

## **Influence of PVDF-HFP on the Dielectric Properties and Relaxation Behavior of PVC Blends**

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### **Abstract**

This study investigates the dielectric behavior of polyvinyl chloride (PVC) blended with polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) at various compositions (95:05, 90:10, 85:15, and 80:20 wt%). The blends were prepared using the solution casting method. The dielectric constant ( $\epsilon'$ ) and loss ( $\tan \delta$ ) were analyzed as functions of temperature and frequency ( $10^2$  to  $10^6$  Hz). The results reveal that  $\epsilon'$  exhibits a sharp increase with temperature due to the lowering of glass transition temperature ( $T_g$ ) caused by PVDF-HFP acting as a plasticizer. The temperature-dependent dielectric relaxation is attributed to cooperative dipolar orientations, while the frequency-dependent decrease in  $\epsilon'$  suggests limited dipole response at higher frequencies. Dielectric loss analysis reveals prominent peaks indicative of dipolar and space charge contributions. Activation energy values were calculated to be in the range of 0.30–0.80 eV, confirming electronic conduction mechanisms.

### **1. Introduction**

The rapid growth of energy storage technology has catalyzed a search for dielectric materials with superior performance characteristics, such as high dielectric constants, low dielectric losses, and good thermal and mechanical stability [1]. Among the candidates, polymer-

based dielectrics have garnered significant attention due to their flexibility, ease of processing, and tunable properties. Polyvinyl chloride (PVC) and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) are particularly promising materials for dielectric applications.

PVC is a widely used thermoplastic polymer known for its excellent processability, chemical resistance, and low cost. However, its relatively low dielectric constant limits its application in high-performance energy storage devices [2]. In contrast, PVDF-HFP, a copolymer of PVDF, exhibits a high dielectric constant and excellent thermal stability due to the presence of highly polar fluorine atoms [3]. The blending of PVC and PVDF-HFP offers a potential avenue for synergistically enhancing the dielectric properties of both materials, with PVC contributing cost-effectiveness and mechanical strength, and PVDF-HFP providing high permittivity and stability.

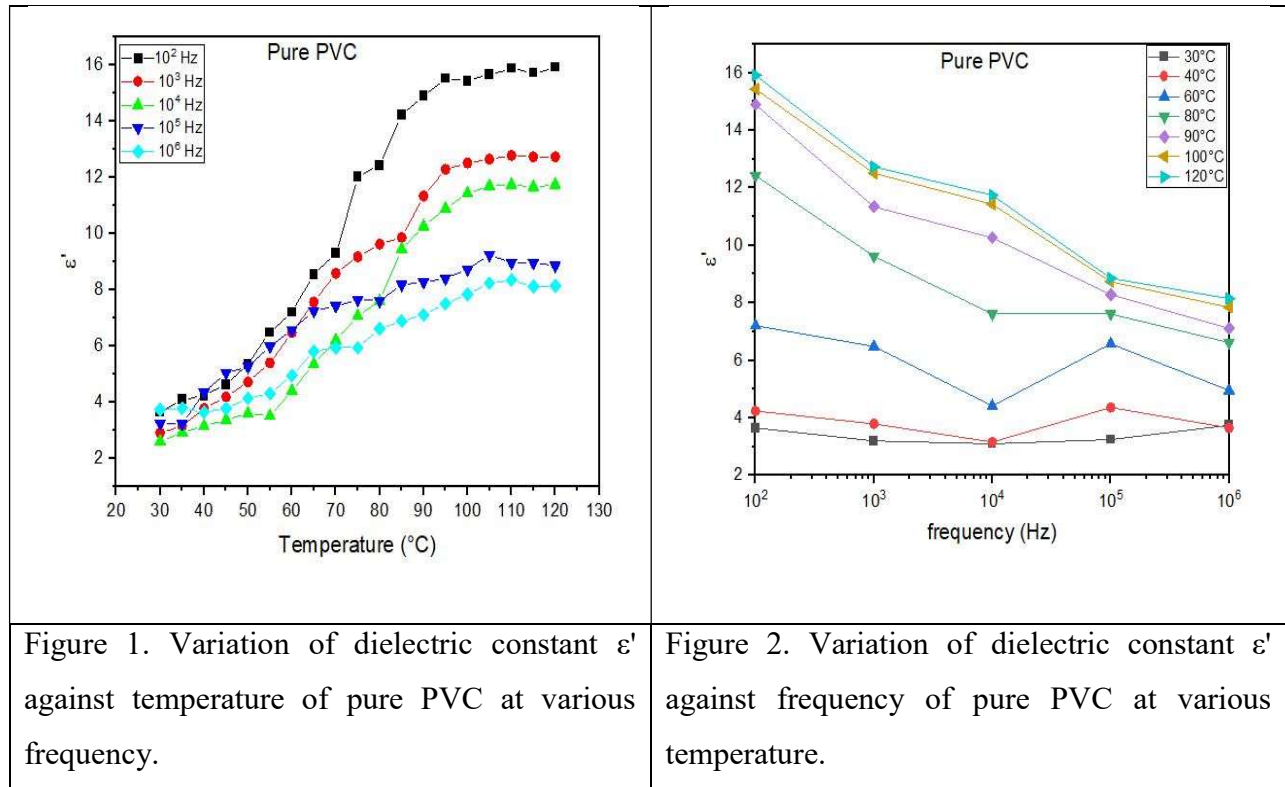
Despite the promising characteristics of these individual polymers, the dielectric performance of their blends remains underexplored. This study aims to investigate the dielectric constant and loss of PVC/PVDF-HFP blends at different compositions, frequencies, and temperatures. Furthermore, the microstructural and thermal properties of the blends will be correlated with their dielectric behavior to identify optimal processing conditions for energy storage applications.

