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Study of electrical properties of polyvinylpyrrolidone/polyacrylamide blend thin films

A RAWAT*, **H K MAHAVAR, A TANWAR and P J SINGH**
Department of Physics, M S J College, Bharatpur 321 001, India

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Abstract. **Electrical properties of polyvinylpyrrolidone, polyacrylamide and their blend thin films have been investigated as a function of temperature and frequency. The films were prepared using solution casting method and the measurements on films were carried out at different temperatures ranging from 305 to 345 K covering a frequency range from 10^2 to 10^5 Hz. The conductivity of film samples was found to increase upon increasing the temperature. Lowering of activation energy by increasing the polyvinylpyrrolidone percentage may be due to the predominance of ion conduction mechanism caused by polyvinylpyrrolidone in the blend. The permittivity (ε_r) and dielectric loss (ε_i) were found to decrease upon increasing frequency. Temperature and frequency dependence of impedance, relaxation time and electric modulus of thin film samples have also been studied. From electric modulus formalism, polarization and conduction relaxation behaviour in the film samples have been discussed.**

Keywords. **PVP; PAM; conductivity; activation energy; relaxation time; electric modulus.**

1. Introduction

The physical mixing of two polymers produces a blend with quite different properties, which can be potentially useful (Bahadur and Sastry 2003). The electrical conductivity studies are aimed at understanding the origin of the charge carrying species and the way in which they move through the bulk of the material. Polymers with controlled conductivity and thermal sensitivity are much desirable in various applications (Cassiers 1960; Dresner and Comizzoli 1972; Pillai *et al* 1980). Knowledge of electrical properties of polymer thin films at low frequencies is helpful in material study and characterization for device fabrication. Thin insulating films, for example, are extensively used in integrated circuits.

Among synthetic polymers, polyvinylpyrrolidone (PVP) and polyacrylamide (PAM) are amorphous and exist as randomly coiled and highly flexible chain in polar solvents. These water soluble polymers have a wide range of biological, pharmaceutical and technological applications. PVP is a polar polymer due to its carbonyl group of double bond in pyrrolidone ring (Tan and Challa 1976). The network structure of PVP has different lengths of π and σ bonds in between nitrogen, oxygen, carbon and hydrogen atoms (Kasha and Pullenan 1962; Palaska 1970; Standen and Scool 1970).

PAM is an insulating polar polymer. It is easily soluble in water and polar solvents, having good mechanical strength and air stability. The use of PAM hydrogels in the field of agriculture (Saraydin *et al* 2000) and biomedical (Torchilin 1987) has been reported by other researchers. Hence an attempt has been made to study the electrical properties of PVP, PAM and their blend thin films. In the present investigation, we have prepared PVP/PAM blend thin films by solution casting technique (Awasthi *et al* 2006; Tanwar *et al* 2006; Rawat *et al* 2012). These films were investigated for electrical properties with the help of LCR meter in the frequency range 100 Hz–100 kHz.

2. Experimental

PVP from Central Drug House (P) Ltd., India, having a molecular weight of 40,000 and PAM from HiMedia Laboratories Pvt. Ltd., India, having a molecular weight of 50,00,000 were used as received. Different ratio's of PVP and PAM by weight were added to doubly distilled deionised water and the mixture was placed on a magnetic stirrer at room temperature for about 12 h in order to get complete dissolution. The solution was poured onto perfectly plane and cleaned Petri dishes, which were kept floating freely in a pool of mercury for perfect leveling. It was, thereafter, allowed to evaporate in air at room temperature in a dust free chamber. After drying, the films were peeled off from Petri dishes. Eleven films of PVP/PAM in different ratios were prepared and their thicknesses were measured with the help of a micrometer (Mitutoyo, Japan) having a least count of 1 μm. The thicknesses of all the films were of the order of 100 μm. The dried films were then cut into pieces (samples) of desired size.

The samples whose electrical properties have been studied, include PVP, PVP 90%/PAM 10%, PVP 80%/PAM 20%, PVP 70%/PAM 30%, PVP 60%/PAM 40%, PVP 50%/PAM 50%, PVP 40%/PAM 60%, PVP 30%/PAM

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*Author for correspondence (anandrawat15oct@gmail.com)

70%, PVP 20%/PAM 80%, PVP 10%/PAM 90% and PAM film samples. The sample was placed between the silver electrodes. The assembly of sample sandwiched between electrodes with connecting lead wires were placed in an oven with temperature control facility. The electrodes were connected to the LCR meter (Aplab, India, Make: M 4080A) through the connecting leads and the measurements were made over a frequency range of 100 Hz–100 kHz and the temperature was varied from 305 to 345 K.

