# Studying The Electrical and Dielectric properties of PVA-Ag /coumarin dye Nanocomposites

M. A. Attallah, T.Y. Elrasasi, N. M. Shash, M. G. El-Shaarawy Physics Department, Faculty of Science, Benha University, Benha, Egypt

### Abstract

PVA-Ag / coumarin nanocomposites with different concentrations of coumarin have been prepared and characterized. The reliance of dc conductivity on temperature has been studied in the temperature range 303 - 393 K. The ac conductivity and dielectric properties of the nanocomposites, have been studied in the frequency range 100 Hz - 10 MHz and temperature range 303 - 393 K. The results depicted that electrical conductivity increased by raising coumarin concentration. The activation energy has decreased as the content of coumarin increases up to 12 wt. %, then it increases as coumarin content increases. The ion transport number t ion of the prepared samples have been calculated by Wagner's dc polarization method. It can be observed that the ion transport number t ion lies in the range 0.7 < t ion < 0.91 which implies that conduction in the samples is ionic. The study of frequency dependence of both dielectric constant and dielectric loss showed a decrease with increasing the frequency while they increase with increasing the temperature. The loss tangent (tanδ) depicted a peak with the frequency, which points to a dielectric relaxation in these nanocomposites with relaxation time decrease with temperature.

# **Keywords**

Dc conductivity, Ac conductivity, Dielectric constant, IV characteristic, Wagner's polarzation

## 1. Introduction

The new high-performance materials from polymer-metal/dye nanocomposites with owns unique characteristics such as flexibility, economically, lightweight and high performance are one of the main focal points of research because of its applications in microelectronic, optical integrated circuits, automobiles, drug delivery, sensors, injection-molded products, membranes, packaging materials, aerospace, coatings, adhesives, fire-retardants and medical devices [1-9].

Among all polymers, polyvinylalcohol (PVA) has been attracted considerable research attention thanks to its unrivaled properties, easy preparation, durability, raises, chemical resistance, thermostability, high mechanical properties, and electrical properties. Besides, PVA was used as a stabilizing agent in Ag nanoparticle [10-12].

Different additives are usually added to the polymer to modify and improve their properties [13-17]. Inorganic additives such as transition metal have a considerable effect on the electrical and dielectric properties of PVA polymer. Few researchers reported the enhancement of the electrical properties of this polymer by adding Ag [18- 20].

Coumarin dye composed of two rings linked with each other. These rings are a lactone and benzene. These two rings have a double bond structure or conjugated  $\pi$ -system. It is worth to mention, this conjugated  $\pi$ -system facilitates the electron exchanges between PVA and coumarin. The electronic features of coumarin have been investigated broadly and realized that it raises the time of reaction as well as decreases the resistivity in general therefore from among all dyes has attracted great interest. [21-25].

This study aims to synthesize, stabilize PVA-Ag /coumarin nanocomposites without employing conventional reducing agents by casting method and enhance both electric and dielectric properties.

# 2. Materials and method

## 2.1 Materials

Polyvinylalcohol  $[CH_2CH(OH)]_n$  (99.8% purity), silver nitrate AgNO<sub>3</sub> (99.8% purity) and coumarin (C<sub>9</sub>H<sub>5</sub>O<sub>2</sub>) were brought from the Alfa Aesar Chemicals.

## 2.2 Preparation

PVA-Ag/coumarin nanocomposite films were prepared by in situ chemical reduction approaches under a hot condition supported by a solution casting techniques as following: a solution of PVA was prepared by solving 3 gm of PVA in 100 ml deionized water with continual stirring at 70 °C for 2 hours even the mixture was fully solved. Then, freshly AgNO<sub>3</sub> solution prepared by dissolving 0.3 gm/30 ml deionized water with continuous stirring for 20 minutes at room temperature was added to the PVA solution under a hot condition (60-70 °C) and the reaction was kept for 1 hour to reduce the silver nitrate to silver nanoparticles by the (-OH group) in PVA Finally, the coumarin dye solution was prepared by dissolving 0.8 gm/400 ml deionized water with continuous stirring for 1 hour at room temperature. Different amount of coumarin dye was added with (0, 4, 8, 12, 16, 30) wt. %. The mixture was let about 24 hours at room temperature to verify a homogenous and air bubble-free. Finally, the solution is purely spilled into a petri-dish and evaporate for 6 days at 40 °C.