## **2. Methodology**

PVC (granules) and PVDF-HFP (powder) were used as received without further purification. The polymers were blended in varying weight ratios (e.g., 95:25, 90:10, 85:15 and 80:20 PVC/PVDF-HFP) using a solution casting method [4]. PVC and PVDF-HFP were dissolved in DMF in predetermined weight ratios (100:0, 95:05, 90:10, 85:15, and 80:20) and stirred continuously for uniform dispersion. The resultant mixtures were poured into glass plate at 80° C to remove residual solvent. The dielectric constant and loss were measured using an impedance analyzer over a frequency range of  $10^2$  to  $10^6$  Hz and at varying temperatures (room temperature to 120 °C). The measurements were performed on capacitor-like samples, with silver paste electrodes applied to both sides of the film for good electrical contact.

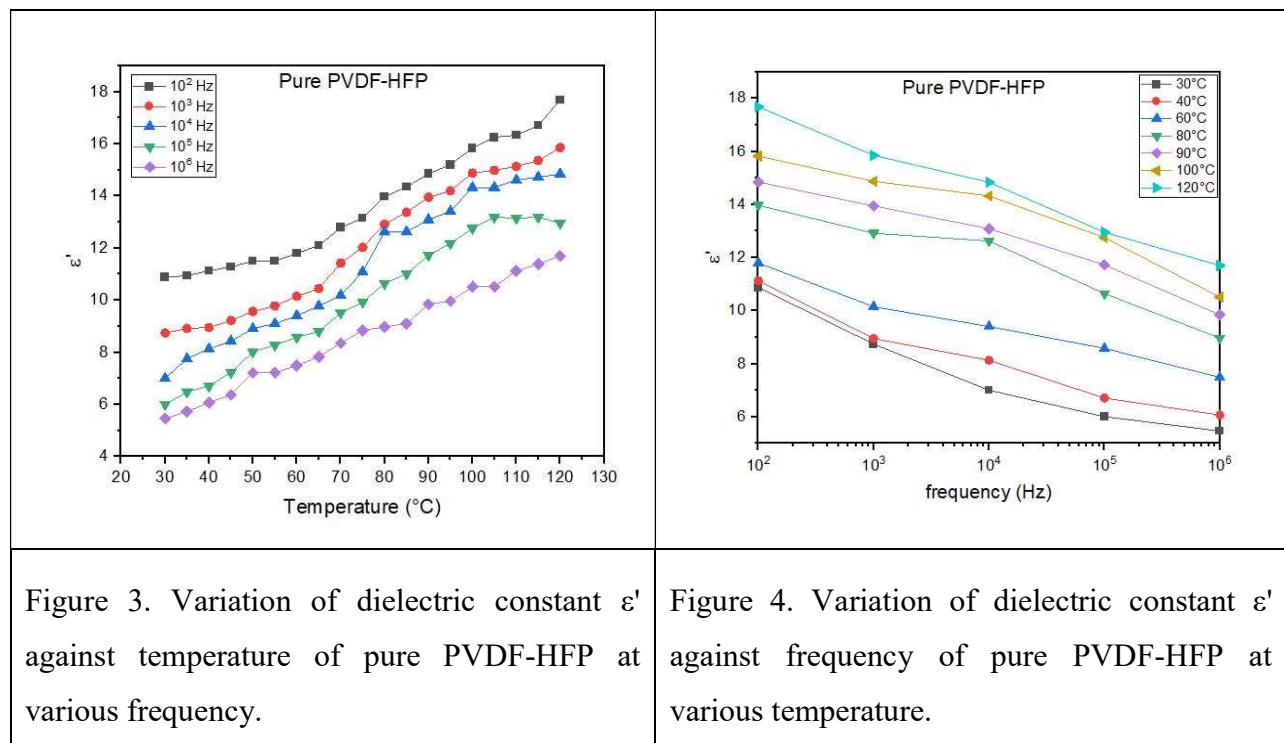
### 3. Results and Discussion

Figures 1 to 12 illustrate the temperature and frequency dependence of  $\epsilon'$  for pure PVC, pure PVDF-HFP, and their blend samples with compositions of PVC:PVDF-HFP in ratios of 95:05, 90:10, 85:15, and 80:20. The data is presented for selected frequencies ( $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Hz). The plots reveal that  $\epsilon'$  exhibits a gradual change with increasing temperature, followed by a rapid rise until it reaches a saturation region, after which it decreases again. The pronounced increase in  $\epsilon'$  values at specific temperatures and the shift toward lower temperatures with higher PVDF-HFP content can be attributed to the reduction in glass transition temperature caused by the addition of PVDF-HFP to PVC. This behavior aligns with observations in other polymers, where the addition of plasticizers lowers the glass transition temperature [5]. Hence, it can be inferred that PVDF-HFP acts as a plasticizer in the PVC-PVDF-HFP blends.



The relaxation process observed near the glass transition temperature for the prepared blend samples ( $\alpha$ -relaxation) is associated with cooperative dipolar orientations. This process corresponds to the segmental relaxation linked to the glass transition, during which the micro-Brownian motion of long-chain segments occurs in the amorphous regions of PVC [6]. At lower

temperatures, the thermal energy absorbed by the samples at a fixed frequency is minimal, allowing only a small number of dipoles to rotate at small angles. As the temperature rises, the value of  $\epsilon'$  is influenced by the number of orienting dipoles per unit volume and their respective dipole moments [7]. With increasing temperatures, the viscosity of the polymeric films decreases, enabling the dipoles to gain sufficient energy to align more easily with the applied electric field, thereby increasing  $\epsilon'$ . Additionally, the chain segments acquire adequate thermal energy to enhance their rotational motion, leading to an increase in polarization [8]. However, at higher temperatures, the specific volume of the polymer further increases, contributing to a continued rise in  $\epsilon'$  values [9-10].



In general,  $\epsilon'$  decreases with the increase of frequencies for all samples. The decreases may be attributed to the decreasing of the number of dipoles, which contribute to polarization, or dipole structure is no longer able to respond to the applied electric field; this leads to reduction in the  $\epsilon'$  value.