3. Results and discussion

The data provided by the LCR meter were used to evaluate different electrical parameters like permittivity (ε_r), dielectric loss (ε_i), ac conductivity (σ_{ac}), dc conductivity (σ_{dc}), impedance (Z) and relaxation time (τ). The formulas used to evaluate the above mentioned parameters are

$$\varepsilon_r = Cd/\varepsilon_0 A, \tag{1}$$

$$\varepsilon_i = \varepsilon_r \tan\delta, \tag{2}$$

$$\sigma_{ac} = \omega\varepsilon_o\varepsilon_i, \tag{3}$$

where ε_0 is the dielectric constant of vacuum, C, the observed capacitance (in farad), d, the thickness of sample (in meter), A, the area of electrode plates (in sq. meter), tan δ, the dissipation factor and ω, the angular frequency.

The values of dc conductivity were estimated from extrapolating the ac conductivity vs frequency plots of all samples in the temperature range 305–345 K, in the lower frequency region up to the Y-axis (f = 0 Hz). Figure 1 shows the temperature dependence of the dc conductivity of all samples under investigation. The pattern indicates an increase in conductivity with rise in temperature. This type of temperature dependence indicates that the electrical conduction in the samples is a thermally activated transport process governed by Arrhenius relation

$$\sigma_{dc} = \sigma_0 \exp(-E_a/kT), \tag{4}$$

where σ_0 is the dc conductivity pre-exponential factor and E_a, the dc conductivity activation energy. The activation energy of the samples calculated from the slope of $\ln\sigma_{dc}$ vs 1000/T graph is shown in figure 2. It shows that, as PVP content increases in the samples, the activation energy decreases, which may be due to the predominance of ionic conduction mechanism caused by PVP in the blend samples, similar results have been reported by Buruiana *et al* (2012) for polysulfone.

The variation of σ_{ac} with frequency at different temperatures for 7:3 PAM/PVP blend sample is shown in figure 3. From this plot, it is observed that the ac conductivity of the sample increases with rise in temperature. It shows negative temperature coefficient impedance behaviour but, at

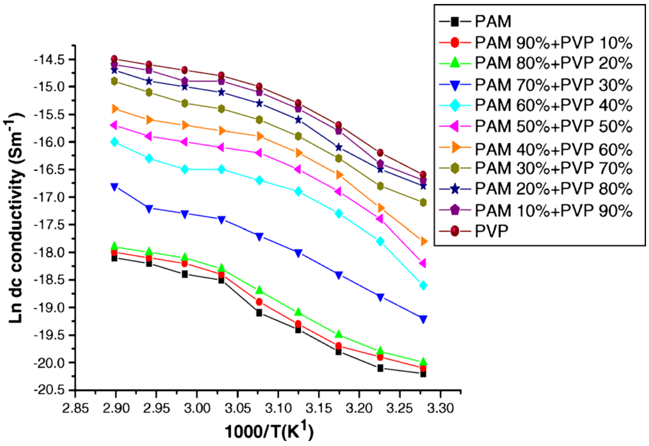


Figure 1. Ln σ_{dc} vs 1000/T.

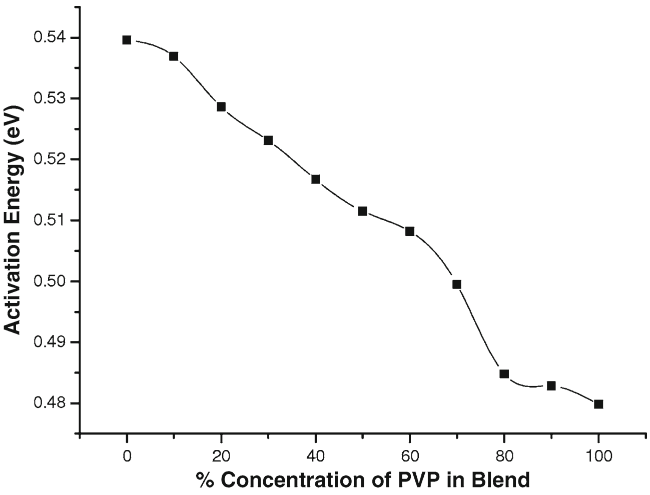


Figure 2. Variation of activation energy with PVP concentration in blend.

