

Dielectric Relaxation Spectroscopy and AC Conductivity of Doped Poly (Vinyl Alcohol)

T. Fahmy^{1,2} and M. T. Ahmed²

*¹Physics Dept., College of Science and Humanitarian Studies,
Prince Sattam bin Abdulaziz Uni., 11942 Alkharj, Kingdom of Saudi Arabia.*

*²Polymer Research Group, Physics Dept.,
Faculty of Science, Mansoura Uni., 35516 Mansoura, Egypt.*

Abstract

The dielectric properties and AC conductivity of pure and doped PVA samples with different concentrations of CuCl₂ and Thiourea are investigated in the frequency range from 0.2 Hz to 100 kHz within a temperature range from room temperature to 433 °K. It is observed that the dielectric constant decreases with an increase of frequency for all samples. The behaviour of the dielectric loss (ϵ'') as a function of temperature at certain frequency revealed that, pure PVA sample is characterized by existence of two different relaxation process and doped PVA samples are characterized by a broad relaxation peak. The conductivity of pure and doped PVA samples is investigated at different temperatures. The values of the exponent n , suggest that the hopping mechanism dominates at lower temperature (from room temperature to nearly glass transition temperature).

1. Introduction

Poly (vinyl alcohol) (PVA) is considered a potential material having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. PVA is water soluble and biodegradable polymer and form high degree complexes with large variety of additives and dopants [1-3]. Due to large range hydrogen bond formation ability of PVA, is used extensively as binder for the synthesis of composite materials [4].

Dielectric properties of heterogeneous polymeric materials play an important role in device applications [5]. From the fundamental point of view, dielectric relaxation spectroscopy has been widely used to realize the microscopic dynamical relaxation process in complicated systems. Dielectric relaxation spectroscopy (DRS)

measures the dielectric permittivity as a function of frequency and temperature and provides information on molecular dynamics and free charge carriers. Thus, dielectric spectroscopy is a powerful tool for the electrical characterization of different materials in relation to their structure [6-10]. The advantage of DRS, as compared to other techniques for studying molecular dynamics of the materials, is the broad frequency range. This broad frequency range allows to measure on the same sample processes with very different characteristic (relaxation) times and, correspondingly, different characteristic length scales.

The present work deals with investigation of dielectric behaviour and conductivity of PVA complexed with thiourea salt and copper chloride over the frequency range from 0.5 Hz to 100 kHz at different temperatures.

2. Experimental work

Materials

The atactic Poly (vinyl alcohol) (PVA) used in this study is a commercial product, purchased from Merck, (Germany), with molecular weight equals to 72, 000, Copper Chloride (CuCl_2) are supplied by BDH Chemicals LTD, Poole, (England) and Thiourea salt after recrystallization, $M_w = 76.12$, (El-Nasr Co., Egypt).

Sample Preparation

Doped PVA samples with different ratio from Copper Chloride and Thiourea are prepared by dissolving them in distilled water at $T = 343 \text{ }^\circ\text{K}$ for about 10 hours. The solution is continuously stirred by means of a magnetic stirrer for about one hour to ensure homogeneous mixture. To prepare the samples for electrical measurements, the mixture is then cast onto a glass substrate in an oven at $T = 418 \text{ }^\circ\text{K}$ for several days. The thickness of the samples ranged from 40 to 60 μm , and is determined using a digital micrometer (Mitutoyo No: 293-521-30, Japan). Carbon paste is used as a conducting electrode (Kontakt Chemie, Germany).

Measurements are carried out on a pure PVA and PVA doped CuCl_2 at different concentrations (0.5 wt%, 5 wt% and 20 wt%) and PVA doped with different concentrations of (0.7 wt% and 40 wt%).

Measuring Techniques

Dielectric permittivity is measured using a phase detector technique (lock-in-amplifier Stanford-type SR 830 research system). The measurements are carried out in the frequency range from 0.2 Hz to 100 kHz under a controlled temperature (model 89000, Digi Sence, Cole-Parmer, USA) that varied from 300 to 400 $^\circ\text{K}$. All measurements are carried out under a vacuum (10^{-3} Torr) to avoid humidity effects. A suitable standard resistance is used to prevent stray capacitance effect.

3. Results and Discussions

Dielectric relaxation spectroscopy

The dielectric behavior of a material is usually described in terms of the dielectric function, $\epsilon^* = \epsilon' + i\epsilon''$, where, ϵ' is the dielectric constant and ϵ'' is the dielectric loss. Dielectric measurements, such as the dielectric constant and the dielectric loss, reveal significant information about the chemical and the physical states of polymers. These properties are drastically affected by the presence of another polymer or dopant in the polymer [11–13].

