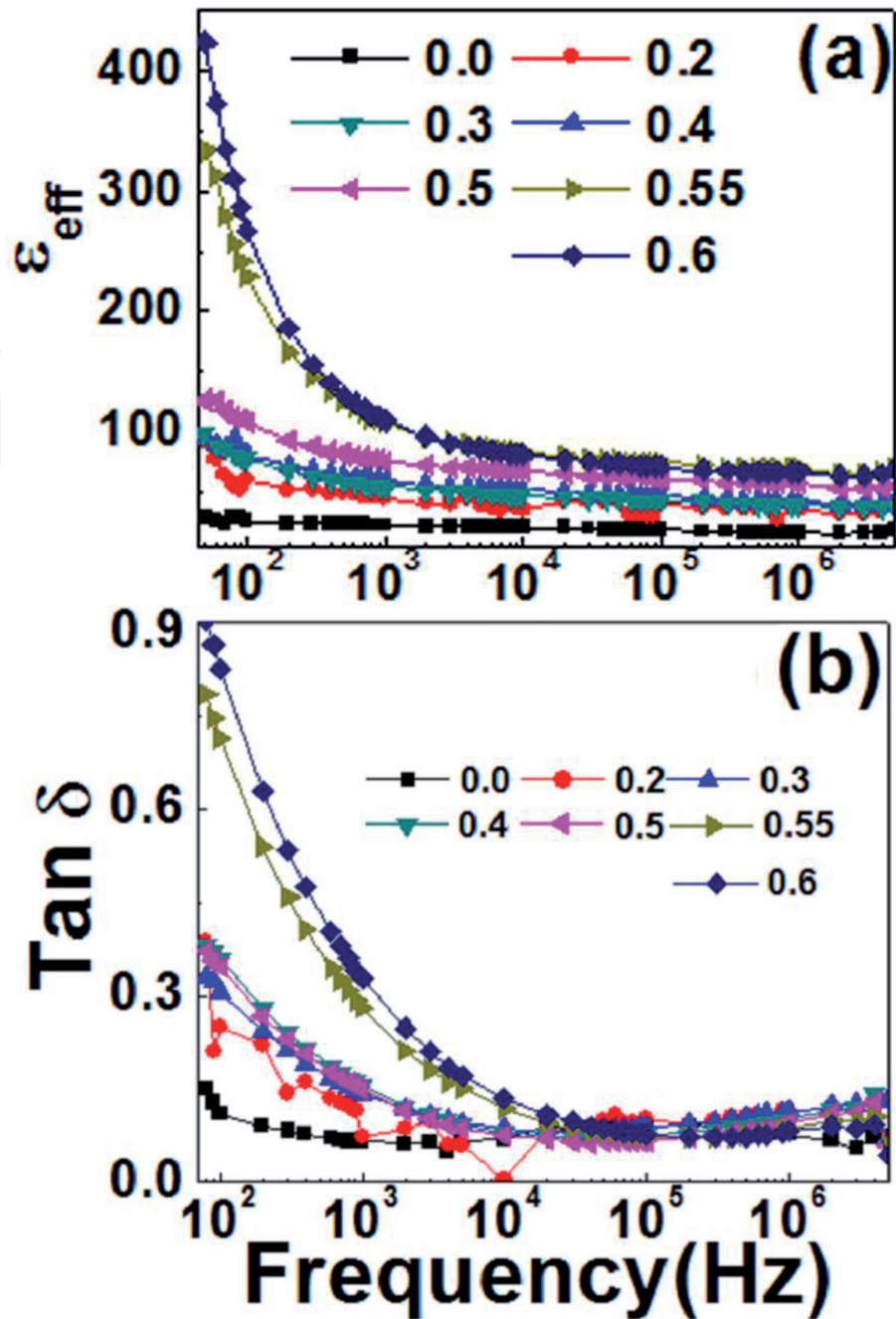
the ferroelectric polarization) as evident from **Figure 4**. Conversely the dielectric properties, such as the effective dielectric constant ( $\epsilon_{\text{eff}}$ ) and loss tangent ( $\tan \delta$ ) of all the PF becomes a linear dependence of  $f_{\text{BaTiO}_3}$  (**Figure 5**), i.e. the static  $\epsilon_{\text{eff}}$  enhances from 10 for pure PVDF to 400 for  $f_{\text{BaTiO}_3} = 0.6$ , whereas the loss tangent increases from 0.09 for pure PVDF to 0.9 for  $f_{\text{BaTiO}_3} = 0.6$  [14]. The variation in the dielectric and ferroelectric behavior is credited to the different types of structures responsible for the two altered electrical properties respectively. The dielectric properties are connected with the more interfaces in the PF, hence  $\epsilon_{\text{eff}}$  &  $\tan \delta$  enhances linearly with  $f_{\text{BaTiO}_3}$  and the ferroelectric properties are associated with the ordered structure of the PF.

### 3.2.2 $P_s \sim f_{\text{BaTiO}_3}$ for different fields

**Figure 6** give you an idea about the variation of  $P_s$  as a function of  $f_{\text{BaTiO}_3}$  for all the PF, at changed electric fields from 5 kV/cm to 8 kV/cm. It is practical that on increasing the concentration of  $n$ -BaTiO<sub>3</sub>, and also on rising the electric fields, the value of  $P_s$  raises up to  $f_{\text{BaTiO}_3} = 0.30$ , but for  $f_{\text{BaTiO}_3} > 0.30$ ,  $P_s$  decreases, due to the aggregation of  $n$ -BaTiO<sub>3</sub> causing poor improvement of the ferroelectric properties. At 5 kV/cm, the value of  $P_s$  increases from 0.1  $\mu\text{C}/\text{cm}^2$  for  $f_{\text{BaTiO}_3} = 0.2$  up to 0.24  $\mu\text{C}/\text{cm}^2$  for  $f_{\text{BaTiO}_3} = 0.30$ , but when  $f_{\text{BaTiO}_3} > 0.30$ ,  $P_s$  decreases to 0.24  $\mu\text{C}/\text{cm}^2$ .

