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**Enhanced Dielectric properties of Surface hydroxylated Bismuth ferrite -Poly (vinylidene fluoride-co-hexafluoropropylene) Composites for energy storage devices**

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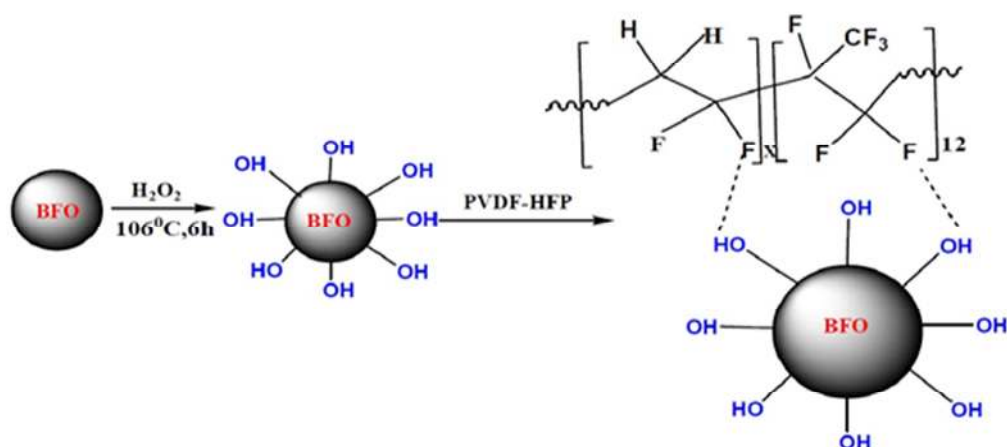
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## Abstract



Dielectric properties of Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) based composites with surface hydroxylated BiFeO<sub>3</sub> (h-BFO) particles were prepared by solution casting techniques. The h-BFO fillers were synthesized from BiFeO<sub>3</sub> in aqueous solution of H<sub>2</sub>O<sub>2</sub>. The result showed that the dielectric properties of the h-BFO-PVDF-HFP composite exhibits better dielectric properties than that of the unmodified BFO-PVDF-HFP composites. Meanwhile, the 30 wt% of h-BFO-PVDF-HFP composite showed higher dielectric constant, better suppressed dielectric loss, high remnant polarization and high electrical conductivity. It is suggested that the strong interaction between h-BFO particles and PVDF-HFP matrix at the interface is the key role in the enhancement of the dielectric properties. It is helpful to understand the influence of surface hydroxylation on the interfaces between the filler and the polymer matrix. The outcome of this study may be exploited in the progress of high energy storage device applications.

**Keywords:** BiFeO<sub>3</sub>; Poly (vinylidene fluoride-co-hexafluoropropylene); Composite; Dielectric properties; Surface hydroxylation.

## 1. Introduction

Polymer composites (PNCs) with high dielectric constant and low dielectric loss have attracted considerable interest recently owing to their potential applications in electrical and electronic industries such as gate dielectrics [1], embedded capacitors [2], aerospace and power industries [3-4]. In the past few decades, much effort has been devoted to an improvement of flexible ceramic filled polymer composites with high dielectric constant, which can be applicable for electronic industries to meet the rigorous requirements of advanced capacitors [5-6]. The traditional multiferroic material such as  $\text{BiFeO}_3$  (BFO) has good dielectric constant but it has poor moldability, low breakdown strength, high processing temperature and it is very brittle and shock resistive in nature [7-8]. Meanwhile, ferroelectric based polymers and their respective copolymers [e.g., Poly(vinylidene fluoride) (PVDF), Poly(vinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), Poly (vinylidene fluoride-trifluoroethylene) (PVDF-TrFE)] have certain qualities such as they have (i) good electrical resistance (ii) easy process-ability (iii) high breakdown strength and (iv) low cost which may be useful for the composites regarding their dielectric performances [9-13] but, they have low dielectric constants ( $< 5$ ) which restrict their future applications in the energy storage device [14]. To overcome this issues the combination of both fillers and polymer can fabricate novel type of ceramic based polymer composite to get high energy storage materials [15-16].

As many studies have been done by the addition of different types of polymer with various kinds of filler containing high dielectric constant, low dielectric loss and good thermal stability, to date much research work has been focused on the interface between the ceramic filler and the polymer matrix for dielectric applications of the polymer based composites [17-20]. Moreover, the effect of interface can remarkably improve the dielectric properties of the composites [21].

In this paper, we report a novel idea of preparing a surface hydroxylated  $\text{BiFeO}_3$  (h-BFO) particles with a ferroelectric polymer (PVDF-HFP) based composite via solution casting technique. The  $\text{BiFeO}_3$  particles are treated with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to produce -OH groups on the surface of BFO particles. A comparison of PVDF-HFP based composite filled with unmodified (BFO) and modified (h-BFO) particles are developed. The h-BFO-PVDF-HFP composite has a high dielectric constant, high electrical conductivity and high remnant

polarization as compared to that of unmodified BFO-PVDF-HFP composite. This may be due to the hydrogen bond which leads to stronger interaction between the h-BFO fillers and the PVDF-HFP matrix [21]. We also have investigated the consequence of such surface hydroxylation on the dielectric properties of the composites with respect to interface zone.

## **2. Experimental**

### **2.1. Materials**

Poly (vinylidene fluoride-co-hexafluoropropylene) [P (VDF-HFP)] was purchased from Sigma-Aldrich, India.  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  was procured from Merck, India and N, N-dimethyl formamide (DMF) was purchased from Himedia Laboratories Pvt. Ltd, India. The 30% Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution was used to hydroxylate the surface of  $\text{BiFeO}_3$ . All chemicals were used as received.

### **2.2. Preparation of Bismuth ferrite (BFO) particles**

The preparation of BFO particles were prepared by the conventional solid state reaction method. The equi-molar quantities of  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were first thoroughly mixed by an agate mortar and pestle in the presence of air for half an hour and then in methanol for another 2 hours. Then the mixed powders were calcined in a high purity alumina crucible at an optimized temperature of  $700^\circ\text{C}$  for 2 hours.