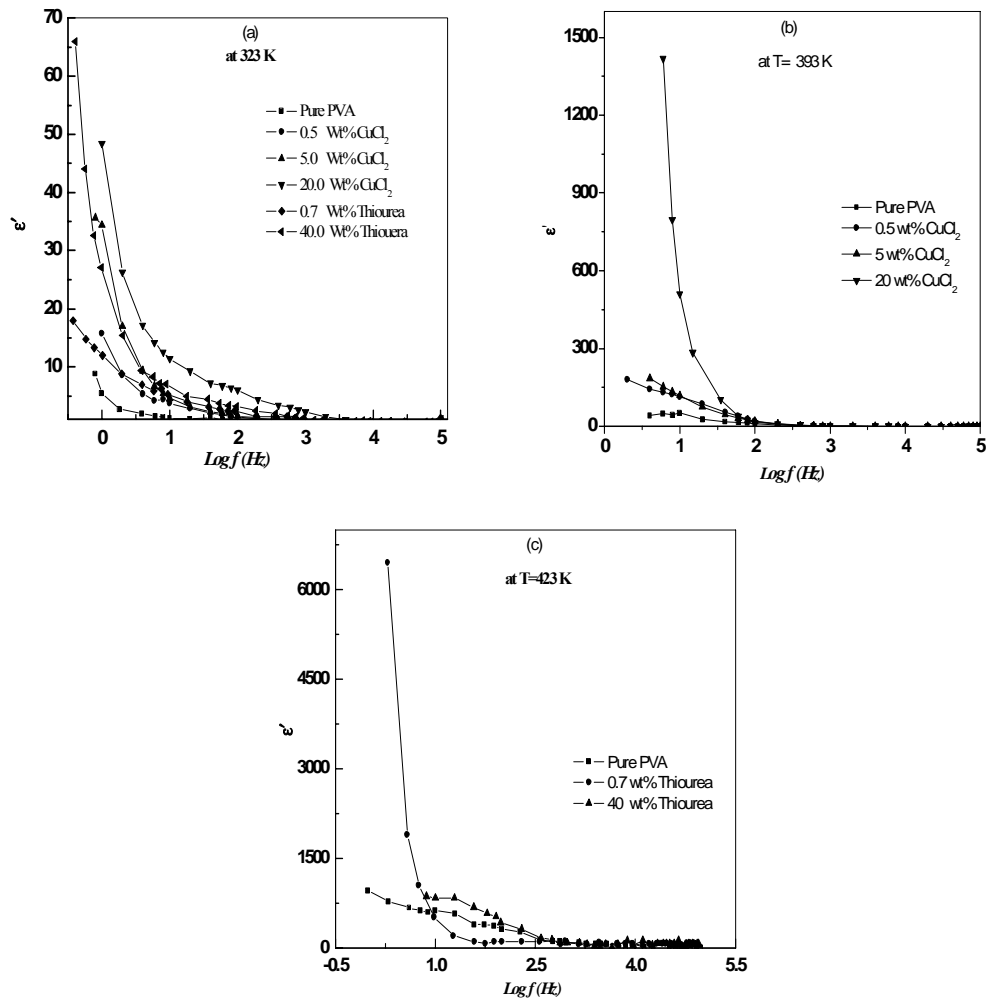


Fig. 1(a-c): Dielectric permittivity (ϵ') as a function of frequency measured for all samples at (a) $T= 323$ K, (b) CuCl_2 doped PVA at 393 K and (c) Thiourea doped PVA at 423 K.

Figure 1 shows the dielectric constant as a function of frequency at different temperature for pure PVA, and PVA doped with different concentrations of CuCl_2 and Thiourea. Generally, it is observed that at low temperatures, the permittivity (ϵ')

value decreases monotonically with increasing frequency and attains a constant value at high frequencies. This behavior is typical of polar dielectrics/polymers because dipole orientation is facilitated by increasing the temperature, thus increasing the permittivity. [14]. Moreover, a dielectric dispersion is clear especially at low temperatures. In addition, this dispersion is found to be temperature and doping ratio dependent, i.e., by increasing temperature and doping, there is a shift of this dispersion to higher frequency for all samples.

The high values of (ϵ') at low frequency and high temperatures may be attributed to free charge building up at the interfaces within the bulk of the sample (interfacial or Maxwell-Wagner-Sillars (MWS) polarization) and at the interface between the sample and the electrodes (space-charge polarization) [15-19]. Naturally a semicrystalline polymer contains two phases. The amorphous phase will give rise to higher nobilities than the crystalline phase. If the amorphous phase contains sufficiently large number of conducting species, interfacial polarization results in. It is generally manifest by the presence of a large loss peak. The phenomenon is due to the presence of two phases, one of much higher conductivity than the other. Hence, contribution of interfacial MWS polarization may be due to the inhomogeneous nature of the samples (PVA and dopant materials) [20]. For very low frequencies there is sufficient time for the charges to move over macroscopic distances and to build up at the interfaces between the sample and the electrodes within half cycle at the applied AC field. This effect results in very high values of the effective dielectric permittivity (ϵ'), i.e., space charge polarization, macropolarization of ions in a finite dielectric layer [15, 21].