### 3.2.3 $P_r \sim f_{\text{BaTiO}_3}$ for different fields

The variation of  $P_r$  as a function of  $f_{\text{BaTiO}_3}$  for all the PF (**Figure 7**), at different electric fields from 5 kV/cm to 8 kV/cm. It can be seen that on increasing the concentration of  $n$ -BaTiO<sub>3</sub>,  $P_r$  increases up to  $f_{\text{BaTiO}_3} = 0.30$ , but for  $f_{\text{BaTiO}_3} > 0.30$ ,



**Figure 5.**  
(color online) the variation of (a)  $\epsilon_{eff}$  and (b)  $\tan \delta$  as a function of frequency at 300 K for the PF.

$P_r$  decreases, i.e. a parallel behavior as observed in the case of variation of  $P_s \sim f_{BaTiO_3}$ , is also observed which is attributed to the same origin. At 8 kV/cm,  $P_r$  increases from 0.10  $\mu\text{C}/\text{cm}^2$  for  $f_{BaTiO_3} = 0.2$  up to 0.20  $\mu\text{C}/\text{cm}^2$  for  $f_{BaTiO_3} = 0.30$ , but for  $f_{BaTiO_3} > 0.30$ ,  $P_r$  decreases and approaches to much less than 0.20  $\mu\text{C}/\text{cm}^2$ .

### 3.2.4 $E_c \sim f_{BaTiO_3}$ for different fields

The variation of  $E_c$  as a function of  $f_{BaTiO_3}$  for all the PF, at different electric fields from 5 kV/cm to 8 kV/cm is shown in **Figure 8**. The value of  $E_c$  is preserved higher up to  $f_{BaTiO_3} = 0.30$ , but for  $f_{BaTiO_3} > 0.30$ ,  $E_c$  decreases, i.e. a similar conduct as observed in the case of variation of  $P_s \sim f_{BaTiO_3}$ , is also observed endorsed to the same origin. At 6 kV/cm, the value of  $E_c$  increases from 2.5 kV/cm for  $f_{BaTiO_3} = 0.2$  up to 3.5 kV/cm for  $f_{BaTiO_3} = 0.30$ , but for  $f_{BaTiO_3} > 0.30$ ,  $E_c$  decreases and becomes much less than 3.5 kV/cm.

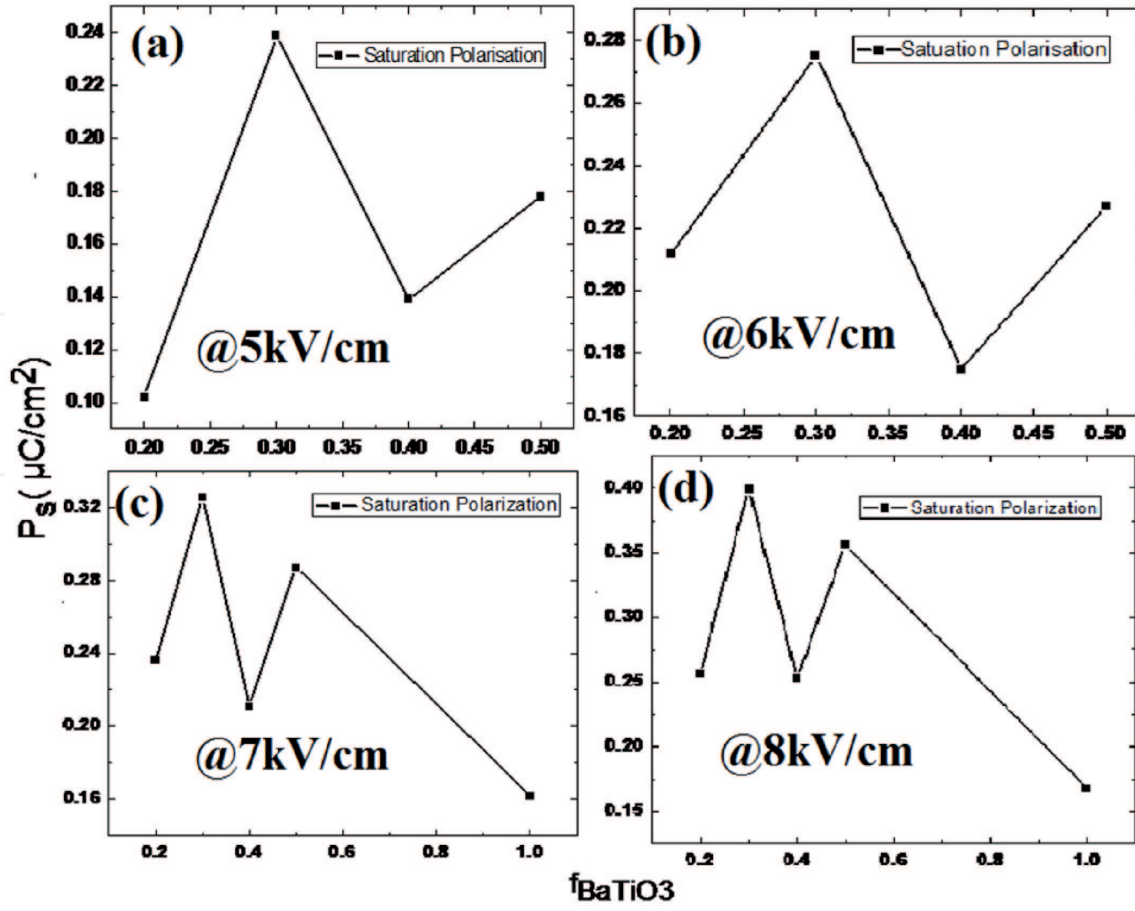


Figure 6.  
 $P_s \sim f_{\text{BaTiO}_3}$  at different electric fields (a) 5 kV/cm (b) 6 kV/cm (c) 7 kV/cm (d) 8 kV/cm.

