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Effect of Solvent on the Optical and Electrical Properties of Poly (Vinyl Alcohol) Films

Velayutham Ramasubbu¹, Chelliah Kamalakshiammal Mahadevan², Xavier Sahaya Shajan³

Research Scholar, Centre for Scientific and Applied Research (CSAR), PSN College of Engineering and Technology,
Melathediyoor, Tirunelveli, India¹

Visiting Professor, Centre for Scientific and Applied Research (CSAR), PSN College of Engineering and Technology,
Melathediyoor, Tirunelveli, India²

Director, Centre for Scientific and Applied Research (CSAR), PSN College of Engineering and Technology,
Melathediyoor, Tirunelveli, India³

ABSTRACT: Poly(vinyl alcohol) (PVA) is considered to be an interesting, low-cost, conductive polymer with useful physical and chemical properties. We describe the preparation of high-quality PVA films by using a simple solution casting method from PVA powder with medium molecular mass (within 75,000-80,000 g/mol). The preparation conditions were varied and the films formed were characterized by thickness, Fourier transform infrared spectra, ultraviolet-visible spectra and dielectric measurements. The films formed under various preparation conditions had the same chemical nature but changes in physical (optical and electrical) properties. For instance, films formed with 1 g PVA dissolved in 20 ml demineralized water were found to exhibit low and uniform thickness as well as high transparency in the UV and visible regions whereas films formed with 1 g PVA dissolved in a mixed solvent (water+Dimethylsulfoxide+HCl) with different stirring durations were found to be well suited for sun screen devices, EMI shielding and electrochemical applications.

KEYWORDS: Conductive polymers, Electrical properties, FTIR spectrum, Optical properties, PVA films, Solution casting.

I. INTRODUCTION

Poly(vinyl alcohol) PVA, is a semi-crystalline, conductive, synthetic polymer having the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is colorless and odorless and is used in paper making, textiles, and a variety of coatings. In terms of microstructure, it is composed mainly of 1,3-diol linkages $[-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}(\text{OH})-]$ but a few percent of 1,2-diols $[-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_2-]$ occur, depending on the conditions for the polymerization of the vinyl ester precursor [1].

PVA is non-toxic, biocompatible, slowly biodegradable, close to incompressible, chemically stable and has high tensile strength, flexibility and excellent film forming, emulsifying and adhesive properties. It is also chemically inert towards oil, grease and solvents. Moreover, the melting point of the fully hydrolyzed and partially hydrolyzed grades of PVA are 230 °C and 180-190 °C respectively. The glass transition temperature (T_g) of PVA is about 80 °C and upon annealing above T_g , its crystallinity will increase up to 55 % (especially in the solvents such as water and ethylene glycol).

PVA has many applications in industry due to its low cost, light-weight and good mechanical, optical and electrical properties. Moreover, doped and blended PVA films have become very interesting because their physical and chemical properties make them useful for specific applications [2-11]. The molecular mass (M_w), determined by the degree of polymerization (p), is a very important parameter of any polymer. The physico-mechanical properties of PVA are

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influenced by the degree of polymerization as well as the hydrolysis degree [5]. Solution casting (SC) is considered to be a low-cost method to prepare isolated PVA films. Also, it can be adopted easily for industrial preparation.

II. RELATED WORK

Formation of PVA films from PVA powders with low, medium and high molecular masses ($M_w \leq 10,000$ g/mol, 89,000 - 130,000 g/mol and $\geq 8,600,000$ g/mol respectively) has already been reported [2,3,5,6,8,9,12]. Similarly, as to the solvent considered, a variety of systems, such as demineralized water, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and water+DMSO have been used as the solvents in the preparation of PVA [2,3,6,8,9,14]. However, for the use in devices, it is necessary to optimize the conditions for the preparation of film with uniform thickness, good optical transparency and significant mechanical stability.

The present work describes the preparation of high-quality PVA films from PVA powder with medium molecular mass (M_w was within 75,000-80,000 g/mol) and hydrolysis > 98 mol%. This PVA powder is easily available commercially and widely used; thus, it would be interesting and useful to optimize the conditions for the preparation of films with it. Moreover, acidifying the solvent system, using hydrochloric acid (HCl), may lead to significant changes in the hydrolysis process and consequently in the physical characteristics of films formed. We varied the preparation conditions using water and water+DMSO+HCl as the solvents and the films formed were characterized chemically, optically and electrically. The results obtained are reported herein.