## 2.3 Measurements

Crystal structures of prepared nanocomposites have been examined by X-ray diffraction( XRD) X-ray- D/Max 2200 V- Rigaku- Japan at room temperature with CuK<sub>a</sub> ( $\lambda = 0.15406$  nm). TGA studied are carried out using radiation SDT Q600 V20.9 Build 20 from room temperature and up to 600 °C with heating rate 10 °C /min. To study the dc electric conductivity, samples with a diameter of (1 cm) and thickness of (0.01 cm) were taken and the silver paste was deposited on both the film surfaces to ensure good electrical contacts. Samples covered with silver paste were sandwiched between the two similar brass electrodes of a spring-loaded sample holder. The entire assembly was placed in a furnace monitored by a temperature controller, the heating rate was adjusted to be 1 °C /min. The dc electrical conductivity was studied in the temperature range 293-393 K. Dielectric and ac electrical measurements were studied in the temperature range 303– 393 K and frequency range of 100 Hz–10 MHz using Gw Instek LCR –B110G. To calculate the ion transport number t ion of the prepared samples Wagner's dc polarization technique has been measured. Where the samples between two stainless electrodes were subjected to dc voltage and the current was measured as a function of time.

#### 3. Results and discussions

#### 3.1. Structure Characterization

The XRD pattern of PVA-Ag/coumarin nanocomposites is depicted in Fig. 1. It can be seen the main peak at  $2\theta = 19.9^{\circ}$  for all the samples, which represents the crystalline peak of the semi-crystalline PVA polymer [26]. The peak intensity is decreased by increasing the content of the coumarin dye referring to the decreasing in the crystalline of the nanocomposite films. Also, a clear peak was observed at  $2\theta = 9.8^{\circ}$ , this peak neither belongs to AgNO<sub>3</sub> nor pure PVA crystalline spectra, but it possibly arises from scattering the atomic plane of some crystalline patterns PVA - Ag<sup>+</sup> complex [27]. The intensity of this peak decreases with increasing the coumarin content,

which reveals a strong interaction occurring between the PVA - Ag nanocomposite and the coumarin dye. This means that the coumarin dye has a strong effect on controlling the reaction, i.e the coumarin may accelerate the reaction between PVA and Ag. XRD showed also one another peak in all the samples at  $2\theta$ = 32.1° characterized for (111) of the FCC structure of silver with interplanar spacing 0.279 nm [28-32].



Fig. 1. XRD of PVA-Ag / coumarin nanocomposites.

TGA of PVA-Ag/coumarin nanocomposites with concentrations (16 and 30 wt% coumarin) as representative samples are depicted in Fig.2. It can be depicted that there are four evident regions in the temperature range  $47^{\circ}$ C – 540 °C. The sample 16 wt.% coumarin is thermally stable even 248 °C while the sample 30 wt.% coumarin is thermally stable till 253 °C. Then, the degradation of the material begins at a temperature of 230 °C. The amount of the ultimate product after the decomposition was 8.7% (0.3089 mg) for sample 16wt.% coumarin and 9.451% (0.6178mg) for sample 30 wt.% coumarin. The weight loss noticed at higher temperatures can be attributed to the pyrolysis process. The final product [carbon] is greater in the sample 30 wt.% coumarin than the sample 16 wt.% coumarin and not evaporate in the temperature range from 400 °C to 539 °C. Samples (0,4,8,12) wt.% coumarin have the same behavior.



Fig. 2. TGA of PVA-Ag / coumarin nanocomposite representative samples (16,30) wt.% coumarin.

## 3.2. DC conductivity

The variations of dc conductivity of PVA - Ag /coumarin nanocomposites with different coumarin concentrations as a function of temperatures are depicted in Fig. 3. It is evident that the dc conductivity increase with increasing the temperatures and the coumarin contents for all samples. The dc electrical conductivity is provided by [33]:

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right) \tag{1}$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  the activation energy,  $k_B$  the Boltzmann constant and T is the absolute temperature. The increase in dc conductivity with temperatures may be assigned to the mutations from the semicrystalline/ crystalline phase to the amorphous one. Also, this increase may be due to the mechanism of hopping among coordination sites, relaxation of local structural and polymer segmental motion [34]. The calculated activation energies are given in Table 1. It is noticed that the activation energy has decreased as the content of coumarin increases up to 12 wt. % then it increases as coumarin content increases. This decrease may be due to the amorphous nature of the polymer that facilitates the fast Ag ion motion in the polymer network and the local energy levels in the forbidden energy gap which act as traps for charge carriers. The increase in activation energy as coumarin content increases may be attributed to the polymer chain favors hopping motion than segmental motion.

