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In-situ polymerization of pyrrole in PVA-PVP matrix: Optimization of oxidant/monomer ratio and its effect on dielectric properties of polymer blend films

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Free standing and flexible polymer blend films of PPy (poly pyrrole) doped in PVA (poly vinyl alcohol) – PVP (poly vinyl pyrrolidone) matrix with varying concentrations of PPy have been prepared by solution cast technique at room temperature. In-situ polymerization of pyrrole monomer (Py) in PVA-PVP matrix has been carried out using FeCl_3 as oxidant. The effect of monomer amount and monomer to oxidant ratio on the dielectric parameters (such as dielectric constant, dielectric loss, loss tangent, ac conductivity, complex electric modulus, complex impedance) of PPy doped PVA-PVP polymer blend films have been studied in the frequency range of 20 Hz to 2 MHz. Two different molar concentrations (0.15 M and 0.30 M) of oxidants have been taken and for each oxidant concentration, four varying concentrations of monomer have been used to optimize the results. The blend films having oxidant to monomer molar concentration ratio of 0.5 in both the cases (i.e. 0.15 M and 0.30 M) have been found to be smooth, flexible, mechanically strong and easy to process. These films have shown very systematic change and improved values of dielectric parameters within the experimental frequency range. Enhanced dielectric parameters (complex permittivity, ac conductivity and electric modulus) values for films having oxidant to monomer molar ratio of 0.5 suggest the organized growth of PPy chain in the matrix of PVA-PVP.

Keywords: Eco-friendly, Polymer blend, Polypyrrole, Oxidant/monomer effect

1 Introduction

Increasing dependency of human life on technology encourages invincible development in the field of science, technology and engineering. To satisfy the technological needs of society, polymeric materials are in focus due to their advantageous properties such as easy processability, mechanical strength, thermal stability, flexibility, corrosion resistance and lower cost. Hence, polymeric materials find a wide range of applications in sensors, actuators, super capacitors, flexible dielectrics, insulators, bio-implants, micro needles, scaffold, drug delivery systems etc.¹⁻⁷ Moving towards green technology, now a day many material scientists are putting their choice on biopolymers²⁻⁵.

PVA (poly vinyl alcohol), PVP (poly vinyl pyrrolidone) and PPy (poly pyrrole) are eco-friendly polymeric materials that are chosen in the present work. Amongst various intrinsically conducting polymers available, polypyrrole (PPy) has many attractive features like high conductivity, facile synthesis, flexibility, and good environmental stability. It is a versatile conducting polymer due to its diverse application as biosensors, gas sensors, micro

actuators, anti-electrostatic coating, solid electrolyte capacitor, electro-chromic windows, polymeric batteries, and functional membranes^{8,9}. For the chemical oxidative polymerization of pyrrole (Py) monomer, various types of oxidants such as FeCl_3 (ferric chloride), APS (ammonium per sulphate) and AgNO_3 (silver nitrate) has been used. The experimental conditions such as reaction temperature, reaction time, humidity, the nature of solvent, the concentration of oxidant and monomer strongly affect the morphology and dielectric properties of PPy¹⁰⁻¹³. Therefore, one of the objectives of the present work is to study the influence of oxidant to monomer molar ratio on the dielectric properties of free standing polymer blend films with in-situ polymerized PPy in PVA-PVP matrix. The effect of varying concentrations of PPy on various dielectric parameters of blend films was also studied. The oxidant to monomer molar ratio was also optimized for the preparation of PPy doped PVA-PVP films.

2 Materials and Method

2.1 Sample preparation

PVA ($M_w = 1, 15,000$ gm/mol) and PVP ($M_w = 40,000$ gm/mol) purchased from Loba Chemicals (India) were used as host polymer matrix. Pyrrole

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monomer supplied by SRL Chemicals (India) was used as received and anhydrous FeCl₃ purchased from Otto Chemicals (India) was used as oxidant for polymerization of pyrrole monomer. Double distilled water was taken as solvent for sample preparation. In present study, films were prepared by solution – cast method at room temperature with humidity level of 25%. Polymerization of pyrrole monomer was carried out by in-situ oxidative polymerization method. PVA and PVP were taken in the ratio of 60:40 and dissolved in 50 ml of pre-heated double distilled water (DDW). PVA-PVP solution was first stirred for 1 h at elevated temperature and then for 2-3 h at room temperature until a clear solution was obtained. Oxidant (FeCl₃) was dissolved separately in 10 ml of DDW at room temperature. Different proportion of pyrrole monomer were mixed with PVA-PVP solution and stirred for 1 h. After complete dissolution of pyrrole monomer (Py) in PVA-PVP blend solution, oxidant was added slowly and then the solution was further stirred for 1 h. By now the solution turns black which is an indication of polymerization of pyrrole monomer. Finally, this blended solution of PVA-PVP-PPY was poured in glass petri dish and left to dry at room temperature.