III. MATERIALS AND METHODS

PVA powder with M_w within 75,000–80,000 g/mol, obtained from Loba Chemie (a chemical company located in India) was used as the precursor for the preparation of PVA films. As per the supplier's information, the hydrolysis was 98-99 mol%. Also, it contained a maximum of 5 % volatile matter and 0.7 % ash. Demineralized water, DMSO, and HCl were used as the solvents.

An appropriate amount of PVA powder (0.25 to 2.0 g) was dissolved in the chosen solvent at a temperature of 60 °C. Stirring was done until the polymer was completely dissolved and formed a uniform, clear, viscous solution (minimum of 8 h). A difference in stirring duration may cause, at least in the case of the mixed solvent (Water+DMSO+HCl), changes in the properties of the prepared films. Thus, we also used two longer stirring durations (14 and 22 h) while using the mixed solvent. Moreover, the pH values of the solutions were within 5.5 – 1. Films were formed by pouring the above solutions into Petri dishes of diameter 10 cm. The samples were subjected to an extended drying period (about 2 and 7 days, respectively, for water and mixed solvents) at room temperature (31 °C) for the solvent evaporation. The system was kept un-disturbed in a dust-free zone at normal atmospheric condition (as the system was expected to be significantly stable in this condition). Transparent, free-standing and flexible films were obtained. Five different amounts of PVA and two different solvents were considered to optimize the preparation condition for a good quality PVA film. As 1.0 g mass (in demineralized water) among the masses considered (0.25, 0.50, 1.0, 1.5 and 2.0 g) gave the best film considering the general features, this mass only was considered for the mixed solvent. So, a total of eight films were formed and characterized.

IV. RESULTS AND DISCUSSIONS

A. GENERAL FEATURES AND CHEMICAL COMPOSITION

The thicknesses of the films were measured by using a digital screw gauge at different places in the film and the average thickness was determined. The average thicknesses of the films, along with sample codes and preparation conditions, are provided in Table 1. Every film prepared was of nearly uniform thickness throughout the film and transparent. Moreover, it was noted that the increase in amount of PVA present in the solution increased the average thickness of the film cast. In addition, the surface area of the film increased with the decrease of average thickness. In certain cases, in order to maintain the lower average thickness, the film extended its surface area beyond the bottom of the Petri dish. So, it is understood that all the 8 films prepared have different average thicknesses and different surface areas even though the same type of Petri dishes were used.

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Sample code	PVA taken (g)	Solvent used	Volume of solvent (ml)	Stirring duration (h)	Average thickness (mm)	Band gap (eV)
PF1	0.25	Water	20	8	0.039	5.58
PF2	0.50	Water	20	8	0.052	5.56
PF3	1.00	Water	20	8	0.095	5.56
PF4	1.50	Water	20	8	0.147	5.56
PF5	2.00	Water	20	8	0.309	5.51
PF6	1.00	Water+ DMSO+HCl	10+10+1	8	0.156	3.52
PF7	1.00	Water+ DMSO+HCl	10+10+1	14	0.263	3.15
PF8	1.00	Water+ DMSO+HCl	10+10+1	22	0.328	3.49

Table 1: The sample codes, preparation conditions, average thickness values and optical band gap values of PVA films prepared in the present study

Figure 1 shows the Fourier transform infrared (FTIR) spectra recorded in the present study. The FTIR spectra were recorded by the attenuated total reflectance (ATR) mode in the wavenumber range 550–4000 cm^{-1} using a Jasco FT/IR-4100 spectrometer (Japan). The spectrum observed for PF3 is repeated, in Fig. 1B (the films cast from mixed solvent) for comparison purposes. The spectra observed were in good agreement with those reported for the PVA films in the literature [2, 3, 6]. The spectra in Fig. 1A (the films cast from demineralized water) show a strong, broad absorbance at around 3295 cm^{-1} which can be assigned to O-H stretching vibrations of the hydroxyl groups in the polymer backbone. The bands corresponding to $-\text{CH}_2$ asymmetric and symmetric stretching vibrations occur, respectively, at around 2927 and 2860 cm^{-1} . The sharp band at around 1086 cm^{-1} corresponds to the C-O stretching present in the PVA backbone. The peaks at around 1419 and 1325 cm^{-1} correspond, respectively, to CH_2 bending and wagging vibrations. The weak bands observed at around 1658 and 1712 cm^{-1} correspond, respectively, to C=C and C=O stretching vibrations of the acetyl group of vinyl acetate present in a negligible amount in the precursor material. The peak at around 830 cm^{-1} corresponds to skeletal C-H rocking.