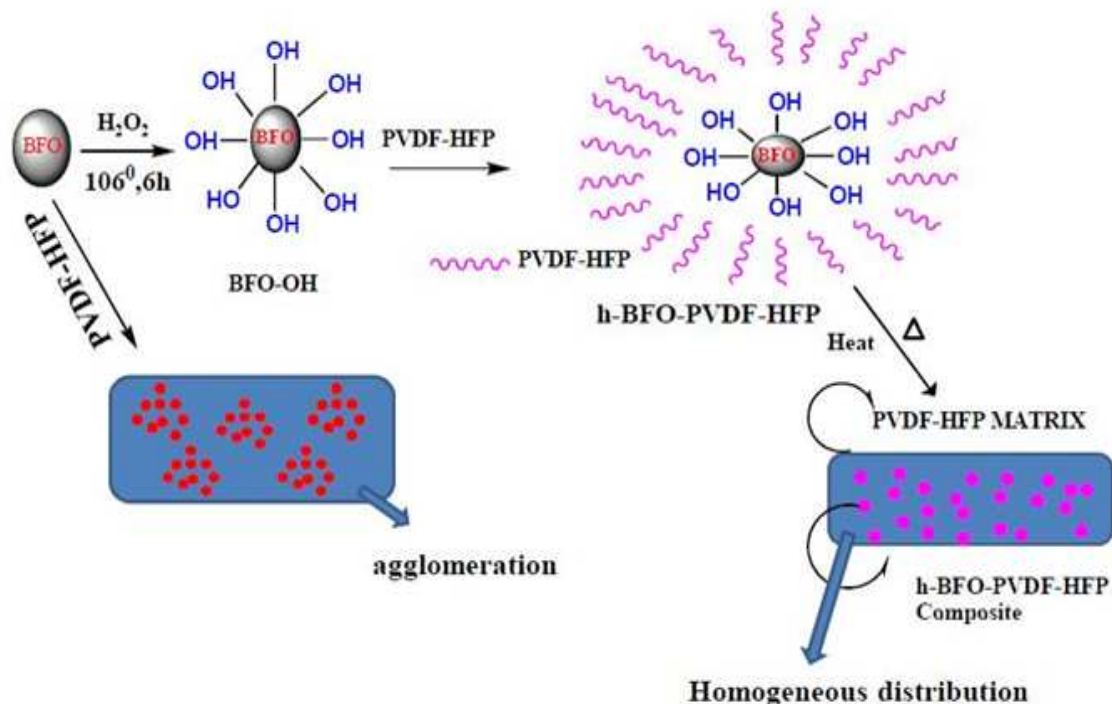
#### **2.2. Surface Hydroxylation of Bismuth ferrite (h-BFO)**

BFO particles (5g) were dispersed in aqueous solution of  $\text{H}_2\text{O}_2$  (30 wt%) were combined in a round bottomed flask and sonicated for 30 min. The solution was refluxed at  $106^\circ\text{C}$  for 6 h and then the particles were recovered by centrifugation. The obtained BFO particles were washed with de-ionized water and then were dried under oven at  $80^\circ\text{C}$  for 24 h. The hydroxylated BFO particles were named as h-BFO.

### **2.3. Preparation of Bismuth ferrite-PVDF-HFP composite films**

The BFO-PVDF-HFP composite film was prepared by solution casting technique. Firstly, the required amounts of BFO particles were dispersed in DMF by ultrasonication for 30 minutes. At the same time, PVDF-HFP was dissolved in DMF by the help of magnetic stirrer. The suspension of DMF and particles were added with the PVDF-HFP-DMF solution. Consequently,

the solution was ultra-sonicated for 1 h and again stirred for 2 h to obtain a homogeneous mixture. Then the resulting mixture was poured into a clean glass petri-dish and dried in an oven at 80°C for overnight to remove any traces of the solvent. The total preparation process is shown in the Fig. 1.



**Fig. 1 Schematic illustration for the preparation of BFO-PVDF-HFP composites.**

### 3. Characterization

X-ray diffraction (XRD) spectra of the composite films were recorded by using an X-ray diffractometer (Mini Flex II, Rigaku, Japan) with  $Cu K_\alpha$  ( $\lambda = 0.15405$  nm) radiation. The morphology and microstructure were analyzed by scanning electron microscope (HITACHI COM-S-4200) operated at 30 kV. Fourier-transform infrared (FTIR) spectroscopy was recorded with a 5700 FTIR (Nicolet) to examine the modification of bismuth ferrite. The dielectric properties of the composite films were carried out by using an impedance analyzer (HIOKI 3532 LCR HiTESTER) at a frequency range (100 Hz–1 MHz) at room temperature. The ferroelectric hysteresis (P-E) loop (polarization vs electric field) curves were obtained on the standard

Hysteresis Automatic P-E Loop Tracer (Marine India Pvt. Ltd.). An external electric field of 3kV/cm was applied at a frequency of 50 Hz to measure the P-E loop. The leakage current of the composites were measured by using an electrometer (Keithley 6517B).

## 4. Results and Discussion

### 4.1. X-ray diffraction analysis

Fig. 2 illustrates the XRD patterns of pure BFO and h-BFO particles prepared via solid state reaction route. It can be seen that, the various diffraction patterns at  $2\theta = 32.11^\circ$  and  $32.40^\circ$  correspond to (104) and (110) planes which are the two characteristic peaks of BFO corresponding to rhombohedral crystal structure with space groups R3c at room temperature (JCPDS file no.-86-1518 ) but, with a slight indication of phase impurity (viz.,  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{40}$ ) [22-23]. As the BFO particles were synthesized by conventional solid state reaction method, the trace amount of impurity phases like  $\text{Bi}_2\text{Fe}_4\text{O}_9$  (mullite phase) and  $\text{Bi}_{25}\text{FeO}_{40}$  (sillenite phase) are formed along with the bulk BFO [24-25]. These impurities may be due to high volatility of bismuth and excess of bismuth concentration. The presence of impurity concentration causes the structural transformation of BFO. Further there is a structural change was observed from XRD in the BFO after addition of -OH groups, which is clearly shown in the Fig.2 (b).