Two sets of polymer blend films of PVA-PVP (taken in ratio of 60:40 and dissolved in 50 ml of double distilled water) doped with PPy having four varying amount of pyrrole monomer (1.2 ml, 2.4 ml, 3 ml, 3.3 ml) were prepared. In first set of films, the molar concentration of oxidant (FeCl₃) was kept as 0.15 M and for the other set it was kept as 0.30 M. All prepared films were of thickness <1 mm.

2.2 Experimental setup

Agilent precision LCR meter E4980A with solid text fixture (Model No: 16451B) having electrode of diameter 0.5 cm were used to measure complex permittivity (dielectric constant, dielectric loss) of the prepared sample. The text fixture was calibrated first to eliminate the stray capacitance effect. Sample was placed between the parallel electrodes of solid text fixture; parallel capacitance and parallel resistance were measured between the frequency ranges of 20 Hz to 2 MHz at room temperature. Using the obtained data of parallel capacitance (C_p) and parallel resistance (R_p) from LCR meter; dielectric constant (ε') and dielectric loss (ε'') were determined. Other electrical parameters like loss tangent, complex electric modulus (M*) and complex impedance (Z*) were calculated using complex permittivity data.

3 Results and Discussion

3.1 Complex permittivity

The real and imaginary part of complex permittivity were determined using equation:-

$$\epsilon^* = \epsilon' - j\epsilon'' \quad \dots (1)$$

where,

$$\epsilon' = C_p/C_0 \quad \dots (2)$$

where, C_p and C_o are capacitance values with and without sample and C_o is given as:

$$C_0 = (\epsilon_0 * A) / d \quad \dots (3)$$

where, C_o is free space permittivity, A is area of the electrodes and d is thickness of the sample.

$$\epsilon'' = 1 / (\omega C_0 R_p) \quad \dots (4)$$

where, R_p is measured parallel resistance and (ω = 2πf) is angular frequency.

Figures 1 and 2 show the variation of real part of complex permittivity (ε') with frequency for PPy doped PVA-PVP blend films having different amount of pyrrole monomer with two molar concentrations (0.15 and 0.30 M) of oxidant (i.e. FeCl₃).

As shown in Fig. 1, PVA-PVP-PPy blend films having 0.15 M concentration of FeCl₃ with 2.4 ml and 3 ml amount of Py monomer exhibited little variation in ε' values with increasing frequency. The values of ε' did not show much enhancement as compared to that of undoped PVA-PVP blend films. This may be

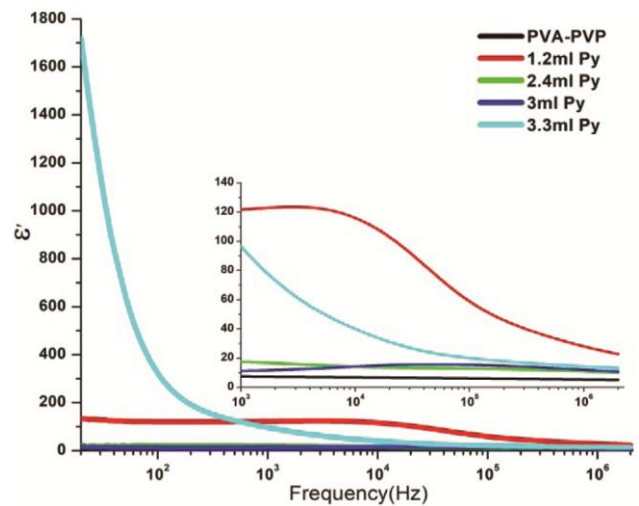


Fig. 1 — Frequency variation of ε' for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films with 0.15 M concentration of FeCl₃. Inset shows ε' variation within the frequency range of 1 kHz-2 MHz.

due to less organized chain formation of PPy in host matrix which resulted in disordered conductive path. Insignificant change in ϵ' can be more clearly justified by electric modulus spectrum which can be derived from complex permittivity. However, a significant variation in values of ϵ' with frequency is observed for PVA-PVP blend films having 1.2 ml and 3.3 ml amount of Py monomer. These films also exhibited enhancement in ϵ' values as compared to undoped PVA-PVP blend films. The polymer blend films with oxidant/monomer molar ratio of 0.5 (having 1.2 ml of Py monomer) exhibited highest values of ϵ' (23 at 2

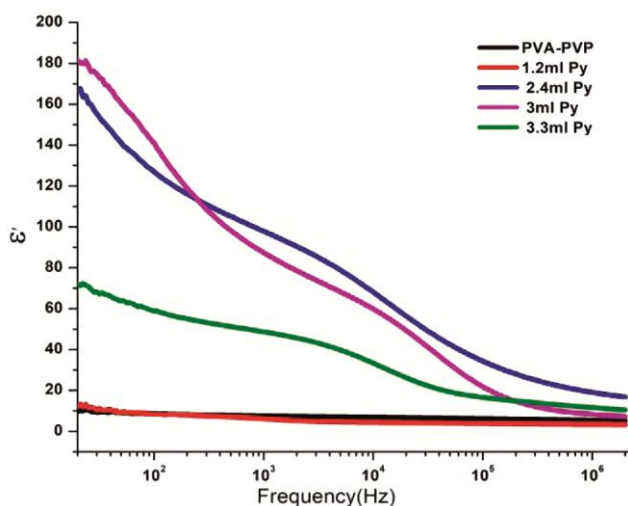


Fig. 2 — Frequency variation of ϵ' for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films with 0.30 M concentration of FeCl_3 .

