

Effect of temperature on dielectric properties of polyvinylpyrrolidone/ polyacrylamide blend films at microwave frequency

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In this paper, dielectric constant (ϵ_r), dielectric loss (ϵ_i), loss tangent ($\tan\delta$), relaxation time (τ), ac conductivity (σ_{ac}), extinction coefficient (K) and refractive index (η) of polyvinylpyrrolidone (PVP), polyacrylamide (PAM) and their blend films have been studied in the temperature range 293-393 K at 9.01 GHz microwave frequency. The temperature and frequency dependent σ_{ac} of film samples is calculated using the dielectric parameters. The variation of ϵ_i , $\tan\delta$, K , σ_{ac} , η and τ showed a decreasing trend with increasing temperature. It is also observed that the temperature dependency of ϵ_r is insignificant at this frequency but its value for the film samples increases with the increasing concentration of PVP in the blend. The DSC measurements show miscible behaviour of PVP/PAM blends.

Keywords: Dielectric constant, Conductivity, Dielectric loss, Loss tangent, Relaxation time, Extinction coefficient Polymer blend, Activation energy, Refractive index

1 Introduction

The use of polymers has increased tremendously over the last few decades. Mechanical, physical and chemical properties of polymers vary over a wide range. One approach to get polymers with intermediate properties has been to blend two or more polymers together, called polymer blends (mixture of structurally different polymers¹). Polymer blends are of interest because synthesized polymers have not satisfied increasing application demands. Blending two or more polymers to obtain a multifunctional polymer with designer physical and/or chemical properties is one of the most widely used and successful polymer process strategies²⁻⁷. The final properties of a polymeric blend obviously depend on the properties of the components, the composition of blend, the interfacial characteristics (e.g. interfacial adhesion) and the morphology. The morphology that is generated during the processing has a significant impact on the blend properties. Blending is a convenient and practical technique for developing materials whose properties may be novel or selectively enhanced, which are possibly superior to those of the components⁸⁻¹¹. The use of polymer blends is expected to increase in the 21st century and thus, further contribute to the increasing use of polymers. Polymer blends have the potential of

playing a big role commercially in the 21st century, just as it has played in the cases of individual polymers in the 20th century. Factors that need attention in designing research and development work on polymer blends include: purity of the component polymers, presence of other additives and their concentrations, presence or absence of air or another cover gas, temperature and thickness of the samples.

Dielectric materials, such as polymers, have many important functions in the microelectronics industry. An accurate measurement of complex permittivity is needed for circuit design, minimization of cross talks and characterization of signal propagation speed. Knowledge of electrical properties of thin insulating polymer films at microwave frequencies is helpful in material study and characterization for device fabrication. The insulating polymer thin films are extensively used in microwave integrated circuits. Therefore, it is of great interest to know the attenuation and phase produced by a particular polymer film and variation of these quantities with parameters such as temperature, material of the film, etc. Hence, the dielectric measurements on thin polymer materials are in great demand^{10,12-15}. A great increase has been observed in the use of polymer films in pure as well as in the form of blends in various medical, biomedical and technological applications. Thus, the aim is to study the dielectric properties of PVP/PAM blend films at microwave

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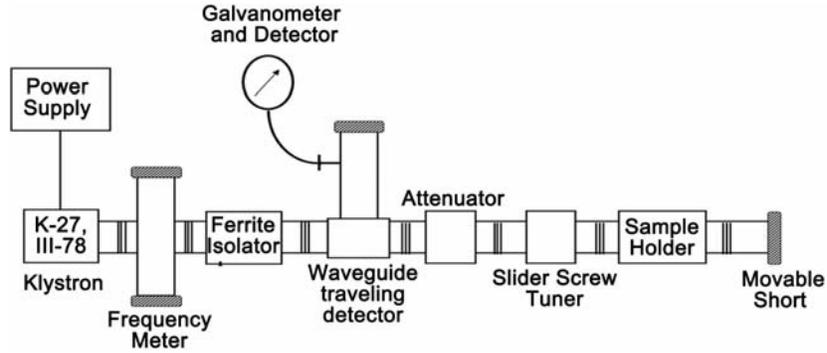


Fig. 1 — Experimental set up for measurement of the dielectric constant

frequency by varying the temperature of the polymer film from 293 K to 393 K.

