Synthesis and Characterization of PANI/PVDF Composites for Dielectric and AC Conductivity


Department of Post Graduate Studies and Research in Physics, Gulbarga University, Kalaburagi – 585 106, Karnataka, India.

1. Introduction

Polyaniline (PANI) is one of the most widely studied conducting polymers due to its facile synthesis, excellent chemical and environmental stability and good electrical conductivity. The polymer of polyaniline is reinforced or doped with conductive and nonconductive materials which play an important role in some physical and chemical factors that affect the mechanical, structural and electrical properties of the newly synthesized polymer composites. The fillers are natural minerals, metal oxides, carbon nanotubes, and ferroelectric materials etc., combined with efficient coupling agent to obtain the optimized PANI composites [1-5]. Polyvinylidene fluoride (PVDF) is one of the highest dielectric permittivity of all the polymers, is widely used in many fields due to its good piezoelectric, pyroelectric response and low impedance [6-12]. In the present study Polyaniline and its polymer composites with polyvinylidene fluoride (PVDF) at different weight percentages were synthesized. The prepared samples of PANI-PVDF were used to study the dielectric properties and AC conductivity as a function of frequency at room temperature.

2. Experimental Methods

2.1 Materials

Analytical grade aniline, ammonium peroxodisulfate, ammonium persulphate, methanol, acetone, and PVDF were used in the preparation of PANI and PVDF polymer composites.

2.2 Preparation of PVDF

A 0.6403 g of PVDF granules were dissolved in 100 mL of dimethylacetamide (DMA) solvent in a beaker. The solution is allowed for constant stirring at 2 or 3 hours with the help of magnetic stirrer at temperature range of 40-50 °C. PVDF granules are completely dissolved in DMA formed 0.5 N PVDF solution. Similarly 1.5 and 2 N PVDF solutions are prepared.

2.3 Synthesis of Polyaniline/PVDF Polymer Composites

An aniline solution of 0.2 M was dissolved in 100 mL of double distilled water. The HCl solution of 0.2 M was added to the aniline solution. This solution was taken in a beaker and placed on the magnetic stirrer and 0.4 M ammonium peroxodisulfate (oxidizing agent) solution was added dropwise to aniline solution. The solution color changes to dark green within few minutes. The mixture was stirred continuously for 5 hours at room temperature and left the solution for 24 hours to polymerize. After 24 hours the precipitate was collected on a filter paper, the precipitate was washed two to three times using 100 mL of acetone to absorb the water molecules and for the removal of any residual organic impurities. The precipitate was firstly dried in air for 30 minutes at room temperature and then in a hot air oven for 7 hours at 60 °C and finally get a product of PANI. The PANI/PVDF polymer composites were prepared using the same procedure as mentioned above where the PVDF of 0.5 N concentrations were added before adding the ammonium peroxodisulfate as an oxidizing agent to the aniline solution. A similar procedure is used for preparation of other polymer composites of PANI/PVDF at N, 1.5, N, 2, N and 2.5 N were synthesized separately during the polymerization to get different polymer composites. The mixture of PANI/PVDF polymer composite of 350 mg was weighed using a single pan balance for preparation of a pellet. The pellet was prepared by applying 3-4 tons of pressure using a pellet making machine [Model-UTM]. Similarly the pellets of other weight percentages of PANI/PVDF polymer composites were prepared. A silver paste was coated on both sides of the surface of the pellet for providing electrical contacts. The prepared pellets of PANI/PVDF polymer composites were used for experimental measurements of capacitance, dissipation, impedance and phase angle to study the dielectric properties as a function of frequency at room temperature using computer interfaced LCR Q-meter [Model: HIOKI 3532-50].
3. Results and Discussion

3.1 XRD Analysis

To study the nature of crystalline or amorphous, we used the powder method of XRD for Pure PANI, PVDF polymer composites and for PANI/PVDF polymer composites. The XRD figures are given in Figs. 1(a–c). The X-ray diffraction pattern of the samples in this present study is obtained using a Philips X-ray diffractometer with CuKa radiation (\(\lambda = 1.5406\) Å). The diffractograms were recorded in terms of 2θ in the range 10 to 90 degrees with a scanning rate of 4 degrees per minute. The Figs. 1(a–c) shows the XRD pattern of synthesized pure PANI, PVDF polymer composites and PANI/PVDF polymer composites respectively. In Fig. 1(a) it shows that the X-ray diffraction pattern of PANI and a broad peak occurred at 2θ = 26.49° which is the characteristic peak says the amorphous nature of PANI and also mentioned in research articles [10, 12].

![XRD Spectra of PANI](image1)

![XRD Spectra of PVDF](image2)

**Fig. 1** X-ray diffraction pattern of a) pure polyaniline, b) of PVDF polymer composites and c) PANI/PVDF polymer composites

It is observed from Fig. 1(b) that, it shows the X-ray diffraction pattern of PVDF polymer and peaks occurred at 2θ = 20.54°, 26°, 41.50° and 58° are the characteristic peak says the semi crystalline nature of PVDF. From Fig. 1(c), it shows that the X-ray diffraction pattern of PANI/PVDF polymer composites and peaks occurred at 2θ = 10.72° for PANI/PVDF of 1 N and 20.58° for PANI/PVDF of 2 N are the characteristic peak says the semi crystalline nature of PANI/PVDF.

