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# Dielectric Properties and Conductivity of PVdF-co-HFP/LiClO$_4$ Polymer Electrolytes

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## ABSTRACT

In this study, it was aimed to preapare a series of PVdF-co-HFP based electrolytes with different LiClO$_4$ loadings and to investigate their chemical and electrical properties in detail. For this purpose, PVdF-co-HFP based electrolytes with different LiClO$_4$ loadings (1-20 weight %) were prepared using solution casting method. XRD, DSC and TG/DT and dielectric spectroscopy analysis of PVdF-co-HFP/LiClO$_4$ were performed to characterize their structural, thermal and dielectric properties, respectively. XRD results showed that the diffraction peaks of PVdF-co-HFP/LiClO$_4$ electrolytes broadened and decreased with LiClO$_4$. TGA patterns exhibited that PVdF-co-HFP/LiClO$_4$ electrolytes with 20 wt % of LiClO$_4$ had the lowest thermal stability and it degraded above 473 K which is highly applicable for solid polymer electrolytes.

Dielectric constant, dielectric loss and conductivities were calculated by measuring capacitance and dielectric loss factor of PVdF-co-HFP/LiClO$_4$ in the range from 10 mHz to 20 MHz frequencies at room temperature. In consequence, conductivities of PVdF-co-HFP/LiClO$_4$ increased significantly with frequency for low loading of LiClO$_4$ while they only slightly changed with higher LiClO$_4$ addition. On the other hand, dielectric constant values of PVdF-co-HFP/LiClO$_4$ films decreased with frequency whereas they rose with LiClO$_4$ addition. The dielectric studies showed an increase in dielectric constant and dielectric loss with decreasing frequency. This result was attributed to high contribution of charge accumulation at the electrode-electrolyte interface. The electrolyte showed the maximum conductivity of $8.10^{-2}$ S/cm at room temperature.

**Keywords:** Conducting Polymers, Impedance spectroscopy, Dielectric properties, and Ionic conductivity.

# 1. Introduction

Today, among some favorable polymers, polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP), based on poly (Vinylidenefluoride) (PVdF) and hexafluorpropylene (HFP), is a highly preferred copolymer matrix by researchers due to various interesting properties of lower crystallinity improving the ionic conductivity and higher free volume occurred by an amorphous phase of HFP into the main constituent VdF blocks[1], lower glass transition ($Tg$)[2,3] and melting temperatures and high anodic stability due to strong electron withdrawing functional group[4], relatively high dielectric constant ($\varepsilon$ = 8.4) and superior mechanical integrity as well as good electrochemical stability[5,6]. Addition of salt dopants to PVdF-HFP may enhance the electrical and optical performance[7] by affecting the diffusion rate of ions which depend on the size of the ion[8]. Lithium salts are easily dissolved in polymer matrices due to the coordination interaction between the lithium ions and the polar groups of the polymer host[9, 10]. LiClO4, as a small size-cation and a large size-anion, has better features than the other lithium salts due to its low interfacial resistance when lithium is used as an anode[10, 11,12]. $LiClO_4$ has high dissociation energy is a fast-ion conducting salt in a number of crystalline and amorphous materials[7]. The fact that the host matrix of PVdF-HFP has high dielectric constant causes greater dissociation of $LiClO_4$ salt and results in enhancement of charge carrier concentration owing to the dissociation of $LiClO_4$ into $Li^+$ and $ClO_4^-$ ions[8]. Dielectric relaxation, a vital tool to show the relaxation of dipole in polymer electrolyte[8], discussed in terms of impedance and dielectric analysis[13] may give details of motions of polimer-dipol and its charges accurately[7].

In this study, as a polymer matrix, PVdF-co-HFP was preferred especially due to commercial availability, high ionic conducting, and mechanic properties, which is an amorphous polymer. LiClO4, as the $Li^+$ salt, is preferred because it is composition of a large-sized anion and a small-sized cation[10, 11, 12]. For electrical characterizations, the ionic conductivity of PVdF-co-HFP with various weight % (1, 3, 5, 10, 15 and 20 wt %) of $LiClO_4$ was studied systematically in a vacuum at room temperature for different frequencies varying from 10 mHz to 20 MHz. Furthermore, dielectric constant and dissipation factor of PVdF-co-HFP/$LiClO_4$ complex films were investigated as a function of frequency and salt content at room temperature.

# 2. Experimental

## 2.1. Chemicals and Analysis

The materials, PVdF-co-HFP (Mw: 400,000), $LiClO_4$, and N-methyl-2-pyrrolidone (NMP) were supplied from Aldrich (USA) and Fluka (Germany), Merck (Germany), respectively. They were used as received without further purification.