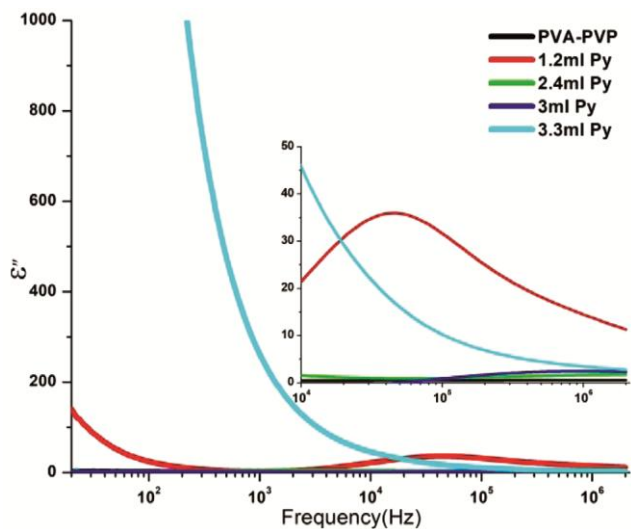


Fig. 3 — Variation of dielectric loss (ϵ'') with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films for 0.15 M concentration of FeCl_3 . Inset shows ϵ'' variation within frequency range of 10 kHz - 2MHz.

MHz) as compared to host matrix of PVA-PVP blend ($\epsilon' = 5$ at 2 MHz). This clearly shows the effect of conducting polymer PPy in host matrix.

Figure 2 shows the variation in ϵ' with frequency for PVA-PVP-PPy blend films with the same amount of pyrrole monomer as in previous case but having 0.30 M concentration of oxidant (FeCl_3). In this case also, enhanced values of ϵ' are observed as compared to undoped PVA-PVP blend films. The maximum increase in value of ϵ' ($\epsilon' = 17$ at 2 MHz) was observed for the PVA-PVP-PPy blend film with 2.4 ml amount of pyrrole monomer which is equivalent to having oxidant/ monomer molar ratio of 0.5.

Hence it can be seen that for complete polymerization of pyrrole monomer, just adequate amount of oxidant should be present in the reaction mixture. If the oxidant is not enough then fewer amounts of counter ion will be generated, which may result in a less-conductive and unstable state of PPy. It is reported that PPy is most conductive and stable in its linear structure⁸⁻⁹. In the presence of excess amount of oxidant, over oxidation takes place which also results in a less conductive structure of PPy.

Further, the dielectric values are associated with polarization effect developed in the blend films on application of electric field. Higher values of ϵ' observed for all PVA-PVP-PPy at low frequencies are due to electrode polarization and interfacial polarization effects within the bulk of polymer blends^{2-5,13}.

Figures 3 and 4 show the variation of imaginary part of complex permittivity (ϵ'') with frequency for

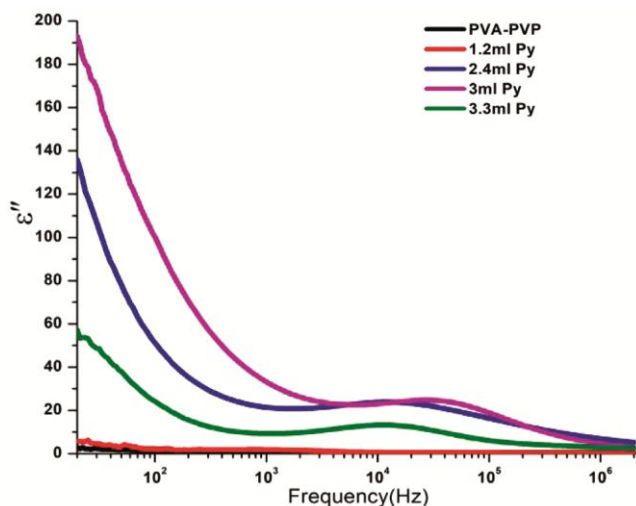


Fig. 4 — Variation of dielectric loss (ϵ'') with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films for 0.30 M concentration of FeCl_3 .