At higher frequencies there is practically no time for buildup of the charges at the sample-electrode interfaces, but only for the transport of the charges over microscopic dimensions and their buildup at the boundaries of conducting species in the material (MWS) polarization. At even higher frequencies the charges cannot follow the changes in the electric field and only bulk polarization mechanisms characteristic of the molecular structure (α and β process) contribute to the electric polarization and thus to (ϵ') [22].

In addition, it is observed that, the highly thiourea doped sample is characterized by very high dielectric constant value. This value could be attributed to the presence of semiconducting grains (thiourea) dispersed in insulating grain boundaries (polymer matrix). This gives rise to barriers at grain – grain boundary interfaces, which impart a very high value of dielectric constant to the resulting polymer complex. This forms the basis of manufacturing barrier layer capacitors [23, 24].

On the other hand, the dielectric loss (ϵ'') for pure PVA sample at different frequencies, against temperature at fixed frequencies is characterized by existence of two dispersion regions at 338 K and 367 °K, as shown in Figure (2). This behaviour is similar to that shown by several glass forming liquids [25], which have a cooperative process at the glass transition and secondary relaxations at lower temperatures in the glass transition. In this mechanism it is envisaged that a dipole may reorientate only with the cooperation of a large region of surrounding molecules. This type of process, which may be observed for amorphous polymers and simple molecular glasses,

generally occurs peak at or slightly above the glass transition temperature, T_g . The occurrence of the peak at 339°K can be attributed to the decrease in the degree of ordering of the polymer molecules due to chaotic thermal vibrations. The peak or shoulder at $T \sim 368\text{ K}$ can be associated with the phase change of PVA near the glass transition temperature, ($T_g \sim 363\text{ K}$).

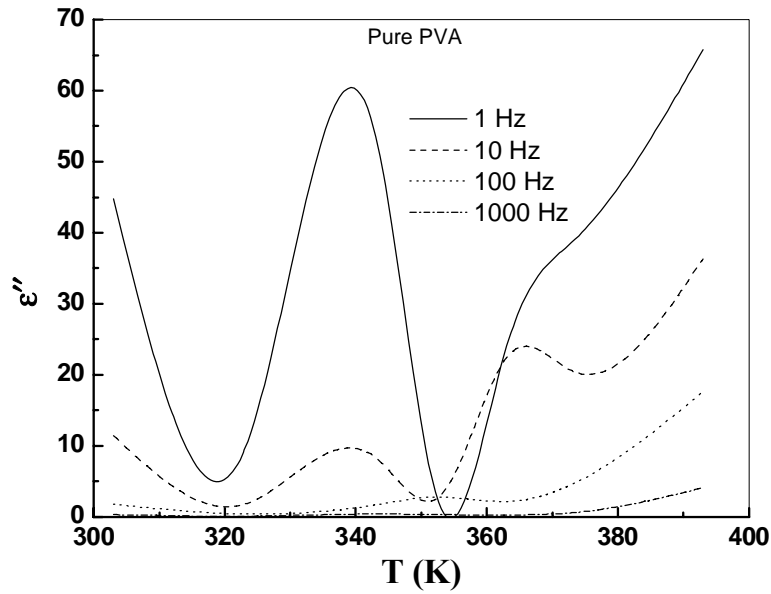


Fig. 2: Temperature behavior of the imaginary part of the dielectric constant (ϵ'') for pure PVA sample at different frequencies.

The dielectric loss tangent $\tan \delta$ can be expressed as a function of the relaxation time τ and the frequency f , i.e., $\tan \delta = f(\tau, f)$, where the change in temperature affects the relaxation time as follows:

$$\tau = \tau_0 \exp \left(\frac{E_a}{k_B T} \right) \quad (1)$$

Where E_a is the activation energy of the relaxation process and $\tau = 1/2\pi f_{\max}$, where f_{\max} is the maximum frequency.