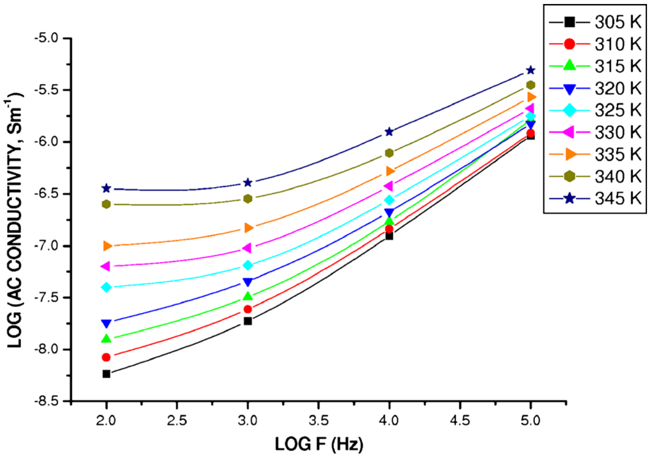


Figure 3. Log σ_{ac} vs Log F at different temperatures for 'PAM 70% + PVP 30%' blend thin film.

high frequency, it is less temperature dependent, i.e. dispersive region. The variation of ac conductivity of all samples with temperature at constant frequency and with frequency at constant temperature is shown in tables 1 and 2, respectively. It is well known that, in case of hopping conduction, the ac conductivity in the intermediate frequency range (usually kilo-hertz range) increases with increasing frequency. The available experimental results on the frequency dependence of ac conductivity have revealed a considerable similarity of behaviour for a wide range of materials. The frequency dependence of ac conductivity can be expressed by the empirical formula (Hill and Jonscher 1979; Long 1991; Hunt 2001)

$$\sigma(\omega) = A\omega^{s}, \tag{5}$$

where ω is the angular frequency of the ac signal ($\omega = 2\pi f$), and the exponent s is frequency as well as temperature dependent and approaches unity at low temperature and decreases with increasing temperature. For the samples under investigation and in the temperature range 305–345 K, the value of s varies from 0·34 to 0·89 as shown in table 3. The frequency dependent ac conductivity fulfils the power law (i.e. $\sigma(\omega) = A\omega^{s}$). The value of s approaching to unity at low temperature confirms assumption that ac conductivity is predominant due to the relaxation dipole moment. The power law dependence of the ac conductivity on frequency corresponds to the short range hopping of carriers through trap sites separated by an energy barrier of various heights. The variation in ac conductivity is comparable as reported in the literature (Polu and Kumar 2011; Buruiana *et al* 2012). The motion of charges could occur in a variety of ways, namely charge displacement (long-range or short-range), dipole re-orientation, space charge formation, etc. The complex impedance $Z^*(\omega)$ of the dielectric material can be described by the following equation

$$Z^*(\omega) = Z'(\omega) + jZ''(\omega), \tag{6}$$

where Z′ and Z″ are the real and imaginary parts of impedance. In figure 4, the impedance data of PAM 30% + PVP 70% film sample is presented in the Nyquist diagrams (imaginary impedance Z″ vs real impedance Z′) for several temperatures. At low temperature, the slope is large, indicating the insulator behaviour of sample. But as the temperature increases, the slope of the curves decreases, bowing down to the real axis. At high temperatures, a tendency to a semicircle behaviour is observed, indicative of the presence of both localized and non-localized conduction processes (Dasari *et al* 2011).

To extract data of dc resistivity, it is necessary to have an equivalent circuit to model the electrical response. Two parallel resistance–capacitance (RC) elements connected in series (Morrison *et al* 2001), as shown in figure 4(c), ascribe to grain and grain boundary responses for the case of Ohmic electrodes. In amorphous materials, the circuit could be simplified to a single parallel RC element. An extra RC element could also be added to the above circuit for electrode contribution. Each parallel RC element appears as a semicircle in the Z″ vs Z′ curve (Morrison *et al* 2001). Thus, the Z″ vs Z′

Table 1. AC conductivity ($\times 10^{-6}$ Sm^{-1}) of samples at 1000 Hz frequency.

Sample/Temperature	305 K	310 K	315 K	320 K	325 K	330 K	335 K	340 K	345 K
PAM	0·006	0·008	0·011	0·018	0·024	0·033	0·051	0·077	0·114
PAM 90% + PVP 10%	0·007	0·009	0·013	0·018	0·028	0·042	0·059	0·078	0·127
PAM 80% + PVP 20%	0·009	0·012	0·015	0·021	0·032	0·048	0·072	0·108	0·145
PAM 70% + PVP 30%	0·019	0·024	0·032	0·046	0·065	0·095	0·148	0·284	0·401
PAM 60% + PVP 40%	0·020	0·037	0·054	0·085	0·144	0·263	0·440	0·476	0·541
PAM 50% + PVP 50%	0·022	0·047	0·066	0·105	0·168	0·321	0·496	0·779	0·895
PAM 40% + PVP 60%	0·030	0·054	0·097	0·124	0·190	0·350	0·663	1·111	1·390
PAM 30% + PVP 70%	0·035	0·060	0·100	0·142	0·247	0·373	0·741	1·170	1·599
PAM 20% + PVP 80%	0·044	0·084	0·141	0·263	0·305	0·497	0·838	1·394	1·841
PAM 10% + PVP 90%	0·058	0·095	0·172	0·265	0·419	0·709	1·508	2·078	2·591
PVP	0·066	0·154	0·212	0·291	0·453	0·790	1·834	3·239	3·707

Table 2. AC conductivity ($\times 10^{-6}$ Sm^{-1}) of samples at 325 K.