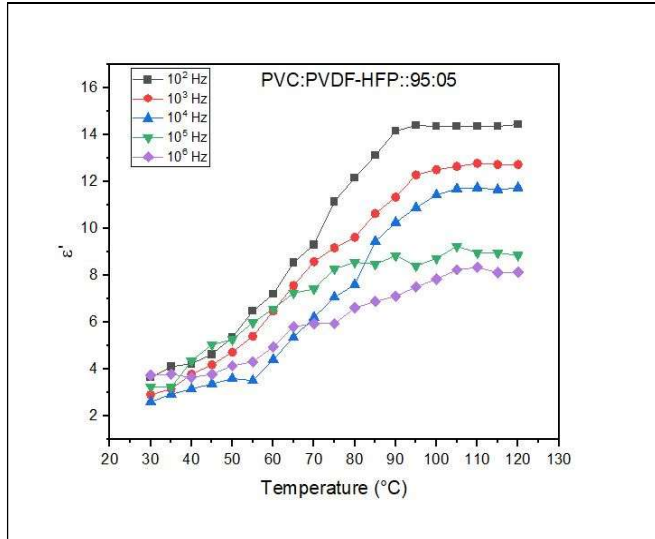


Figure 5. Variation of dielectric constant  $\epsilon'$  against temperature of PVC:PVDF-HFP::95:05 at various frequency .

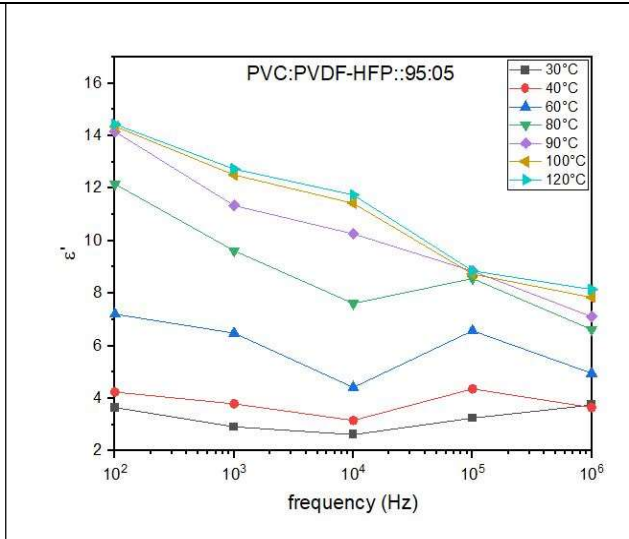


Figure 6. Variation of dielectric constant  $\epsilon'$  against frequency of PVC:PVDF-HFP::95:05 at various temperature .

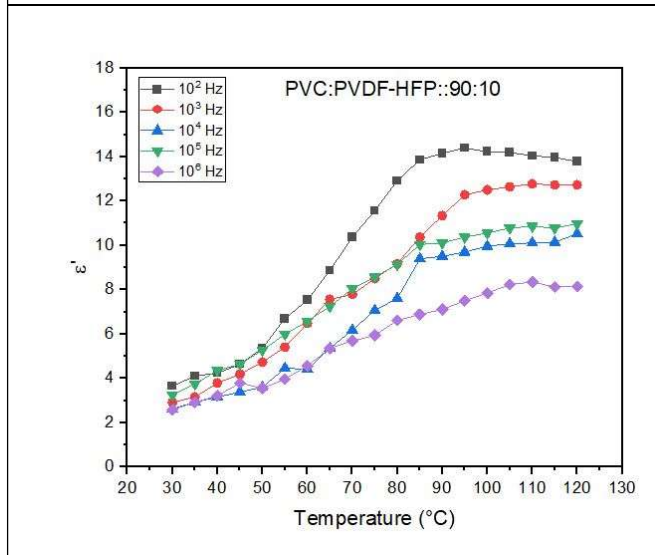


Figure 7. Variation of dielectric constant  $\epsilon'$  against temperature of PVC:PVDF-HFP::90:10 at various frequency .

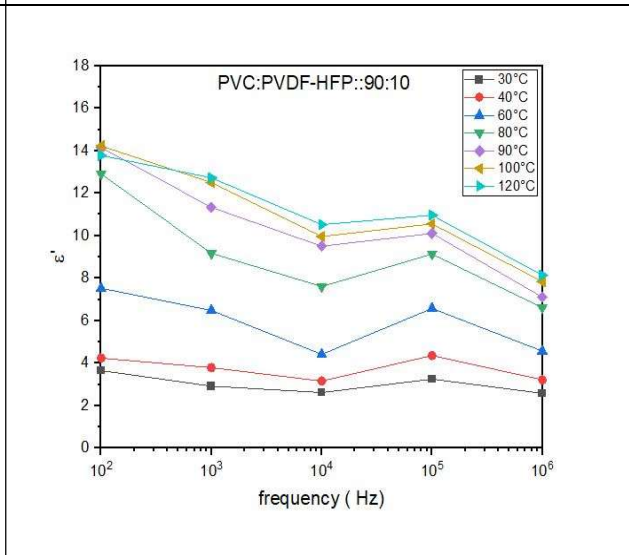


Figure 8. Variation of dielectric constant  $\epsilon'$  against frequency of PVC:PVDF-HFP::90:10 at various temperature .