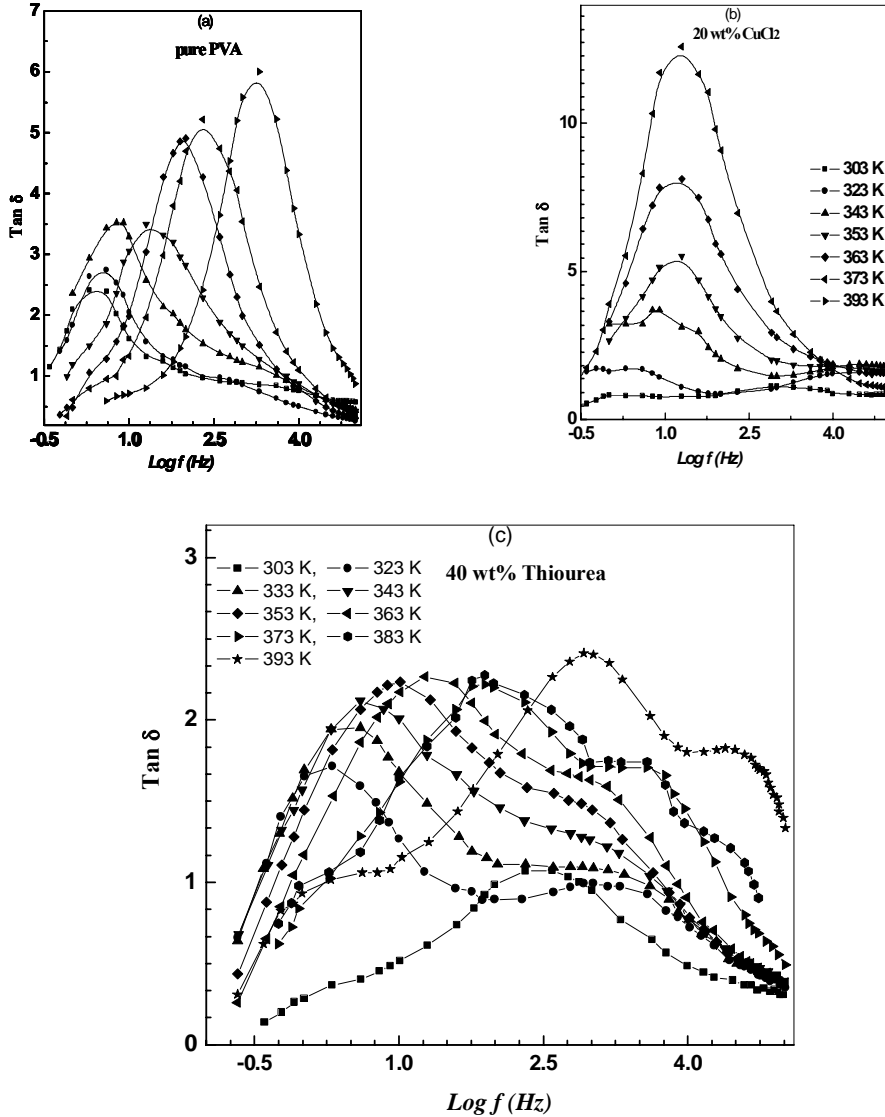


Figure 5(a-c). Fig. 3: Tangent dielectric loss ($\tan \delta$) as a function of frequency measured for, (a) pure PVA, (b) PVA doped CuCl_2 20wt% and (c) PVA doped thiourea 40 wt%.

Figure 3 displays the dielectric loss tangent of pure PVA and PVA doped samples with thiourea and CuCl_2 as a function of frequency at different temperatures. This spectrum is characterized by a relaxation peak. The shift of this relaxation peak is a consequence of the higher mobility at high temperatures and increasing of the peak amplitude is associated with an increase in the number of relaxed dipoles. Above T_g , there is a contribution of the movements of the main chain to the relaxation process, i.e., α -relaxation, and there is a narrowing of the loss curves [26]. Hence, owing to the cooperative motion, the peak height of $\tan \delta$ above T_g is much larger

than that below T_g [27]. The cooperative nature of the segmental relaxations characterizes the α -relaxation. When polymer molecules are in a crowded environment, the motion of a segment is interfered due to the presence of its neighbor. Dissipation of energetic input, typically through a rotation of the segmental bond from one stable state to another, is then possible only through the cooperation of the neighbors. Such cooperation covers in the form of a simultaneous relaxation. The broadness of relaxation peak in highly doped PVA-Thiourea sample, is associated to the relaxation time distribution for the main chain motion. The relatively low doped thiourea samples have similar spectra (figure not shown). The marked broadening of loss curves at low temperatures suggests that the motions are more complex and possibly correspond to two components. The first is a high frequency component involving the motions of the side groups of the polymer together with the local motion of the salt molecules, i.e., β -relaxation [28]. These processes do not relax all the mean square dipole moments of these dipolar units, so the remainder are relaxed by a second, low frequency process whose mechanism will resemble that for α - process of other amorphous polymers such as poly (vinyl acetate) and poly (ethylene terephthalate) [29]. Moreover, in semicrystalline polymers, the loss curves due to the micro-Brownian motion of chain molecules in an amorphous phase show a remarkable broadening as the temperature is reduced to the vicinity of glass transition, T_g , as shown in Figure 3c. Moreover, on doping, a shift in the peak position has been observed. This shift could be attributed to hindering of the internal rotation of the side groups by hydrogen bonding [28].

