

Original Article

Effect of ultrahigh diluted homeopathic medicines on the electrical properties of PVDF-HFP

Ahana Chatterjee¹, Biplab Kumar Paul^{2,3}, SubrataKar^{2,3}, Sukhen Das^{2,3}, Ruma Basu^{4,3}, Durga Shankar Bhar³, Rajkumar Manchanda⁵, Anil Kumar Khurana⁵, Debadatta Nayak⁵, Papiya Nandy^{3*}.

¹ Heritage Institute of Technology, Kolkata- 700107

² Jadavpur University, Dept. of Physics, Kolkata-700032

³ Center for Interdisciplinary Research and Education, Kolkata-700032.

⁴ Jogmaya Devi college, Dept. of Physics, Kolkata-700026

⁵ Central Council for Research in Homeopathy, New Delhi – 110058, India

*Corresponding author, Email: pnandy00@gmail.com

Abstract

In an effort to improve the electrical properties of the electroactive Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP), we introduced a novel and simple approach to synthesize PVDF-HFP composite films by incorporating ultrahigh dilutions of two homeopathic medicines *Ferrum metallicum* (FM) and *Zincum oxidatum* (ZO) in different potencies. The homeo-PVDF-composite films (HPCF) were synthesized by simple solution casting technique. XRD, FESEM, FTIR studies were performed to check the presence of nanoparticles in the film. The electrical properties of the HPCF samples get enhanced significantly due to the incorporation of the medicines and the effect increases with the increase in potency of the medicines.

Keywords: Electroactive; PVDF-HFP, Homeopathy, Dielectric constant, Tangent loss

IJHDR



Cite as: Chatterjee A, Paul BK, Kar S, Das S, Basu R, Bhar DS, Manchanda R, Khurana A, Nayak D, Nandy P. Effect of ultrahigh diluted homeopathic medicines on the electrical properties of Poly PVDF-HFP. *Int J High Dilution Res.* 2016;15(1): 10-17.

Introduction

Electroactive polymer films currently have become the topic of intense global research. These films have good dielectric and electronic properties, and have become an alternative for traditional ferroelectric ceramics. Out of these entire polymers, poly (vinylidene fluoride) (PVDF) and its copolymers are selected for their versatile applications¹⁻⁵.

To improve the efficiency of these films, several fillers have been tried⁴⁻¹⁵. In our search for suitable single non-toxic filler, we selected a novel filler – ultrahigh diluted medicine¹⁶⁻¹⁷.

It has been proposed and established by experimental evidence the formation of nanoparticles, with increase the potency, when these medicines are diluted and agitated (succussion)¹⁶⁻¹⁷.

We have used this property of nanoparticle formation of ultrahigh diluted (UHD) (homeopathic) medicine one step further by utilizing them for the first time in technological applications. We have reported here how the electric properties of the polymer film can be altered efficiently by incorporating homeopathic medicine *Ferrum metallicum* (FM) and *Zincum oxidatum* (ZO) by varying the potency of these medicines.

At a time when electroactive polymer films are gaining worldwide attention due to their suitable electrical properties^{4,6,12-15}, this simple fabrication and non-toxic method will make these homeo-polymer film an alternative for traditional ferroelectric ceramics^{5, 8-10} and hence, the outcome of this experiment may be of high significance.

Materials and methods

The materials used in the synthesis of HPCF are poly (vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP) (Sigma-Aldrich, USA.), dimethyl sulfoxide (DMSO) (Merck, India) and freshly prepared three potencies (6cH, 30cH and 200cH) of homeopathic medicines FM and ZO, which were obtained from Hahnemann Publishing Company, Kolkata, India.