2 Experimental Method

The experimental arrangement of the method for microwave measurements of dielectric parameters of films is shown in Fig. 1, which was developed by Dube¹⁶ and Dube & Natarajan^{17,18}. The sample holder is an approximately 10 cm long wave-guide, having a sharply cut longitudinal slot at the middle of the upper face through which the film sample can be introduced in the waveguide. The advantage of this method is that it does not impose any restrictions on the length of the film sample and the film specimen is placed longitudinally at the centre of the broad side of a hollow rectangular waveguide excited in the TE₁₀ mode so that the whole specimen remains in maximum electric field. Figure 2 shows a rectangular waveguide with its axis in the Z direction and the sample is mounted in the YZ plane. In this configuration, the electric field acts in the plane of the film. Standing waves are produced in rectangular waveguide by short-circuiting the system. These are detected in the slotted line by means of a traveling waveguide detector. The movable probe is now located at the maximum. The sample of length L cm is then placed in the sample holder, which is a waveguide of length 10 cm with a fine accurately cut longitudinal slot in the middle of the upper face through which the sample can be introduced in the waveguide. This causes the minima positions to shift by a distance X . The phase shift introduced by the specimen per unit length is:

$$\beta_s = \beta_0 \left[\frac{X}{L} \right] \quad \dots (1)$$

where, $\beta_0 = 2\pi / \lambda_g$, λ_g being the guide wavelength in air. Thus, the total phase factor (β_d) in presence of the sample is given by:

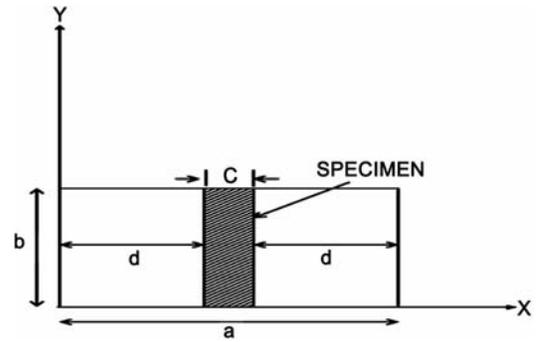


Fig. 2 — Cross-section of a rectangular waveguide with specimen

$$\beta_d = \beta_0 \left[1 + \frac{X}{L} \right] \quad \dots (2)$$

For measuring the dielectric loss, the voltage standing wave ratio (VSWR) is taken without and with the film sample. Let these VSWR be ρ_1 and ρ_2 , respectively, then:

$$r = \frac{[\rho_1 - 1]}{[\rho_1 + 1]} = \exp(-\alpha) \quad \dots (3)$$

$$r' = \frac{[\rho_2 - 1]}{[\rho_2 + 1]} = \exp[-(\alpha + 2\beta_s L)] \quad \dots (4)$$

where, r' and r , are the reflection coefficients of the system with and without the sample; and α , the attenuation constant. Hence, β_s can be calculated from Eqs (3) and (4).

The Maxwell's equations can be solved for the TE₁₀ mode by taking Z variations of the form $\exp(-i\beta Z)$. Then, by usual methods¹⁹, the following dispersion relation is obtained:

$$\tan \left[d(k^2 - \beta^2)^{\frac{1}{2}} \right] \tan \left[\frac{1}{2} c(\epsilon k^2 - \beta^2)^{\frac{1}{2}} \right] = \frac{(k^2 - \beta^2)^{\frac{1}{2}}}{(\epsilon k^2 - \beta^2)^{\frac{1}{2}}} \quad \dots (5)$$

where, $k = \omega/c_0$, is the free space propagation vector; ω , the angular frequency; and c_0 , the velocity of light. For complex dielectric constant (ϵ), the solution of Eq. (5) is very difficult even graphically. Therefore, it is simplified under the approximation:

$$\left[\frac{1}{2} c (\epsilon k^2 - \beta^2)^{\frac{1}{2}} \right] < 1$$

which holds very well in the case of thin films. Using $\epsilon = \epsilon_r - i\epsilon_i$; and $\beta = \beta_r - i\beta_i$, real and imaginary parts of ϵ obtained are given in the following equations:

$$\epsilon_r = \frac{1}{k^2} \left[\beta_r^2 - \beta_i^2 + \left(\frac{a_1 a_3 + a_2 a_4}{a_3^2 + a_4^2} \right) \frac{2}{cd} \right] \quad \dots (6)$$

$$\epsilon_i = \frac{1}{k^2} \left[2\beta_r \beta_i - \left(\frac{a_2 a_3 - a_1 a_4}{a_3^2 + a_4^2} \right) \frac{2}{cd} \right] \quad \dots (7)$$

where, $a_1 = d \operatorname{Re}(k^2 - \beta_r^2)^{\frac{1}{2}}$;

$$a_2 = d \operatorname{Im}(k^2 - \beta_r^2)^{\frac{1}{2}}$$

$$a_3 = \frac{2 \sin 2a_1}{\left[\exp(2a_2) + \exp(-2a_2) + 2 \cos 2a_1 \right]}$$

$$a_4 = \frac{\left[\exp(2a_2) - \exp(-2a_2) \right]}{\left[\exp(2a_2) + \exp(-2a_2) + 2 \cos 2a_1 \right]}$$

c = thickness of film; and

$$d = \frac{1}{2}(a - c); \text{ } a \text{ being the width of the waveguide.}$$

The values of β_r and β_i are used in Eqs (6) and (7) to calculate ϵ_r and ϵ_i . Being electrode less technique, measurements at microwave frequencies are free from electrode polarization and associated problems and thus, yield real material parameters. To study dielectric parameters as a function of temperature, the guide section containing the specimen is heated by a cylindrical furnace. Microwave power is obtained from a klystron source and the temperature of the samples was varied from 293 K to 393 K in a step of 10 K with an accuracy of 0.1 K.

2.1 Sample preparation

PVP (MW: 40000 amu) supplied by Central Drug House (P) Ltd, New Delhi (India) and PAM (MW: 5000000 amu) supplied by Hi-Media Laboratories Pvt Ltd., Mumbai (India) were used as received for the film preparation. The films of PVP, PAM and their blends were prepared by solution cast

method^{13,20,21}. For preparing blends of PVP and PAM, both the polymers were dissolved in a common solvent, i.e. double distilled de-ionized water and the mixture was stirred for few hours in order to get proper mixing. The mixture then was poured in a petri dish floating in a mercury pool to ensure the uniform thickness of the film. The whole assembly was placed in a dust free chamber for few days so that the solvent gets evaporated and the film is taken out of the petri dish. The blends of PVP and PAM were prepared in the ratio 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90, respectively. Two films of pure PVP and PAM were also prepared by the same method.

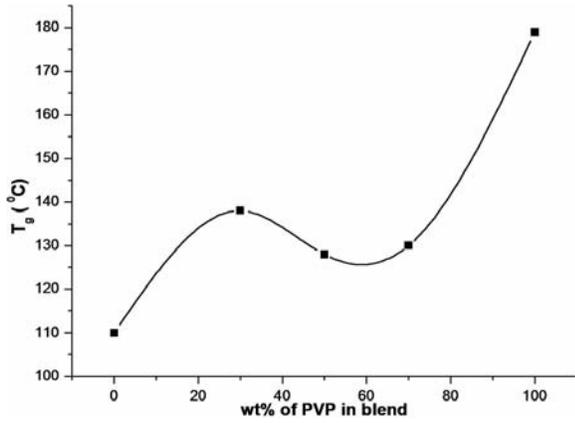
2.2 DSC measurements

Differential scanning calorimetry (DSC) has been applied to characterize the miscibility of PVP/PAM blends. The glass transition temperature (T_g) values of the virgin samples and the blends were measured using a temperature modulated differential scanning calorimeter (TA Instruments, Model 2910) at IUC-DAE, Indore Centre. Samples weighing 7-10 mg were scanned from 30 to 200°C heated at a rate of 10°C min⁻¹.