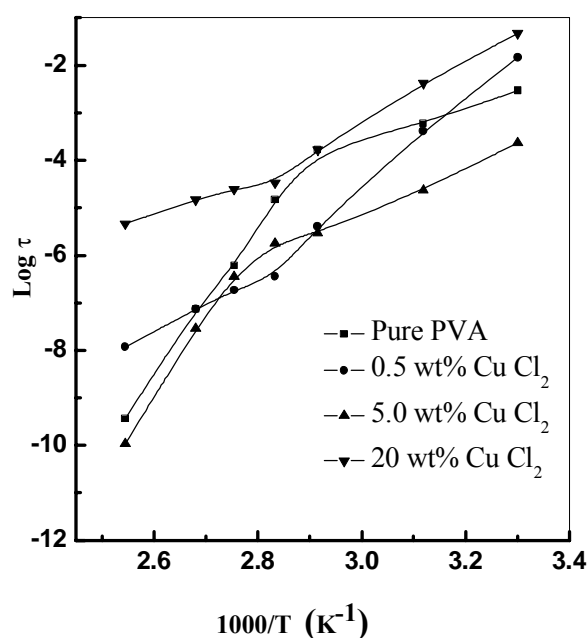


Fig. 4: Arrhenius plot of pure PVA and doped samples.

The value of the characteristic relaxation time τ of all samples can be calculated from the figures (3a-c), where determined from the peak frequency (f_m) at the maximum loss at different temperatures (the maximum of the loss peaks), $\omega\tau=1$, where $\omega=2\pi f_m$ is the angular frequency. Figure 4 shows the variation of $\log \tau$ versus reciprocal of temperature for pure and doped PVA with CuCl_2 samples (as a representative curve). The behavior is found to be that of two straight line regions, one beyond T_g , while the second above T_g . The activation energy (E_a) is calculated from the slope of these lines and found to be 0.12, 0.28, 0.18 and 0.13 eV beyond T_g and 0.46, 0.41, 0.56 and 0.25 eV above T_g for pure PVA, and CuCl_2 doped samples (0.5, 5 and 20 wt% respectively). On the other hand, as the Thiourea concentration increased, the activation energy increased. The values of activation energies are 1.37 and 1.57 eV for PVA low and high doped samples, respectively.

AC Conductivity:

AC conductivity (σ_{ac}) has been examined as a function of frequency at different temperature for pure PVA and PVA doped samples with different concentrations of CuCl_2 and thiourea salts, in a wide range of frequency from 1 Hz to 100 kHz, as shown in Fig. 5.

Generally, the number of charge carriers, which have high relaxation time due to higher energy barrier and respond in low frequency regime, might be less in number, hence the conductivity is lower at lower frequencies. However, the number of charge carriers with low barrier heights is bigger and they respond easily with high frequency and showed higher conductivity at higher frequencies. As can be seen, firstly for pure PVA, at low temperatures the AC conductivity increases with frequency, whereas at temperatures higher than about $T=393$ °K, a plateau is observed, namely σ is approximately independent of frequency in a frequency region which extends to higher frequencies with increasing temperature. However, higher concentration of salts and its distribution throughout the polymer matrix will change the local electric field and, therefore, the electrical properties as shown in Fig. 5a-c [30]. Hence, the plateau region has disappeared for highly doped PVA samples. On the other hand, the characteristic feature of conductivity spectra can be explained using Jonscher's power law [31];