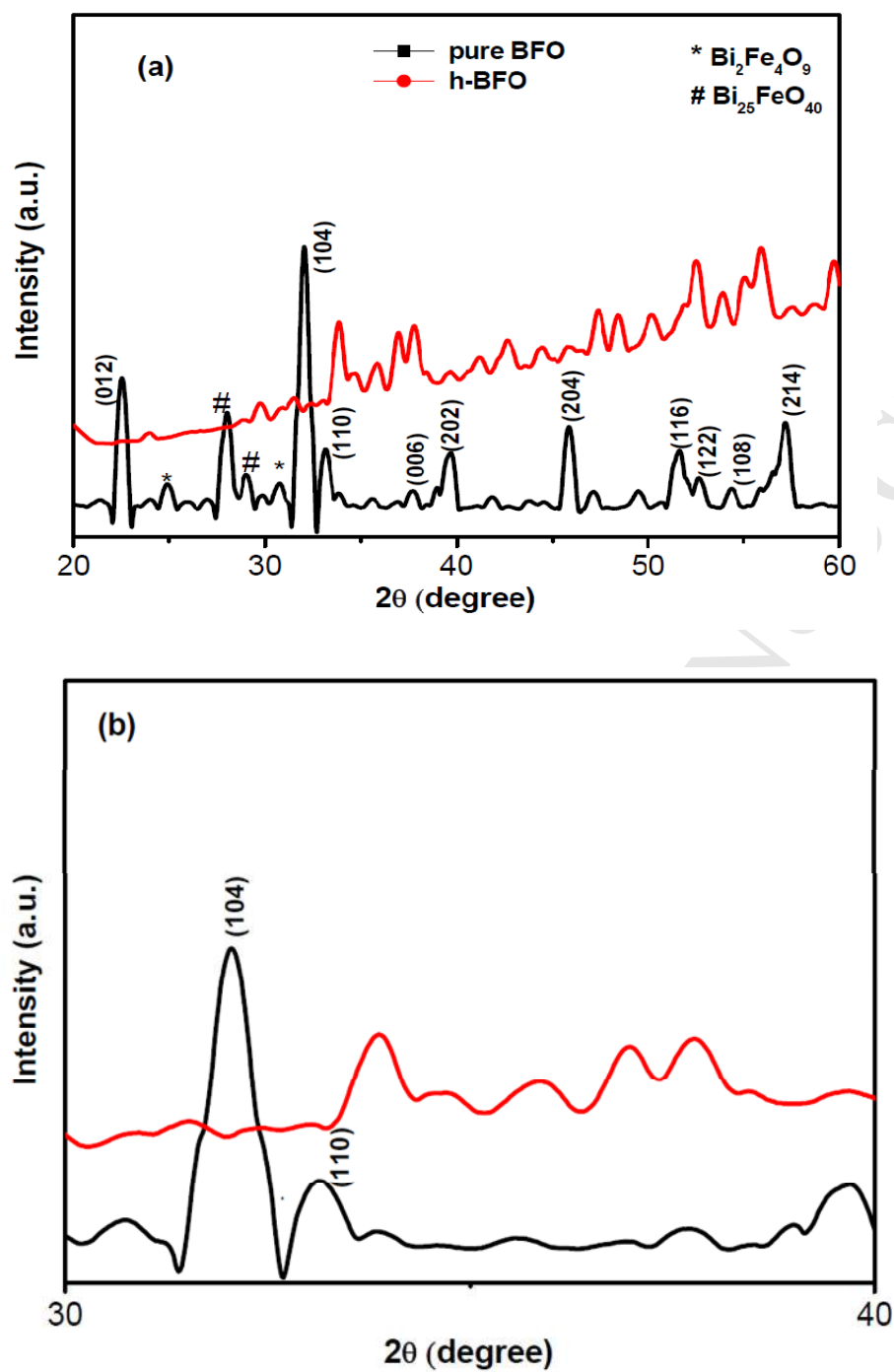
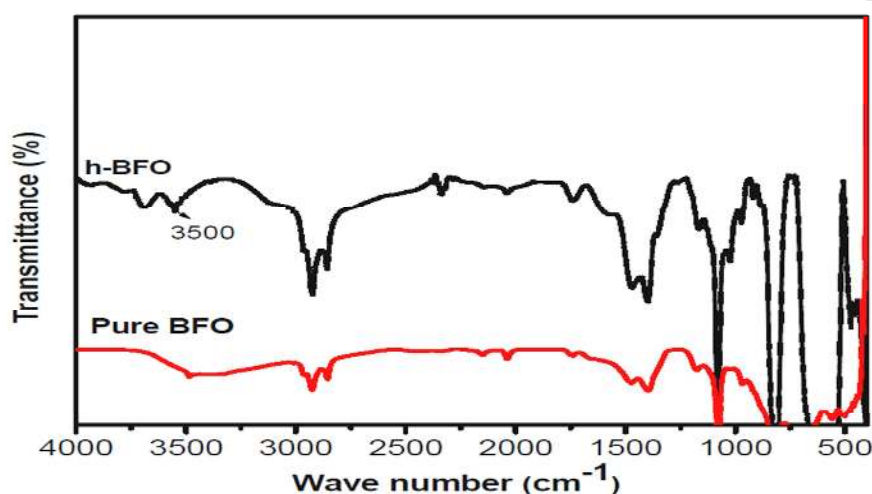


Fig. 2 XRD patterns of (a) pure BFO, h-BFO and (b) magnified view of the peak positions with a range of  $(30^\circ \leq 2\theta \leq 40^\circ)$ .



## 4.2. FTIR study

The effect of  $\text{H}_2\text{O}_2$  on the surface behavior of  $\text{BiFeO}_3$  (h-BFO) particles were analyzed by using FTIR. As shown in Fig. 3, it is observed that, the absorption band at  $\sim 3500\text{ cm}^{-1}$  which corresponds to h-BFO represents the stretching mode of surface hydroxyl groups and this clearly indicates that the hydroxyl groups are present in the BFO surfaces. Again, the absorption peak at  $455\text{ cm}^{-1}$  is assigned to the  $\text{FeO}_6$  octahedral of the perovskite structure. This absorption band is due to the Fe-O stretching and bending vibration of BFO. This represents the presence of metal-oxygen bond.

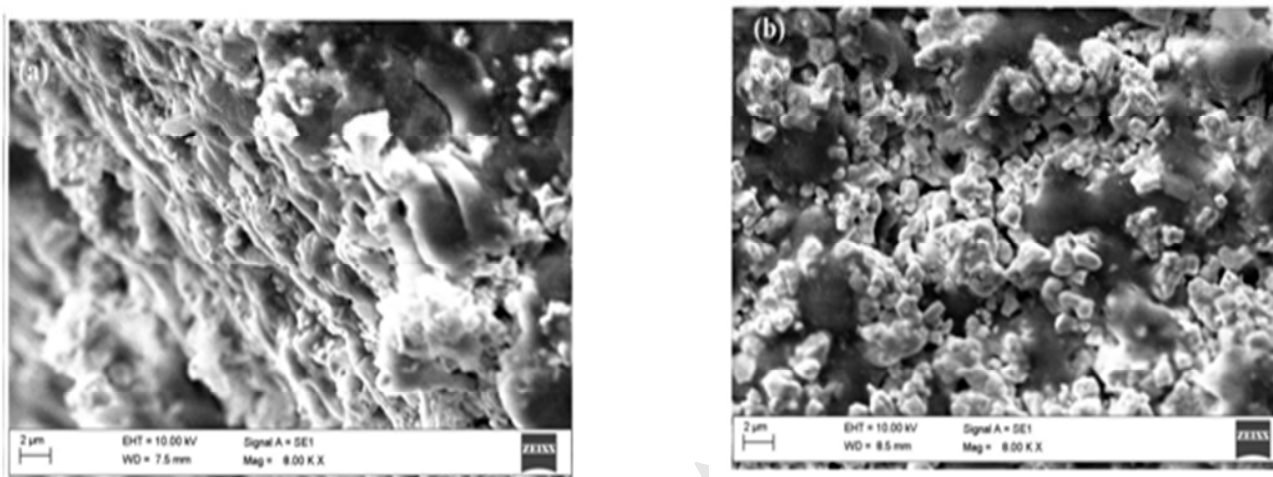


**Fig.3 FTIR spectra of the h-BFO particles**

## 4.3. Morphology Study

Fig.4 (a,b) illustrates SEM images of the BFO-PVDF-HFP and h-BFO-PVDF-HFP composites. It can be distinctly revealed that most of the BFO particles are well dispersed in both the samples. This result shows that homogeneous distribution of BFO-PVDF-HFP composites can be achieved by solution casting technique. Moreover, there are some voids and small pores are present in the unmodified BFO surfaces in the polymer matrix (Fig.4a). On the other hand, the surface voids and small pores are reasonably reduced in case of h-BFO particles in the polymer matrix (Fig.4b). This result shows that there is a much stronger interaction between h-BFO

particles with the PVDF-HFP matrix as compared to that of unmodified BFO. The h-BFO particles when added with PVDF-HFP, leads to formation of hydrogen bond between the F atoms of the polymer chain and the -OH groups of the modified BFO particles, which results in strong interaction between h-BFO particles with the PVDF-HFP matrix.