PPy doped PVA-PVP blend films having different amount of pyrrole monomer for two molar concentrations (0.15 and 0.30 M) of oxidant (i.e. FeCl₃). Here also, the blend films having oxidant/monomer molar ratio of 0.5 exhibited dominant effect of conducting PPy on dielectric loss (ϵ'') values as compared to other blend films. The value of ϵ'' is observed to be 11 and 5 at the frequency 2 MHz for PVA-PVP-PPy film having Py monomer amounts of 1.2 ml (for 0.15 M FeCl₃) and 2.4 ml (for 0.30 M FeCl₃), respectively. In ϵ'' spectra of PVA-PVP-PPy blend film with 0.15 M concentration of oxidant (FeCl₃), only the film with 1.2 ml amount of Py monomer exhibited a single relaxation peak between 10³ Hz to 10⁵ Hz (Fig. 3). However, the ϵ'' values are seen to decrease slowly and linearly above the frequency of 10⁵ Hz. On the other hand for ϵ'' spectra (Fig. 4) of PVA-PVP-PPy blend films with 0.30 M concentration of oxidant, the Py monomer amount greater than 1.2 ml exhibited relaxation peaks in the measured frequency range. Relaxation peaks are seen to be shifting to higher frequency region as the concentration of pyrrole monomer is increasing. Higher values of ϵ'' at low frequencies are due to migration of charge carriers within material. In the frequency range of 1 kHz to 100 kHz, there is a gradual decrease in the dielectric loss values which can be attributed to the conduction loss due to free charge migration, ion jumps and polarization loss. The low values of dielectric loss at higher frequencies (>100 kHz) may be due to the ionic vibrations only, as the migration of ions ceases completely at higher frequencies¹²⁻¹⁵. In case of miscible polymers blends, relaxation peaks are generally the combined effect of interfacial polarization and α , β – relaxation processes. Interface polarization is also known as Maxwell-Wagner-Sillars (MWS) effect which attributes to the accumulation of charges trapped between the interfaces of constituent polymers in the polymer blends/composites. α , β – relaxation processes are associated with the segmental motion of the polymer chain. In the present study, relaxation peaks are in the audio frequency range. It may be caused by the dominant effect of MWS relaxation process as α & β – relaxation processes mostly occur in the lower frequency region^{2-5,16}.

3.2 Loss tangent spectra

Loss tangent can be defined as the ratio of imaginary part (ϵ'') of complex permittivity to the real part (ϵ') of complex permittivity. It can be calculated using following equation:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \dots (5)$$

Figures 5 and 6 show the variation of $\tan\delta$ with frequency in the range of 20 Hz to 2 MHz for PVA-PVP-PPy blend films. It shows relaxation peaks within experimental frequency range for most of the blend films having 0.15 M and 0.30 M molar concentrations of oxidant. Highest value of loss tangent was observed for PVA-PVP-PPy blend film having monomer amount of 1.2 ml Py with 0.15 M FeCl₃ and 3 ml Py with 0.30 M FeCl₃.

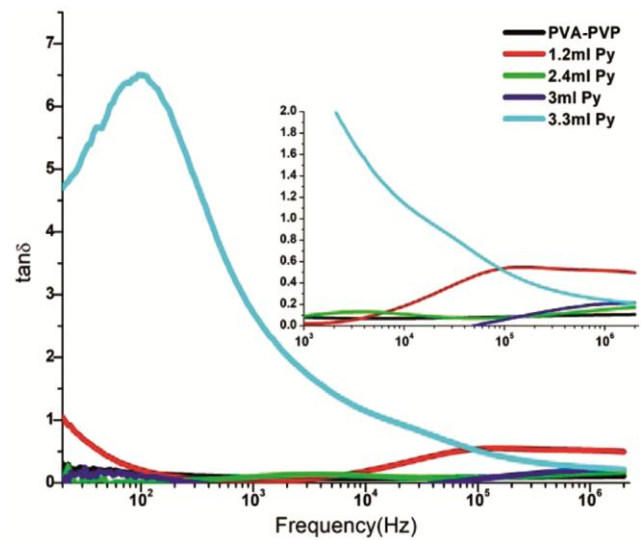


Fig. 5 — Variation of $\tan \delta$ with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films with 0.15 M concentration of FeCl₃. Inset in Fig. 5 shows $\tan \delta$ variation within frequency range of 1 kHz – 2 MHz.

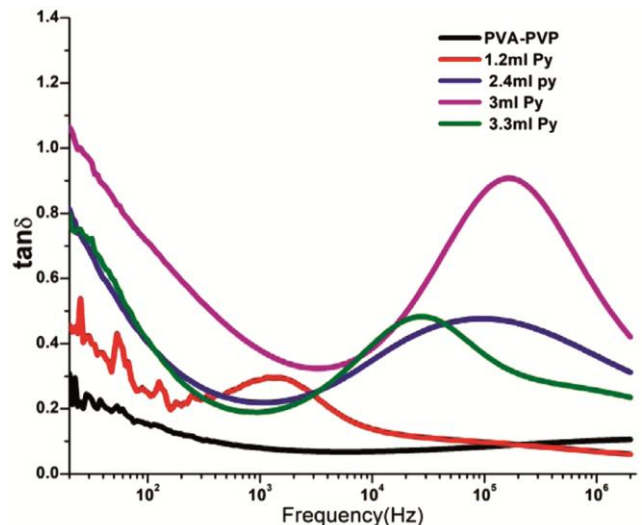


Fig. 6 — Variation of $\tan \delta$ with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blend films with 0.30 M concentration of FeCl₃.

