Significant enhancement of dielectric and conducting properties of electroactive polymer polyvinylidene fluoride films: An innovative use of *Ferrum metallicum* at different concentrations

B. K. Paul¹,², S. Kar¹,², P. Bandyopadhyay¹,², R. Basu¹,³, S. Das¹,²,⁴, D. S. Bhar¹, Raj K. Manchanda⁵, Anil Khurana⁵, D. Nayak⁵, Papiya Nandy¹*

**ABSTRACT**

**Background:** There are experimental evidences of nanoparticle aspect of homoeopathic medicine. It has also been established that the size of these nanoparticles (NPs) decrease with increase in potency.

**Aim:** We have used this aspect of homoeopathic medicines in some technical applications. Here, to improve the electrical properties of an electroactive polymer, poly (vinylidene fluoride-hexa-fluoropropylene) (PVDF-HFP), we have incorporated in the polymer film, a very novel and unique probe *Ferrum metallicum* (FeM), a homoeopathic medicine, the size of which can be changed by dilution, followed by controlled agitation.

**Settings and Design:** The composite film was synthesized by solution-casting technique. Using standard procedures, the characterization studies by X-ray diffraction, field-emission scanning electron microscope, and Fourier transform infrared spectroscopy were performed to check the incorporation of the NPs in the film.

**Material and Method:** Each sample was freshly prepared 2 times by doping FeM in PVDF-HFP matrix using solution-casting technique, and the experiment was repeated with each sample for 5 times.

**Statistical Analysis:** This being a continuous data recording, error bars cannot be shown. We have presented the graphs which have been repeated maximum number of times.

**Result and Conclusion:** Our result shows that the electrical properties such as dielectric constant, tangent loss, and electrical conductivity of these polymer films get significantly modified due to incorporation of this homoeopathic nanomedicine and the effect increases with the increase in concentration of the probe up to a critical value. These FeM-incorporated PVDF-HFP films will have potential applications as high-energy storage devices such as multilayered high-charge storage device.

**Keywords:** A.C. conductivity, Dielectric constant, Nanoparticles, Polymer film, Tangent loss
INTRODUCTION

In recent times, electroactive polymer films have become the subject of intense research interest due to their good electrical and other properties. Polyvinylidene fluoride (PVDF) and its polymers are selected from the whole range of these polymers for their versatile applications.[1-5] The electrical properties of these polymers can be greatly enhanced by using suitable fillers.[4-15] In our endeavor in the search for a suitable nontoxic, easily available and low-cost filler, we have thought of a very novel and unique idea of using triturated iron particles, a commonly used homeopathic nanomedicine Ferrum metallicum (FeM).

That the homeopathic medicines are active even at a very low dilution has been challenging for the scientists and many different hypotheses had been proposed. Out of all these, the proposal of formation of nanoparticles (NPs) at high potency (the process of potentization is dilution, followed by succussion) of these medicines had been experimentally proved.[16-19]

We have utilized this property of nanoparticle formation of homeopathic medicine for the first time in technological applications and reported here the enhancement of electrical properties of (PVDF-hexa-fluoropropylene) (PVDF-HFP) by incorporating triturated iron NPs FeM in the polymer matrix. We have been able to improve the electrical properties, namely dielectric constant, conductivity, and tangent loss of the film by changing the concentration of FeM up to a certain critical concentration.

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 nontoxic method will make these FeM-incorporated polymer film an alternative for traditional electroactive ceramics[5,8-10] and hence the outcome of this experiment is of great significance.