$$\sigma = \sigma_0 + A\omega^n \quad (0 < n < 1) \quad (2)$$

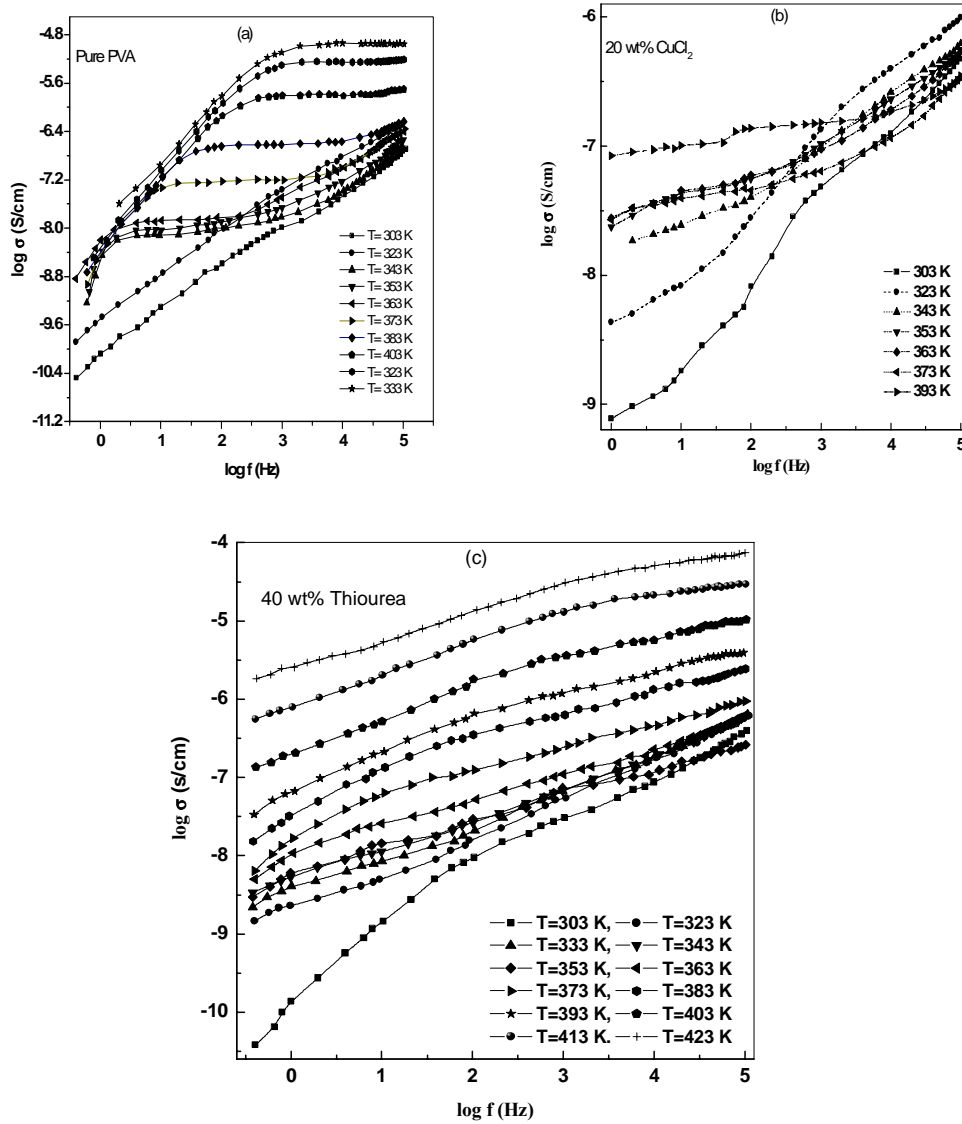


Fig. 5(a-c): Plots of ($\log \sigma$) versus ($\log f$) at different temperature for pure and doped PVA samples.

where σ is the real part of AC conductivity, σ_0 in most cases is found to be temperature dependent only, while in this case it depends on both temperature and frequency, A is a temperature dependent preexponential factor and n is the power law exponent. The exponent n represents the degree of interaction between mobile ions and lattices. The factor A determines the strength of the polarizability of the sample. The conductivity of all samples apparently enhanced with increasing temperature. This can be easily understood based on the segmental chain motion of polymer composites. When the temperature is increased, mobility of polymer chains is enhanced, and the fraction of free volume in polymer composite increases

accordingly, which leads to an increase in the conductivity of the pure polymer. The frequency independent behavior of the conductivity in the low frequency region is observed, particularly, for pure PVA. This plateau region is shifted towards high frequency side with increasing temperature. The high-frequency conductivity dispersion may be attributed to AC conductivity whereas the frequency independent plateau region of the conductivity pattern corresponds to the dc conductivity (σ_{dc}) of the sample [32]. The same frequency and temperature dependence of conductivity is also found in other amorphous solids having a thermally activated hopping conduction [33, 34].

Many publications in the polymer field have presented results qualitatively similar to such behavior, where electronic and/or ionic hopping models were taken into account [35, 36]. It was observed that, the Eq. 2 can't fit the overall behavior of conductivity in the full range of frequency. The values of the exponent (n) has been estimated and summarized in Table 1.

Table 1a: Parameters of dielectric relaxation of all CuCl_2 doped samples.

T (K)	Pure PVA		0.5 wt%		5 wt%		20 wt%	
	N	W_m	N	W_m	n	W_m	n	W_m
303	0.64	0.44	0.67	0.47	0.48	0.30	0.52	0.33
323	0.61	0.43	0.70	0.56	0.49	0.33	0.39	0.27
343	0.53	0.38	0.59	0.43	0.72	0.63	0.38	0.29
353	0.57	0.42	0.66	0.54	0.43	0.32	0.36	0.29
363	0.50	0.38	0.64	0.52	0.42	0.32	0.40	0.31
373	0.42	0.33	0.55	0.43	0.33	0.29	0.54	0.42
393	0.24	0.27	0.23	0.26	0.08	0.22	0.31	0.29

Table 1b: Parameters of dielectric relaxation for Thiourea doped samples

T(K)	0.7 wt%		40 wt%	
	N	W_m	n	W_m
303	0.55	0.34	0.55	0.33
323	0.52	0.55	0.48	0.32
333	0.51	0.35	0.47	0.33
343	0.53	0.38	0.46	0.33
353	0.45	0.33	0.43	0.32
363	0.43	0.33	0.36	0.29
373	0.41	0.33	0.30	0.37
383	0.23	0.25	0.27	0.27
393	0.07	0.22	0.27	0.28
403	0.05	0.22	0.23	0.27
413	0.04	0.22	0.17	0.26
423	0.04	0.23	0.15	0.25

It can be noticed that, n value decreases slightly at low temperatures and sharply at high temperatures. The variation in the exponent n reflects the change in the nature of the conduction process with change in temperature and composition. It is observed that, values of n in the region from room temperature to 358 °K points to Jonscher's "universal dielectric response" in the regime of hopping localized charge carriers [33].