X-ray diffraction measurements were recorded by a Rigaku D/Max-2200/PC XRD diffractometer in the range 10-80$^o$ with a scanning rate of 2$^o$/min to determine the crystallinity of PVdF-co-HFP polymer electrolytes in conjunction with $LiClO_4$ amount in the sample. Differential scanning calorimetry (DSC) measurements were taken by Setaram DSC 131 system at a heating rate of 10$^o$C/min under nitrogen atmosphere. Seiko Exstar 6000 TG/DTA6300 was used to collect TGA data in the range of 40-500$^o$C at a heating rate of 10$^o$C/min. Weights of the polymer films were maintained in the range of 5-15 mg and all experiments were under nitrogen flow.

### 2.2. Preparation of Polymer-Salt Complexes

Lithium perchlorate ($LiClO_4$) was dried by annealing under vacuum at 393 K for 12 hours prior to use. The polymer solution was prepared first by addition of 2 g of PVdF-co-HFP in predetermined amount of NMP and stirred for 3-4 hours at rising temperature from 298 to 323 K. After the homogenous solution was obtained, the various amounts of $LiClO_4$ were added to the polymer solution. Then, the polymer-salt complexes were stirred additionally for 3-4 hours. Subsequently, the homogenous mixtures were poured on petri dishes and evaporated at 393 K for 24 hours. Finally, the dried polymer electrolytes were removed from the dishes and kept in vacuum desiccator until further use.

### 2.3. Ionic Conductivity Measurements

Electrical contacts with a 6 mm diameter were taken on both sides of the samples prepared in 10 x 10 mm$^2$ dimensions. Copper wires fixed by indium on silver-paste electrodes were used as the electrical contacts. All samples were annealed at the maximum temperature (373 K) under vacuum pressure (10$^{-4}$ Torr) for one hour before the measurement. After this annealing procees, it was observed that moisture effects disappear, because depending on the stabilization process, the PVdF-co-HFP/$LiClO_4$ electrolytes, the capacitance (C) and dissipation factor ($\tan\delta$) were measured with reproducible results using a Novocontrol Alpha, a High Performance Frequency Analyzer, operating in a wide frequency range from 10 mHz to 20 MHz at room temperature. The samples have parallel plate capacitor configurations.

The dielectric constant ($\varepsilon_1$) is given by $\varepsilon_1 = \frac{d\,C}{\varepsilon_0\,A}$ where $d$, $A$, $\varepsilon_0$ and $C$ are the thickness of the dielectric material, the surface area of capacitor, the dielectric permittivity of vacuum, and the capacitance of the sample, respectively. The correlation between the dielectric constant ($\varepsilon_1$) and the imaginary part (loss factor: $\varepsilon_2$) is called "dissipation factor" (loss tangent: $\tan\delta$) and given by $\tan\delta = \frac{\varepsilon_2}{\varepsilon_1}$ for each angular frequency ($\omega$). Ac conductivity is then given by $\sigma_{ac} = \omega\varepsilon_0\,\varepsilon_r \tan\delta$ where $\varepsilon_r = \frac{C}{C_0}$ is relative permittivity. The dielectric constant and the ac conductivity values were found depending on $LiClO_4$ amount in the electrolyte composition in terms of capacitance-value and dissipation factor at room temperature in the frequency range from 10 mHz to 20 MHz.

## 3. Result and Discussion

### 3.1. X-ray Diffraction

The XRD patterns, recorded at room temperature for PVdF-co-HFP/$LiClO_4$ polymer electrolytes, shown in Fig. 1, showed sharp diffraction peaks appeared at $2\theta \sim 18.7^o$ and $20.5^o$. Fig. 1 revealed that $LiClO_4$ addition disturbed the crystalline region and led to diminish in peak intensities. The complete dissolution of $LiClO_4$ resulted in amorphous phases[14]. Hence, broadening diffraction peaks with increasing $LiClO_4$ indicated the formation of polymer-salt complexation between $Li^+$ ion in salt and the flour group existing in the polymer backbone. In addition, at $2\theta \sim 18.7^o$ and $20.5^o$ while the intensity of the peaks decreased from 10 to 20 wt % of $LiClO_4$. Some additional peaks there in showed up due to the formation of some nanocomposites[15].

### 3.2. Termogravimetric Analysis (TGA)

The thermal properties of PVdF-co-HFP/$LiClO_4$ electrolytes were studied and TGA patterns are shown in Fig. 2. While thermal degradation of PVdF-co-HFP occurred about $500^o$C in one step, thermal stability of PVdF-co-HFP/$LiClO_4$ significantly decreased with $LiClO_4$ in the electrolyte composition. Among the films, PVdF-co-HFP with 20 % of $LiClO_4$ had the lowest thermal stability and the thermal degradation of this electrolyte begun above 200 $^o$C. Also, thermal degradation of PVdF-co-HFP/$LiClO_4$ complex electrolytes took place in two steps and it can be seen this behavior more obviously in TGA pattern of PVdF-co-HFP with 20 % of $LiClO_4$. TGA results may reveal that the complexation occured between polymer macromolecules and ionic salts which led to a significant reduction in thermal stability. Concerning the thermal degradation of electrolytes in two step, it can be emphasized that the first one can be ascribed to remove of moisture adsorbed in/on the electrolyte film due to the highly hygroscopic nature of $LiClO_4$[16]. The second step is directly attributed to the degradation of PVdF-co-HFP copolymer backbone.