As shown in Fig. 1B, the broad band occurring at around 3294 cm^{-1} was significantly shifted towards the higher wavenumber side for the samples PF6 (3338 cm^{-1}), PF7 (3349 cm^{-1}), and PF8 (3383 cm^{-1}) which could be explained as due to the solvent effect (the longer the mixing of solvents, the larger the shifting of wavenumber). The weak peak observed at around 703 cm^{-1} for the samples PF6, PF7 and PF8 could be explained as due to asymmetric C-S stretching, again as a consequence of the solvent effect. Hema *et al* [2] have observed that the peak corresponding to asymmetric C-S stretching at 753 cm^{-1} of DMSO cast PVA films was shifted to 715 cm^{-1} in NH_4Cl doped PVA. It should be noted that PF6, PF7, and PF8 are Water+DMSO+HCl (mixed solvent) cast PVA films. This indicates the presence (even after drying for 7 days) of residual DMSO and HCl in the polymer films prepared using the mixed solvent.

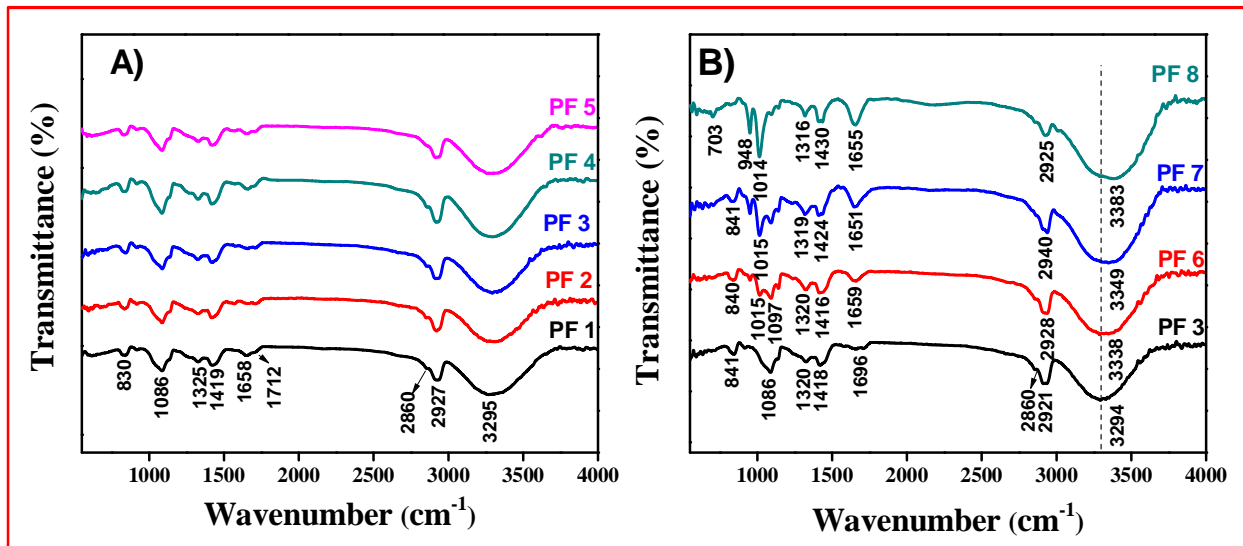


Fig.1: The FTIR spectra of the films. A) PF1 – PF5 ; B) PF3 and PF6 – PF8

B. OPTICAL PROPERTIES

Optical studies were performed by UV-visible transmittance spectra that were recorded in the wavelength range 200–800 nm using a Shimadzu UV 2600 spectrophotometer (Japan). The UV-visible transmittance spectra recorded in the present study are shown in Fig. 2. The spectrum for PF3 is again repeated, in Fig. 2B, for comparison purposes. Films prepared with water solvent (PF1 – PF5) were found to be highly transparent (80-99 %) in the entire wavelength region starting from ~225 nm to 800 nm. Films prepared with the other solvent (Water+DMSO+HCl) exhibited low optical transmittance, particularly in the lower wavelength (UV) region. Thus, water should be used as a solvent when a wide transparency window is required. However, the films PF6, PF7 and PF8 may find their utility in sunscreen devices as they are able to significantly absorb the UV region and transmit the visible region. Also, as the amount of PVA was increased, the thicknesses of the films increased; and consequently, the transmittance decreased.