Frequency (Hz)	PAM	PAM 90% + PVP 10%	PAM 80% + PVP 20%	PAM 70% + PVP 30%	PAM 60% + PVP 40%	PAM 50% + PVP 50%	PAM 40% + PVP 60%	PAM 30% + PVP 70%	PAM 20% + PVP 80%	PAM 10% + PVP 90%	PVP
100	0·007	0·009	0·010	0·040	0·066	0·099	0·128	0·175	0·233	0·284	0·317
1000	0·024	0·028	0·032	0·065	0·144	0·168	0·190	0·247	0·305	0·419	0·453
10000	0·111	0·058	0·123	0·276	0·391	0·295	0·555	0·644	0·828	1·224	1·782
100000	0·826	0·498	0·816	1·780	1·492	1·359	1·985	2·397	3·244	4·401	11·559

Table 3. Variation of s with temperature.

Temperature (K)↓ Film composition →	PAM	PAM 90% + PVP 10%	PAM 80% + PVP 20%	PAM 70% + PVP 30%	PAM 60% + PVP 40%	PAM 50% + PVP 50%	PAM 40% + PVP 60%	PAM 30% + PVP 70%	PAM 20% + PVP 80%	PAM 10% + PVP 90%	PVP
305	0·89	0·67	0·89	0·89	0·80	0·77	0·73	0·64	0·75	0·73	0·63
310	0·84	0·63	0·86	0·85	0·69	0·63	0·64	0·67	0·65	0·66	0·55
315	0·82	0·58	0·81	0·85	0·64	0·59	0·54	0·57	0·58	0·57	0·54
320	0·79	0·53	0·76	0·76	0·58	0·53	0·55	0·56	0·49	0·54	0·69
325	0·77	0·63	0·70	0·72	0·51	0·45	0·51	0·49	0·51	0·51	0·70
330	0·74	0·53	0·64	0·67	0·44	0·39	0·50	0·48	0·48	0·48	0·69
335	0·71	0·38	0·60	0·63	0·40	0·43	0·44	0·42	0·46	0·41	0·63
340	0·64	0·36	0·56	0·55	0·48	0·47	0·43	0·42	0·45	0·45	0·53
345	0·58	0·34	0·56	0·54	0·50	0·60	0·49	0·46	0·49	0·51	0·54

curve is composed of two semicircles. A small semicircle at high frequencies indicates the effect of grain and large semicircle at low frequencies indicates the grain boundary effect. The intercept of the semicircle on real axis gives the resistance of grain (R_g) and grain boundary (R_{gb}) of the corresponding component contributing towards the impedance of the sample.