The HPCF were synthesized by the simple solution-casting method. In a typical synthesis, 100 mg PVDF-HFP were added in 2 ml DMSO and mixed together under vigorous stirring at 60°C for 3 hours. 600µl of FM and ZO in three potencies 6cH, 30cH and 200cH were separately added to three samples of the solution. The HPCFs were obtained by casting the whole mixture in clean dry petri dishes and evaporating the solvent in an incubated oven at 60°C for three hours. The films were then coated by silver paste on both sides for electrical measurements. The synthesized films had the thickness in the range of 40–60µm as measured by using a digital screw gauge^{11,15,18}. (Fig.1a)

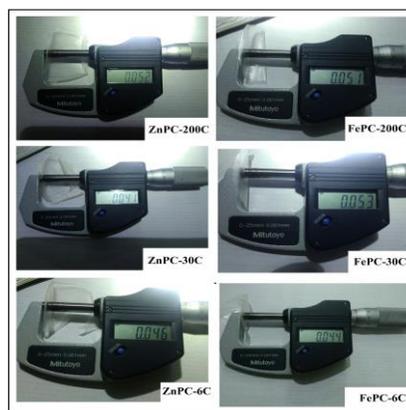


Figure 1a: Photographs of synthesized films and their measurements. The thickness of all films lie between 41 µm and 52 µm.



Cite as: Chatterjee A, Paul BK, Kar S, Das S, Basu R, Bhar DS, Manchanda R, Khurana A, Nayak D, Nandy P. Effect of ultrahigh diluted homeopathic medicines on the electrical properties of Poly PVDF-HFP. *Int J High Dilution Res.* 2016;15(1): 10-17.

Instrumentation

The X-ray diffractometer (D8, Bruker AXS, Wisconsin, USA, using Cu K α radiation (1.5418 Å) and operating at 40kV with a scan speed of 3s/step) analyzed phase identification of the different HPCF samples. The characteristic stretching and bending modes of vibration of chemical bonds of these samples were effectively evaluated by FTIR spectroscopy (FTIR-8400S, Shimadzu). Dielectric measurements of these films were carried out by an electrometer (Model 4274 A, Hewlett-Packard, USA). Electrical properties such as dielectric permittivity (ϵ_r), dissipation factor ($\tan \delta$) and A.C. conductivity (σ a.c.) of all HPCF samples were measured in the frequency range 20Hz to 2.0MHz using LCR meter (Model 4274 A, Hewlett-Packard, USA).

Characterization

X-ray diffraction technique

The crystallization behavior of the films was investigated using an X-ray diffractometer.

Fig.1 shows the X-ray diffraction (XRD) patterns of all HPCFs. The diffraction pattern of pure PVDF-HFP shows peaks at 2θ values of 17.61 (100), 18.21 (020), 20.11 (021) and 26.81 [(201), (310)] corresponding to the α -phase and 38.91 (211) for the γ -phase. From the XRD observations, it found that all the peaks were presented in the HPCF system. No additional peaks appeared may be due to the low dilution of the loaded medicine^{11, 15, 18}.

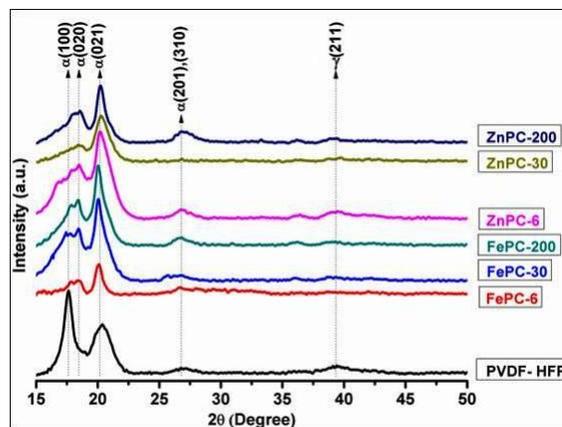


Figure 1. XRD analysis of all HPCF system.

FTIR analysis

Fig. 2(a) and 2(b) show the Fourier transform infrared (FTIR) spectra of (a) FM and (b) ZO loaded HPCFs including pure PVDF-HFP film. The spectrum of all HPCFs shows characteristic absorbance bands at 488, 532, 613 and 763, 796 and 975 cm^{-1} corresponding to the α -phase and at 840, 481, 511, 600 and 839 cm^{-1} corresponding to the β -phase have been observed^{11, 15, 18}.