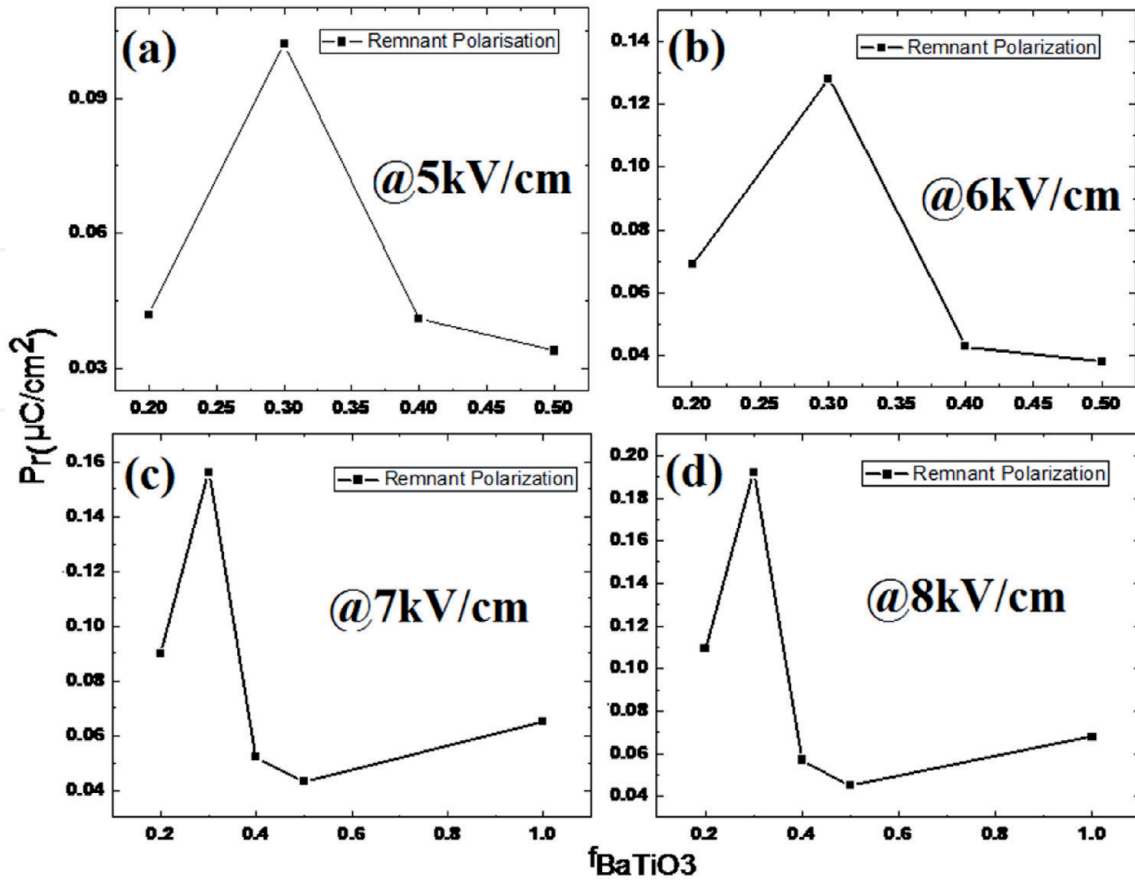


Figure 7.  
 $P_r \sim f_{\text{BaTiO}_3}$  at different electric fields (a) 5 kV/cm (b) 6 kV/cm (c) 7 kV/cm (d) 8 kV/cm.

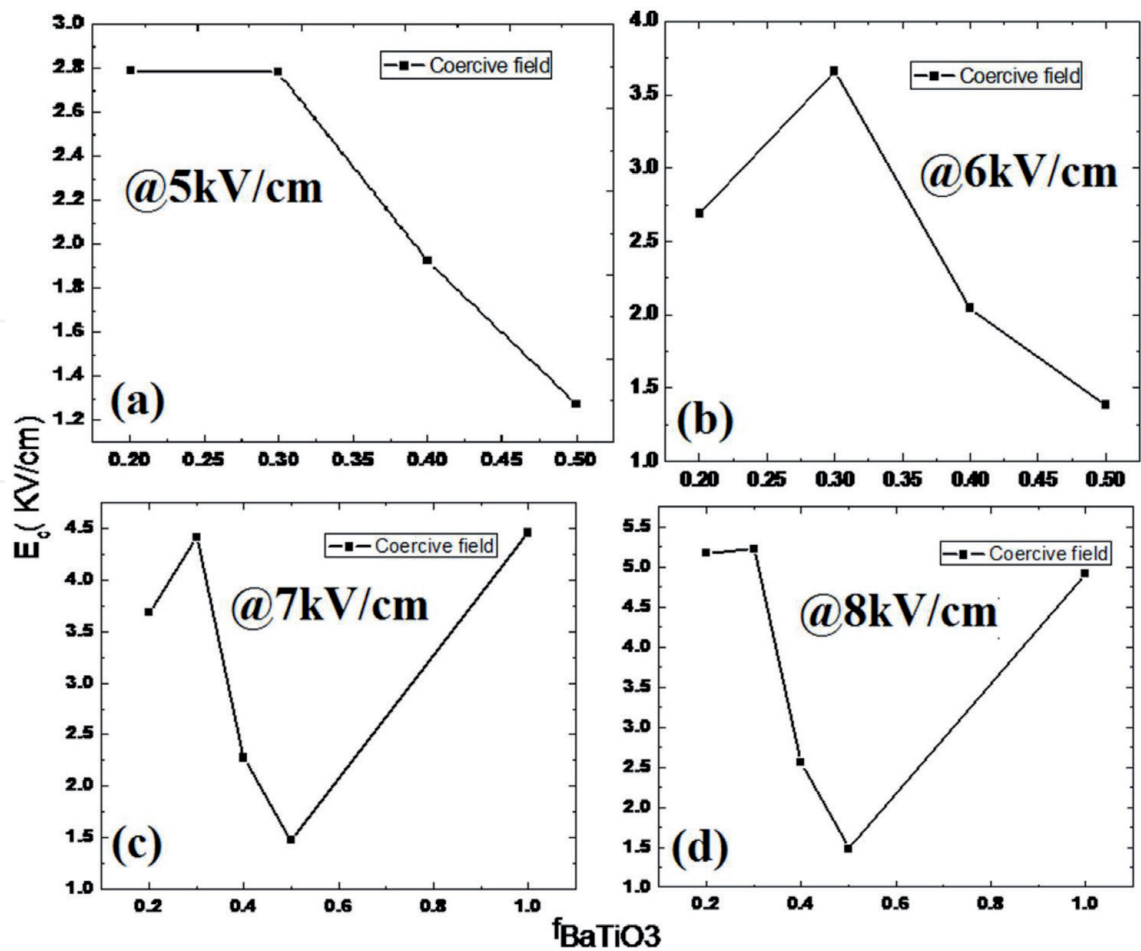


Figure 8.  
 $E_c \sim f_{BaTiO3}$  at different electric fields (a) 5 kV/cm (b) 6 kV/cm (c) 7 kV/cm (d) 8 kV/cm.