At higher temperatures, the reduction in  $\epsilon'$  can be explained by thermal agitation, which disrupts the orientation of dipoles. Nonetheless, the role of interfacial polarization, resulting in space charge accumulation, cannot be completely ruled out. This decrease in  $\epsilon'$  is primarily

observed at lower frequencies, where the effects of space charge polarization are more pronounced, while at higher frequencies, such behavior is less evident [11]. The inclusion of PVDF-HFP in PVC causes a noticeable reduction in  $\epsilon'$  values, indicating a transformation in the morphology of PVC. This morphological alteration, combined with changes in space charge distribution, leads to a diminished internal field within the blend.

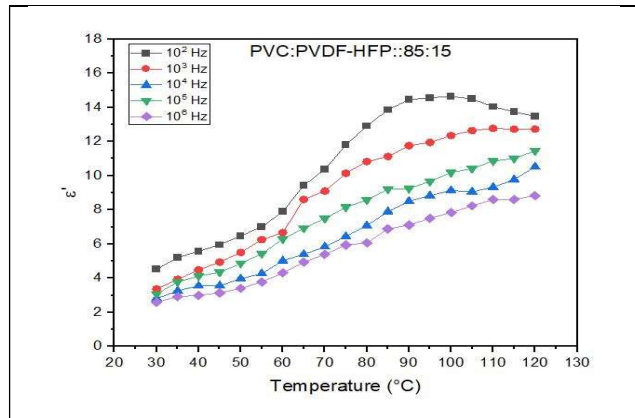


Figure 9. Variation of dielectric constant  $\epsilon'$  against temperature of PVC:PVDF-HFP::85:15 at various frequency.

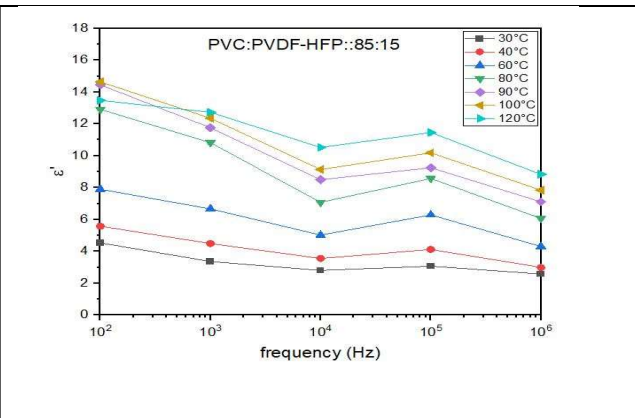


Figure 10. Variation of dielectric constant  $\epsilon'$  against frequency of PVC:PVDF-HFP::85:15 at various temperature .

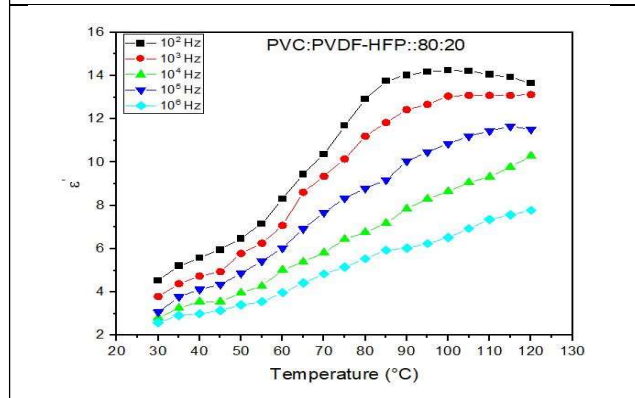


Figure 11. Variation of dielectric constant  $\epsilon'$  against temperature of PVC:PVDF-HFP::80:20 at various frequency.