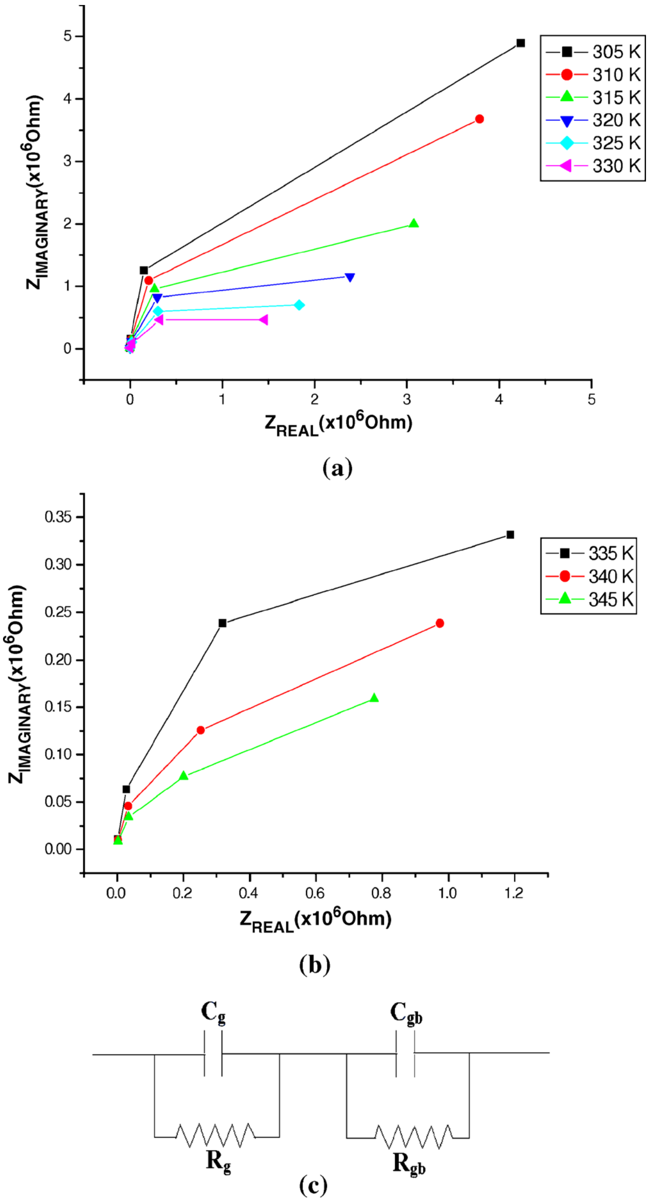
From the results presented in figure 5, it is observed that permittivity (ε_r) increases with the increase in temperature. This is justified from the effect of temperature, as the temperature facilitates the diffusion of ions in the space charge polarization. Thermal energy may also aid in overcoming the activation energy barrier for the orientation of polar molecules in the direction of the field. Consequently, the value of permittivity increases. The measurement of permittivity reveals that its value for the blend samples is almost intermediate between the values of permittivity for PVP and PAM individually at all temperatures and at all frequencies under investigation. It can also be seen from figure 5 that permittivity decreases with increase in frequency and reaches a constant value at high frequencies. The values of permittivity are higher at low frequencies, but as the frequency of the applied field is increased, the permittivity begins to decrease. This could be due to the dipoles not being able to follow the field variation at high frequencies and also due to the polarization effects. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Srivastava and Srivastava (1981) have suggested that the permittivity of non-polar polymers remains almost invariable with frequency while, in case of polar polymers, the permittivity begins to drop as the frequency is increased and, at very high frequencies, it approaches the values typical of non-polar dielectrics.

The dependence of dielectric loss (ε_i) on temperature at different frequencies is depicted in figure 6. The results show that, at low temperatures, there is negligible variation in the value of dielectric loss but it increases with further increase in temperature. It is also observed that, at high temperature and low frequency, the variation in the value of dielectric loss is more. The large variation in the value of dielectric loss at higher temperatures may be due to break down of hydrogen bonds resulting in an increased mobility for the polymer chains and hence there is increase in the loss part (Assender and Windle 1988a, b). Figures 5 and 6 show that the dispersion in ε_i is more than that in ε_r implying that it is influenced by dc conductivity. Low frequency slope of ε_i vs $\log F$ plot indicates the predominance of the dc conduction in this frequency region. Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases with increasing frequency. In terms of the theory of this phenomenon as developed by Debye (1929), dielectric relaxation is the lag in dipole orientation behind an alternating electric field. The dielectric relaxation time (τ) has been calculated and found to be temperature and frequency dependent. The plots of dielectric relaxation time with respect to frequency at various temperatures are shown in figure 7. It is evident from the plots that the relaxation time increases with increase in temperature (Tiwari *et al* 2012) of the blend film sample.

The electric modulus (M^*) is the reciprocal of the permittivity (ε^*). It was originally introduced by Macedo *et al* (1972) to study space charge relaxation phenomena. Now M^* representation is widely used to analyse ionic conductivities (Angell 1990). The electric modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant, so that the electric modulus represents the real dielectric relaxation process, which can be expressed as (Macedo *et al* 1972)

$$\begin{aligned} M^*(\omega) &= 1/\varepsilon^*(\omega) = M' + jM'' \\ &= M_\infty \left[1 - \int_0^\infty (-d\phi(t)/dt)\exp(-j\omega t)dt\right], \end{aligned} \tag{7}$$

where $M_\infty = (\varepsilon_\infty)^{-1}$ is the asymptotic value of $M'(\omega)$ and $\phi(t)$ is the time evolution of the electric field within the material. The temperature dependence of the electric modulus M' and M'' at various frequencies are shown in figures 8 and 9, respectively for PAM 30% + PVP 70% blend film sample.



(a)

(b)

(c)

Figure 4. (**a** & **b**) Z″ vs Z′ at different temperatures for 'PAM 30% + PVP 70%' blend thin film. (**c**) Equivalent circuit.