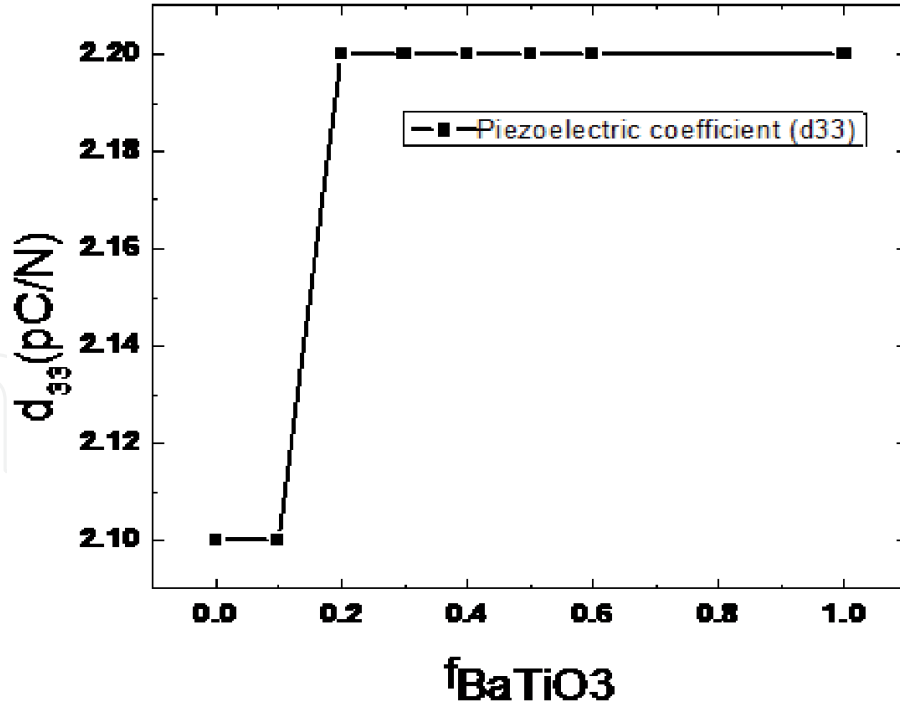
### 3.3 Piezoelectric properties

Figure 9 gives the explanation of change in piezo- electric coefficient ( $d_{33}$ ) of the PF as a function of  $f_{BaTiO3}$ . On increasing the concentration of  $n$ -BaTiO<sub>3</sub>, the piezoelectric nature of composite also increases and when the amount of  $n$ -BaTiO<sub>3</sub> filler content increases much, the value of  $d_{33}$  becomes constant. The value of  $d_{33}$  increases from 2.10 pC/N for  $f_{BaTiO3} = 0.0$  up to 2.20 pC/N for  $f_{BaTiO3} = 0.20$  and remains constant, beyond  $f_{BaTiO3} = 0.20$  up to  $f_{BaTiO3} = 1.0$  because of the aggregated filler ( $n$ -BaTiO<sub>3</sub>) causes poor improvement in the peizo- electric nature of the PF.

### 3.4 Dielectric properties

The variation of dielectric properties of the PCC as a function of frequency at 300 K are shown in Figure 10a and b, respectively. The value of  $\epsilon_{eff}$  at 50 Hz for the 0.0 sample is 16 while this value increases up to 120 linearly up to the PCC with  $f_{BaTiO3} = 0.5$  & after that it raises up to the value of 330 & 420 for the samples with  $f_{BaTiO3} = 0.55$  &  $f_{BaTiO3} = 0.60$  respectively. The higher value of  $\epsilon_{eff}$  for the  $f_{BaTiO3} = 0.55$  &  $f_{BaTiO3} = 0.60$  are attributed to the large interfacial polarization arising due to the occurrence of spherulites and created large interface like structures(during cold pressing), while the spherulites are lost for the hot molded samples (Figure 11).

The static dielectric constant ( $\epsilon_r$ ) of the cold pressed pure PVDF is ~16 i.e. higher than the  $\epsilon_r$  of hot molded pure PVDF (~10) due to the loss of spherulites (Inset, Figure 11) of the polymer.  $\epsilon_{eff}$  decreases with increase of frequency due to the