### 3.3. Differential Scanning Calorimetry (DSC)

Fig. 3 shows DSC curves of PVdF-co-HFP/$LiClO_4$ electrolyte films. It can be resolved in the Fig. 3 that there was a sharp endothermic peak at around 150°C due to the melting point of PVdF-co-HFP. The melting temperatures ($T_m$) of PVdF-co-HFP electrolytes with 1 and 10 wt % of $LiClO_4$ were found to be 149.2 and 147.3°C, respectively. Thus, $T_m$ of polymer-salt complexes decreased with salt content in the electrolyte composition. This result is very good agreement with the literature[17]. This slight reduction in $T_m$ can be explained by the formation of polymer-salt complexation leading to more amorphous regions in the elecytrolyte structure. This result also confirmed XRD results reported in our study.

### *3.4.* Dependence of Dielectric Constant ($\varepsilon_1$) on frequency and wt % of $LiClO_4$

Fig. 4 shows the variation of dielectric constant ($\varepsilon_1$) versus frequency of PVdF-co-HFP electrolytes with different $LiClO_4$ loadings at room temperature. Although all types of polarization may exist in the low frequency region as general behavior of dielectric, electronic polarization occurs only in the high frequncy region[18]. The dielectric constants were low for PVdF-co-HFP based electrolytes if small amount of $LiClO_4$ was added to the complex structure. Beyond 5 % of $LiClO_4$ loading, the dielectric constants of the electrolytes were high in the low frequency part. At the high frequency region, the dielectric constant decreased five magnitude of order compared to value obtained at frequencies lower than $10^3$ Hz for PVdF-co-HFP based electrolyte with 10-20 wt % of $LiClO_4$. Unlike, the dielectric constant of polymeric electrolyte with low amount of $LiClO_4$ did not change remarkably. This phenomenon can be explained as follow. At the low frequency region, existing dipols can follow the field change. Thus, the dipoles are polarized and cause dielectric constant to increase. The dielectric constant dependent on frequency: It decreased when the frequency rose. The reason can be due to the strong dispersion of permittivity[19-21].

Fig. 5 shows the variation of the dielectric constant as a function of wt % of $LiClO_4$ salt for various frequencies at room temperature. Although the dielectric constant remained almost constant for all frequencies up to 5 wt % of $LiClO_4$, there was a dramatic increase for the lower frequencies from 0.1 to 10 Hz beyond this point. The variation of dielectric constants can be due to two reasons: One is that there exist different polarization mechanisms depending on the field and each one of the mechanisms contributes differently to polarization. The other is whether there is a possible medium to polarize. As the wt % of $LiClO_4$ salt concentration increases the dielectric constant decreases, especially at 10 wt % of $LiClO_4$ salt.

Thus, the second reason is out of the possibility. As a result, the first reason is effectively valid mechanism.

### 3.5. Dependence of dissipation factor ( $\tan\delta$ ) on frequency and wt % of $LiClO_4$

Figure 6 exhibits the variation of dissipation factor ( $\tan\delta$ ) versus frequency of PVdF-co-HFP electrolytes with different $LiClO_4$ loadings at room temperature. At the low frequency part (between $10^{-2}$ and $10^{3}$ Hz), the dissipation factor ( $\tan\delta$ ) changed in an increasing order for all samples consecutively varying from the lowest to the highest wt % of $LiClO_4$ addition except PVdF-co-HFP with 5 wt % of $LiClO_4$. At the high frequency region (between $10^{3}$ and $10^{7}$ Hz), two different behaviours can be seen. One was having low dissipation factor with adjacent seperation including 5 wt % of $LiClO_4$, the other was having high dissipation factor in an arbitrary manner for the samples between 10 and 20 wt % of $LiClO_4$. It seemed that there was a minimum around $10^{3}$ Hz, yet the positions of minimum and maximum may shift as a function of frequency with respect to $LiClO_4$ amount. Changes in the dissipation factor before and after $10^{3}$ Hz can be due to the ions experiencing longer and shorter time for the relaxation process.

On the other hand, the dissipation factor of the samples with 10-20 wt % of $LiClO_4$ decreased more sharply at the low frequency region (before 300 Hz). This decrease is also shown in Fig.4 revealing the existence of a polarization with a short relaxation time in the related area. The polarized ions at this frequency may follow the field's change and consequently indicates the energy loss. Hereof, the free volume increases and the samples experience more amorphous structure.