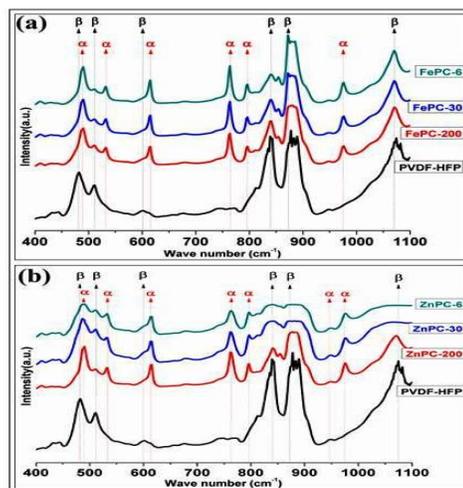


Figure 2. FTIR analysis of all (a) FePC and (b) ZnPC films.



FESEM analysis

Fig.3 shows the morphology and microstructures of HPCF samples loaded with FM and ZO medicines of 200cH and 6cH potencies and were labeled as (a) FePC-200, (b) FePC-6, (c) ZnPC-200 and (d) ZnPC-6 films respectively. From Fig. 3 it has been observed that for (a) FePC-200 film, a large number of cube like crystalline nano structured iron particles are homogenously distributed and well separated from each other whereas (b) FePC-6 film have comparatively large particles were embedded in the polymer matrix. On the other hand (c) ZnPC-200 film showed densely packed nano particles whereas (d) ZnPC-6 stands for the evidence of a large number of agglomerated particles embedded in the polymer matrix^{11,15,18}.

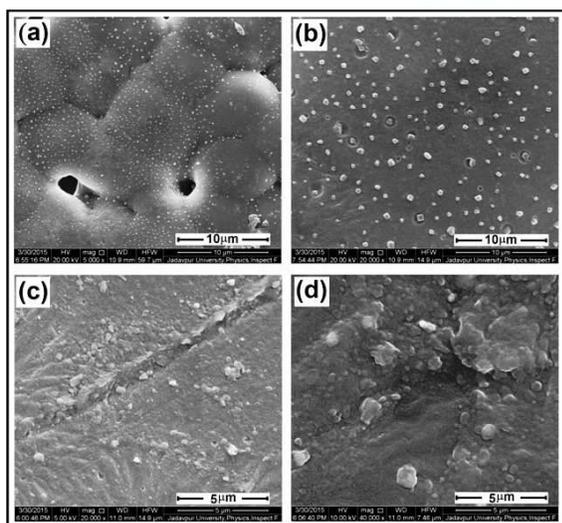


Figure 3. FESEM micrograph of (a) FePC-200, (b) FePC-6, (c) ZnPC-200 and (d) ZnPC-6 films.

Dielectric Measurements and discussions

Dielectric constant

The dielectric constant (k) or relative permittivity (ϵ_r) of each sample was calculated from the capacitance using the formula, $\epsilon_r = (C \cdot d) / A \epsilon_0$, where ϵ_r , C , d , A and ϵ_0 are the dielectric constant of the material, capacitance, thickness of the film, the area of cross-section and permittivity of free space respectively.

The variations of dielectric constant of all FePC and ZnPC film with frequency are shown in Fig. 4(a) and (b) respectively. From the figure, it is clearly seen that within the frequency range 20 Hz to 2 MHz, dielectric constant for all FePC and ZnPC films continuously decrease with increasing frequency for all concentration of FePC and ZnPC film at about 200Hz and after that it seems to remain constant at about 100 KHz. It is also seen that throughout the whole frequency range, dielectric constant has substantially higher values in the case of all FePC and ZnPC film compared to be a pure polymer film. Enhancement of dielectric constant at a lower frequency may be explained by the fact that, at lower frequency range the dipoles can orient easily with the electric field and so they can contribute to improved polarization which is mainly responsible for the enhancement of the dielectric constant. As the frequency is increased further dipole response is limited and the dielectric constant has a saturation tendency. In this case, the internal individual dipoles contribute the dielectric constant^{11,15,18}.