<b>Table 1</b> . Activation energy $(E_a)$ , mobility $(\mu)$ and the number of charge carriers (N) of PV	VA-
Ag/coumarin nanocomposites.	

Concentration	$E_a$	μ	Ν
( wt. % )	( eV )	$(m^2/volt.sec)$	(m <sup>-3</sup> )
0	0.484	$6.2  imes 10^{-11}$	$2.6  imes 10^{22}$
4	0.345	$8.3 \times 10^{-9}$	$1.7  imes 10^{20}$
8	0.287	$2.2  imes 10^{-7}$	$1.33 \times 10^{19}$
12	0.359	$5 \times 10^{-7}$	$1.3  imes 10^{19}$
16	0.543	$2.8  imes 10^{-6}$	$8.4 imes10^{17}$
30	0.634	$1.7 \times 10^{-3}$	$4.9  imes 10^{15}$



Fig. 3. The temperature dependence of  $\sigma_{dc}$  conductivity, for PVA –Ag/ coumarin nanocomposites.

Fig. 4. shows the  $\sigma_{dc}$  conductivity dependence of coumarin content at room temperature. It can be seen that the dc conductivity increases with increasing the amount of coumarin. This increase may be due to: (a) the coumarin fills up the interstitial sites among the polymer chains in the amorphous phase and joins these chains to some kind of bonds by a charge exchange process among the OH groups of PVA and dopant molecules. (b) The PVA/Ag complex formation, which obstructs the polymeric chain mobility. This complex formation increases with the doping level which may lead to an increase in PVA conductivity. (c) the motion of the carriers which impeded at the crystalline–amorphous interfaces at higher dopant concentrations, the presence of the molecular aggregates generally obstructs tend to preferentially diffuse into the amorphous regions of the polymer. The presence of aggregates in these regions cause a reduction of the crystalline– amorphous interface, which affects the conductive pathways through the amorphous regions. This process of reduction in the interstitial barrier increases the transition probability of electron hopping across the barrier [35].



Fig. 4. Variation of  $\sigma_{dc}$  conductivity with coumarin concentration.

# 3.3 Current-Voltage Characteristics

I-V characteristics of PVA-Ag/coumarin nanocomposites with concentrations (8 and 12 wt% coumarin) as representative samples are depicted in Fig. 5. It was obvious that there are two regions the Ohmic region and the space charge region. Under the effect of the high electric field, the concentration of free charge carriers caused by electrodes is greater than that of thermal-generated charging carriers. So, the Child-Langmuir law is applied and the density of current  $J_s$  is denoted by [36]:

$$J_{s} = \frac{10^{-13} V_{s}^{2} \mu \varepsilon}{b^{3}}$$
(2)

where  $V_s$  is the voltage,  $\mu$  is the charge carriers mobility,  $\boldsymbol{\varepsilon}$  is the permittivity of the sample and b is the thickness of the sample. The electrical conductivity in the Ohmic region is given by,

$$\sigma = N q \mu \tag{3}$$

where N is the concentrations of charge carriers and q is the electron charge. By using equations (2 & 3), the values of N and  $\mu$  can be estimated and tabulated in Table 1. It can be observed that  $\mu$  increases with increasing the concentration of coumarin. This increase in  $\mu$  may be due to that coumarin fill up the free volume holes and occupy the interstitial positions among the polymer chains in the amorphous phase and joins these chains to some kind of bonds by a charge exchange process among the OH groups of PVA and dopant molecules.



**Fig. 5.** Current-voltage characteristic for PVA –Ag/ coumarin nanocomposites representative samples (8, 12) wt.% coumarin.