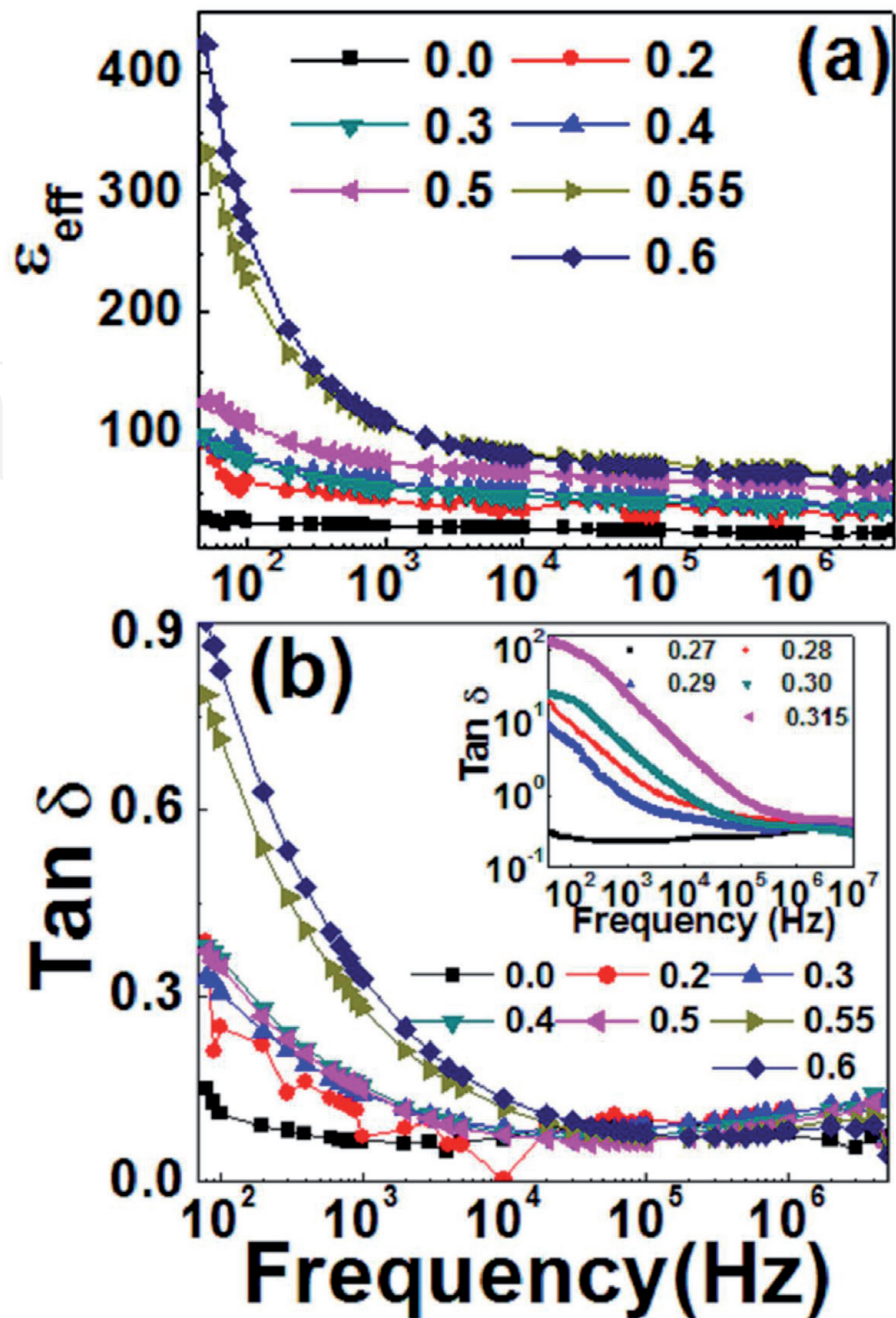
**Figure 9.**  
Variation of the piezoelectric coefficient ( $d_{33}$ ) as a function of  $f_{BaTiO_3}$ .

absence of contribution from interfacial polarization at higher frequencies, where only the involvement from dipolar and atomic polarization exists. A very low  $\tan \delta$  for the PCC with  $f_{BaTiO_3} = 0.6$  (having highest  $\epsilon_{eff} = 420$  observed at 50 Hz) was approached to 0.9 at 50 Hz and that also decreases with increase of frequency and the tendency of decrement is also observed for all the PCC. Nevertheless, in the cold pressed PMC [33], the  $\tan \delta$  was reported to be 10 at 50 Hz (Inset, **Figure 10b**) for the percolative sample, with  $\epsilon_{eff} \sim 2000$ . The PMC at  $f_c$  shows 10 times higher value of  $\tan \delta$  in contrast to the result of PCC, although both type of polymer composites are prepared by the same cold pressing procedure. **Figure 12** shows the behaviour of  $\epsilon_{eff}$ ,  $\sigma_{eff}$  and  $\tan \delta$  of the composites as a function of  $f_{BaTiO_3}$  at different frequencies. The  $\epsilon_{eff}$  rises linearly from 16 to 120 for  $f_{BaTiO_3}$  rises from 0.0 to 0.50 at 100 Hz, due to the large interfacial polarization occurring due to the presence of spherulites. The interfaces formed at the PCC, increases  $\epsilon_{eff}$  largely from 120 to 350 & 420 for  $f_{BaTiO_3} = 0.55$  & 0.60 respectively. The expression developed by Yamada et al. (which is a model for explaining the sum properties of the composite) was fitted to the dielectric data (**Figure 12(b)**) at 1 kHz frequency. The model is given by

$$\epsilon_{eff} = K_{PVDf} \left[ 1 + \frac{nf_{BaTiO_3}(K_{BaTiO_3} - K_{PVDf})}{nK_{PVDf} + (K_{BaTiO_3} - K_{PVDf})(1 + f_{BaTiO_3})} \right] \quad (1)$$

where  $\epsilon_{eff}$  is the effective dielectric constant of the composite,  $K_{PVDf}$  and  $K_{BaTiO_3}$  are the dielectric constants of the polymer matrix and the ceramic, respectively,  $f_{BaTiO_3}$  is the volume fraction of the ceramic and 'n' is a parameter related to the geometry of ceramic particles [2].  $K_{PVDf}$ ,  $K_{BaTiO_3}$  and  $n$  found from the fitting of Eq. (1) to the dielectric data are 17, 1600 and 10, is in good agreement with the earlier literature [5].