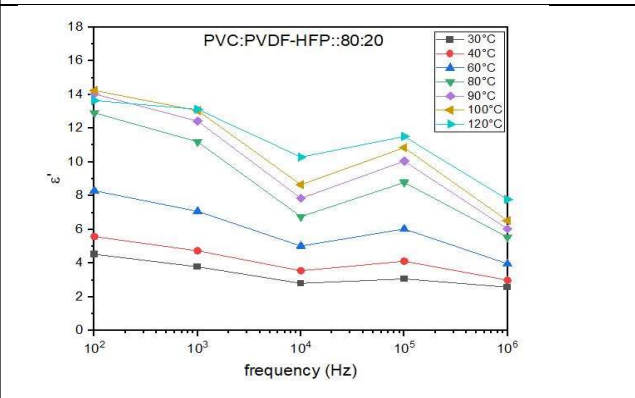


Figure 12. Variation of dielectric constant  $\epsilon'$  against frequency of PVC:PVDF-HFP::80:20 at various temperature.

Figures 13 and 16 illustrate the dependence of dielectric loss ( $\epsilon''$ ) on fixed temperature and frequency for the selected blend samples. These curves clearly show a loss maximum, which shifts toward higher temperatures at a fixed frequency and toward higher frequencies at a fixed temperature. This behavior indicates that the dielectric relaxation in the blend is thermally

dependent and primarily driven by dipole orientation. The shift in the dipolar maximum to lower temperatures at various fixed frequencies and to higher frequencies at fixed temperatures, with an increasing amount of PVDF-HFP, suggests that the addition of PVDF-HFP lowers the transition temperature of PVC [5, 11].

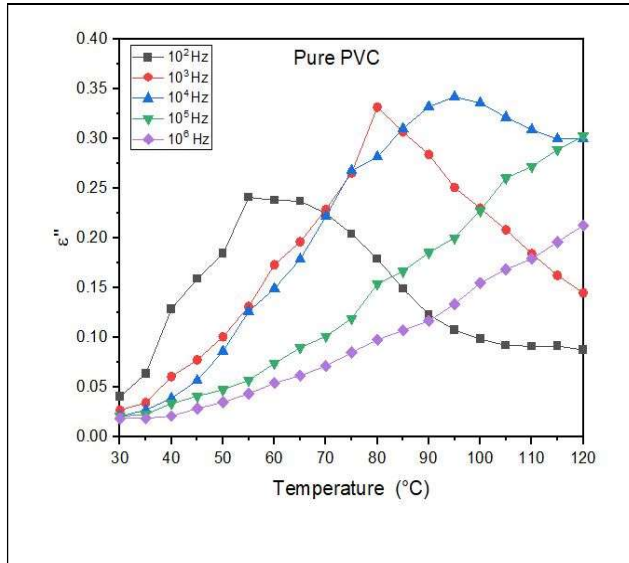


Figure 13. Variation of dielectric loss  $\epsilon''$  against temperature of Pure PVC at various frequency.

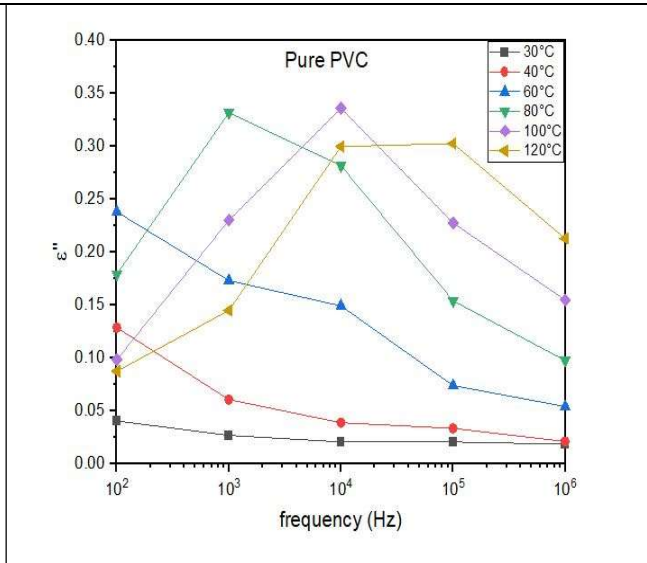


Figure 14. Variation of dielectric loss  $\epsilon''$  against frequency of Pure PVC at various temperature.