MATERIALS AND METHODS

The FeMP was synthesized by solution-casting method. In a typical synthesis, 100 mg of PVDF-HFP was added in 2 ml DMSO and mixed together under vigorous stirring at 60°C for 3 h. Measured amounts of the FeM at 200C potency were added to the solution. FeMP was obtained by casting the whole mixture in clean dry Petri dishes and evaporating the solvent in an incubated oven at 60°C for 12 h. As we know DMSO cannot be totally removed, we did all our measurements with the residual DMSO. The films were then coated by silver paste on both sides for electrical measurements. The synthesized films had the thickness in the range of 40–60 μm as measured by using a digital screw gauge.[11,15,20]

Sample Details

- 100 mg PVDF-HFP + 2 ml DMSO + No FeM (0 FeMP)
- 100 mg PVDF-HFP + 2 ml DMSO + 0.1 ml FeM at 200C (0.1 FeMP)
- 100 mg PVDF-HFP + 2 ml DMSO + 0.2 ml FeM at 200C (0.2 FeMP)
- 100 mg PVDF-HFP + 2 ml DMSO + 0.5 ml FeM at 200C (0.5 FeMP)
- 100 mg PVDF-HFP + 2 ml DMSO + 1.0 ml FeM at 200C (1.0 FeMP)
- 100 mg PVDF-HFP + 2 ml DMSO + 2.0 ml FeM at 200C (2.0 FeMP).

Instrumentation

The characteristic stretching and bending modes of vibration of chemical bonds of these samples were effectively evaluated by Fourier transform infrared spectroscopy ([FTIR]-8400S, Shimadzu). Dielectric measurements of these films were carried out by an electrometer (HP Model 4274 A, Hewlett-Packard, USA). Electrical properties such as dielectric permittivity \((\varepsilon_r)\), dissipation factor \((\tan \delta)\), and A.C. conductivity \((\sigma_{A.C})\) of all FeMP samples were measured in the frequency range of 20 Hz to 2.0 MHz using LCR meter (HP Model 4274 A, Hewlett-Packard, USA). Field-emission scanning electron microscopy (FESEM) was done by using INSPECT F50 SEM, FEI Europe BV. The operating conditions are mentioned in the FESEM images as follows: HV 20.00 kV, mag 5000x, WD 10.9 mm, and HFW 59.7 μm. Sample preparation was done by using Turbo-Pumped Sputter Coater EMS 150TS and was used for gold coating.
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra of all FeMPs that show characteristic absorbance bands at 488, 532, 613, 763, 796, and 975 cm\(^{-1}\) corresponding to the \(\alpha\)-phase and at 481, 511, 600, 839, and 1070 cm\(^{-1}\) corresponding to the \(\beta\)-phase have been observed.\(^{[11,15,20]}\) The spectra indicate that there is no phase shift or chemical interaction between the nanomedicine and the polymer film, but the intensity of \(\alpha\)- and \(\beta\)-phases change with the concentration of FeM [Figure 1].

Field-emission Scanning Electron Microscope Analysis

Figure 2 shows the morphology and microstructures of FeMP samples loaded with nano medicine FeM at 200C potency and of different concentrations. In Figure 2a and b, the particles are more scattered, whereas Figure 2c shows the evidence of large number of agglomerated particles embedded in polymer matrix. Evidence for the inclusion of Fe in the polymer was not very conclusive as the sample was of extreme dilution and was difficult to detect the presence of particle. However, we realized that the particles seen in the FESEM are Fe particles as their number density changed with higher concentration of added Fe.

Dielectric Constant Measurements

The dielectric constant \((\varepsilon_r)\) of each sample was calculated using the formula,

\[
\varepsilon_r = \frac{C_p \cdot d}{A \cdot \varepsilon_0},
\]

where \(\varepsilon_r\), \(C_p\), \(d\), \(A\), and \(\varepsilon_0\) are the dielectric constant of the material, capacitance, thickness of the film, area of cross-section, and permittivity of free space, respectively.

The variations of dielectric constant with frequency of all FeMP films are shown in Figure 3. From the figure, it is clearly seen that throughout the whole frequency range, dielectric constant has substantially higher values in case of all FeMP films compared to the pure polymer film. The value increases with the concentration of FeM up to a critical value of 0.5 ml of FeM added in the polymer film, after which the value decreases. It is also seen that within the frequency range 20 Hz to 2 MHz, dielectric constant of FeMP films decreases continuously with increasing frequency for all concentrations of FeM up to 200 Hz and after that the rate of decrease slows down.