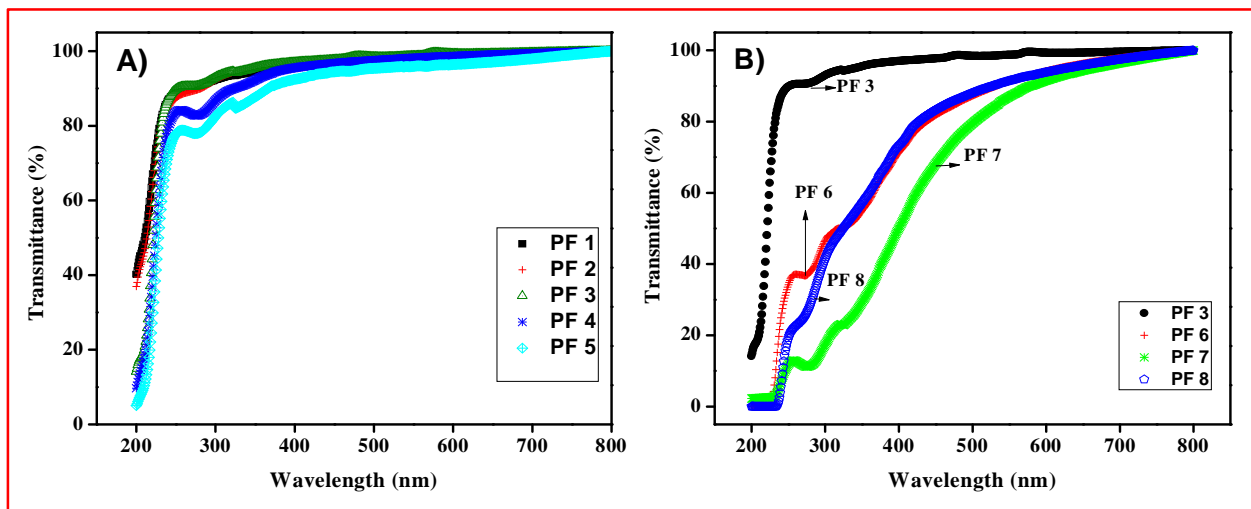


Fig. 2: The UV-visible transmittance spectra of the films. A) PF1 – PF5 ; B) PF3 and PF6 – PF8

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The optical band gap energies (E_g) were obtained in the present study from the absorption edges and are given in Table 1. The E_g values varied from 3.15 to 5.58 eV. Earlier researchers have reported values like 2.92 and 3.47 eV for pure PVA polymer films [3, 8]. In the present study, when water was used as the solvent, the E_g values varied from 5.51 - 5.58 eV, i.e., without any significant difference among them. When the mixed solvent (Water+DMSO+HCl) was used, the E_g value varied from 3.15 - 3.52 eV, similar to that reported in the literature (3.47 eV), where water+DMSO was used as the solvent [8]. Thus, the difference in E_g values obtained may be due to the difference in solvents (Water, Water+DMSO and Water+DMSO+HCl) considered. No significant change in E_g value was observed due to the amount of PVA used and/or stirring duration used.

C. ELECTRICAL PROPERTIES

AC electrical measurements were carried out at room temperature (31 °C) by the two-probe technique with various frequencies ranging from 20-10000Hz using an IM6 Zahner-Elektrok (Germany) electrochemical workstation. From this measurement, we can derive various parameters such as (i) real part of dielectric constant (ϵ'), (ii) imaginary part of dielectric constant (ϵ''), (iii) AC electrical conductivity (σ_{ac}) and (iv) bulk resistance (R_b) (from cole-cole plots).

The complex dielectric constant or relative permittivity ϵ^* is given by

$$\epsilon^* = \epsilon' - i\epsilon'' \tag{1}$$

The ϵ' characterizes the most important electrical properties of dielectrics, namely, the dielectric constant and ϵ'' characterizes the dissipation of the energy of electrical oscillations in a dielectric subjected to the action of a varying electric field. In this case, a phase lag arose between the electric displacement vector and the electric field strength. It can be described by the dissipation factor or dielectric loss tangent:

$$\tan \delta = \epsilon''/\epsilon' = 1/Q \tag{2}$$

where Q is the quality factor.

The magnitude of the dielectric constant of polymers is determined by their chemical and physical structure and chemical composition. The parameters characterizing the dielectric losses (ϵ'' and $\tan \delta$) depend on the specific features of molecular motions in polymers and, hence, on their chemical and physical structure [13]. The dielectric property (ϵ') indicates the charge storage capacity of a material. The ϵ' and ϵ'' values are the charge storage and loss of energy in each cycle of an applied electric field [14].

The AC electrical conductivity (σ_{ac}) is normally evaluated by using the relation

$$\sigma_{ac} = \epsilon' \epsilon_0 \tan \delta \omega \tag{3}$$

where ϵ_0 is the permittivity of free space ($=8.854 \times 10^{-12} \text{ Fm}^{-1}$) and ω is the angular frequency ($=2\pi f$, f is the frequency of the applied field).