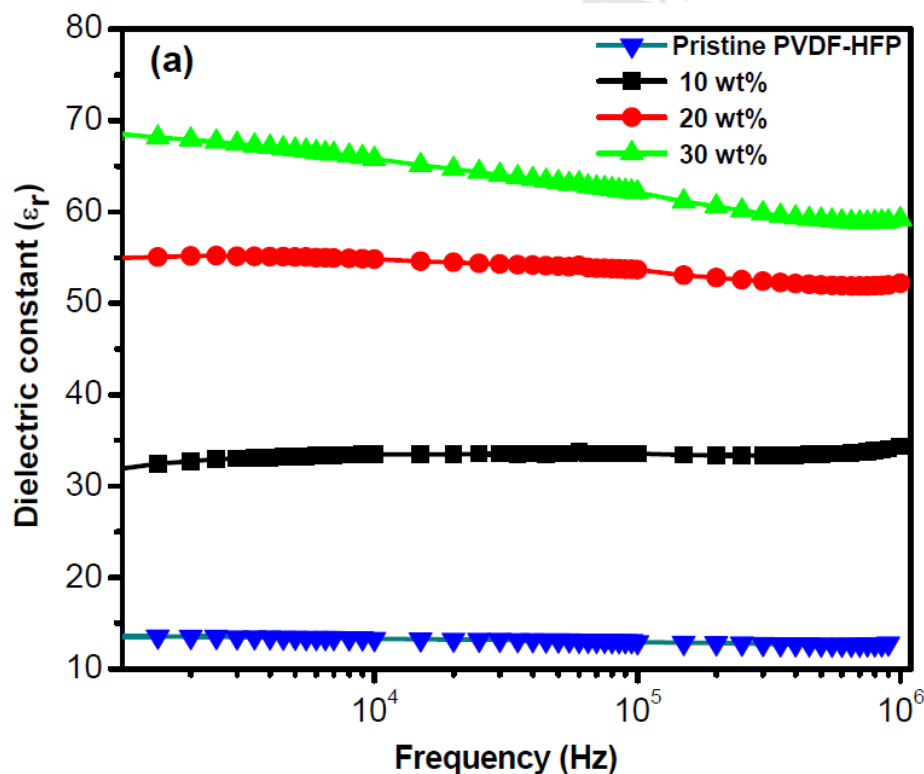


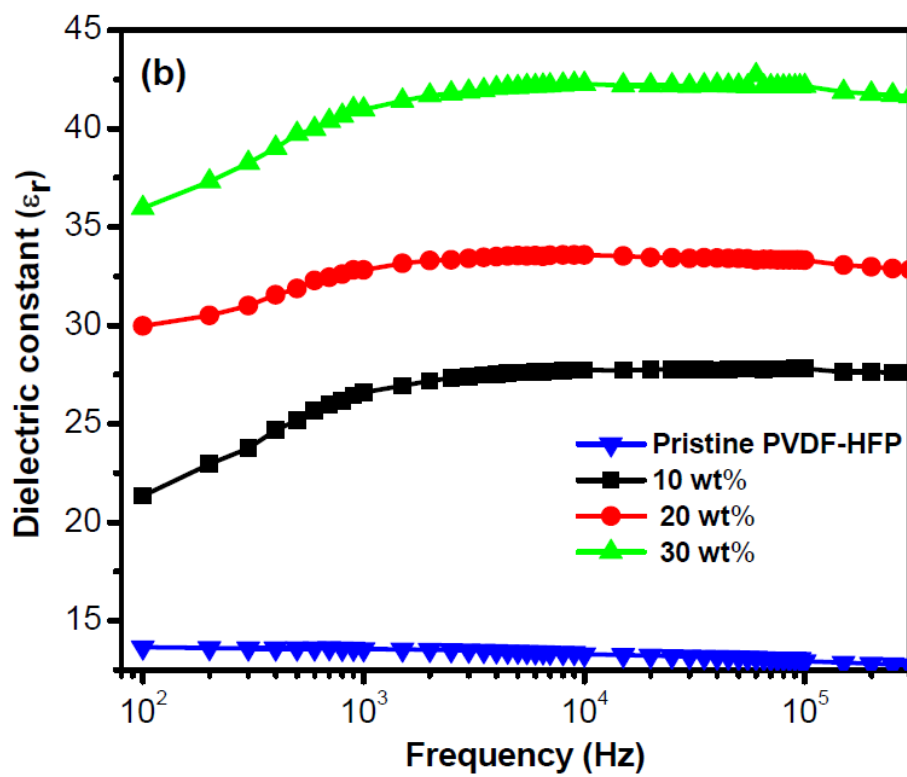
**Fig. 4 SEM images of (a) unmodified BFO-PVDF-HFP and (b) h-BFO-PVDF composites.**

#### 4.4. Dielectric analysis

Fig. 5(a,b) illustrates the variation of dielectric constant, pristine PVDF-HFP, unmodified BFO-PVDF-HFP and h-BFO-PVDF-HFP composite films with frequency at room temperature. From Fig. 5(a), it can be seen that the dielectric constant of h-BFO-PVDF-HFP composite shows significantly improved dielectric properties than those of unmodified one (as shown in Fig. 5b) by introducing filler contents. The dielectric constant of h-BFO-PVDF-HFP and unmodified BFO-PVDF-HFP composites increases steadily with increasing the BFO contents over the whole frequency ranges under study, but at higher concentration of filler loading, the dielectric constant exhibits more rapid increase. Besides, it is interesting to see that, in case of h-BFO-PVDF-HFP composite the value of dielectric constant increases from 33 to 68 for 10 and 30 wt% of BFO at  $10^2$  Hz (Table-1), which is nearly 5 times higher than that of pristine PVDF-HFP (its dielectric constant is  $\sim 13$  at  $10^2$  Hz). In both cases, it is observed that the value of dielectric constant decreases with increase in frequency. The decrease in dielectric constant with the increase in frequency can be explained on the basis of various types of polarization effects, i.e., electronic,

ionic, dipolar and interfacial polarization. However, the linearity of dielectric constant of composite at high frequency range is mainly due to the reduction of space charge and Maxwell-Wagner polarization. At the low frequency range all types of polarizations easily respond as the time changes in electric field, but as the frequency of the field increases different polarizations are cleaned out. Further, it is found that the interface between the ceramic filler and the polymer matrix plays a major role in the enhancement of the dielectric constant of the composites with filler loading [26-27]. The surface hydroxylation of BFO particles (h-BFO) can increase the interaction between fillers and polymer matrix this is mainly due to polarization between hydroxylated BFO (h-BFO) and polymer phase. Secondly, when the h-BFO particles are mixed with PVDF-HFP matrix, hydrogen bond will form between the F atom of the PVDF-HFP matrix and -OH groups on the surface of the h-BFO particles. So, there is a strong interaction between h-BFO particles and PVDF-HFP matrix. The plausible interaction between PVDF-HFP and h-BFO is shown in Fig.6. As a result, the dielectric constant of such composite with surface hydroxylated BFO particles is much higher than that of unmodified BFO particles which is clearly shown in Fig. 5 (a,b).