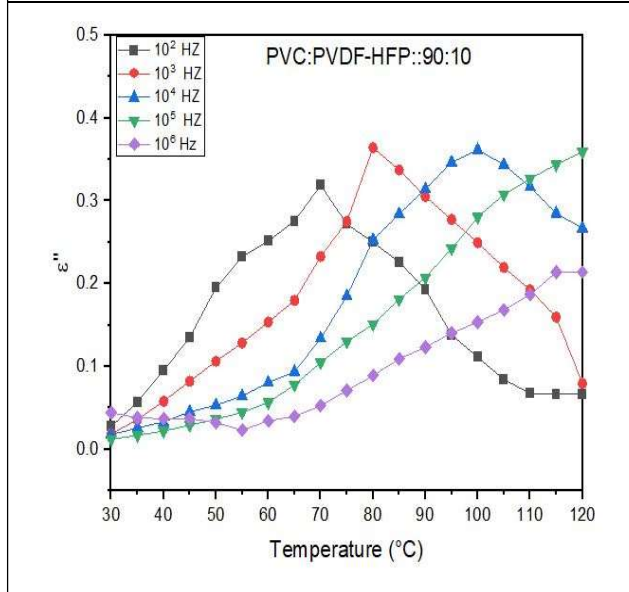


Figure 15. Variation of dielectric loss  $\epsilon''$  against temperature of