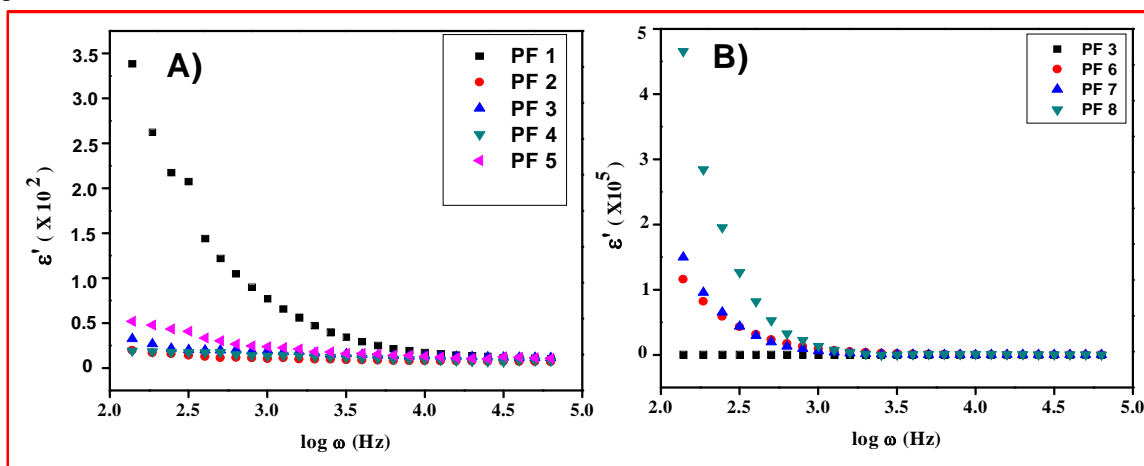


Fig. 3: Frequency dependence of ϵ' of the films A) PF1 – PF5 ; B) PF3 and PF6 – PF8.

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The values of ϵ' , ϵ'' and σ_{ac} were determined in the present study for all of the eight films prepared and are shown in Figs. 3 to 5. The data for PF3 are again repeated for comparison purposes.

The real and imaginary parts of the dielectric constant were found to decrease with the increase in frequency in an exponential manner. The maximum dielectric constant was observed for PF1 among the films prepared using the water solvent. The dielectric constants (of the order of 10^2) observed in the present study were significantly higher when compared to those observed (< 7) by Divya *et al* [8] (solution cast films using water+DMSO as the solvent) which may be due to the difference in molecular mass of the PVA considered.

Very high dielectric constants (of the order of 10^5) were observed for the films prepared using the mixed solvent (PF6, PF7 and PF8) with the maximum for PF8. This indicates that the presence of ions (acquired from the solvent) in the PVA film leads to very high dielectric constants. Hema *et al* [2] have also observed very high values of dielectric constant for PVA films doped with NH_4X ($X = Cl, Br$ and I).

The variation of dielectric constant with applied field frequency can be explained as due to the electrical relaxation processes which can be due to the dipolar contributions of charge carriers transferring between isolated states. So, the space charge contribution can be expected to play an important role in the polarization process. Moreover, the observed very high values of dielectric constant may be due to the interfacial effects between the bulk of the sample and the electrode [14].

Dielectric loss (ϵ'') is the direct measure of energy dissipated and its variation with applied frequency is displayed in Fig. 4. It generally contributes in the ionic transport and the polarization of the charge or the dipole. The very high values of ϵ'' (of the order of 10^6) observed at lower frequencies for PF6, PF7 and PF8 can be attributed to the “free” charge motion within the material [15]. These values do not correspond to the bulk dielectric of the material, but are only due to the “free” charge build up at the electrode-electrolyte interface. At low frequencies, enough time is available for the charges to build up at the interface before the electric field is reversed. This contributes to the large apparent value of ϵ'' . When the frequency is increased, there was not sufficient time available for the build up of the charges at the interface but only for the build up of the charges at the boundaries of conducting species in the material and at the ends of conducting paths. This behavior leads to the “conductivity relaxation” phenomenon [15]. Moreover, the observed higher values of ϵ'' indicate that these films (PF6, PF7 and PF8) may find their use in electromagnetic interference (EMI) shielding.