3 Results and Discussion

The XRD pattern of PVP, PAM and their blend films confirm the amorphous nature of the samples²¹. The glass transition temperature (T_g) measured for PAM and PVP samples are 110 and 179°C, respectively (Fig. 3). One of the main indicators of miscibility behaviour in polymer blends is the glass transition temperature. If two glass transition temperatures are observed for the blend of two different polymers, the blend is said to be immiscible blend, because the presence of two T_g s in a blend suggests the coexistence of both polymer phases. On the other hand, if the blend is miscible, one T_g should be observed. In the case of blends of PVP/PAM, only one T_g is observed as shown in Fig. 3. The T_g values of different blend samples of PVP/PAM lie between the T_g values of PAM and PVP samples. The existence of one T_g in each blend sample confirms the miscibility of PVP/PAM blends. The T_g versus weight percentage of PVP curve of PVP/PAM samples exhibits an S-shape (Fig. 3) that is common for strong hydrogen bond blends²².

Figures 4 and 5 show that σ_{ac} and τ of PVP, PAM and their blend films decrease with the increase in the temperature at microwave frequency. Such behaviour is expected. When polar molecules are very large, then under the influence of electromagnetic field of high frequency, the rotary motion of the polar


 Fig. 3 — Variation of T_g with PVP% in PVP/PAM blends

molecules of a system is not sufficiently rapid to attain equilibrium with the field. The polarization of molecules then acquires a component out of phase with the field, resulting in thermal dissipation of energy. Thus, there is a systematic decrease of σ_{ac} as temperature increases, since ϵ_i is proportional to σ_{ac} . The decrease in τ with increasing temperature may be due to the increase in effective length of dipole. From Fig. 4 and Table 1, it is found that the increase in PVP concentration into the blend results in: (i) increase in its σ_{ac} ; and (ii) increase in ϵ_r . This may perhaps be due to the modification of trap structure introduced by the addition of PVP in the blend. The PVP molecules in the blend might be producing additional traps of shallow as well as deeper depths; thus, providing conducting path ways for the charge carriers. The poly blend of PAM and PVP can be considered to be the mixture of two homo polymers. Such blends possess the properties of both the component polymers, i.e., PAM and PVP. Since PVP has higher conductivity than PAM, the mixture can be expected to possess the conductivity and other parameters intermediate between that of PAM and PVP, i.e., higher than that of PAM and lower than that of PVP. The behaviour of σ_{ac} and τ with composition and temperature is not monotonous, which may be due to the variation in T_g s of the samples as shown in Fig. 3.

The dielectric properties can vary widely in solids as a function of temperature, frequency of applied electric field, crystal structure and external factors. The dielectric response of a solid can be described by expressing ϵ as a complex quantity, made up of a real component and an imaginary component, i.e.

$$\epsilon = \epsilon_r - i\epsilon_i \quad \dots (8)$$

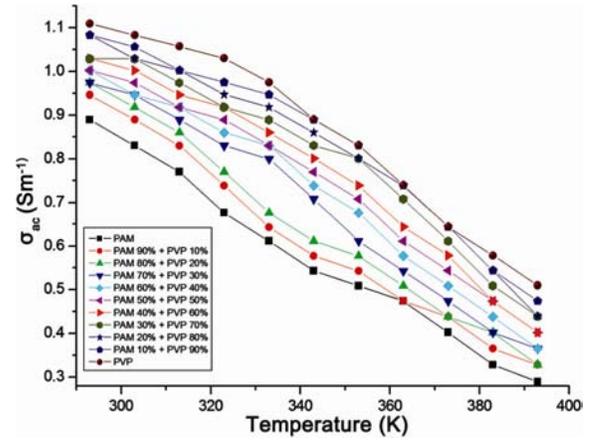


Fig. 4 — Variation of ac conductivity with temperature

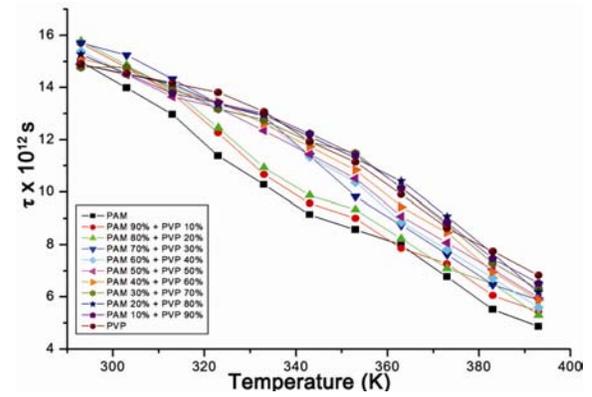


Fig. 5 — Variation of relaxation time with temperature

where, ϵ_r and ϵ_i , are the real part (permittivity) and imaginary part (dielectric loss) of dielectric constant representing the amount of energy stored in a dielectric material as a result of polarization and the energy loss, respectively; while applying an electric field.