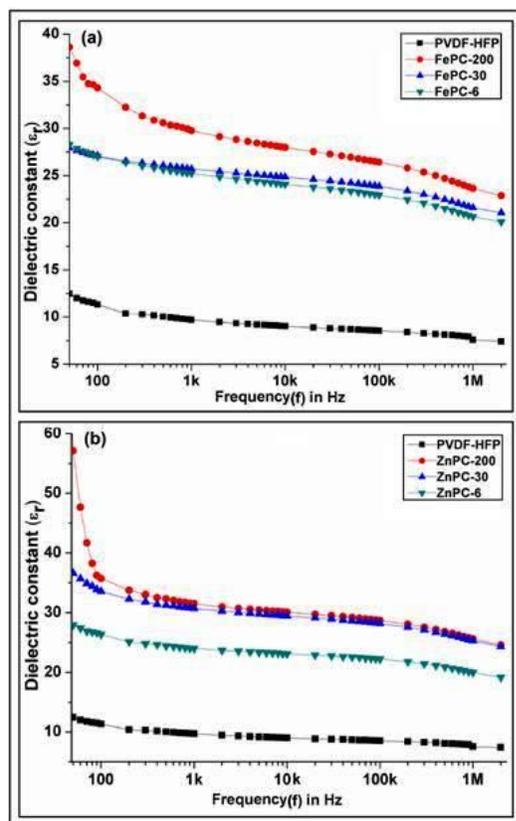


Figure 4. Frequency dependent dielectric constant analysis of all (a) FePC and (b) ZnPC films.

Tangent loss

The complex permittivity of a medium is expressed as, $\epsilon = \epsilon'(1 - j \tan\delta)$, where $\tan\delta$ is the tangent loss which includes dielectric damping loss and conductivity loss of the material.

Fig.5 (a) and (b) shows the variation of tangent loss with frequency for all FePC and ZnPC film respectively in the frequency range 20 Hz to 2 MHz. From the figure, it is clearly seen that throughout the frequency range tangent loss continuously decreases with increasing frequency for all FePC and ZnPC film upto 10 KHz. At comparatively lower frequency ranges the dipoles can orient easily

with external electric field due to more relaxation time. This phenomenon is mainly responsible for intermolecular friction or vibration which contributes to the higher tangent loss. As frequency increases within 10 KHz, less polarization effect continues due to less relaxation time. So intermolecular friction or vibration diminishes which is responsible for the decrease in tangent loss. On the other hand after 10 KHz the tangent loss increases perhaps due to the heat generation followed by more inter molecular vibration and resulting in increasing tangent loss^{11,15,18}.

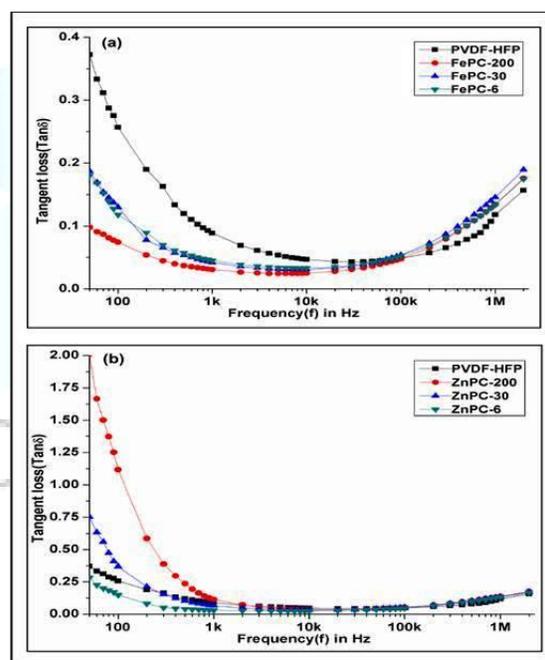


Figure 5. Frequency dependent dielectric loss analysis of (a) FePC and (b) ZnPC films.

A.C. Conductivity

A.C. conductivity (σ a.c) is calculated using the formula, $\sigma_{a.c} = 2\pi f \tan\delta \epsilon_r \epsilon_0$, where σ a.c, f , $\tan\delta$, ϵ_r and ϵ_0 , are the AC conductivity, frequency in Hz, tangent loss factor, dielectric



constant of the material and vacuum permittivity respectively.

The variation of ac conductivity with frequency for all FePC and ZnPC film respectively is shown in Fig. 6(a) and (b). It shows ac conductivity increases exponentially with frequency. The increase of frequency increased a.c. conductivity by increasing hopping of conducting electrons present in FePC and ZnPC films. At higher frequency range, the rapid increase of conductivity with increasing frequency is referred to electronic polarization effect. This increase in conductivity with frequency also arises due to the presence of iron and zinc particles in the polymer matrix that may increase the mobility of the Fe^{++} and Zn^{++} ions which find an easy path to move and hence increase the electrical conductivity^{11,15,18}.