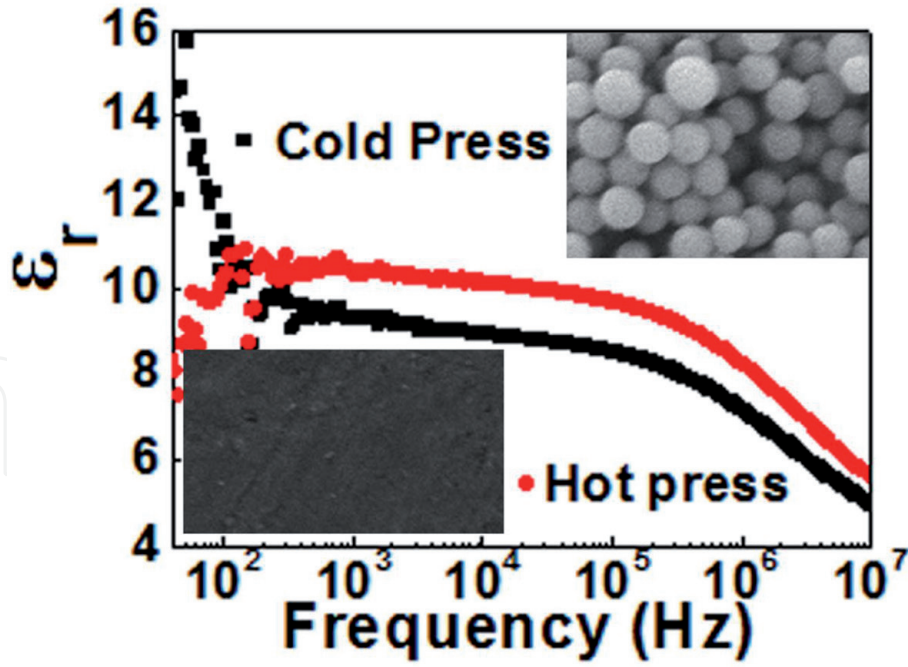
The  $\sigma_{eff}$  &  $\tan \delta$  increases with the increase of  $f_{BaTiO_3}$  in the PCC slowly, suggesting the semiconducting nature of the BaTiO3 nano-ceramics. For  $f_{BaTiO_3} = 0.6$ , the  $\sigma_{eff}$  value varies within  $10^{-8} \Omega^{-1} \text{cm}^{-1}$  to  $10^{-4} \Omega^{-1} \text{cm}^{-1}$  for frequency varying between 50 Hz to 5 MHz, while the value of  $\tan \delta$  is maintained in between 0.1 to 0.9.



**Figure 10.**  
(color online) the variation of (a)  $\epsilon_{\text{eff}}$  and (b)  $\tan \delta$  as a function of frequency at 300 K for the PD, inset:  $\tan \delta \sim$  frequency for some typical percolative PMC samples showing higher  $\tan \delta$  [33].

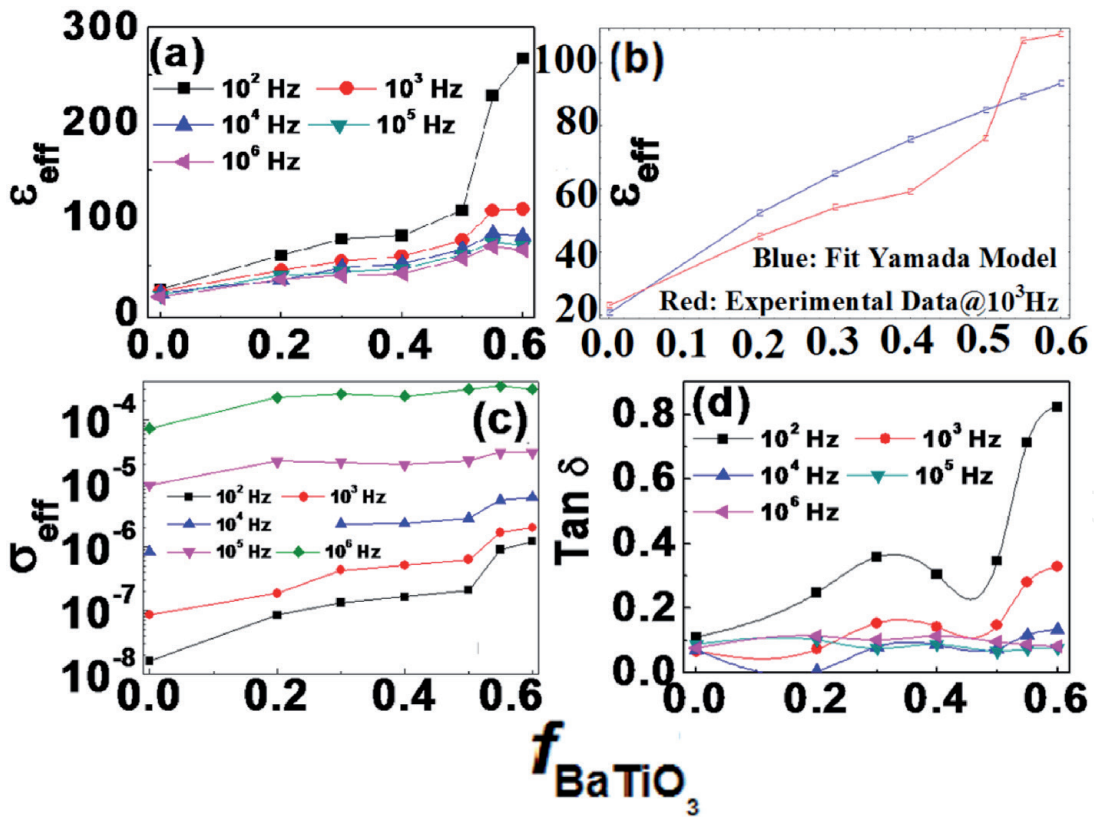
$\sigma_{\text{eff}}$  &  $\tan \delta$  are also found to be increasing with increase of frequency, suggesting conventional hopping conduction in the disordered PCC. Similarly,  $\sigma_{\text{eff}}$  value was found to be very low i.e. less than  $10^{-4} \Omega^{-1}$  for all the PCC and that value remains constant over the entire frequency range. The  $\tan \delta$  raises slowly as a function of  $f_{\text{BaTiO}_3}$  is found to be less than 0.9 even with the PCC having  $f_{\text{BaTiO}_3} = 0.6$ .

