Effect of Homeopathic Dilutions of *Cuprum Arsenicosum* on the Electrical Properties of Poly(Vinylidene Fluoride-Co-Hexafluoropropylene)

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**Abstract**

**Background** We report the effects of nanoparticles in homeopathic preparations of copper salts on the electrical properties of polymer film. Previous work showed that the incorporation of metal-derived homeopathic medicines increases the dielectric constant and alternating current (AC) conductivity of an electroactive polymer film that is commonly used as a capacitor in the electronic industry. We report here the effect of dilution of one homeopathic medicine, *Cuprum arsenicosum* (*CuAs*), at 200C potency on the electrical properties of the polymer film of poly(vinylidene fluoride-co-hexafluoropropylene).

**Methods** *CuAs* 200c was incorporated in the film by the solution casting method. The electrical characteristics were measured at different frequencies using an inductance, capacitance, and resistance meter. Fourier transform infrared spectroscopy (FTIR) was performed to detect phase change in the polymer film due to the incorporation of *CuAs*. Morphology and particle size were studied using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy.

**Results** At 10 kHz frequency, both dielectric constant and AC conductivity increased approximately 18 times for the polymer film when incorporated with 2 mL *CuAs* at 200C potency. FTIR indicated the increase in conducting phase, while FESEM and EDX confirmed the presence of spherical *CuAs* particles.

**Conclusion** The incorporation of *CuAs* in the electroactive polymer film enhances the conductivity and dielectric constant. We conclude that these changes arise from the change in phase of the polymer film, and because of the presence of two different metals that affects the interfacial polarization.

**Keywords**

► homeopathic medicine
► nanoparticles
► electrical properties
► polymer film

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Introduction

Homoeopathic medicine is one of the world’s most widely practiced complementary therapies. However, the mechanism of action of these medicines at very high dilution remains a puzzle to the conventional scientific community. Several theories have been advanced, but are yet to be confirmed.

Succussion, an integral part of preparing homeopathic medicines, transfers mechanical energy to the solution, causing the size reduction of the original aggregated drug particles to the nano-dimension. We have previously shown that the permeability of drugs of nano-dimension through the membrane is a function of the potency. Our research and those of other groups have demonstrated the formation of nanoparticles at high homeopathic dilutions. We believe that this nanoparticle formation is a major clue to understanding the behavior of the homeopathic medicine at ultramolecular dilution.

We have investigated the nanoparticle aspect of homeopathic dilutions further, using them in several technological applications. In one case, we have shown that thermovoltage and photo-voltage generation are enhanced with the homeopathic medicine Zinzip oxydatum (ZnO), This finding may have important implications in solar energy conversion.

In another case, to improve the electrical properties of electroactive polymer films, which have been commercially used in recent times as an alternative for traditional electroactive ceramics for technological applications, we have explored a novel method of exploiting the nanoparticle aspect of homeopathic medicines. By incorporating homeopathic dilutions including Ferrum metallicum (FeM), Cuprum metallicum (CuM), Cobaltum metallicum (CoM), and ZnO in the polymer matrix of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), we were able to improve the electrical properties of these polymers, enhancing the dielectric constant and alternating current (AC) conductivity, followed by decrease in tangent loss of these electroactive polymer films.

We report here how these enhanced electrical properties of the polymer film can be further improved by incorporating Cuprum arsenicosum (CuAs) nanoparticles at different proportions in the polymer matrix. At 10 kHz frequency, for example, both dielectric constant and AC conductivity increased approximately 18 times for polymer film incorporated with 2 mL of CuAs at 200 C potency compared with the undoped film.

Methods

Solution Casting Method

To synthesize CuAs nanoparticles incorporated PVDF-HFP films, freshly prepared CuAs at 200C potency was obtained from the Hahnemann Publishing Company, India. PVDF-HFP pellets were supplied by Sigma Aldrich, United States, and dimethyl sulfoxide (DMSO) from Merck, Germany.