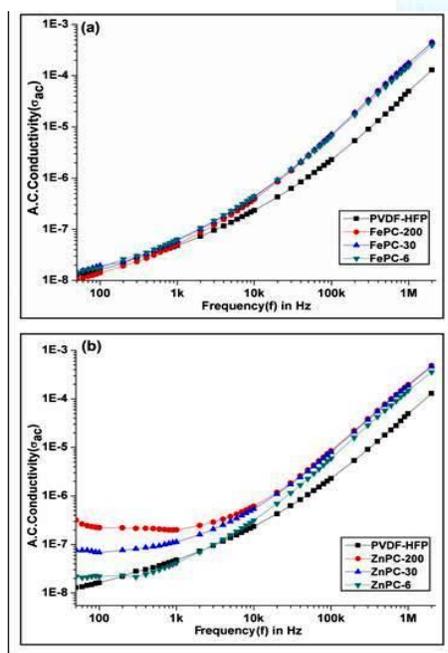


Figure 6. Frequency dependent dielectric conductivity analysis of all (a) FePC and (b) ZnPC films.

Conclusion

HPCFs with different potencies of FM and ZO have been synthesized by solution casting technique and their phase evolution and dielectric properties have been investigated. The dielectric constant of all FePC film is higher than the pure polymer throughout the frequency range 20 Hz to 2 MHz and the FePC-200 film has the highest dielectric constant. The tangent loss of FePC-200 film is also considerable in that frequency range. The AC electrical conductivity increases with frequency for all HPFC films due to the presence of nanoparticles in the polymer composites. Thus pure polymer film which has comparatively low dielectric constant can be modified into materials with enhanced dielectric constant and comparatively low tangent loss by making a composite with ultrahigh diluted homeopathic medicine FM and ZO. As the effect is more prominent with FM, FePC-200 film can be used as a dielectric material for the fabrication of high charge storing multilayer capacitors and can be a promising candidate for electronic industries.

Incorporating *Ferrum metallicum* at 200cH in PVDF-HFP film, our recent study shows that the electrical properties such as dielectric constant, tangent loss, and electrical conductivity of these polymer films increase with concentration of the probe up to a critical value¹⁹.

Conflict of Interest

None declared.

Acknowledgement

The authors are thankful to the Central Council for Research in Homeopathy (CCRH), under Ministry of AYUSH, Govt. of India for



providing financial assistance. The study was undertaken in joint collaboration between CIRE, Kolkata and CCRH, New Delhi.