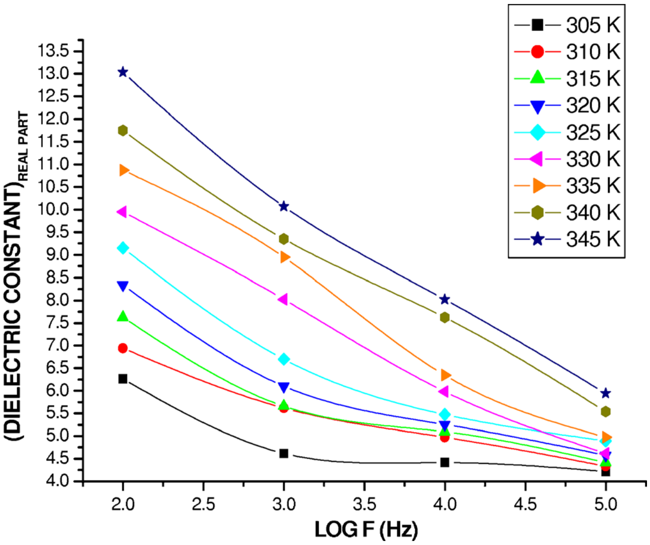


Figure 5. ε_r vs Log *F* for 'PAM 50% + PVP 50%' blend thin film.

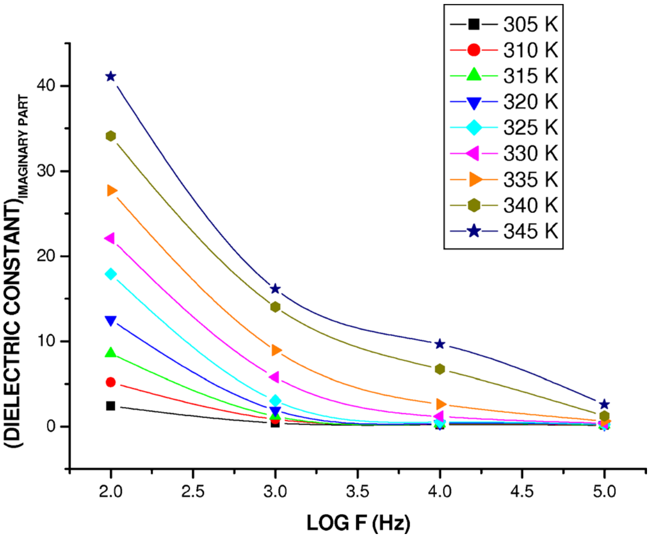


Figure 6. ε_i vs Log *F* for 'PAM 50% + PVP 50%' blend thin film.

$M'(\omega)$ shows a dispersion tending to M_∞ at high frequencies for all temperatures under investigation while the asymmetric $M''(\omega)$ is suggestive of stretched exponential relaxation behaviour. $M''(\omega)$ shows peaks at different frequencies for different temperatures. The peak of $M''(\omega)$ shifts towards higher frequency with increasing temperature, which indicates that the conductivity of the charge carrier has been thermally activated (Buruiana *et al* 2012). These peaks indicate the transition from short-range to long-range mobility with decreasing frequency, where the low frequency side of the peak represents the range of frequencies in which the ions are capable of moving long distances i.e. performing successful hopping from one site to the neighbouring site, whereas for the high frequency side, the ions are spatially confined to their potential wells and can execute only localized motion (Kim 2001). Our results are comparable with the values reported in the literature (Khare *et al* 1998; Abou-Aiad *et al* 2006; Sengwa *et al* 2010).

XRD measurements

The X-ray diffraction patterns of prepared thin film samples were taken by PANalytical (Make: X'Pert PRO MPD) operating at 45 kV–40 mA. The radiation source used was CuKα (λ = 1·542 Å) with the 2θ values at the rate of 20/min. Figure 10 shows different spectra of PVP, PAM and their blend film samples. The XRD patterns confirms the amorphous nature of all the film samples. XRD patterns of PVP