The CuAs-doped nanocomposites were synthesized by the solution-casting method (see Fig. 1). In a typical synthesis, 100 mg of PVDF-HFP was added to 2 mL of DMSO and mixed together with vigorous stirring at 60°C for 3 hours. Measured amounts of CuAs were added to the solution. All the composite films were obtained by casting the whole mixture in clean dry Petri dishes and evaporating the solvent in an oven at 60°C for 12 hours. As 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 a thickness in the range of 50 to 55 μm as measured using a digital screw gauge.

Electrical Characteristics, Phase Change, Morphology, and Particle Size

The electrical characteristics were measured at different frequencies using an inductance, capacitance and resistance (LCR) meter (HP Model 4274 A, Hewlett-Packard, United States). Fourier transform infrared spectroscopy (FTIR) (FTIR-8400S, Shimadzu) was performed to detect phase change in the polymer film due to the incorporation of CuAs, Morphology, particle size, and energy dispersive X-ray (EDX) spectroscopy were studied using field emission scanning electron microscopy (FESEM) (ZEISS Sigma 300).

Synthesized sample details and codes are given below. Particular colors and numbers in -Figs. 2, 3, 4, and 5 were used to identify the samples.

Sample code 0: 100 mg PVDF + 2 mL DMSO + 0 mL CuAs
Sample code 0.1: 100 mg PVDF + 2 mL DMSO + 0.1 mL CuAs
Sample code 0.5: 100 mg PVDF + 2 mL DMSO + 0.5 mL CuAs
Sample code 2.0: 100 mg PVDF + 2 mL DMSO + 2.0 mL CuAs
Sample code 5.0: 100 mg PVDF + 2 mL DMSO + 5.0 mL CuAs

Fig. 1 Flowchart to synthesize PVDF-CuAs homeopathic medicine nanocomposite films. DMSO, dimethyl sulfoxide. PVDF-CuAs, poly(vinylidene fluoride-Cuprum arsenicosum).

Flowchart to synthesize PVDF-CuAs nanocomposite

100 mg PVDF tablet
2 mL DMSO
Stirring for 8 hours at 50°C

0.5% PVDF-DMSO Solution
Stirring for 16 hours at 60°C
Dry the gel at 60°C for 24 hours in Petri dish

Gel of PVDF-CuAs Nanocomposite

Undoped homogeneous gel
0.1, 0.5, 2 and 5 mL of CuAs diluted liquid for each sample.
Results and Discussion

FTIR Analysis

Phase identification and confirmation studies were performed by FTIR. – Fig. 2 shows the FTIR spectroscopic pattern in the range of 400 to 1,100 cm⁻¹ of all CuAs doped PVDF-HFP nanocomposite films. The FTIR spectra show the characteristic absorbance bands at 487, 530, 615, 763, 795, and 875 cm⁻¹ corresponding to the α-phase and around 512 and 842 cm⁻¹ corresponding to the β-phase. From FTIR spectra, we observe a variation in phase intensity of α- and β-phases which confirms chemical interaction between the CuAs nanoparticles with the polymer film.¹⁵,¹⁹–²² From – Fig. 2 it is also confirmed that, with increase in concentration of CuAs, the β-phase peaks have grown significantly compared with the pure PVDF-HFP and reached maximum for 2 mL insertion, which signifies that the best effective interaction occurred between the CuAs nanoparticle and PVDF matrix at this concentration. With further insertion of CuAs nanoparticles, the phase intensity decreased because of the network destruction. This was confirmed by FESEM (– Fig. 6).

Fig. 2 Phase identification and confirmation study by FTIR of all the samples. FTIR, Fourier transform infrared spectroscopy.

Fig. 3 Variation of dielectric constant with frequency for all CuAs incorporated PVDF films. See also – Table 1. CuAs, Cuprum arsenicosum, PVDF, poly(vinylidene fluoride).