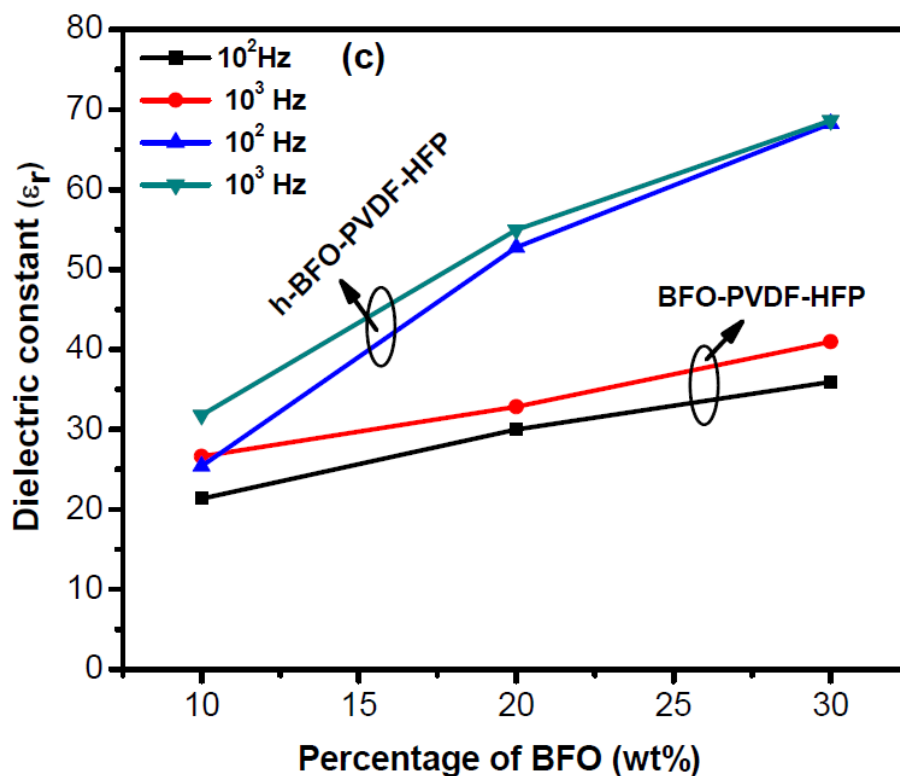


Fig.5 Frequency dependences of dielectric constant comparison: (a) h-BFO-PVDF-HFP (b) unmodified BFO-PVDF-HFP (c) unmodified and h-BFO-PVDF-HFP composites measured at  $10^2$  Hz and  $10^3$  Hz as a function of BFO filler contents.

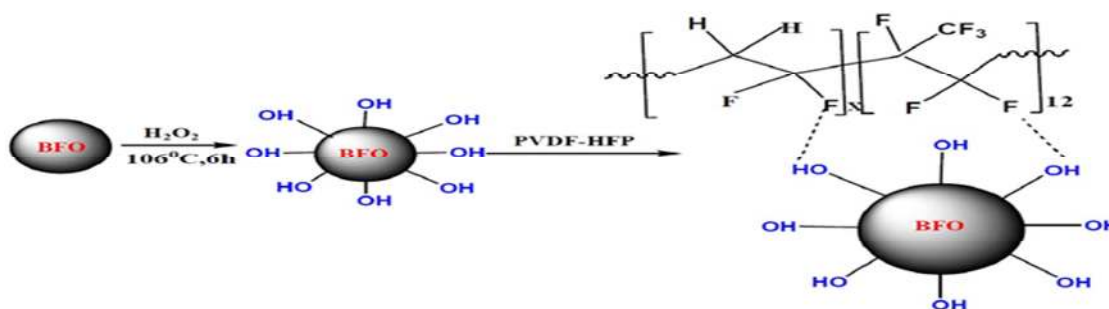


Fig. 6 Plausible interaction between PVDF-HFP and h-BFO particles

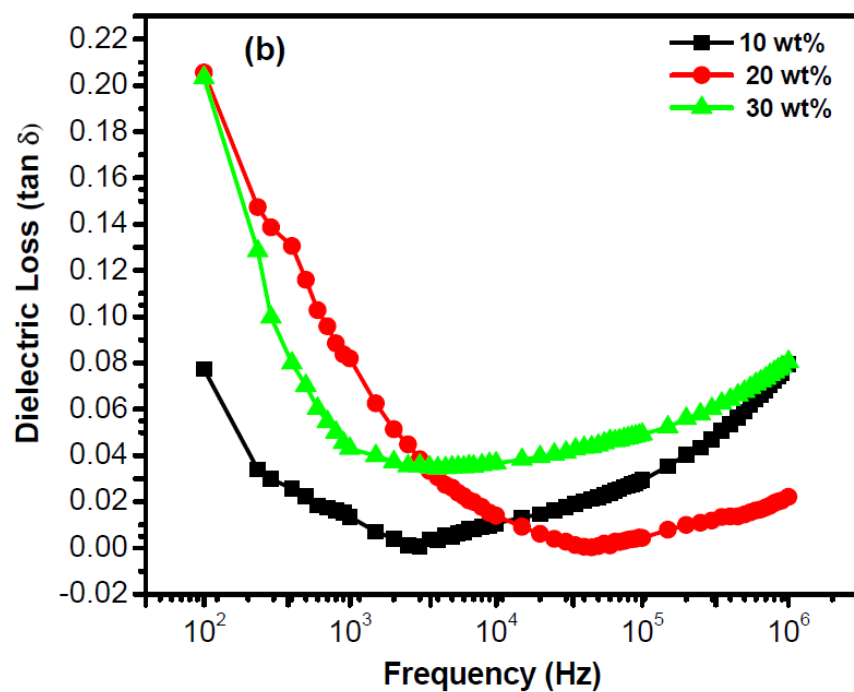
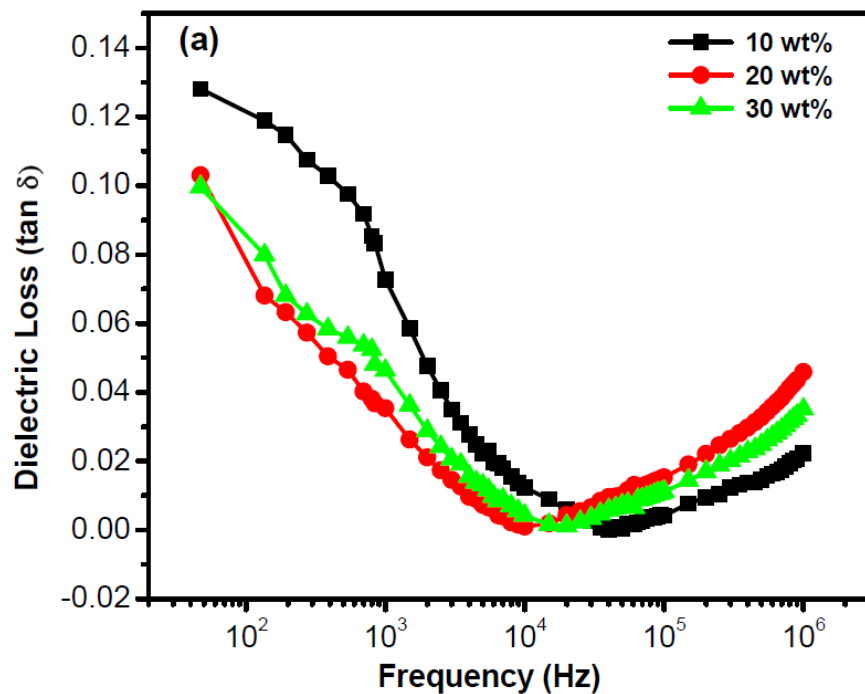
The dependence of the dielectric constant of the composite on the volume fraction of BFO fillers in a frequency range of 100 to 1000 Hz at room temperature is shown in Fig. 5c. It is found that