PVC:PVDF-HFP::90:10 at various frequency.

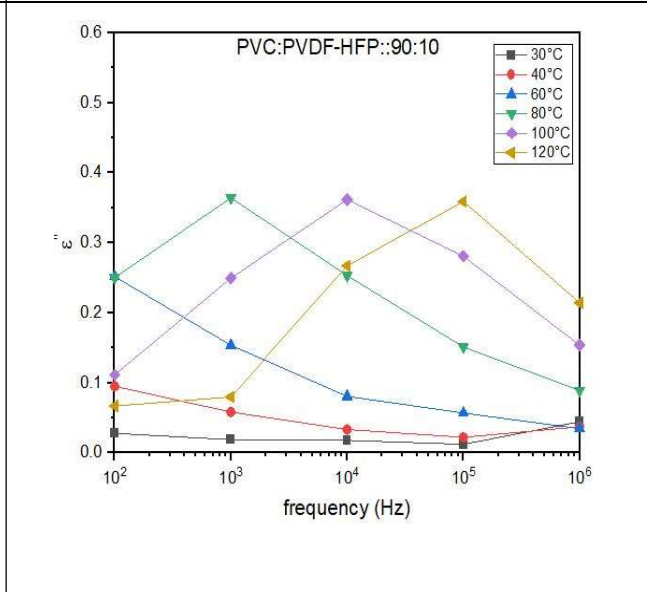
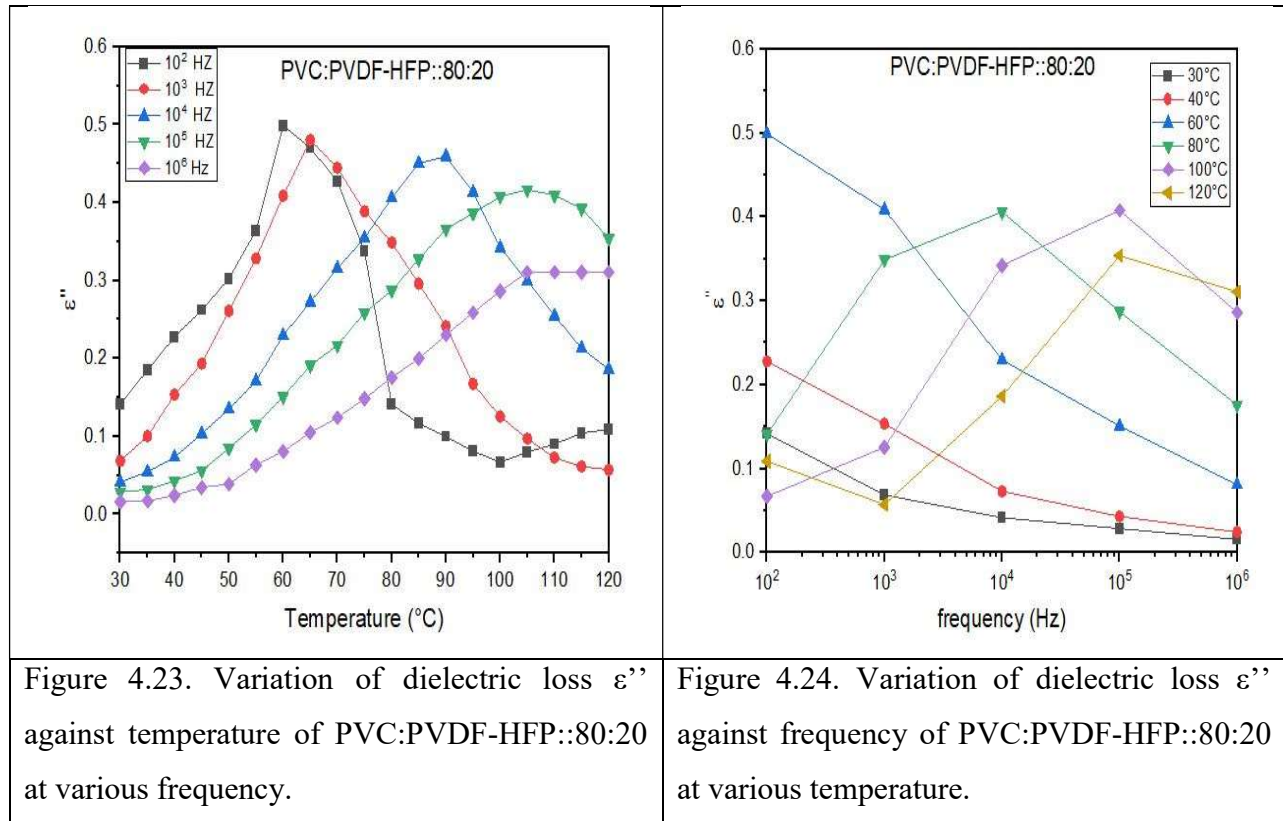