Fig. 4 Variation of tangent loss with frequency for all CuAs incorporated PVDF films. CuAs, Cuprum arsenicosum; PVDF, poly(vinylidene fluoride).

Fig. 5 Variation of AC conductivity (Siemens/meter) with frequency for all CuAs incorporated PVDF films. See also – Table 1. CuAs, Cuprum arsenicosum, PVDF, poly(vinylidene fluoride).
Field Emission Scanning Electron Microscopy Analysis
We examined the particle size and morphology of CuAs-incorporated PVDF films with FESEM (►Fig. 6). The figure depicts the microstructures in the polymer film of the five samples of (a) pure PVDF-HFP, (b) 0.5 mL, (c) 2 mL, and (d) 5 mL doping concentration of CuAs incorporated in the polymer films. The result shows the presence of several morphology and microstructures of CuAs incorporated in the polymer samples. For lower insertion concentration (0.5 mL), a small number of spherical shaped nanoparticles are seen to be embedded in the PVDF-HFP matrix. A large number of spherical shaped CuAs nanoparticles, homogeneously distributed and densely packed in the polymer matrix, are observed for the doping concentration of 2 mL. For further increase in doping concentration, evidence of a large number of agglomerated nanoparticles embedded in the polymer matrix is observed. The clear presence of homeopathic medicines of such low dimension in the polymer matrix indicates existence of nanoparticles.15,19–22

Energy Dispersive X-ray Spectroscopy and Elemental Analysis
Elemental mapping images of CuAs compound nanoparticle-incorporated PVDF-HFP composite film were performed from EDX measurements.

Fig. 6 Morphology and microstructural analysis of (a) 0, (b) 0.5, (c) 2.0, and (d) 5.0 CuAs incorporated PVDF films by FESEM. CuAs, Cuprum arsenicosum, FESEM, field emission scanning electron microscopy; PVDF, poly(vinylidene fluoride).

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Study of Electrical Properties of Polyvinyl Film PVDF-HFP
We studied the following electrical properties of CuAs-doped PVDF-HFP with the help of an LCR instrument and compared with that of the pure PVDF film.

Dielectric Constant
Dielectric property ($\varepsilon_r$) of a material is its ability to be polarized by an applied electric field and can be calculated as,

$$\varepsilon_r = \frac{c_p d}{(4\pi\varepsilon_0)}$$

where, $c_p$ is the charge stored in the material, $d$ is the thickness of the plate or film, $A$ is the area of the sample, and $\varepsilon_0$ is the permittivity in free space.
The variation in dielectric constant with frequency for all films clearly shows that within the frequency range 20 Hz to 2 MHz, the dielectric constant continuously decreases with increasing frequency (Fig. 3). It has substantially higher values throughout the whole frequency range for all films doped with CuAs, compared with the pure polymer film. The value increases with increasing concentration of CuAs and at a certain concentration (2 mL) it becomes maximum at approximately 18-fold compared with the 0-mL sample (Table 1). This effect is due to Maxwell–Wagner–Sillars interfacial polarization followed by maximum interfacing area per unit volume. Upon further increasing the doping concentration, the value of dielectric constant decreases due to the decreasing of their interparticle distance or agglomeration. As the frequency is increased further, dipole response is limited and the dielectric constant has a saturation tendency.

**Tangent Loss**

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. This loss quantifies a dielectric material’s inherent dissipation of electromagnetic energy (e.g., heat) and can be calculated as

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon}
\]

where, \( \varepsilon'' \) is the imaginary part of permittivity and \( \varepsilon \) is the real part of permittivity.