### 3.6. Dependence of dielectric loss ( $\varepsilon_2$ ) on frequency and wt % of $LiClO_4$

The variations of the dielectric constant as a function of $LiClO_4$ loading at different frequencies and room temperature are shown in Fig.7. The change of the dielectric loss ( $\varepsilon_2$ ) between $10^{-2}$ and $10^{4}$ Hz was considerably higher for the samples with 10-20 wt % of $LiClO_4$ than that of the ones having less than 10 wt % of $LiClO_4$. Due to free charge motion, the larger dielectric loss ( $\varepsilon_2$ ) and more polarized structure are expected to happen as moving to the low frequency part. For the samples with 1-5 wt % of $LiClO_4$ in the high frequency part, $10^{4}$ Hz and above, the changes of the dielectric loss ( $\varepsilon_2$ ) were owing to different polarization behavior. There was a peak around $10^{6}$ Hz appeared only for PVdF-co-HFP electrolyte having

1-5 wt % of $LiClO_4$. This peak observed in the dielectric loss is usually attributed to the energy absorbed by the permanent dipoles in the materials[22].

Fig.8 shows the dielectric loss versus wt % of $LiClO_4$ for various frequencies. Fig.5 and Fig.8 have the similar behavior with respect to the dependency of salt loading. The relaxation frequency at room temperature occured around $10^6$ Hz and was observed to shift with $LiClO_4$ loading.

The significant broadening of the dielectric peaks indicates that the phase transition is of diffuse-type. The broadening of the dielectric peak occurs mainly due to compositional fluctation and/or substitution induced disorder in the lattice[18, 23].

### 3.7 Dependence of ac conductivity on frequency and wt % of $LiClO_4$

Fig. 9 shows the conductivity values versus frequencies varying from 10 mHz to 20 MHz for PVdF-co-HFP with various $LiClO_4$ loading at 293 K in logarithmic scale. While the conductivity values remained constant for the samples with 10-20 wt % of $LiClO_4$ and they increased moderately for the samples with 0-5 wt % of $LiClO_4$ in the frequency part between $10^{-2}$ and $10^5$ Hz. Then they rose linearly for the all samples with frequency after $10^5$ Hz. In the Fig. 9, at low frequencies, there existed the frequency independent pletau region as a dc contribution of the carries [24]. The conductivity values were varying from $10^{-11}$ to $10^{-4}$ S/cm at the lowest frequency for the samples from the minimum to the maximum $LiClO_4$ content, respectively.

For disordered materials including solid and gel polymer electrolytes the overall behavior of the conductivities has frequency dependency [24, 25] expressed as

$$\sigma(\omega) = \sigma(0) + A\omega^n$$

where $\sigma(0)$ corresponds to the dc conductivity region, $A$ is the pre-exponential factor and $n$ is the fractional exponent between 0 and 1 [24]. This frequency dependent conductivity behavior is repetitive for each different wt % of $LiClO_4$.

At the low frequency region, the ions loose more energy while following the electric field's change. Thus, the change in the conductivity can be considered as a measure of energy loss. However, the conductivity increases fairly with increasing frequencies in the high frequency parts not because of the ions but the increase in electrons's polarization.

In Fig. 10, the conductivity versus wt % of $LiClO_4$ is plotted for various frequencies varying from 0.1 Hz to 20 MHz at 293 K in logarithmic scale. In the low wt % of $LiClO_4$, the conductivities were placed progressively in a broad interval varying from $1x10^{-10}$ to $1x10^{-3}$ $S.cm^{-1}$ for frequencies between 0.1 Hz and 20 MHz. The conductivities did not change at the highest frequency for all samples but approached a value around $10^{-3}$ S/cm for the samples with high wt % of $LiClO_4$. The change of the conductivity was independent of the frequencies for the samples with 10 and 20 wt % of $LiClO_4$ and highly dependent the samples with low wt % of $LiClO_4$. Measuring at small frequencies like 0.1 Hz, addition of wt % of $LiClO_4$ produced the polarity and so the conductivity increased in a broad range from $10^{-11}$ to $10^{-3}$ S/cm. According to the XRD results, the crystallinity had been reduced with addition of wt % of $LiClO_4$ up to 5 wt % in which the phase change occurred at this value or at higher concentrations. The observed sharp increase in the conductivity happened about the phase change from the crystallinity to the amorphous[14]. At high frequencies about 20 MHz, the ions couldn't follow the electric field's change. In this frequency region, the conductivity changed from $10^{-4}$ to $10^{-1}$ S/cm at room temperature. Morever, increasing LiClO4 concentration above 5 wt % caused an increase in conductivity due to some crystalline forms of Li. This conductivity behavior with frequency and with LiClO4 shown in Fig. 10 is consistent with different polymer matrix published in the literature[15, 22, 26, 27].