Figure 16. Variation of dielectric loss  $\epsilon''$  against frequency of PVC:PVDF-HFP::90:10 at various temperature.

As the weight percentage of PVDF-HFP increases in the blend samples, the maximum loss also increases. This can be attributed to the higher heterogeneity in the blends with increasing PVDF-HFP content, leading to a greater number of trapping sites [12]. The peak observed, based on its location, is likely due to dipolar reorientation and space charge effects, which are a result of molecular motions associated with the side chains and the charge effects arising from the trapping of injected charge carriers in distributed traps.



The activation energy was calculated based on the Arrhenius-type shift of the loss peaks. The calculated activation energy values are presented in Table 1. It was observed that the activation energy values do not exhibit a consistent variation with the weight percentage of PVDF-HFP in the blend samples. For the PVC:PVDF-HFP blend, the activation energy was found to range from 0.30 to 0.80 eV, which is characteristic of electronic conduction [13].



Table 1 . Value of activation energy (in eV)

| Blend of<br>PVC:PVDF-HFP | Activation Energy (eV) |
|--------------------------|------------------------|
| 100:0                    | 0.52                   |
| 95:05                    | 0.45                   |
| 90:10                    | 0.63                   |
| 85:15                    | 0.69                   |
| 80:20                    | 0.39                   |

#### 4. Conclusion

The addition of PVDF-HFP to PVC significantly influences its dielectric and mechanical properties. The incorporation of PVDF-HFP lowers the glass transition temperature of PVC, enhancing dipolar orientation and segmental mobility. Dielectric constant ( $\epsilon'$ ) increased with temperature due to improved dipole alignment but decreased with frequency due to limited dipole response. Dielectric loss ( $\tan \delta$ ) analysis revealed prominent relaxation peaks influenced by composition and temperature. The calculated activation energy values (0.30–0.52 eV) confirm electronic conduction mechanisms.

These findings establish PVC:PVDF-HFP blends as promising materials for applications in dielectric and electronic devices, with tunable properties achieved by varying PVDF-HFP content. Future work will focus on optimizing the blend ratios for specific industrial applications.

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