the dielectric constant of h-BFO-PVDF-HFP composite is quite higher than that of unmodified BFO-PVDF-HFP composite. When the weight percentage of BFO increases the dielectric constant also increases in both cases, but the extent of enhancement is more in case of h-BFO-PVDF-HFP composite. This result may be due to the surface hydroxylation of BFO particles and uniform distribution of BFO in the polymer matrix.

Fig.7 represents the dielectric loss of h-BFO-PVDF-HFP and unmodified BFO-PVDF-HFP composites over a wide range of frequencies. It is observed that, in case of h-BFO-PVDF-HFP composite the dielectric loss decreases as compared to that of the unmodified BFO-PVDF-HFP composite (Table-1). The dielectric loss of the composites decreases with the increase in frequency (Fig. 7 a, b). However, there is an increase in the dielectric loss is observed in the low frequency range, which may be due to the relaxation mechanism present in the polymer. For comparative study, the 30 wt% of h-BFO-PVDF-HFP composite shows relatively low dielectric loss value because the h-BFO particles are uniformly distributed in the polymer matrix. Meanwhile, in unmodified BFO-PVDF-HFP composites the dielectric loss value is quite high because the BFO particles are agglomerated in the polymer matrix. The high value of the dielectric loss at the lower frequency range can be attributed due to the relaxation of the space charge polarization [28-29].

The dependence of the dielectric loss of the composite on the volume fraction of BFO fillers in the frequency range 100 to 1000 Hz at room temperature is shown in Fig. 7c. It is observed that in case of h-BFO-PVDF-HFP composite, the dielectric loss value remains at a low level ( $< 1$ ). This phenomenon has been observed in many polymer/ceramic composite systems and can be commonly attributed to the small amount of defects at the interface and uniform dispersion of h-BFO particles in the PVDF-HFP matrix, which is clearly visualized from Fig. 4(b) and Fig.1. Further, in case of unmodified BFO-PVDF-HFP composite the dielectric loss value is quite high because unmodified BFO particles are agglomerated in the PVDF-HFP matrix as a result the dielectric loss value remains high. Secondly, the higher loss value may be originated from their high electrical conductivities [30,31]. For comparison, the composite films with surface hydroxylated and unmodified BFO particles are prepared and their dielectric properties are given in Table-1. In order to show the superiority of the composite, the surface hydroxylated and unmodified BFO particles are prepared by solution casting technique. The surface hydroxylated

BFO particles not only show higher dielectric constant, but also have quite changed dielectric loss over the whole frequency ranges.



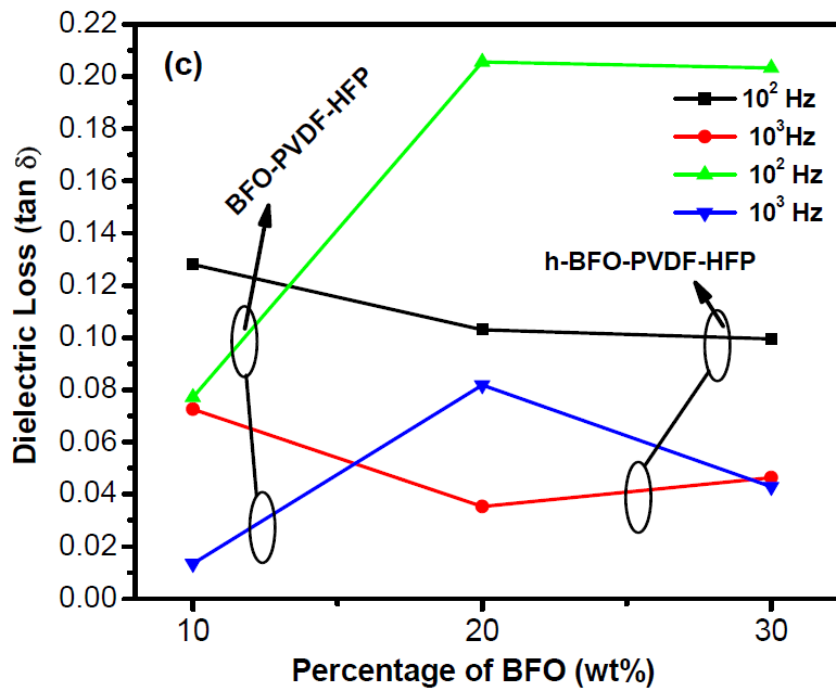


Fig.7 Frequency dependences of dielectric loss comparison: (a) h-BFO-PVDF-HFP (b) unmodified BFO-PVDF-HFP (c) unmodified and h-BFO-PVDF-HFP composites measured at  $10^2$  Hz and  $10^3$  Hz as a function of BFO filler contents.

Table-1: Comparison of dielectric properties of h-BFO-PVDF-HFP and BFO-PVDF-HFP composite films ( $10^2$  Hz).