In Fig. 5 relaxation peaks for some samples having specific amount of Py monomer (1.2 ml and 2.4 ml) are very broad and less intense. As the concentration of pyrrole monomer increases, the intensity of relaxation peaks increases and broadness decreases as seen in Fig. 6. With increasing amount of monomer (Py), the relaxation peaks are also shifting towards higher frequency side. The shifting of $\tan\delta$ relaxation peak towards higher frequency corresponds to reduced relaxation time ($\tau_p = 1/\omega_p$). So, it can be inferred that the increasing concentration of conducting polymer enhances the flexibility of polymer chain dynamics and the mobility of the charge carriers which results in reduced relaxation time^{15,16}.

3.3 AC conductivity

Frequency dependent ac conductivity of the samples can be calculated using complex permittivity data by following equation:

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' \quad \dots (6)$$

Variation in ac conductivity values with frequency for PVA-PVP-PPy blend films is shown in Figs 7 and 8 for oxidant molar concentration of 0.15 M and 0.30 M, respectively. In both cases, ac conductivity spectra exhibited frequency independent behavior within 20 Hz to 10 kHz. This shows the accumulation of charges because of slow periodic reversal of electric field in low frequency region. As frequency increases, the ac conductivity increases for all blend films. This may be due to hopping of free charges which results

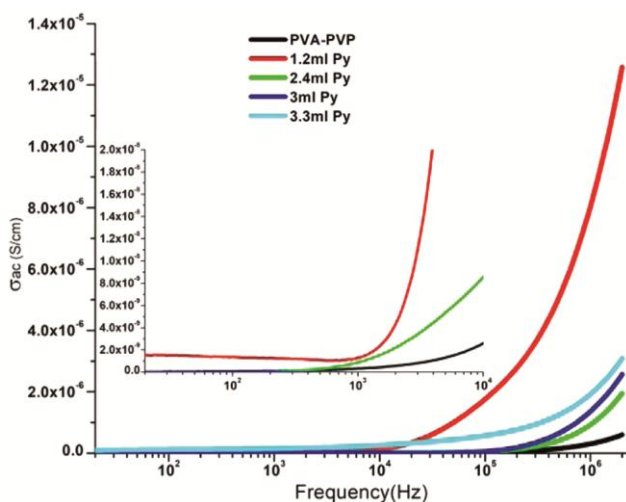


Fig. 7 — Variation of σ_{ac} with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.15 M concentration of FeCl_3 . Inset shows variation of σ_{ac} within frequency range of 20 Hz to 10^4 Hz.

in fast ion exchange process and thus enhancing the ac conductivity¹⁴. Maximum conductivity of the order of 10^{-5} S/cm was observed for PVA-PVP-PPy blend film having 1.2 ml pyrrole monomer with 0.15 M concentration of oxidant. In case of 0.30 M concentration of oxidant, the maximum conductivity of the order of 10^{-6} S/cm was seen with 2.4 ml pyrrole monomer.

The electrical conductivity relaxation process and the association of charge dynamics in this process of relaxation for polymeric material could be fairly analyzed by electric modulus formalism. Electric modulus spectrum is utilized to distinguish the effect of electrode polarization and bulk properties of the material on relaxation process. Complex electric modulus can be derived from complex dielectric permittivity. It can be evaluated from the following relation:

$$M^* = 1/\epsilon^* = M' + i M'' \quad \dots (7)$$

M' and M'' are the real and imaginary part of the electric modulus. It can be further given by following equation:

$$M' = \epsilon' / (\epsilon'^2 + \epsilon''^2) \quad \dots (8)$$

$$M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2) \quad \dots (9)$$

Here, ϵ' and ϵ'' are the real and imaginary part of complex permittivity i.e., dielectric constant and the dielectric loss.

The variation of electric modulus with frequency for PVA-PVP-PPY polymer blend films with 0.15 M

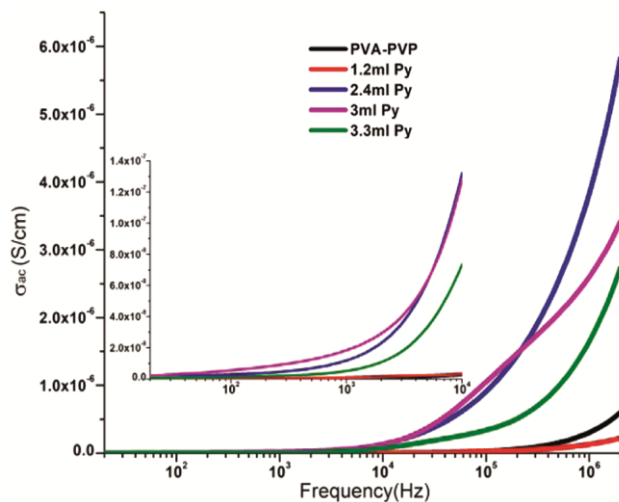


Fig. 8 — Variation of σ_{ac} with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.30 M concentration of FeCl_3 . Inset shows variation of σ_{ac} within frequency range of 20 Hz to 10^4 Hz.