The ϵ_r of any material, in general, is directly related to dielectric polarization. The higher the polarization, the higher will be ϵ_r of the material. There are four primary mechanisms causing polarizations: electronic polarization, ionic polarization, dipolar polarization and space charges polarization. Their occurrence depends upon the frequency of the applied field. At low frequencies, space charge polarization and dipolar polarization are known to play the vital role and both these polarizations are temperature dependent. At high frequencies, electronic polarization and ionic polarization are main contributors and their temperature dependence is insignificant. This is evident from Table 1, which shows that for all film samples, ϵ_r is almost independent of the temperature variation. Similar trend of the variation of ϵ_r with

Table 1 — Variation of dielectric constant (ϵ_r) with temperature

Film composition → Temperature (K) ↓	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
293	2.091	2.122	2.176	2.187	2.294	2.369	2.401	2.455	2.498	2.562	2.627
303	2.091	2.123	2.176	2.187	2.294	2.369	2.401	2.455	2.498	2.562	2.627
313	2.091	2.123	2.177	2.187	2.295	2.370	2.402	2.456	2.498	2.563	2.627
323	2.092	2.124	2.177	2.188	2.295	2.370	2.402	2.456	2.499	2.563	2.627
333	2.093	2.125	2.178	2.188	2.295	2.371	2.403	2.456	2.499	2.563	2.628
343	2.093	2.125	2.178	2.189	2.296	2.371	2.403	2.457	2.499	2.564	2.628
353	2.093	2.125	2.179	2.189	2.296	2.371	2.403	2.457	2.500	2.564	2.629
363	2.093	2.125	2.179	2.190	2.297	2.372	2.404	2.457	2.500	2.565	2.629
373	2.093	2.126	2.179	2.190	2.297	2.372	2.404	2.458	2.501	2.565	2.630
383	2.094	2.126	2.179	2.190	2.298	2.373	2.405	2.459	2.501	2.566	2.630
393	2.094	2.126	2.180	2.190	2.298	2.373	2.405	2.459	2.502	2.566	2.631

temperature for polyvinyl chloride (PVC) has been reported by Dube¹⁶. The dependence of ϵ_r on temperature is presented in Fig. 6, which shows that ϵ_r decreases as the temperature increases. The decrease in ϵ_r with temperature may be due to the relaxation of the dipole molecules coupled with the resulting drop in τ (Fig. 5). As the temperature increases, the energy required in overcoming the internal mechanical friction of the medium decreases when the dipoles rotate through a unit angle²³, so the decreases in ϵ_r with the rise in temperature can be interpreted. By the assumption of temperature independence of molar refraction and molar weight, the temperature dependence of the specific volume of the polymeric material may influence the temperature dependence of η . Usually the specific volume will increase on increasing the temperature, which results in a decrease of η on increasing the temperature. Figure 7 shows the course of η as a function of temperature of the samples under investigation. The temperature dependency of η for the present samples is in good agreement with the results of other polymers²⁴. Tables (2 and 3) show the variation of $\tan\delta$ and K with temperature, respectively.