Sample	Dielectric constant (h-BFO/unmodified)	Dielectric Loss (h-BFO/unmodified)
BFO-PVDF-HFP (10wt%)	33/21	0.12 /0.076
BFO-PVDF-HFP (20wt%)	55/30	0.10/0.20
BFO-PVDF-HFP (30 wt%)	68/36	0.09/ 0.21

#### 4.5. AC electrical conductivity

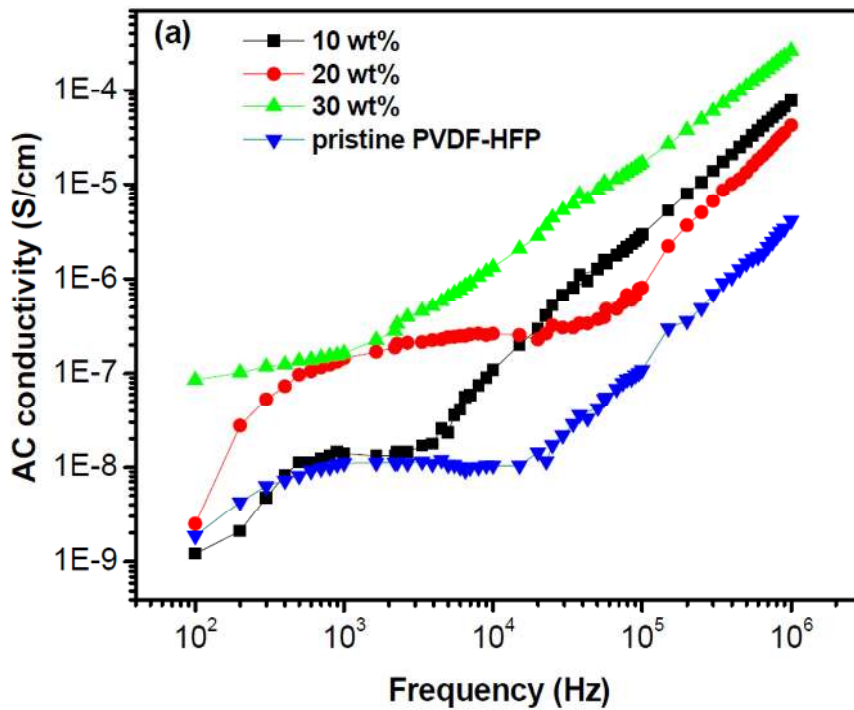
The frequency dependence of AC electrical conductivity of h-BFO-PVDF-HFP and BFO-PVDF-HFP composite with different wt% of BFO fillers at room temperature is shown in Fig.8. The value of AC electrical conductivity ( $\sigma_{ac}$ ) of the composites was evaluated by using the dielectric data and the following empirical formula:

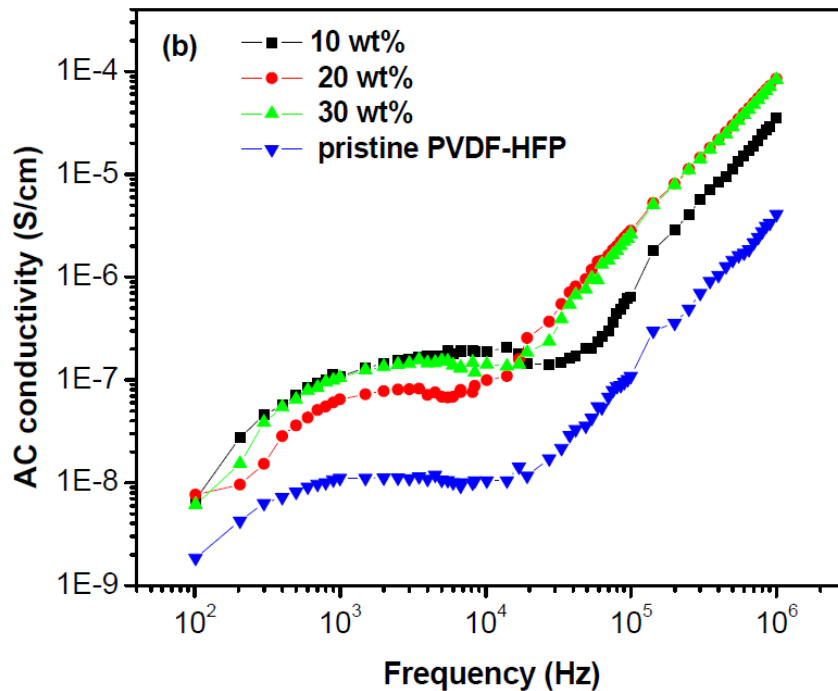


$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta$$

Where the symbols have their usual meaning:  $\sigma_{ac}$  = AC conductivity,  $\epsilon_0$  = Permittivity in free space,  $\epsilon_r$  = Relative dielectric constant,  $\omega$  = Angular frequency,  $\tan \delta$  = Loss tangent.

As shown in Fig. 8 (a), the AC electrical conductivity of h-BFO-PVDF-HFP composite increases with increase in frequency for all weight percentages of BFO content and slightly higher than that of the pure PVDF-HFP over the whole frequency range, indicating good insulating properties of the composites. It is observed that the composites with surface hydroxylated BFO particles have high electrical conductivity than those of unmodified one as shown in Fig. 8 (b). This is because the particles are homogeneous dispersion in the polymer matrix in case of modified BFO due to which the electrons can easily move in presence of applied electric field [29, 31].