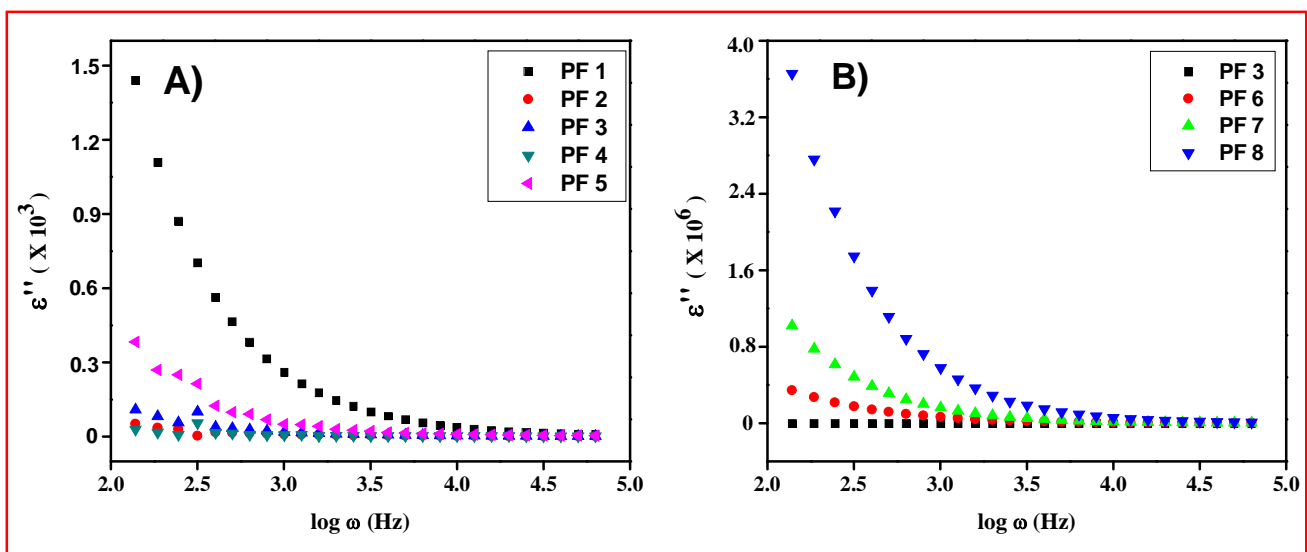


Fig. 4: Frequency dependence of ϵ'' of the films A) PF1 – PF5 ; B) PF3 and PF6 – PF8.

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The change in AC electrical conductivity (σ_{ac}) with the applied field frequency is given in Fig. 5. The conductivity was very high (of the order of 10^{-3} S cm^{-1}) for PF6, PF7 and PF8 (the highest) when compared to that for other PVA films prepared from aqueous solutions (for which, σ_{ac} was of the order of 10^{-6} S cm^{-1}). This indicates that the use of mixed solvent and higher stirring duration induced more mobile charges (ions) in the PVA film considered. Hema *et al* [2] have reported similar higher values of electrical conductivity (2.5×10^{-3} S cm^{-1}) in PVA polymer films doped with NH₄I. They have attributed the charge transport as being predominantly due to ions. Based on the dielectric properties, it can be stated that the films prepared using the mixed solvent (PF6, PF7 and PF8) would be well suited for the electrochemical application.