and 0.30 M concentration of oxidant (FeCl_3) is shown in Fig. 9 and Fig. 10, respectively. M' values increase with increasing frequency and tends towards zero in the low frequency region for both molar concentrations (0.15 M and 0.30 M) of FeCl_3 . This observation reveals that the measurements are almost free from electrode polarization effect and it can be neglected in data analysis along with the reduced orientation of dipoles^{2-5,17}. The PPy doped polymer blend films have lower values of M' and this declining nature of plots supports the enhanced value of dielectric constant than PVA-PVP host matrix¹⁷. The doping of PPy in PVA-PVP matrix induces large

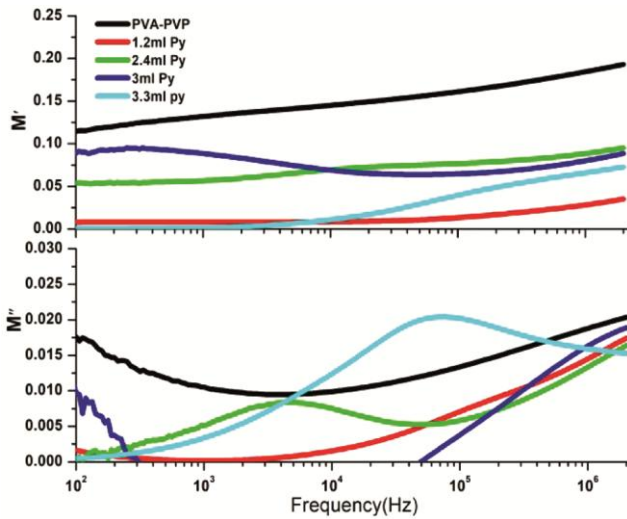


Fig. 9 — Variation of M' and M'' with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of PY blends films with 0.15 M concentration of FeCl_3 .

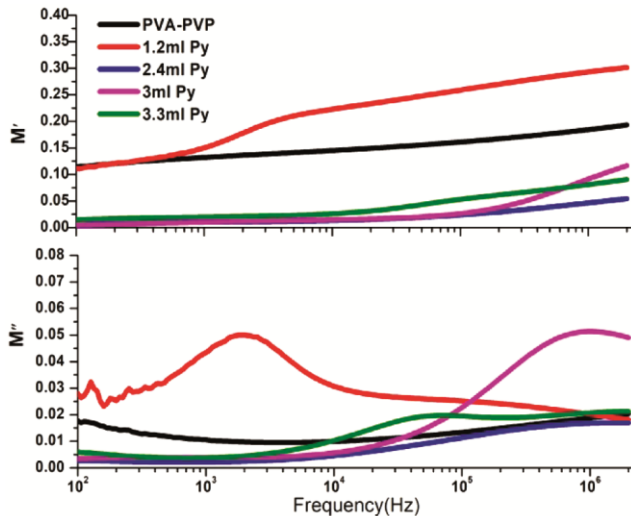


Fig. 10 — Variation of M' and M'' with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of PY blends films with 0.30 M concentration of FeCl_3 .

number of charge carriers and increased polymer segmental motion which results in comparatively low value of M' as compared to host matrix.

The maximum value of all dielectric parameters (e.g. ϵ^* and σ_{ac}) is observed for PVA-PVP-PPY blend film with 1.2 ml amount of Py monomer in case of 0.15 M molar concentration of FeCl_3 with minimum value of M' . Similarly, the lowest value of M' can be seen for PVA-PVP-PPY blend film having 2.4 ml amount of Py monomer with 0.30 M molar concentration of FeCl_3 (Fig. 10) and also showing maximum value of all dielectric parameters (e.g. ϵ^* and σ_{ac}). These results suggest the systematic growth of PPy in host matrix leading to maximum variation in dielectric properties.

In Fig. 9, the variation of M'' with frequency shows single relaxation peak for PVA-PVP host film and the blend films having 2.4 ml and 3.3 ml amount of Py monomer. Relaxation peak for host matrix is seen nearly at 100 Hz but initiated below this frequency. There is no relaxation process taking place for PVA-PVP-PPy blend film with 1.2 ml amount of Py within the experimental frequency region. It may relax on the higher frequency beyond this experimental frequency range. For the samples with 2.4 ml and 3.3 ml amount of Py, the relaxation peaks are found to shift towards higher frequency side as compared to host matrix.

It can be seen from Fig. 10 also, that as the concentration of conducting polymer (PPy) increases in host matrix, the relaxation peaks are shifting towards the higher frequency side. It can be observed that the sample having 2.4 ml concentration of PPy has a relaxation process initiated nearly at 1 MHz frequency. The shifting of relaxation peaks towards higher frequencies with increased amount of PPy correspond to increased interaction between constituent functional group of polymer leading to impeded mobility of polymer chain which in turn enhances relaxation frequency^{14,17-18}.