The electrical parameters as a function of temperature of the PCC was confirmed by measuring and are given in **Figure 13**. For  $f_{\text{BaTiO}_3} = 0.4$  (**Figure 13a**) &  $f_{\text{BaTiO}_3} = 0.50$  (**Figure 13b**), the low frequency (50 Hz) value of  $\epsilon_{\text{eff}}$  is sustained at a thermal stabilized value of 90 & 130 (with their corresponding decrement as a function of frequency) as a function of temperature from 40–100°C. The stabilization of  $\epsilon_{\text{eff}}$  is ascribed due to the major effective contribution coming from the sum properties of the dielectric constant of both the components. Yet, for the samples with  $f_{\text{BaTiO}_3} = 0.55$  & 0.6, the reached  $\epsilon_{\text{eff}} \sim 350$  & 420 value arises due to the sum properties



**Figure 11.**

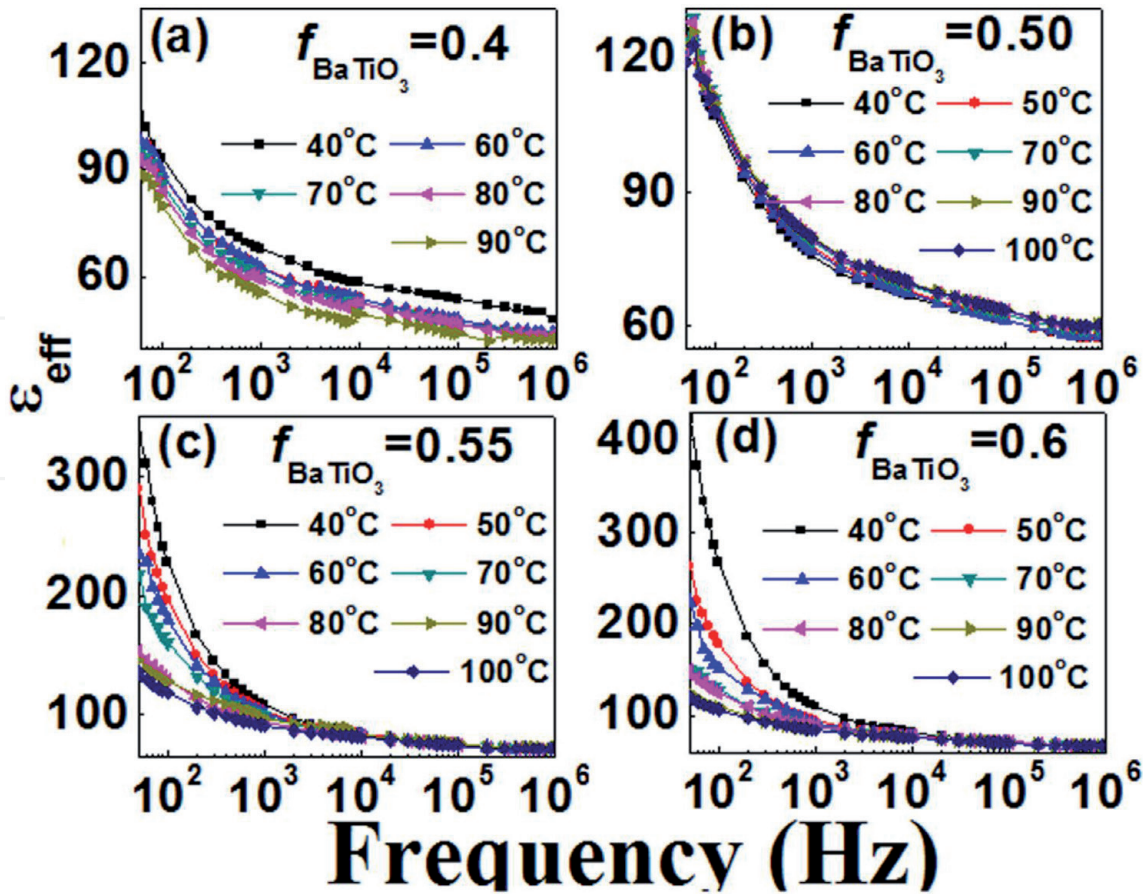
The variation of dielectric constant ( $\epsilon_r$ ) with frequency for both cold and hot press PVDF, inset: The FESEM micrograph of the cold/hot molded PVDF showing the presence/loss of spherulites at temperature higher than the room temperature.



**Figure 12.**

(color online) the variation of (a)  $\epsilon_{\text{eff}}$  experimentally (b) fitting of  $\epsilon_{\text{eff}}$  experimental data at 1KHz with Yamada model as a function of  $f_{\text{BaTiO}_3}$  (c)  $\sigma_{\text{eff}}$  and (d)  $\tan \delta$  as a function of  $f_{\text{BaTiO}_3}$  for various frequencies at 300 K.

of the dielectric constant of both the components as well as also due to the major contribution of the spherulites. Hence with the rise of temperature, the  $\epsilon_{\text{eff}}$  decreases due to the deteriorating of the spherulites of the PCC (**Figure 13c and d**). Hence the spherulites are useful at room temperature in case of PCC for realizing high value of  $\epsilon_{\text{eff}}$  with lower  $\tan \delta$ .