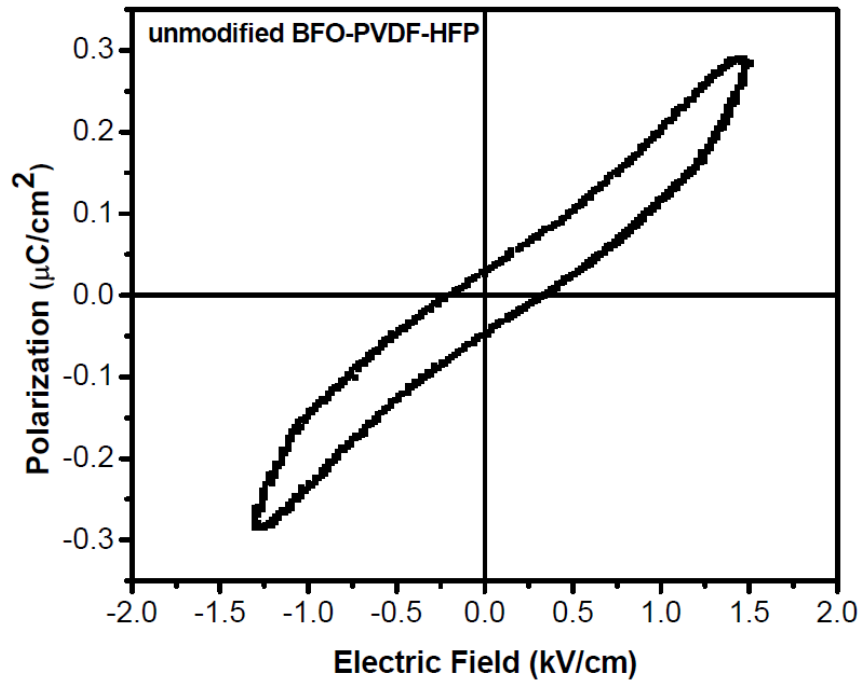


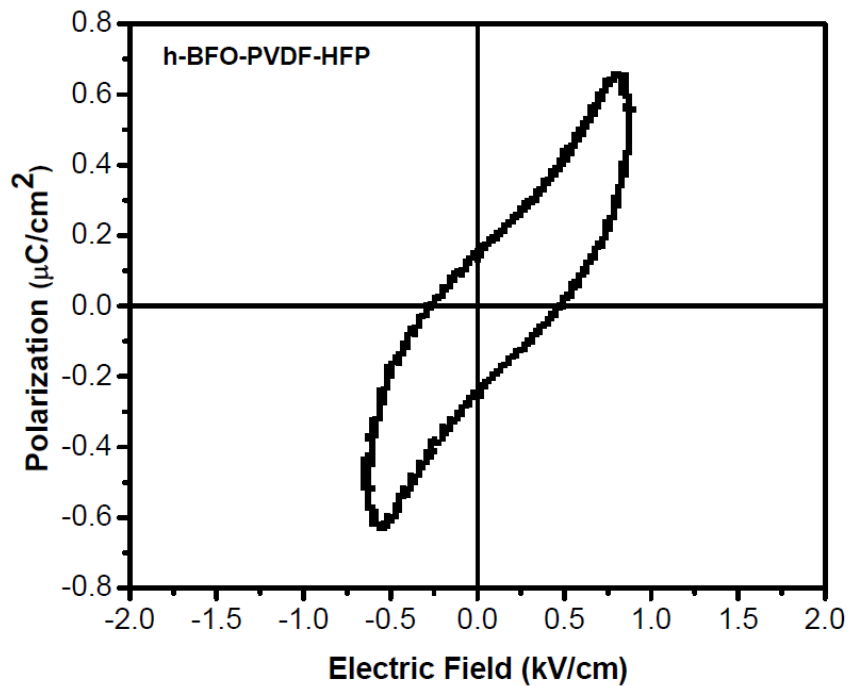
**Fig. 8** Frequency dependences of AC conductivity comparison: (a) h-BFO-PVDF-HFP and (b) unmodified BFO-PVDF-HFP composites with BFO filler contents.

#### 4.6. Ferroelectric properties

Fig. 9 shows the dielectric displacement-applied electric field (which is called P-E loop) of the unpoled h-BFO-PVDF-HFP and unmodified BFO-PVDF-HFP composites at different applied electric fields. P-E loops are required for confirming the ferroelectric nature of a material at a particular temperature and frequency. The energy dissipation and the phase separation between charge and voltage results a loop with a particular area under the curves. These area exhibits charge storage capability of such materials. For perfect ferroelectric polymers we would expect the charge accumulation which is due to the polarization of molecular dipoles [32-33]. It is observed that the h-BFO-PVDF-HFP composites show higher remnant polarization than those of unmodified one, which may be due to the increase of dielectric constant of the composites. However, in case of unmodified BFO, the value of remnant polarization is ( $2P_r \sim 0.152 \mu\text{C}/\text{cm}^2$ ) and for h-BFO-PVDF-HFP composites, the value of remnant polarization is ( $2P_r \sim 1.19 \mu\text{C}/\text{cm}^2$ ). The remnant polarization is directly proportional to the piezoelectric response of the material. As

the remnant polarizations of h-BFO-PVDF-HFP composites are higher than that of unmodified one, it shows better piezoelectric properties. On the other hand, the value of coercive field for unmodified BFO is ( $2E_c \sim 1.195\text{kV/cm}$ ), which is less than that of h-BFO-PVDF-HFP composite whose coercive field value is ( $2E_c \sim 1.021\text{Kv/cm}$ ). Hence h-BFO composites have more practical applications in electronic industries.





**Fig. 9 P-E hysteresis loop of the unmodified BFO and h-BFO-PVDF-HFP composites.**

#### **4.7. Current –voltage characteristics**

The current-voltage (I-V) characteristic curve for the unmodified BFO-PVDF-HFP and modified h-BFO-PVDF-HFP composites is shown in Fig.10. It is observed that in case of modified composite the leakage current is much lower than that of the unmodified composites. The reduced leakage current may be attributed to the surface modification by hydroxyl groups on the surface of the BFO particles and due to the formation of passivation layers in h-BFO [17]. The leakage current behavior leads the asymmetric PE loops [34] which have been shown in the Fig. 9.

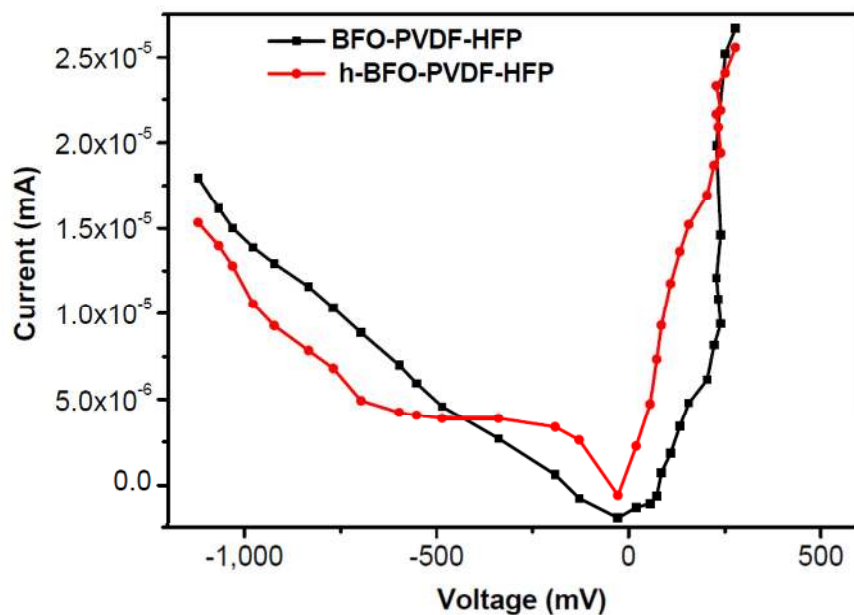


Fig. 10 Current –voltage characteristic curve showing the leakage currents

## 5. Conclusion

In summary, the h-BFO-PVDF-HFP and unmodified BFO-PVDF-HFP composites were prepared *via* solution casting technique. It is observed that, the surface modification is a valuable process for uniform distribution of the ceramic fillers in the polymer matrix and support the interface by such surface treatment (*via surface hydroxylation*). The results showed that high dielectric constant, low dielectric loss, high AC electrical conductivity and high remnant polarization were achieved by the use of h-BFO-PVDF-HFP composites. These modified composites with high dielectric performance are potential materials for high energy storage device applications.

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