The M'' versus frequency graph follows the same trend as of loss tangent. In case of pure blend film of PVA-PVP, the accumulation of charges occurs at the heterogeneous interface of semi-crystalline PVA and amorphous PVP resulting in relaxation phenomenon at lower frequency. But the relaxation peak for host matrix is broad enough and spread in wide frequency range. It shows the strong polymer chain connectivity that hinders the free movement of dipoles within the system^{2-5,16-18}. With increasing concentration of PPy in the host matrix, the effect of free charge carriers are

more dominant than the chain segmental motion effect. It increases the flexibility of polymer chain segmental motion and enhances chain dynamics through conduction process^{3,16}.

3.4 Impedance spectroscopy

Impedance spectroscopy is a useful technique to explore the contribution of different processes governing the electrical properties of polymer blends/composites. This is the commonly used technique to understand the conduction mechanism, the role of polymer chain in charge carrier generation and to separate the bulk effect of material. The shape of impedance spectra clarifies the electrode polarization effect and the charge carriers (electronic or ionic) associated with conduction mechanism.

Impedance spectra for all the PVA-PVP-PPy films were shown in Figs 11 and 12, exhibit single arc throughout the experimental frequency region, showing the electronic conduction of the material. It confirms the suppressed electric double layer (EDL) capacitive effect or electrode effect and more expressed bulk properties of the material^{5,18}. Shape of the plot shows the poly dispersive nature of the dielectric relaxation as for mono dispersive nature of dielectric relaxation, a semicircle with center located at real axis are expected. Here, large circular arcs can be seen with end points inclined towards real axis^{17,18,,20,21}.

Z' and Z'' values decreases with increase in frequency in both cases (Figs 13 and 14). For 1.2 ml amount of Py monomer in Fig. 13, Z' and Z'' values

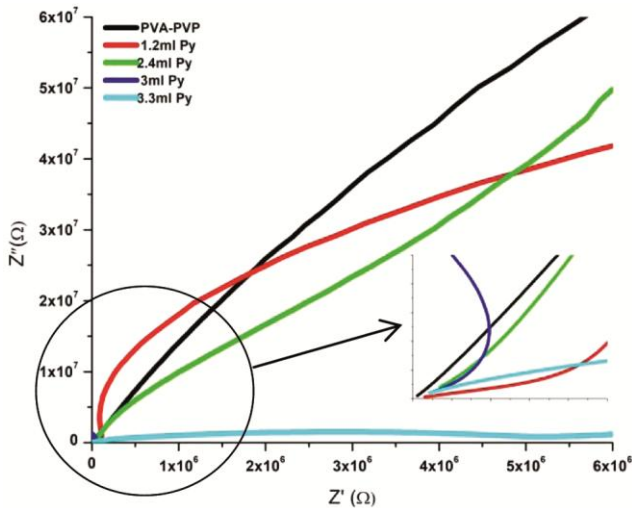


Fig. 11 — Plot of Z'' versus Z' for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.15 M concentration of $FeCl_3$.

were lower through out the frequency range as compare to host. For 0.15 M concentration of oxidant only this combination was assumed as conductive and proper growth of PPy in PVA-PVP matrix is considered. As oxidant concentration is low here and for only 1.2 ml amount of Py monomer results in systematic growth of PPy chain. In Fig. 14, lower

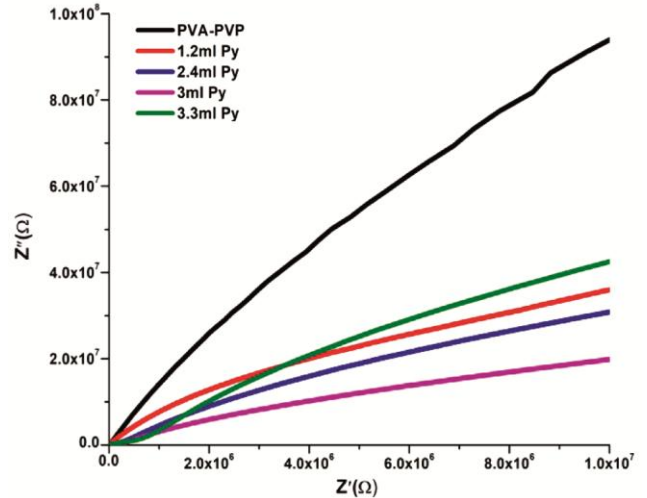


Fig. 12 — Plot of Z'' versus Z' for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.30 M concentration of $FeCl_3$.