Enhancement of dielectric constant at lower frequency may be explained from interfacial polarization occurred in the interfaces between insulators (e.g., PVDF-HFP) and conducting materials (e.g., FeM). This effect overrules the effect of orientation of dipoles at lower frequency. As the frequency is increased further, dipole response is restricted and the dielectric constant has a saturation tendency. In this case, the internal individual dipoles contribute to the dielectric constant which is nothing but the electronic polarization effect.\(^{[11,15,20]}\)

At a higher doping concentration, dielectric constant decreases due to the presence of more agglomerated particles present in the composite system thereby reducing the interfacial area. This phenomenon can be also explained by FESEM micrograph [Figure 3].
**Tangent Loss Measurement**

The tangent loss, \( \tan \delta \), of a medium includes dielectric damping loss and conductivity loss of the material and is the ratio of conduction current and displacement current.

\[
\tan \delta = \frac{\sigma_{a.c.}}{2 \pi f \varepsilon_r \varepsilon_o}.
\]

From Figure 4, it is clearly seen that throughout the frequency range, tangent loss continuously decreases exponentially with increasing frequency for all FeMP films up to 10 KHz. At comparatively lower frequency range, the dipoles can orient easily with external electric field. This phenomenon is mainly responsible for intermolecular friction or vibration, which contributes to the exponential decrease of tangent loss.

As the frequency increases further, polarization effect is less as the dipoles cannot follow the rapidly changing applied electric field and there is no further tangent loss.

The increase in tangent loss above 100 KHz frequency arises due to the contribution from the conduction of metal NPs through the polymer.[11,15,20]

Figure 4 shows that the sample 0.2 FeMP has the maximum tangent loss perhaps due to the formation of more conducting pathway, i.e., leakage current. Further increase of doping element may inhibit the conducting pathways resulting in low tangent loss.

**A.C. Conductivity Measurement**

A.C. conductivity (\( \sigma_{a.c.} \)) is given by,

\[
\sigma_{a.c.} = 2 \pi f \tan \delta \varepsilon_r \varepsilon_o
\]

where \( f \), \( \tan \delta \), \( \varepsilon_r \) and \( \varepsilon_o \) are the frequency in Hz, tangent loss factor, dielectric constant of the material, and vacuum permittivity, respectively.

The A.C. conductivity increases with all frequencies as shown in Figure 5. The conductivity is maximum for 0.2 FeMP due to the formation of more conducting pathway, i.e., leakage current. Further increase of doping element may inhibit the conducting pathways resulting in low conductivity. The exponential increase in conductivity with frequency arises due to the increase in mobility of iron particles present in the polymer matrix.[11,15,20]

**CONCLUSIONS**

FeMPs with different concentrations of FeM have been synthesized by solution-casting technique and their phase evolution, dielectric properties, and A.C. conductivity have been investigated.
Gradual addition of FeM in PVDF-HFP leads to gradual increase in α-phase at the cost of electroactive β-phase as observed from the FTIR spectra. The dielectric constant of FeMPs at all concentrations of FeM is higher than the pure polymer throughout the frequency range of 20 Hz to 2 MHz [Figure 3]. The tangent loss of this film is also considerable in that frequency range [Figure 4].

The dielectric constant is highest for 0.5 FeMP. Perhaps, the composite reaches the optimum conformation of α- and β-phases at this concentration of FeM to exhibit the maximum dielectric constant [Figure 3], which in turn is responsible for the low tangent loss as shown in Figure 4. However, A.C. conductivity is high for 0.2 FeMP [Figure 5], giving rise to high tangent loss [Figure 4].

The electrical conductivity increases with frequency for all FeMP films [Figure 5] due to the presence of mobile metal ions in the polymer composites. As tan δ is a measure of the ratio of conduction current and displacement current, its value also increases with increase in conductivity [Figure 4].