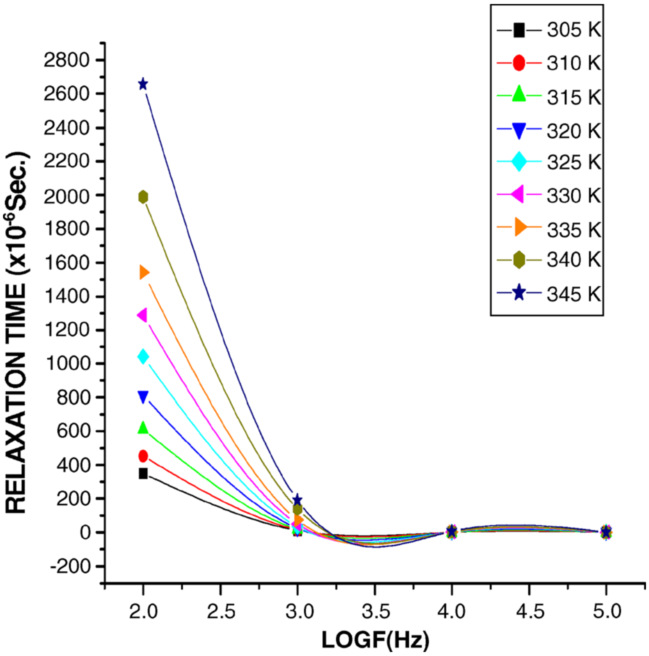


Figure 7. Relaxation time vs Log *F* for 'PAM 70% + PVP 30%' blend thin film.

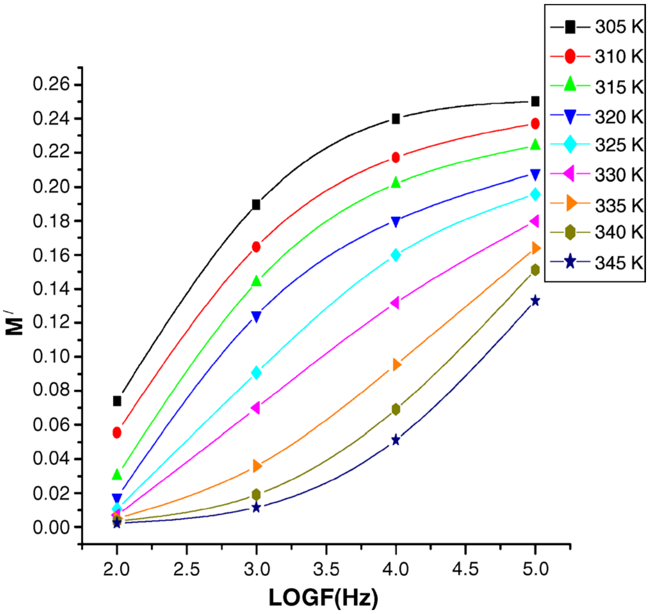


Figure 8. M' vs Log *F* for 'PAM 30% + PVP 70%' blend thin film.

and PAM are found to be in agreement with the earlier reports in literature (Mishra *et al* 2007; Sivaiah *et al* 2010).

4. Conclusions

PVP, PAM and their blend thin film samples have been investigated for dielectric permittivity, dielectric loss, relaxation time, ac and dc conductivities, activation energy impedance

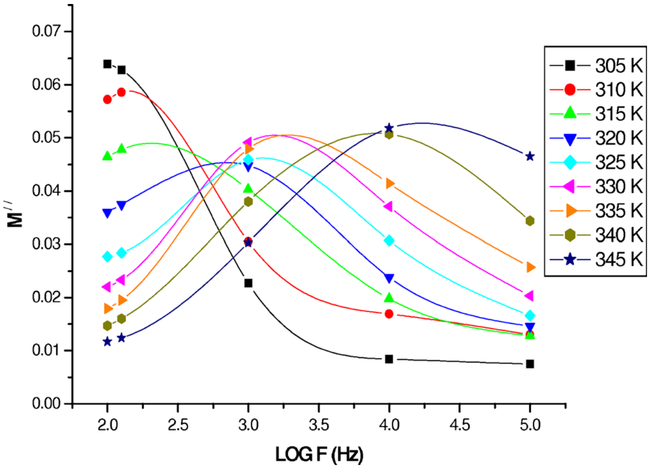


Figure 9. M'' vs Log *F* for 'PAM 30% + PVP 70%' blend thin film.

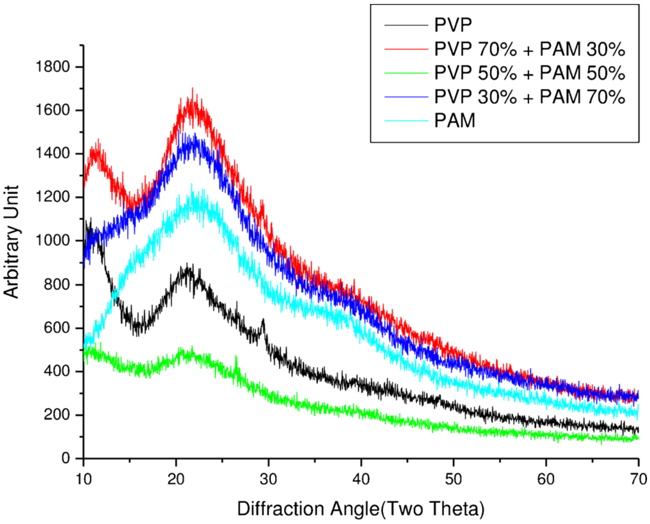


Figure 10. XRD plots of PVP, PAM and their blend films (Rawat *et al* 2012).