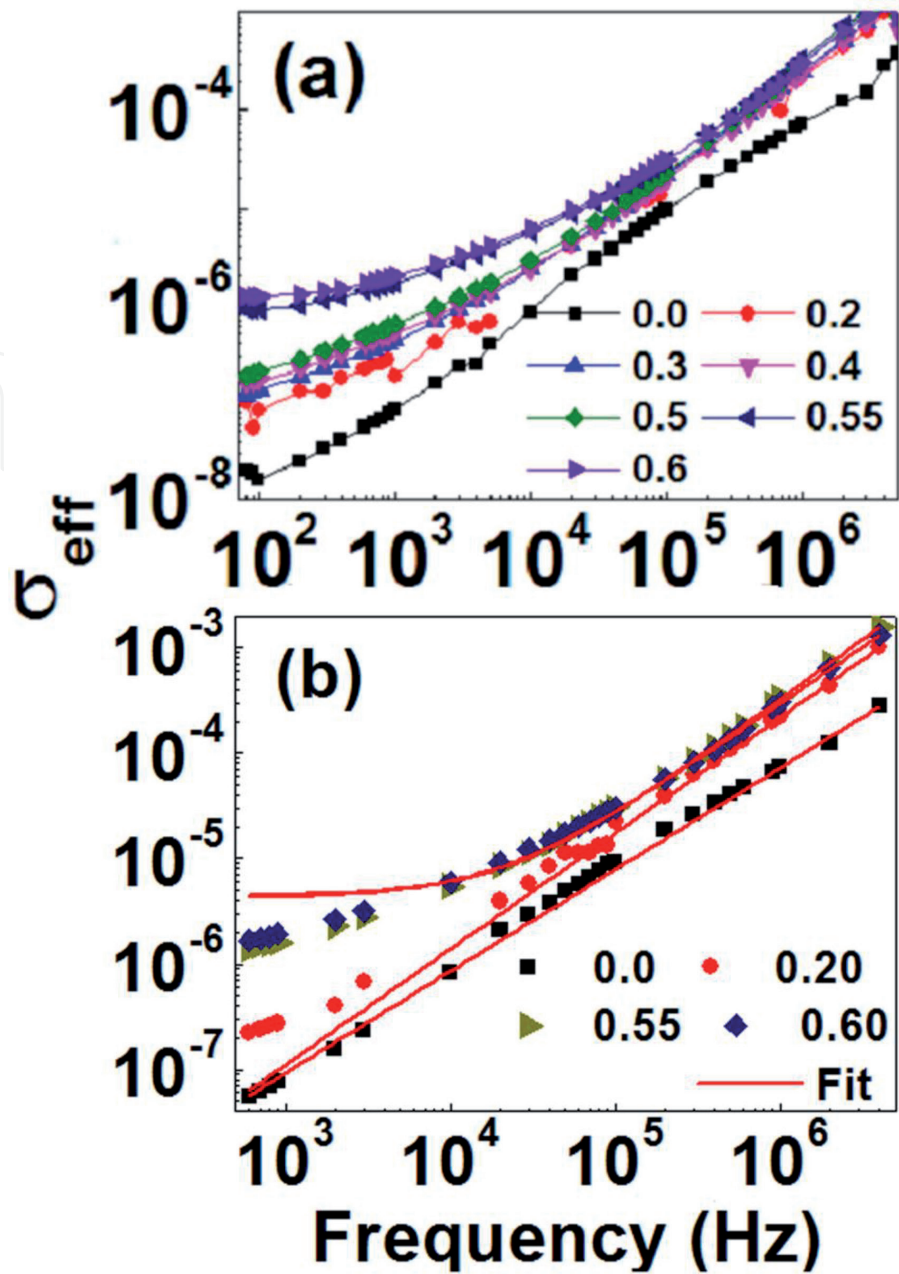
**Figure 13.**  
(color online) the variation of  $\epsilon_{\text{eff}}$  as a function of frequencies for the temperature varying from 40°C to 100°C for varying  $f_{\text{BaTiO}_3}$  (a) 0.40 (b) 0.50 (c) 0.55 (d) 0.60.

### 3.5 Electrical conductivity

Ac conductivity ( $\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta$ ) as a function of frequency at different  $f_{\text{BaTiO}_3}$  is shown in **Figure 14**. The  $\sigma_{\text{eff}}$  as a function of frequency was found to be the ac hopping conduction satisfying the Johnson's fractional power law. The plot shows dispersion of ac conductivity with frequency corresponding to  $f_{\text{BaTiO}_3} \leq 0.20$ , be in agreement with Eq. (2) i.e.

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^k \quad (2)$$

with the  $\sigma_{dc}$  part becoming zero and the value of  $k \sim 1$ . The non-presence of dc conductivity for the samples with  $f_{\text{BaTiO}_3} \leq 0.20$ , can be understand as the non-presence of percolating paths (being formed from the semiconducting  $\text{BaTiO}_3$  nano-ceramics in the PVDF matrix) due to insufficient fraction of  $\text{BaTiO}_3$ . The long range dc conduction starts to develop for  $f_{\text{BaTiO}_3} = 0.3$  to 0.5, but a good fit of Eq. (2) could not be resulted for them as the percolating paths were not sufficient. Interestingly, for  $f_{\text{BaTiO}_3} \geq 0.55$ , a mixed conductivity is found. The plateau due to the appearance of long range dc conductivity. At higher frequency the conductivity becomes more or less with  $f_{\text{BaTiO}_3}$  dependent. This “hopping or critical frequency  $\omega_H$ .” at which the change in slope takes place can be observed to be increasing with the increase of  $f_{\text{BaTiO}_3}$ , since the length of dc plateau increases with increase of  $f_{\text{BaTiO}_3}$  from 0.3 to 0.6. On the other hand, the value of ‘ $k$ ’ lies well within the Johnson's universal regime [0,1] symptomatic of the validity of Johnson's power law universally.



**Figure 14.** (color online) the variation of (a)  $\sigma_{eff}$  experimentally and (b)  $\sigma_{eff}$  fitted with Jonscher's power law, as a function of frequencies.

### 3.6 Conclusions

The micro-structural, ferroelectric, piezoelectric, dielectric and conductivity properties of the polymer composites have been analyzed and are correlated. The properties strongly depend on the novel cold pressing preparation techniques and the dispersion of *n*-BaTiO<sub>3</sub> filler particles into the PVDF matrix and also on the nano-sizes of ceramics. The addition of *n*-BaTiO<sub>3</sub> enhances the ferroelectric, piezoelectric and dielectric properties of the composites. It is also found that this cold pressing method is more suitable to the PCC based on PVDF matrix (since very low value of Tan $\delta$  is observed). The spherulites present in PVDF matrix are always helpful in maintaining the dielectric constant and increasing the  $\epsilon_{eff}$  of PCC. The enhancement of dielectric results are explained with the help of standard Yamada model. The mixed conductivity appears for the PD/PF and Jonschers universal fractional power law is well satisfied for all composites. The hopping conduction in these disordered materials have been confirmed in all PCC. The dynamics of

charge carriers are filler/temperature dependent. These PD/PF should be explored for applications by focusing the research on achieving lowered  $\tan \delta$ , which will increase the dielectric field strength/high energy density and better ferroelectric/piezoelectric properties may be expected for various multifunctional applications.

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