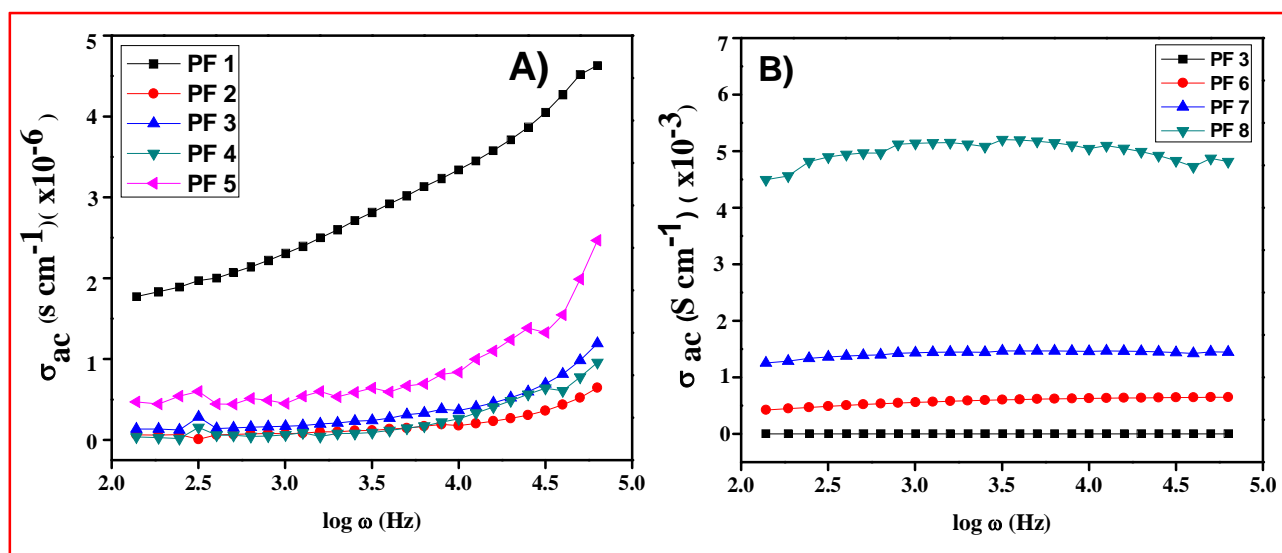


Fig. 5: Frequency dependence of σ_{ac} of the films A) PF1 – PF5; B) PF3 and PF6 – PF8.

In the case of a polymer such as PVA, the migration of ions (for instance, the Cl^- ions present in PF6 – PF8 films) may occur through the free volume of the matrix polymer (as in the case of solid electrolytes) that can be represented by a resistor. The polarization of immobile polymer chains in the alternating field can be represented by a capacitor. The ionic migration and bulk polarization can be physically parallel to each other at higher applied field frequencies. However, at lower applied frequencies, the electrode and electrolyte (PVA film) interface dominates.

Figure 6 shows the Cole – Cole (impedance) plots (Z' vs Z'') for the PVA films prepared with mixed solvent. Typically, the plots consist of two well-defined regions. They are: the high- frequency semicircular region (that is due to the bulk effect of the PVA film) and the low-frequency arc or spike region (which is due to the effect of blocking electrodes). The intercept of the spike with the Z' axis gives the bulk resistance (R_b) of the PVA film. It is clear from Fig. 6 that the R_b value decreased with the increase of stirring duration used for the preparation of the PVA films. Also, the semicircular region disappeared for longer stirring duration.

Previous workers have already reported that the ionic conductivity of PVA is increased due to an enhancement of the ionic mobility and number of carrier ions [16]. In the present study, it can be understood that the interaction between solvent (Water+DMSO+HCl) and the PVA chains was more effective as the stirring duration was increased. Longer stirring led to provide conductive pathways for facilitating ion migration and hence enhancement in conductivity.

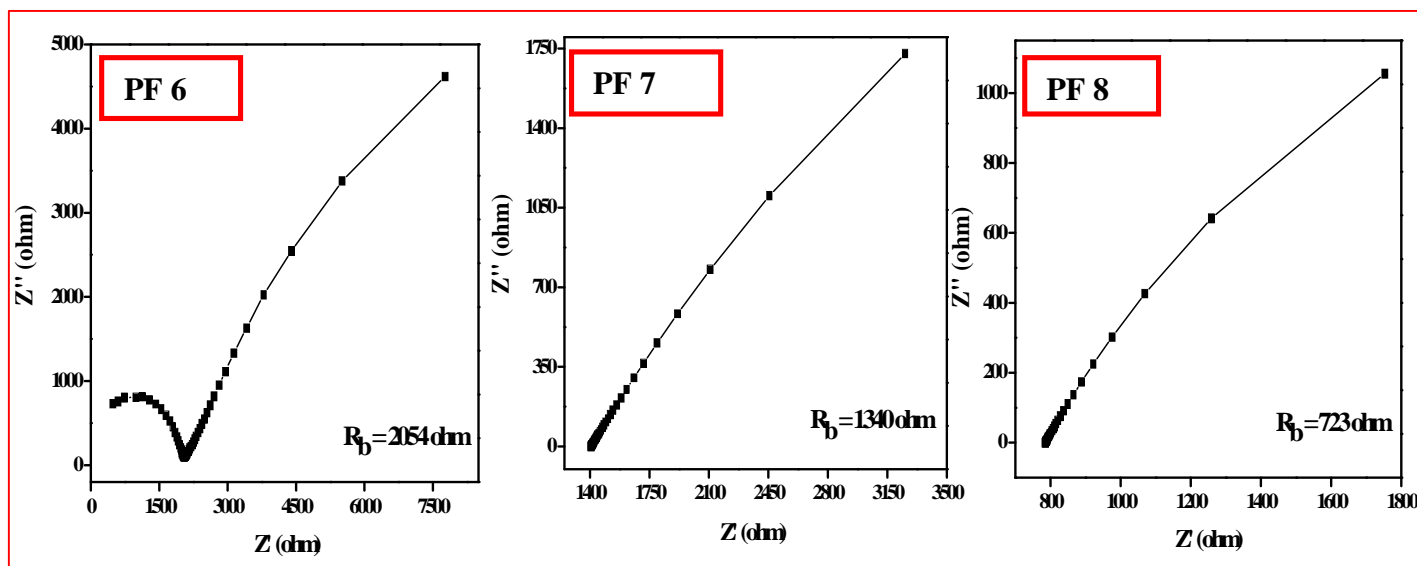


Fig. 6: Cole-Cole plots for the films prepared with mixed solvent.