In Fig. 1(c), it is observed that the sharp peaks are occurring at angles of 20.56, 25.29, 41.50 and 58° degrees shown crystalline in nature for polymer composites of PANI/PVDF at 2 N concentration. In Fig. 1(c), it is observed that the peaks for the PVDF polymer composites are diminished and disappeared at 41.50 and 58° in polymer composite of PANI/PVDF at 1 N concentration. The intensive peaks of PANI and PVDF occurred for PANI/PVDF polymer composites of both concentrations. As concentrations of PVDF are increases in PANI the intensity also increases. But as 2θ angle increases the polymer composites of 1 N and 2 N concentrations becomes an amorphous nature.

3.2 Dielectric Properties

The dielectric properties have been studied for all the PANI-PVDF polymer composites as a function of frequency at room temperature.  

3.2.1 Dielectric Constants

The dielectric constant with frequency for PANI and for the composites of PANI with PVDF polymer composites of different weight percentages are shown in the Fig. 2. Using the values of capacitance the dielectric constant were determined for PANI and all other polymer composites of PANI/PVDF, using the Eq. (1) given by

\[
\varepsilon' = \frac{cd}{\varepsilon_A}
\]

where \(d\) is the thickness of the sample, \(A\) is the effective cross-sectional area of the sample; \(C\) is the capacitance of the sample. The dielectric constant of composites of PANI with PVDF polymer composites decreased as frequency increased up to 106 Hz, which is shown in shown in Fig. 2. The dielectric constant remains almost constant after frequency of 106 Hz and it shows independent of frequency because of electrical relaxation process. It is observed that for PANI/PVDF polymer composites at 1 N the dielectric constant is high and it is due to electric dipoles have sufficient time to align with the field before the field changes its direction. The dielectric constant decreases due to the shorter time available for the dipoles to align [13-16].

![Dielectric constant](image3)

**Fig. 2** The graph of dielectric constant with frequency for PANI/PVDF polymer composites

3.2.2 Dielectric Loss

The dielectric loss as a function of frequency for PANI and for the polymer composites of PANI/PVDF in different weight percentages at room temperature are shown in the Fig. 3. The dielectric loss is obtained with help from experimentally measured data of dissipation factor and the values of dielectric constant using the relation given by \(\varepsilon'' = \varepsilon' \tan \delta\).

![Dielectric loss](image4)

**Fig. 3** The plots of dielectric loss with frequency for PANI/PVDF polymer composites

It is observed from Fig. 3 that for dielectric loss decreased gradually as frequency increased up to 175 Hz for all the composites. The dielectric loss \(\varepsilon''\) decreases due to the migration of ions in the material [9].
3.2.3 AC Conductivity

The AC conductivity as a function of frequency for PANI and for the polymer composites of PANI/PVDF at different weight percentages of PVDF at ambient temperature are studied and the plots of AC conductivity as function of frequency are given in the Fig. 4.

![AC conductivity plots](https://doi.org/10.30799/jnst.145.18040514)

**Fig. 4** The plots of AC conductivity with frequency for PANI/PVDF polymer composites

The electrical property of AC conductivity ($\sigma_{ac}$) as a function of frequency have been determined with the help of dielectric data using the following equation.

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta$$  \hspace{1cm} (2)

where $\varepsilon_0$ is the permittivity of free space = $8.85 \times 10^{-12}$ Fm$^{-1}$, $\omega$ is the angular frequency and $\varepsilon'$ is the dielectric constant. From Fig. 4, it is observed that for all the polymer composites of PANI/PVDF the AC conductivity ($\sigma_{ac}$) remains constant up to 6.75 MHz afterwards it increased for higher frequencies. This is due to the increase in charge carriers through the hopping mechanism in the polymer composites. It is also observed that as a weight percentage of PVDF increased the AC conductivity is also increased. The polymer composites of PANI/PVDF at 1.5 N shows relatively higher AC conductivity compared to other weight percentages of polymer composites of PANI/PVDF where it is lower.

4. Conclusion

The synthesized samples of PANI and composites of PANI with PVDF polymer were characterized by using X-Ray diffraction (XRD). The characteristic peak for PANI occurred at $2\theta = 26.49^\circ$ and the for PVDF polymer the characteristic peaks occurred at $2\theta = 20.54^\circ$, $26^\circ$, $41.50^\circ$ and $58^\circ$, hence PVDF is semi crystalline in nature. It is found that the dielectric permittivity decreased exponentially at lower frequency region up to 300 Hz and then the dielectric permittivity remains constant at higher frequency region as the frequency increased. It is also observed that the dielectric permittivity of the polymer composite increased as compared to PANI. The AC conductivity remains constant up to 6.75 MHz and afterwards it increases as frequency increased. This is due to the increase in charge carriers through the hopping mechanism in the polymer composites. Further it is also observed that as a weight percentage of PVDF increased the AC conductivity is also increased.

References