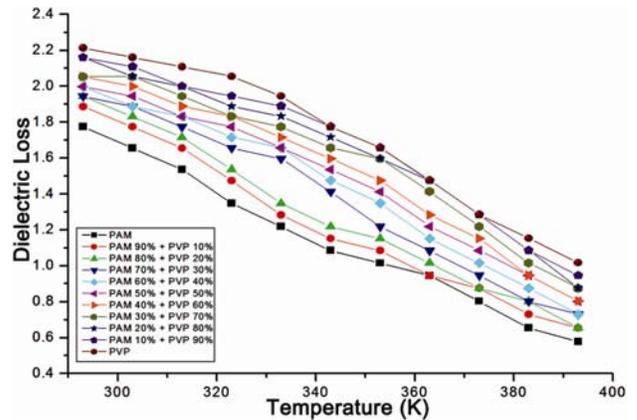


Fig. 6 — Variation of dielectric loss with temperature

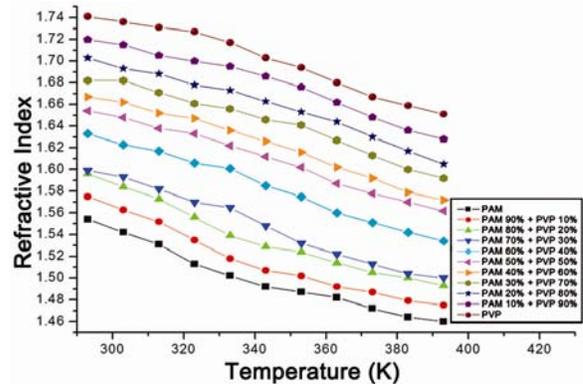


Fig. 7 — Variation of refractive index with temperature

Table 2 — Variation of loss tangent ($\tan\delta$) with temperature

Film composition → Temperature (K)↓	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
293	0.848	0.889	0.893	0.889	0.871	0.844	0.855	0.836	0.865	0.843	0.843
303	0.792	0.835	0.841	0.863	0.823	0.820	0.832	0.836	0.822	0.823	0.823
313	0.734	0.780	0.788	0.811	0.798	0.773	0.786	0.792	0.800	0.780	0.802
323	0.644	0.694	0.705	0.757	0.748	0.749	0.762	0.746	0.756	0.759	0.782
333	0.582	0.604	0.619	0.730	0.722	0.699	0.714	0.722	0.733	0.737	0.740
343	0.518	0.542	0.559	0.645	0.642	0.678	0.665	0.676	0.687	0.692	0.675
353	0.485	0.510	0.529	0.557	0.587	0.596	0.614	0.650	0.639	0.646	0.631
363	0.452	0.445	0.466	0.495	0.502	0.514	0.534	0.575	0.590	0.575	0.561
373	0.383	0.411	0.401	0.432	0.442	0.457	0.479	0.496	0.514	0.501	0.489
383	0.312	0.343	0.368	0.366	0.381	0.399	0.393	0.413	0.434	0.423	0.438
393	0.276	0.307	0.300	0.333	0.317	0.338	0.334	0.356	0.350	0.369	0.386

Table 3 — Variation of extinction coefficient (K) with temperature

Film composition → Temperature (K)↓	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
293	0.367	0.380	0.382	0.380	0.375	0.366	0.369	0.363	0.373	0.365	0.365
303	0.348	0.363	0.365	0.372	0.359	0.358	0.362	0.363	0.358	0.358	0.359
313	0.328	0.344	0.347	0.354	0.350	0.341	0.346	0.348	0.351	0.344	0.352
323	0.294	0.313	0.317	0.336	0.332	0.333	0.338	0.332	0.335	0.336	0.345
333	0.270	0.279	0.284	0.326	0.323	0.315	0.320	0.323	0.327	0.329	0.330
343	0.244	0.254	0.261	0.295	0.294	0.296	0.302	0.306	0.310	0.312	0.306
353	0.230	0.240	0.248	0.260	0.272	0.275	0.282	0.297	0.292	0.295	0.290
363	0.215	0.212	0.222	0.234	0.237	0.242	0.250	0.267	0.273	0.267	0.261
373	0.185	0.198	0.193	0.207	0.211	0.218	0.227	0.234	0.242	0.236	0.231
383	0.153	0.167	0.178	0.177	0.184	0.192	0.190	0.199	0.208	0.203	0.210
393	0.135	0.150	0.147	0.162	0.155	0.165	0.162	0.173	0.170	0.179	0.187

Both these parameters have same type of variation, i.e. as the temperature increases, the value of these parameters decrease.

4 Conclusions

On the basis of the present observations, it is concluded that dielectric and conductivity parameters of PVP, PAM and their blend films showed temperature dependent as well as PVP/PAM ratio dependent behaviour. At microwave frequency, the temperature dependence of ϵ_r is insignificant. The presence of PVP in the blend enhances the values of ϵ_r , ϵ_i , σ_{ac} and η in the temperature range under investigation. Thus, by selecting a proper ratio of PVP and PAM in the blend, one can make a blend or blend film of desired values of these parameters. The temperature dependence of ϵ_i , σ_{ac} , K , $\tan\delta$, τ and η have been determined in the temperature range 293-393 K and all these parameters are found to decrease with the increase of temperature.

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