## Conclusions

In the study, a series of PVdF-co-HFP based electrolytes with different $LiClO_4$ loadings (1-20 wt/wt) was prepared using solution casting method. XRD, DSC and TG/DT and dielectric spectroscopy analysis of PVdF-co-HFP/$LiClO_4$ were performed to characterize their structural, thermal and dielectric properties, respectively. XRD patterns indicated that crystalline region of PVdF-co-HFP was turned into amorphous fraction and the diffraction peaks were broadened with $LiClO_4$ loading in the complex composition. TGA results showed that thermal stability of the polymer-salt complex film decreased with $LiClO_4$ content. Among the films, PVdF-co-HFP with 20 wt % of $LiClO_4$ had the lowest thermal stability and it degraded beyond 473 K which is highly applicable for solid polymer electrolytes.

The dielectric constant, loss, and conductivity values were obtained in a range from 10 mHz to 20 MHz frequencies. The effects of added $LiClO_4$ amount on PVdF-co-HFP for the conductivity were investigated, so the conductivities of PVdF-co-HFP/$LiClO_4$ increased significantly with increasing frequency for all samples independent on $LiClO_4$ content. The electrolyte showed the maximum conductivity of $10^{-2}$ S/cm at room temperature. The dielectric constant decreased with increasing frequency but it increased with increasing wt % of $LiClO_4$.

It was shown at high frequency region that the conductivity obtained for samples with 3 and 20 wt % of $LiClO_4$ were close to each other. Thus the optimum conductivity can be observed with a low $LiClO_4$ ratio.

## Acknowledgments

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# Dielectric Properties and Conductivity of PVdF-co-HFP/LiClO$_4$ Polymer Electrolytes

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**Figure1**

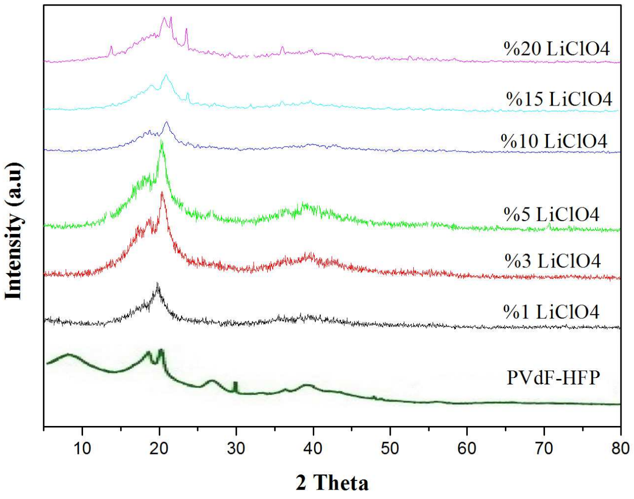


**Figure 2.**

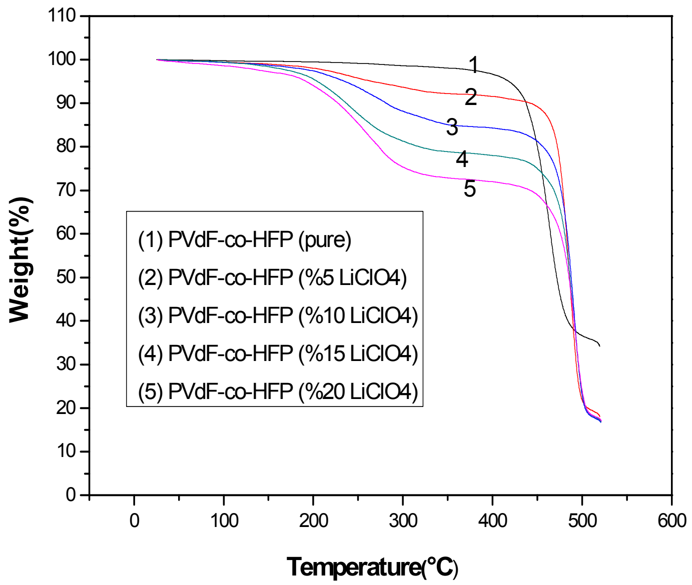


Figure 3.