References

1. [Martins P, Costa CM, Benelmekki M, Botelho G, Lanceros-Mendez S. On the origin of the electroactive poly\(vinylidene fluoride\) b-phase nucleation by ferrite nanoparticles via surface electrostatic interactions. CrystEngComm. 2012;14 \(8\): 2807-2811.](#)
2. [Martins P, Lopes AC, Lanceros-Mendez S. Electroactive phases of poly\(vinylidene fluoride\): determination, processing and applications. Prog. Polym. Sci. 2013; 39\(4\), 683-706.](#)
3. Nalwa HS. Ferroelectric Polymers: Chemistry, Physics, and Applications. Marcel Dekker, New York, 1995.
4. [Li Y, Huang X, Hu Z, Jiang P, Li S, Tanaka T. Large dielectric constant and high thermal conductivity in poly\(vinylidene fluoride\)/barium titanate/silicon carbide three-phase nanocomposites. Appl. Mater. Interfaces. 2011; 3\(11\): 4396-4403.](#)
5. [Dang ZM, Lin YH and Nan CW. Novel ferroelectric polymer composites with high dielectric constants. Adv. Mater. 2003; 15: 1625-9.](#)
6. [Chen Q, Du PY, Jin L, Weng WJ and Han GR. Percolative conductor/polymer composite films with significant dielectric properties. Appl. Phys. Lett. 2007; 91 022912](#)
7. [Panda M, Srinivas PV and Thakur AK. On the question of percolation threshold in polyvinylidene fluoride / nanocrystalline nickel composites. Appl. Phys. Lett. 2008; 92, 132905.](#)
8. [Huang XY, Jiang PK and Xie LY. Ferroelectric polymer/silver nanocomposites with high dielectric constant and high thermal conductivity. Appl. Phys. Lett. 2009; 95, 242901.](#)
9. [Dang ZM, Wu JP, Xu HP, Yao SH, Jiang MJ and Bai JB. Dielectric properties of upright carbon fiber filled poly\(vinylidene fluoride\) composite with low percolation threshold and weak temperature dependence. Appl. Phys. Lett. 2007; 91, 072912.](#)
10. [Yao SH, Dang ZM, Jiang MJ, Xu HP and Bai JB. Influence of aspect ratio of carbon nanotube on percolation threshold in ferroelectric polymer nanocomposites. Appl. Phys. Lett. 2007; 91, 212901.](#)
11. [Thakur P, Kool A, Bagchi B, Das S and Nandy P. Effect of in situ synthesized Fe₂O₃ and Co₃O₄ nanoparticles on electroactive b phase crystallization and dielectric properties of poly\(vinylidene fluoride\) thin films. PhysChem Chem Phys. 2015;17\(2\):1368-78.](#)
12. [Dang ZM, Wang L, Yin Y, Zhang Q and Lei QQ. Giant dielectric permittivities in functionalized CNT/PVDF. Adv. Mater. 2007;19\(6\): 852-57.](#)
13. [Li Q, Xue QZ, Hao LZ, GaoXL and Zheng QB. Large dielectric constant of the chemically functionalized carbon nanotube/polymer composites. Compos. Sci. Technol. 2008; 68\(10\): 2290-96.](#)
14. [He F, Lau S, Chan HL and Fan J. High dielectric permittivity and low](#)



Cite as: Chatterjee A, Paul BK, Kar S, Das S, Basu R, Bhar DS, Manchanda R, Khurana A, Nayak D, Nandy P. Effect of ultrahigh diluted homeopathic medicines on the electrical properties of Poly PVDF-HFP. *Int J High Dilution Res.* 2016;15(1): 10-17.

- [percolation threshold in nanocomposites based on poly\(vinylidene fluoride\) and exfoliated graphite nanoplates. Adv. Mater. 2009;21: 710-15.](#)
15. [Thakur P, Kool A, Bagchi B, Das S and Nandy P. Enhancement of \$\beta\$ phase crystallization and dielectric behavior of kaolinite/halloysite modified poly\(vinylidene fluoride\) thin films. Applied Clay Science. 2014;99:149-159.](#)
16. [Nandy P, Bhandary S, Das S, Basu R and S. Bhattacharyya. Nanoparticle and membrane anisotropy. Homeopathy. 2014;100 \(3\): 194.](#)
17. [Chikramane PS, Kalita S, Suresh AK, Kane SG. Why extreme dilutions reach non zero asymptotes: A nanoparticulate hypothesis based on](#)
- [forth flotation. Langmuir 2012; 28: 15864-75.](#)
18. [Halder K, Paul BK, Bagchi B, Bhattacharya A, and Das S. Copper Ion Doped Mullite Composite in Poly \(vinylidene Fluoride\) Matrix: Effect on Microstructure, Phase Behavior and Electrical Properties. Journal of Research Updates in Polymer Science. 2014; 3: 157-169 157.](#)
19. [Paul B K, Kar S, Bandyopadhyay P, Basu R, Das S, Bhar D S, Manchanda RK, Khurana A, Nayak D, Nandy P. Significant enhancement of dielectric and conducting properties of electroactive polymer polyvinylidene fluoride films: An innovative use of Ferrum metallicum at different concentrations. Indian J Res Homoeopathy 2016;10:52-8.](#)

Received: 03 Nov, 2015. Accepted: 24 March, 2016.

© International Journal of High Dilution Research.
Not for commercial purposes.



Cite as: Chatterjee A, Paul BK, Kar S, Das S, Basu R, Bhar DS, Manchanda R, Khurana A, Nayak D, Nandy P. Effect of ultrahigh diluted homeopathic medicines on the electrical properties of Poly PVDF-HFP. *Int J High Dilution Res.* 2016;15(1): 10-17.