and electric modulus at different frequencies and temperatures. The ac conductivity of all samples vary from $5{\cdot}8 \times 10^{-9}$ (Sm^{-1}) to $3{\cdot}7 \times 10^{-6}$ (Sm^{-1}) at 1 kHz frequency. The activation energy decreases from 0·54 to 0·48 eV on increasing the PVP percentage in the blend. The shift in M$''$ (max.) indicates the presence of temperature relaxation process in the material.

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References

Abou-Aiad T H M, Abd-El-Nour K N, Hakim I K and Elsabee M Z 2006 *Polymer* **47** 379

Angell C A 1990 *Chem. Rev.* **90** 523

Assender A P and Windle A H 1988a *Polymer* **39** 4295

Assender A P and Windle A H 1988b *Polymer* **39** 4303

Awasthi K, Awasthi S, Srivastava A, Kamalakaran R, Talapatra S, Ajayan P M and Srivastava O N 2006 *Nanotechnology* **17** 5417

Bahadur P and Sastry N V 2003 *Principles of Polymer Science* (New Delhi: Narosa Publishing House) 281

Buruiana L I, Avram E, Popa A, Musteata V E and Ioan S 2012 *Polym. Bull.* **68** 1647

Cassiers P M 1960 *Photogr. Sci. Engg.* **4** 199

Dasari M P, Rao K S, Krishna M and Krishna G G 2011 *Acta Physica Polonica A* **119** 387

Debye P 1929 *Polar Molecules* (New York: Chemical Catalog) Chap. 5

Dresner J and Comizzoli R B 1972 *Photogr. Sci. Engg.* **16** 43

Hill R M and Jonscher A K 1979 *J. Non-Cryst. Solids* **32** 53

Hunt A G 2001 *Philos. Mag.* **B81** 875

Kasha M and Pullenan B P 1962 *Horizon in Biochemistry* Albert Szent Gyooryi Dedicatory Vol. (New York: Academic) p. 364

Khare P K, Paliwal S K, Kuraria R, Vishwakarma H L, Verma A and Jain S K 1998 *Bull. Mater. Sci.* **21** 139

Kim J S 2001 *J. Phys. Soc. Jpn.* **70** 3129

Long A R 1991 In *Hopping Transport in Solids* (eds) M Pollak and B I Shklovskii (The Netherlands: Elsevier Science Publishers) p. 207

Macedo P B, Moynihan C T and Bose R 1972 *Phys. Chem. Glasses* **13** 171

Mishra S, Bajpai R, Katare R and Bajpai A K 2007 *Express Polymer Lett.* **1** 407

Morrison F D, Sinclair D C and West A R 2001 *J. Am. Ceram. Soc.* **84** 531

Palaska E J 1970 *Encyclopedia of Chemical Technology* (New York: John Wiley) **21** 427

Pillai P K C, Gupta A K and Goel M 1980 *Macromol. Chemie* **181** 951

Polu A R and Kumar R 2011 *Bull. Mater. Sci.* **34** 1063

Rawat A, Mahavar H K, Chauhan S, Tanwar A and Singh P J 2012 *Indian J. Pure and Appl. Phys.* **50** 100

Saraydin D, Karadag E and Güven O 2000 *Polymer Bulletin* **45** 287

Sengwa R J, Sankhala S and Choudhary S 2010 *Indian J. Pure Appl. Phys.* **48** 196

Sivaiah K, Rudramadevi B H, Buddhudu S, Bhaskar K G and Varadarajulu A 2010 *Indian J. Pure and Appl. Phys.* **48** 658

Srivastava A P and Srivastava S K 1981 *Indian J. Pure Appl. Phys.* **19** 953

Standen A and Scool A 1970 *Encyclopedia of Chemical Technology* (New York: Interscience) 1st edn, **Vol. 10** 421

Tan Y Y and Challa G 1976 *Polymer* **17** 739

Tanwar A, Gupta K K, Singh P J and Vijay Y K 2006 *Bull. Mater. Sci.* **29** 181

Tiwari D C, Sen V and Sharma R 2012 *Indian J. Pure Appl. Phys.* **50** 49

Torchilin V P 1987 *Adv. Drug Deliv. Rev.* **1** 41