Values of n less unity are associated with charge carriers or with extrinsic dipoles arising from the presence of defects and impurities in the sample [34]. With the increase of temperature, the interaction between the dipoles decreases leading to decrease of n . Hence, the above equation corresponds to the short range hopping conduction of charge carriers. The hopping takes place by charge carriers through trap sites separated by energy barriers of varied heights. At higher temperatures, the thermal energy of the charge carriers is increased and consequently, the relative potential barrier height is also reduced. At low temperatures, the electronic hopping conduction dominates the conductivity and the ionic hopping makes little contribution. Moreover, n values are predicted to have temperature dependence and the magnitude of n at any temperature is determined by the binding energy (W_m) of the charge carrier as follow: [37, 38].

$$W_m = \frac{6k_B T}{1-n}$$

where k_B is Boltzmann's constant and W_m is the energy difference between the ground state of the potential well and the ionized state (i.e., the charge carrier localized state). The values of W_m of all parameters characterizing the samples are estimated and summarized in Table (1).

The variation of the real part of the conductivity against the inverse of temperature ($1/T$) of pure and doped PVA samples is plotted according to Arrhenius equation as follow:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

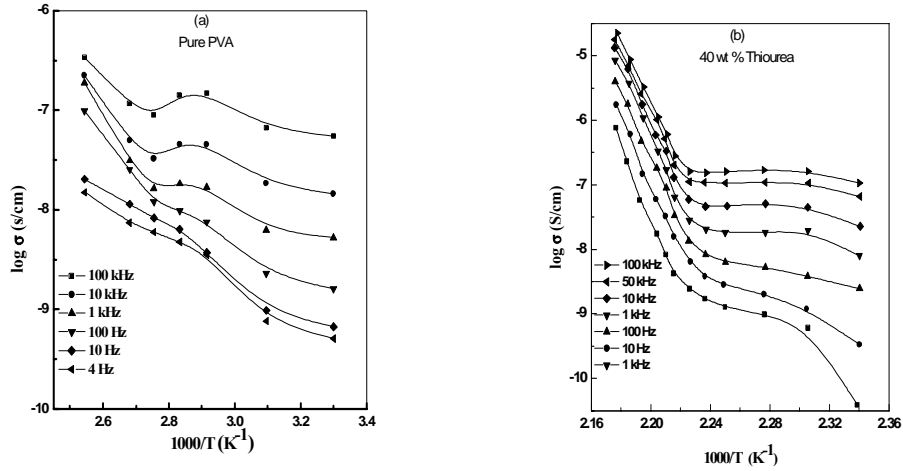


Fig. 6: Plots of $\log \sigma$ versus $1000/T$ for pure and PVA sample at different frequencies.

Hence, one can observe that, two conductivity regions are presented, as shown in Fig. 6 as a representative one. At low temperatures the thermal activation of the conductivity is almost negligible, but shows a strong dependence on frequency. After increasing the temperature above a critical value the conductivity increases strongly and the effect of the frequency on the conductivity becomes negligible at high temperatures. The activation energy values have been determined and listed in Table 2.

Table 2a: The values of activation energies for PVA and PVA doped CuCl_2 and thiourea at different frequencies.

			E_a (eV)			
f (Hz)	Pure PVA	0.5 wt% CuCl_2	5.0 wt% CuCl_2	20.0 wt% CuCl_2	0.7 wt% Thiourea	40.0 wt% Thiourea
100 kHz	0.07	--	0.35		0.47	0.34
10 kHz	0.16	0.40	0.48	--	0.51	0.48
1 kHz	0.37	0.36	0.44	--	0.51	0.53
100 Hz	0.44	0.47	0.42	--	0.26	0.54
10 Hz	0.35	0.25	0.36	0.15	0.06	0.54
4 Hz	0.24	0.05	0.34	0.25	0.11	0.55

4. Conclusion

The dielectric properties of pure and doped PVA samples with different concentrations of CuCl_2 and Thiourea are investigated in the frequency range from 0.2 Hz to 100 kHz within a temperature range from room temperature to 433 $^{\circ}\text{K}$. The experimental data were presented in isothermal and isochronal plots to stress special

aspects of the dielectric behavior. It is found that the dielectric constant decreases with an increase of frequency for all samples. This agrees with the Maxwell-Wagner double layer model. The behaviour of the dielectric loss (ϵ'') as a function of temperature at certain frequency revealed that, pure PVA sample is characterized by existence of two different relaxation process. The conductivity of pure and doped PVA samples is investigated at different temperatures. The values of the exponent n , suggest that the hopping mechanism dominates at lower temperature (from room temperature to nearly glass transition temperature). The Arrhenius plot of conductivity suggested that there is a change in the conductivity mechanism around the glass transition region.