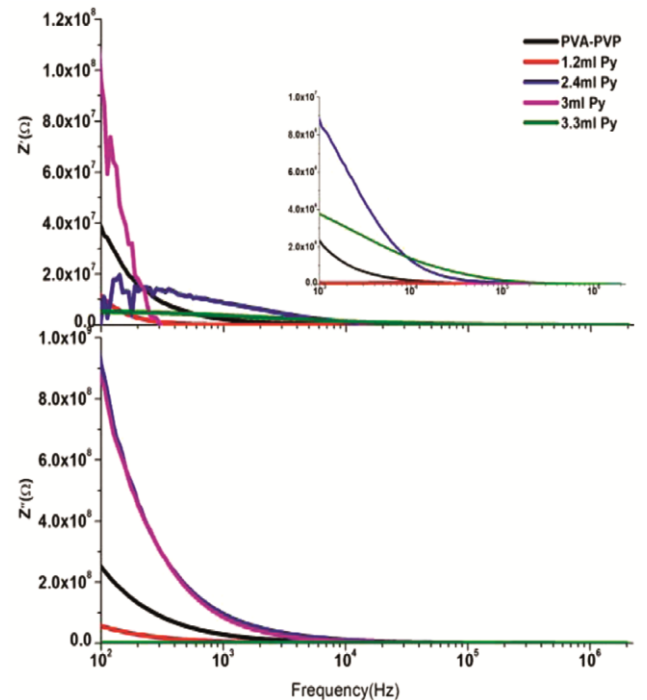


Fig. 13 — Variation of Z' and Z'' with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.15 M concentration of $FeCl_3$. Inset in Fig.13 shows the variation of Z' from 1 kHz to 2 MHz frequency.

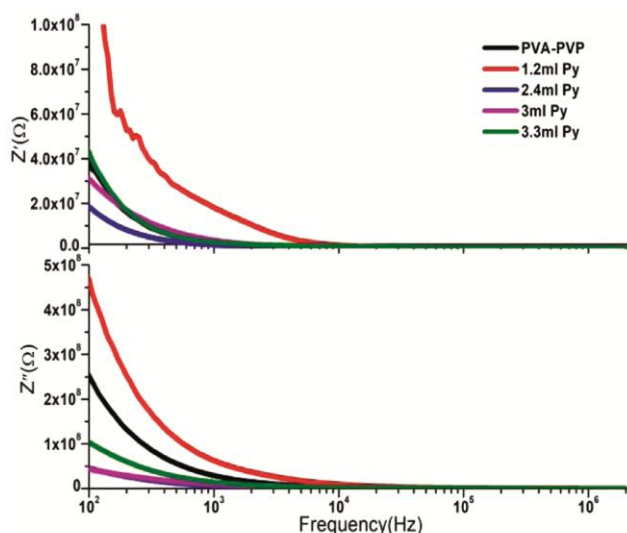


Fig. 14 — Variation of Z' and Z'' with frequency for PVA-PVP and PVA-PVP doped with 1.2 ml, 2.4 ml, 3 ml and 3.3 ml of Py blends films with 0.30 M concentration of FeCl_3 .

value of Z' and Z'' were observed for all PPy doped samples except the sample having 1.2 ml amount of Py monomer. Here oxidant concentration is increased and so more amount of Py is required to undergo complete polymerization. So, it can be inferred that with increasing amount of PPy, films become lossy and hence more conductive. This result supports ac conductivity inference of the samples.

In both the cases, Z'' values are higher than Z' values for all the samples which show the capacitive behavior of the films¹⁷⁻²². Decreasing values of Z'' and increasing values of Z' were observed for PPy doped samples as compare to host. With increasing amount of Py monomer, degree of inclination of the plot with real axis decreases as compare to host in both the cases (Figs 11 and 12). It may be attributed to increased roughness at the interface between material and electrode because of the presence of PPy which results in lossy behavior of the material¹⁹⁻²².

4 Conclusions

Dielectric study of free-standing PPy doped PVA-PVP polymer blend films having different concentration of in-situ polymerized PPy with two different molar concentrations of oxidant (0.15 M and 0.30 M) was carried out. When in-situ polymerization of pyrrole is carried out with adequate amount of FeCl_3 (monomer/oxidant ratio of 0.5), it results in a stable, free standing flexible polymer blend film exhibiting high dielectric constant and ac conductivity values. Dielectric parameters of PVA-PVP-PPy blends films

were further analyzed and justified by electric modulus formalism and impedance spectroscopy. Electric modulus spectra indicate the well-arranged growth of PPy in PVA-PVP matrix for the samples having oxidant/monomer molar ratio 0.5. The complex modulus spectra are seen to be in accordance with loss tangent spectra. Impedance spectroscopy for all the samples supports the electric modulus formalism which suggests that the measurements are free from electrode effect. So it can be inferred that in the absence of optimum amount of oxidant, the monomer does not get enough counter ions to undergo complete polymerization process and results in less conductive films exhibiting low ac conductivity values. However, in the presence of excessive amount of oxidant, polymerization process suffers from over oxidation, which also results in decreased value of ac conductivity and dielectric loss. Hence, oxidant- monomer ratio plays very important role in order to synthesize a properly arranged and well polymerized chain of PPy in PVA-PVP matrix.

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