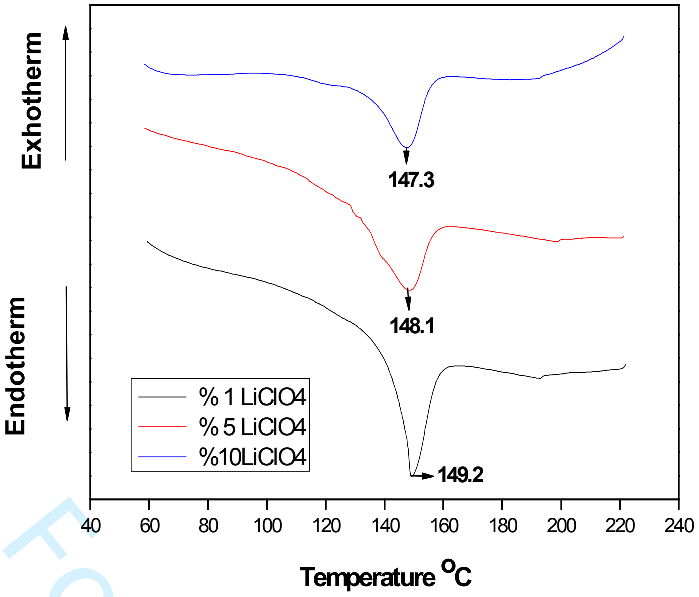
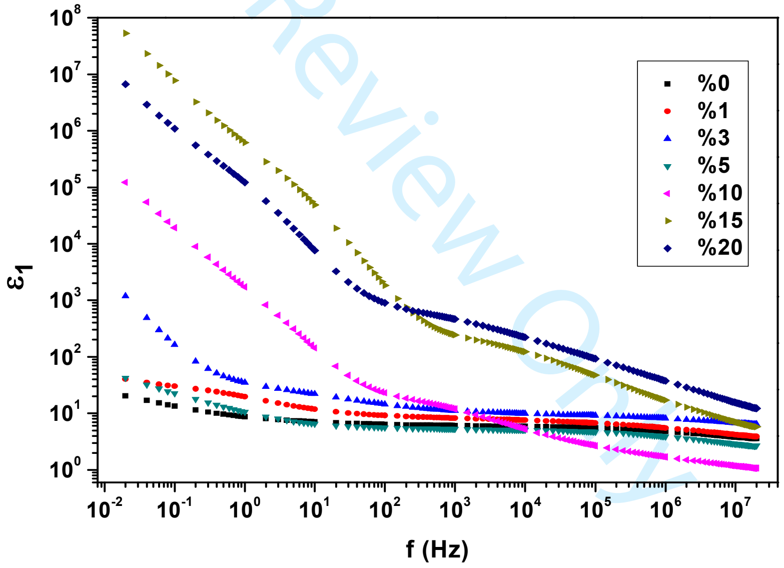


Fig.4.



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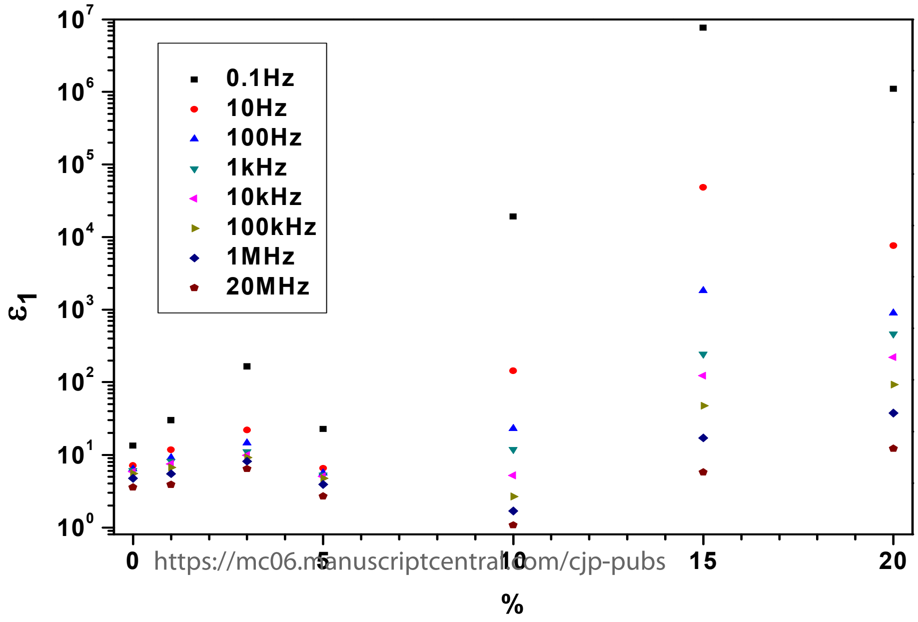


Fig. 6.

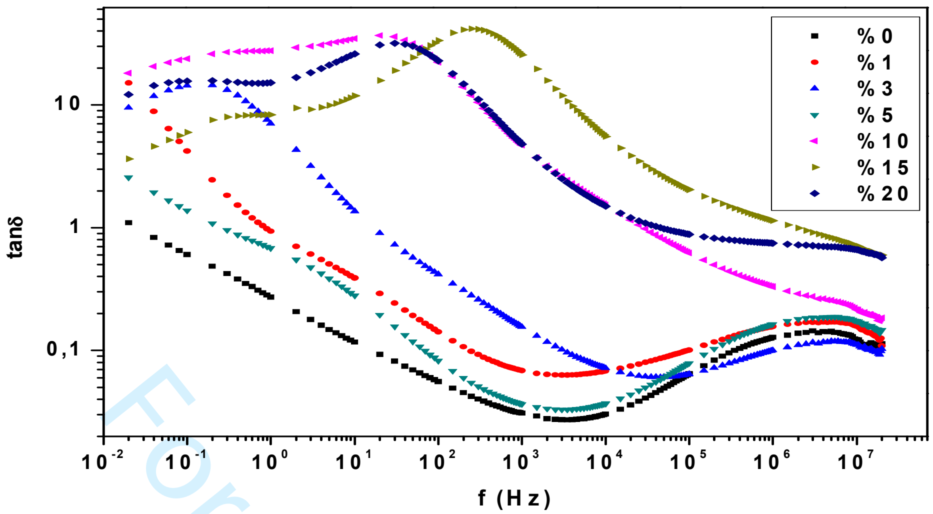


Fig.7.