V. CONCLUSION

High-quality PVA films have been successfully prepared from PVA powder with a M_w of 75,000-80,000 g/mol. Each film had nearly uniform thickness throughout it. However, the average thickness increased with the amount of PVA used for the preparation. FTIR spectra revealed the presence of residual DMSO and HCl (creating mobile ions like Cl^-) in the polymer films prepared using the mixed solvent (Water+DMSO+HCl). The UV-visible spectra indicate that the films formed using water as the solvent (PF1 – PF5) exhibited a wide transparency window covering the UV and visible regions whereas the films formed using the mixed solvent (PF6, PF7 and PF8) were well suited for sunscreen devices. The dielectric measurements indicated high ϵ' , ϵ'' and σ_{ac} values for the films prepared using mixed solvent. The observation of highest conductivity for PF8 indicated that the use of mixed solvent and higher stirring duration induced more mobile charges in the PVA film. The present study indicates that water as solvent is better suited for preparing PVA films useful as optical window materials whereas the mixed solvent is better suited for preparing PVA films useful in sunscreen devices, EMI shielding and electrochemical applications.

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REFERENCES

- [1] Hallensleben, M.L. Polyvinyl compounds, others in Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH, Weinheim, 2000.
- [2] Hema, M., Selvasekarapandian, S., Arunkumar, D., Sakunthala, A., Nithya, H., J. Non-Crystal. Sol., 355, 84-90, 2009.
- [3] Jabbar, W. A., Habubi, N.F., Chiad, S.S., J. Arkansas Acad. Sci., 64, 101 – 105, 2010.
- [4] Bhargav, P.B., Sarada, B.A., Sharma, A.K., Rao, V.V.R.N, J. Macromol. Sci., Part A: Pure Appl. Chem., 47(2), 131-137, 2009.
- [5] Sonmery, M., Fikai, D., Stan, A., Blestu, C., Matei, L., Fikai, A., Andronescu, E., Mater. Lett., 74, 132 – 136, 2012.
- [6] Roy, A. S., Gupta, S., Sindhu, S., Parveen, A., Ramamurthy, P.C., Composites: Part B, 47, 314-319, 2013.
- [7] Mirzaee, Sh., Shayestech, S. F., Mahdavarfar, S., Polymer, 55, 3713-3719, 2014.
- [8] Divya, R., Meena, M., Mahadevan, C.K., Padma, C.M., Int. J. Eng. Res. Technol., 3(7), 722-727, 2014.
- [9] Divya, R., Meena, M., Mahadevan, C.K., Padma, C.M., Int. J. Eng. Res. Appl., 4(5:5), 1-7, 2014.
- [10] Liu, X., Chen, Q., Lu, L., Feng, X., Meng, X., Catalysis Commun., 58, 30-33, 2015.
- [11] Alwin, S., Bhat, S.D., Sahu, A.K., Jalajakshi, A., Sridhar, P., Pitchumani, S., Shukla, A.K., J. Electrochem. Soc., 158 (2), B91-B98, 2011.



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- [12] Wang, E., Batra, S., Cakmak, A., Polymer, 67, 200-207, 2015.
- [13] Perepechko, I.I. Introduction to Polymer Physics, Mir Publishers, Moscow, 1981.
- [14] Rajeswari, N., Selvasekarapandian, S., Karthikeyan, S., Prabhu, M., Hirankumar, G., Nithya, H., Sanjeeviraja, C., J. Non-Crystal. Sol., 357,3751-3756, 2011.
- [15] Nithya, H., Selvasekarapandian, S., Arunkumar, D., Sakunthala, A., Hema, M., Christopher Selvin, P., Kawamura, J., Baskaran, R., Sanjeeviraja, C., Mater. Chem. Phys., 126: 404-408, 2011.
- [16] Baskaran, R., Selvasekarapandian, S., Hirankumar, G, Bhuvaneswari, M.S., J. Power Sources,134: 235-240, 2004.