**Table 1** Variation in dielectric constant and AC conductivity of polymer film due to incorporation of CuAs at 10 kHz frequency

<table>
<thead>
<tr>
<th>Dielectric constant (Fig. 3)</th>
<th>For Sample 0</th>
<th>For sample 2.0</th>
<th>Increase by factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3</td>
<td>146</td>
<td></td>
<td>17.6–18.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AC conductivity (Fig. 5)</th>
<th>For Sample 0</th>
<th>For sample 2.0</th>
<th>Increase by factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.8 \times 10^{-7}) Siemens/meter</td>
<td>(3.2 \times 10^{-6}) Siemens/meter</td>
<td>(17.8–18.0)</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: AC, alternating current; CuAs, *Cuprum arsenicosum*. Note: The LCR meter records data in a continuous way, the data are not taken individually at each point. From the graphs (Figs. 3 and 5), an approximate value was therefore taken.

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**Fig. 7** (a) Elemental confirmation of all elements present in the 2 mL CuAs incorporated PVDF film by EDX spectra (C, Carbon; Cu, Copper; F, Fluorine; As, Arsenic); (b) selected area for measurement; and (c-f) elemental mapping image (c) Carbon, (d) Fluorine, (e) Arsenic, and (f) Copper of 2 mL CuAs-doped PVDF-HFP film. K, L, and Ka 1 refer respectively to the K-band, L-band, and K\(_a\)-band of the X-ray beam used for the EDX spectroscopy. CuAs, *Cuprum arsenicosum*, EDX, energy dispersive X-ray; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene).
The variation in tangent loss with frequency for all homeo-polymer films clearly shows that, throughout the frequency range, tangent loss continuously decreases with increasing frequency for all films up to 10 kHz (Fig. 4). At comparatively lower frequency, more tangent loss is observed due to higher polarization effect followed by more relaxation time. As frequency increases within 10 kHz, polarization effect reduces further due to less relaxation time and inter-molecular friction or vibration diminishes, which is responsible for the decrease in tangent loss. However, after 10 kHz the tangent loss increases, perhaps due to the heat generation followed by more inter-molecular vibration or leakage current.15,19-22

Electrical Conductivity

Electrical conductivity ($\sigma_{a.c.}$) is an intrinsic property of a material that indicates how strongly a given material allows the flow of electric current. It is commonly represented by the Greek letter $\sigma$ (sigma) and is calculated using the formula,

$$\sigma_{a.c.} = 2\pi f \tan\delta \epsilon_r \epsilon_0,$$

where $\sigma_{a.c.}$, $f$, $\tan\delta$, $\epsilon_r$, and $\epsilon_0$ are the AC conductivity, frequency in Hz, tangent loss factor, dielectric constant of the material, and vacuum permittivity, respectively.

Measurements of AC conductivity have been widely used to investigate the nature of ionic motion in ionically conducting materials since it is assumed that they are responsible for this type of conduction. Our results (Fig. 5) show that the AC conductivity increases exponentially with frequency for all homeo-polymer films. This arises due to increase in hopping of conducting electrons present in the homeo-polymer films.23 For a given frequency, enhanced AC conductance is evident in films with higher concentrations of CuAs: at 10 kHz, for example, there is approximately 18-fold greater AC conductance for the 2 mL sample than for the 0 mL sample (Table 1). At higher frequency ranges, the rapid increase in conductivity with increasing frequency is referred to as the electronic polarization effect. The increase in conductivity with frequency also arises due to the presence of free metallic ions in the polymer matrix.15,19-22

Conclusion

Here we have shown that by the incorporation of CuAs at 200C potency in the film of polymer PVDF-HFP, the electrical properties, namely dielectric constant and electrical conductivity measured at 10 kHz frequency, increase by approximately 18 times compared with those of the pure polymer film.

The enhancement of dielectric constant results from the presence of two different metallic nanoparticles in the composite film. Also, the incorporation of CuAs induces a phase change in the polymer film, as is evident from the FTIR spectrum, which is responsible for the enhancement of AC conductivity.

A logical conclusion from these observations is that these homeopathic medicines are more than just alcohol or water: their inherent electrical property is responsible for their effect on different physical processes. And through our experiments, we have shown that the important and unquantifiable effects of homeopathic medicines can be connected with the latest quantifiable technology, potentially opening up a whole new era of research in homeopathy.

Acknowledgment

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