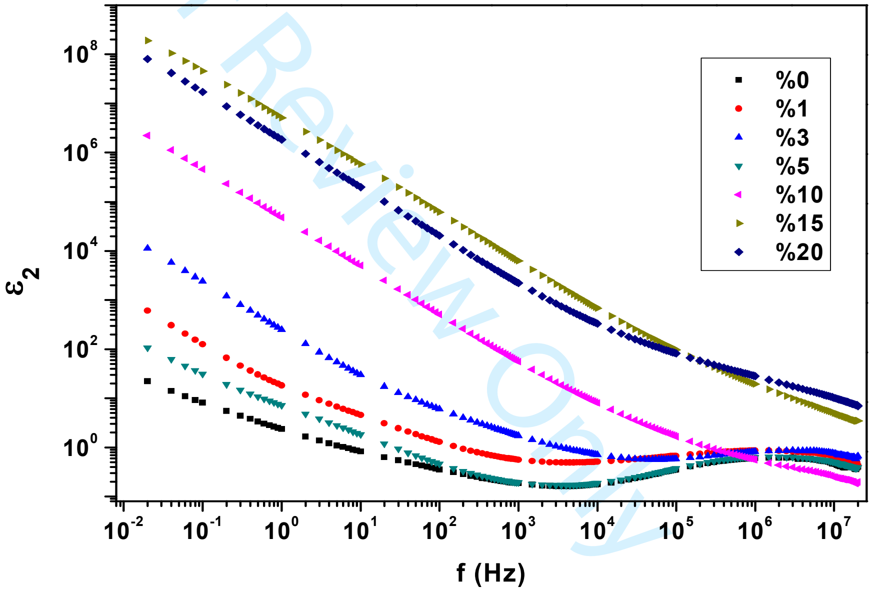


Fig.8.

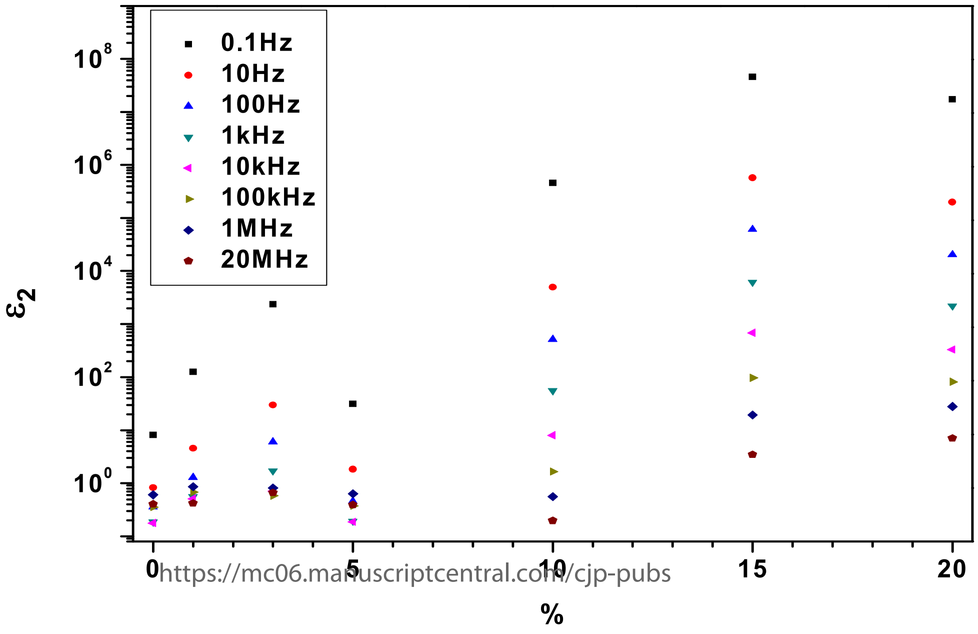
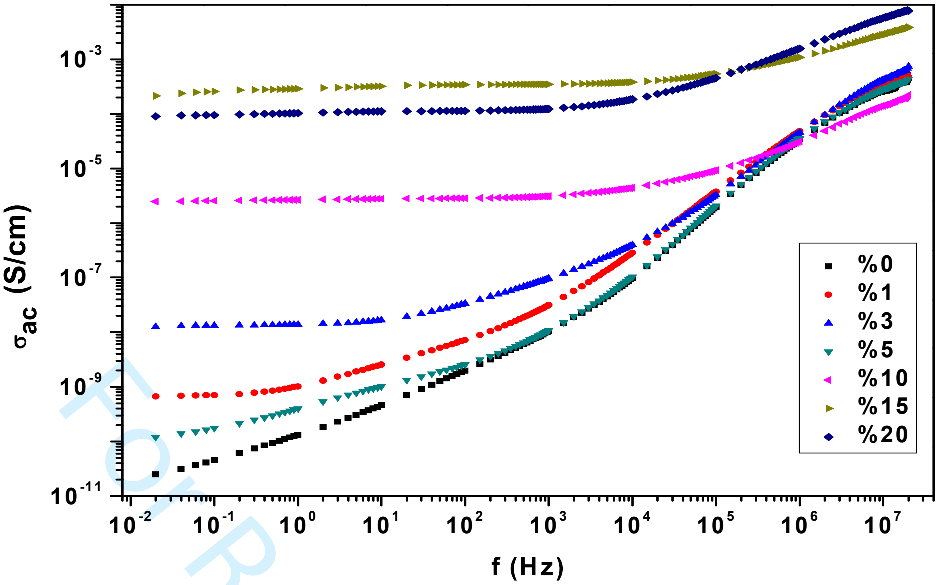