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References:

- [1] V. Kuncser, G. Filoti, R. Podgorsek, M. Biebricher, H. Franke, *J. Phys. D: Appl. Phys.* 31, 2315 (1998).
- [2] T. Fahmy, *Intern. J. Polymeric Mater*, 50, 109 (2001).
- [3] R. J. Sengawa and K. Kaur, *Ind. J. Eng. Mater. Sci.* 10, 492(2003),
- [4] K. A. Abdelkader and Z. Anwar, *J. Appl. Polym. Sci.*, 2, 163(2006).
- [5] C. V. S. Reddy, X. Han, Q-Y. Zhu, L.Q. Mai and W. Chen, *Microelectronics Eng.*, 83, 281 (2006).
- [6] T. Fahmy, *Polym. Plast. Tech. & Eng.*, 46, 7 (2007).
- [7] S. Mahendia, A. K. Tomar, S. Kumar, *J. Alloys and Compounds*, 508, 406 (2010).
- [8] T. Fahmy and M. T. Ahmed, *J. Korean Phys. Soc.*, 58, 1654 (2011).
- [9] E. Sheha, H. Khode, T. S. Shanap, M. G. El-shaaray and M. K. Elmansy, *Optik*, 123, 1161 (2012).
- [10] S. Sugumaran, C. S. Bellan, *Optik, Inter. J. Light and Electron Optics*, 125, 5128(2014).
- [11] M. M. Mosad, *J. Mater. Sci. Lett.* 9, 32 (1990).
- [12] H. Saito and B. Stuhn, *Polymer* 35, 475 (1994).
- [13] T. Fahmy and M. T. Ahmed, *J. Polym. Mater.*, 20, 367 (2003)
- [14] V. M. Mohan, W. Qiu, J. Shen, and W. Chen, *J Polym. Res.* 17, 143 (2010).
- [15] P. Hedvig, "Dielectric Spectroscopy in Polymers", Bristol: Adam Huger, (1977).
- [16] R. M. Silverstein and F. X. Webster, "Spectrometric Identification of Organic Compounds", 6th Ed., John Wiley & sons Inc., p. 106 (1998).
- [17] D. Moroso, A. Cella and E. Peccatori, *Chem. Ind.*, 25, 1897 (1987).

- [18] C. N. R. Rao, "Ultra-Violet and Visible Spectroscopy" 3rd Ed., Butterworth & Co Publishers, Ltd, p. 29. (1975).
- [19] Y. Kihira, and H. Yamamura, *J. Polym. Sci. B*, 24, 867 (1986).
- [20] E. Tuncer, and S. T. Gubanski, *J. Phys. Condens. Matt.*, 12, 1873 (2000).
- [21] A. Kyritsis, P. Pissis and J. Grammatikakis, *J. Polym. Sci. Polym. Phys. Ed.*, 33, 1737 (1995).
- [22] B. Neagu, P. Pissis, L. Apekis, and J. L. Ribelles, *J. Phys. D: Appl. Phys.*, 30, 1551 (1997).
- [23] N. Yamaoha, *Am. Ceram. Soc. Bull.*, 65, 1149 (1986).
- [24] O. Parkash, D. Kumar and C. D. Prasad *J. Phys. D: Appl. Phys.*, 27, 1509, (1994).
- [25] M. S. Ahmed, J.J. Crossley, M. S. Chao and S. Walker, *J. Chem. Soc. Faraday, Trans. 80*, 1047 (1984).
- [26] M. S. Dionisio, J. J. Moura Ramos and G. Williams, *Polym. Int.*, 32, 145(1993).
- [27] M. S. Dionisio, J. J. Moura Ramos and G. Williams, *Polym.* 34, 4105, (1993).
- [28] M. S. Dionisio, J. J. Moura Ramos and G. Williams, *Polym*, 35, 1705 (1994).
- [29] A. Kyritsis, P. Pissis, and J. Grammatikakis, *J. Polym. Sci. Polym. Phys. Ed.*, 33, 1737 (1995).
- [30] M. D Migahed, T. Fahmy and S. Roth, "Science and Technology of Polymers and Advanced Materials", (Ed) Parasad, P. N. (Plenum Pub. Corporation, NY) p. 411 (1998).
- [31] A. K. Jonscher, "The universal dielectric response", *Nature*, 267, 673 (1977)
- [32] V. Senthil, T. Badapanda, S. N. Kumar, P. Kumar and S. Panigrahi, *J Polym. Res.* 19, 9838 (2012).
- [33] L. Paquin, H. St-Onge and M. R. Wertheimer, *IEEE Transaction on Electrical Insulation*, EI-17, 399 (1982).
- [34] P. Venkateswarlu, A. Laha and S.B Krupanidhi, *Thin solid films*, 474, 1 (2004).
- [35] S. Kivelson, *Phys. Rev. Lett.*, 46, 1344 (1981).
- [36] A. J. Epstein, H. Rommelmann, M. Abkowitz, and H. W. Gibson, *Phys. Rev. Lett.*, 47, 1549 (1981).
- [37] G. E. Pike, *Phys. Rev. B*, 6, 1592 (1972).
- [38] W. H. Jung, *J. Phys. D: Appl. Phys.*, 33, 444 (2000).