We can compare this result using homoeopathic source of Fe nanoparticle with our earlier study of homogenous dispersion of Fe₂O₃ NPs, as obtained from chemical (nonhomoeopathic) sources, in the polymer matrix.[11] We have shown that the incorporation leads to strong interfacial interaction between the NPs and the polymer resulting in enhanced dielectric constant of the thin films. The observed variation of the dielectric properties of the thin films has been explained on the basis of surface charge, size, geometrical shape, and extent of agglomeration of the NPs in the polymer matrix. Similarly, dielectric constant, tangent loss, A.C. conductivity, and resistivity of composites with increasing concentration of Fe metal ion at different temperatures have been studied by us.[21] The results showed that dielectric constant decreased with frequency for all the samples attaining constancy at higher frequency, followed by electronic polarization. A.C. conductivity increased with frequency, and was found to depend on the concentration of mobile ions present in the 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 homoeopathic nanomedicine FeM, which are nontoxic, eco-friendly, and easily available in the nano form. Our similar work using other metal NPs also gives promising result and compares well with this result.[11,21-23]

As a dielectric material, these FeMP films can then be a promising candidate for the fabrication of high-charge storing multilayer capacitors and can be used for electronic industries.

Acknowledgement
The authors are thankful to the Central Council for Research in Homeoeopathy (CCRH), Ministry of AYUSH, Govt. of India for providing financial assistance. The study was undertaken in joint collaboration between CIRE, Kolkata and CCRH, New Delhi.

Financial Support and Sponsorship
Central Council for Research in Homeoeopathy, New Delhi.

Conflicts of Interest
There are no conflicts of interest.

REFERENCES


Mejora significativa de las propiedades dieléctricas y conductoras de las películas del polivinilideno, un polímero electroactivo: uso innovador de *Ferrum metallicum* a diferentes concentraciones

**Fundamento:** Existen evidencias experimentales en cuanto al aspecto de nanopartículas en la medicina homeopática. También se ha establecido que el tamaño de estas nanopartículas (NP) desciende conforme aumenta la potencia.

**Objetivos:** Hemos utilizado este aspecto de los medicamentos homeopáticos en determinadas aplicaciones técnicas. En este contexto, para mejorar las propiedades eléctricas de un polímero electroactivo, el poli (vinilideno fluoruro-hexa-fluoropropileno) (PVDF-HFP), hemos incorporado una sonda muy novedosa y exclusiva de *Ferrum metallicum* (FeM), un medicamento homeopático en la película polimérica. El tamaño de FeM puede cambiarse por dilución seguida de una agitación controlada.

**Contesto y diseño:** Se sintetizó la película compuesta mediante la técnica de colada de soluciones (*solution-casting*). Se aplicaron procedimientos estandarizados para efectuar los estudios de caracterización a través de difracción de rayos X, microscopía electrónica de barrido del campo de emisión y espectroscopia infrarroja con transformación de Fourier, y controlar la incorporación de las NP en la película.

**Materiales y métodos:** Cada muestra se preparó de nuevo dos veces mediante el dopaje de FeM en la matriz PVDF-HFP utilizando la técnica de colada de soluciones. El experimento se repitió 5 veces con cada muestra.

**Análisis estadístico:** Al ser un registro continuado de datos, no se pueden mostrar barras de errores. Hemos presentado los gráficos que se han repetido el máximo número de veces.

**Resultados y conclusiones:** Nuestro resultado muestra que las propiedades eléctricas, como la constante dieléctrica, la pérdida tangencial y la conductividad eléctrica de las películas de polímero se modifican significativamente debido a la incorporación de este nanomedicamento homeopático, y que el efecto incrementa con el aumento de la concentración de la sonda hasta un valor crítico. El FeM incorporado en las películas PVDF-HFP tiene aplicaciones potenciales como dispositivos de almacenamiento de alta energía, como el dispositivo de almacenamiento multicapa de alta carga.