**Fig.9.**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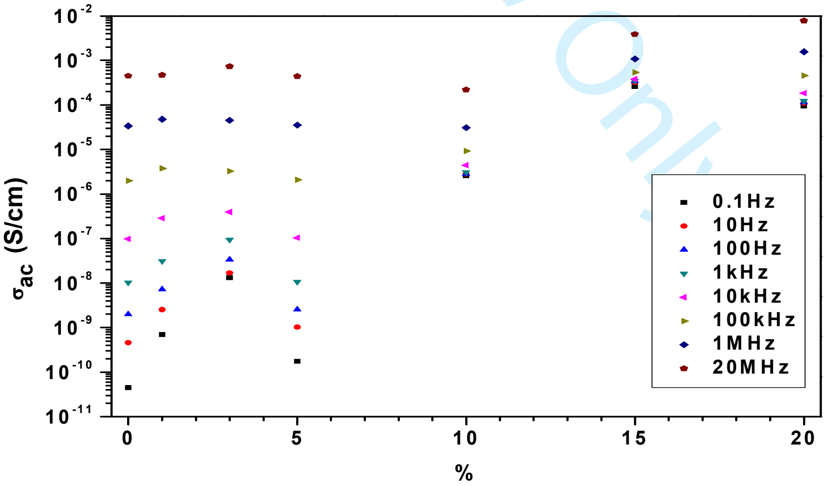
$10^{-3}$
$10^{-5}$
$10^{-7}$
$10^{-9}$
$10^{-11}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$10^{1}$
$10^{2}$
$10^{3}$
$10^{4}$
$10^{5}$
$10^{6}$
$10^{7}$
f (Hz)
%0
%1
%3
%5
%10
%15
%20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$10^{-10}$
$10^{-11}$
0
5
10
15
20
%
0.1Hz
10Hz
100Hz
1kHz
10kHz
100kHz
1MHz
20MHz

**Fig.10**

**Figure Caption**

**Fig.1.** XRD spectra of PVdF-co-HFP/$LiClO_4$ complex films depending on the wt% of $LiClO_4$.

**Fig.2.** TGA curves of pure PVdF-co-HFP and PVdF-co-HFP/$LiClO_4$ complex films depending on the wt % of $LiClO_4$.

**Fig.3.** DSC curves of PVdF-co-HFP/$LiClO_4$ complex films depending on the wt % of $LiClO_4$.

**Fig.4.** The variation of the dielectric constant as a function of frequencies for wt % of $LiClO_4$ added to PVdF-co-HFP at room temperature.

**Fig.5.** The variation of the dielectric constant as a function of wt % of $LiClO_4$ added to PVdF-co-HFP for various frequencies at room temperature.

**Fig.6.** The variation of the dissipation factor as a function of frequencies for wt % of $LiClO_4$ added to PVdF-co-HFP at room temperature.

**Fig.7.** The variation of the loss factor as a function of frequencies for wt % of $LiClO_4$ added to PVdF-co-HFP at room temperature.

**Fig.8.** The variation of the loss factor as a function of wt % of $LiClO_4$ added to PVdF- co-HFP for various frequencies at room temperature.

**Fig.9.** The variation of the conductivity as a function of frequencies for wt % of $LiClO_4$ added to PVdF-co-HFP at room temperature.

**Fig.10.** The variation of the conductivity as a function of wt % of $LiClO_4$ added to PVdF- co-HFP for various frequencies at room temperature.