### 3. 4. AC conductivity

The frequency dependence of the ac conductivity of PVA - Ag /coumarin nanocomposites as a function of temperature is given in Fig. 6. It can be seen that ac conductivity obeys the power law [37]

$$\sigma_{ac}(\omega) = A \,\omega^s \tag{4}$$

where A is the pre-exponential factor,  $\boldsymbol{\omega}$  is the angular frequency and s is the frequency exponent. It is observed that at relatively low frequency the conductivity represents almost frequencyindependent behavior, while a strong dependent appears at the high-frequency range. The increase in  $\sigma_{ac}$  with increasing frequency may be due to the increase of the absorbed energy from the ac applied field which leads to an increase in the number of charge carriers that contribute to the conduction process. The increase in  $\sigma_{ac}$  with increasing coumarin contents may be attributed to the reduction of the crystalline regions in PVA and enhance the amorphous region, here with allowing more charge carriers to share in the conduction which confirmed by XRD. The values of the exponent s have been calculated using the least square fitting for equation (4) at different temperatures for all prepared samples and listed in Table 2. It can be observed that the exponent s lies in the range of 0.6 < s < 0.85, which implies that conduction in the samples is ionic. Also, it can be observed that the values of s go down with increasing the content of coumarin and temperature. There are many theories like classical hopping over a barrier, i.e., correlated barrier hopping (CBH) and quantum tunneling that described the dependence of  $\mathbf{s}$  on temperature [38]. Under the CBH model, the charge carriers jump between the sites above the potential barrier that separates it. The frequency exponent s is provided by the equation [39]

$$\mathbf{s} = \mathbf{6} - \frac{k_B T}{\left(W_h - k_B T ln\left(\frac{1}{\omega \tau_o}\right)\right)} \tag{5}$$

where  $k_B$  is Boltzmann constant,  $W_h$  is the height of the barriers, and  $\tau_o$  is the relaxation time. The conductivity power law nature is a general behavior that originates from the hopping of electron within the trap sites found in the matrix band gap. Also, the extent of the frequency exponent clarifies the magnitude of many body interactions among electrons, impurities, and other charged defects. Since these interactions are strongly based on temperature, the frequency exponent **s** is also temperature dependent. The coumarin dye is known to contain a large number of trap sites needed for the ac conduction. Electrons are enclosed and liberated from these traps

during the hopping process which is known as the (CBH) phenomena. However, in the present case, it is observed that the values of s decrease when coumarin content increases. This may be due to as the temperature and coumarin content increase, the amorphousty and density of traps increase. The values of s depict that the (CBH) model is the most appropriate model to characterize the electrical conduction mechanism for the prepared sample.



**Fig. 6.** The frequency dependence of  $\sigma_{ac}$  conductivity, for PVA –Ag/ coumarin nanocomposites representative sample (30) wt.% coumarin.

Concentrations	0	4	8	12	16	30
( wt. %)						
Temperature				S		
( K )						
323	0.80	0.8	0.79	0.65	0.74	0.63
343	0.79	0.83	0.82	0.73	0.66	0.62
363	0.66	0.75	0.68	0.70	0.51	0.55
383	0.50	0.56	0.48	0.51	0.43	0.39
393	0.43	0.47	0.40	0.43	0.36	0.32

Table 2. Frequency exponent s of PVA-Ag/coumarin nanocomposites at different temperatures.

Regarding the general behavior of  $\sigma_{ac}(\omega)$ , there is a critical frequency,  $\omega_p$ , after which the conductivity described by equ.4, the conductivity reaches twice its value at a critical frequency  $\omega_p$  (which is defined as the hopping rate) and is given by  $\omega_p = (\sigma_{dc}/A)^{1/s}$ . The values of  $\omega_p$  are calculated at different temperatures for prepared samples. Fig. 7. depicted the temperature dependence of the hopping rate ( $\omega_p$ ) for the prepared samples. The values of  $\omega_p$  for all samples are thermally activated in the mentioned temperature range accordingly to the following relation:

# $\omega_p \sim Exp \left(-E_{\omega}/k_BT\right) \tag{6}$

where  $E_{\omega}$  is the energy of activation that shifts the  $\omega_p$  to a higher frequency with increasing temperature. The values of  $E_{\omega}$  has been calculated by using the least square fitting of equation 6 and given in Table 3. It can be noticed that the addition of coumarin markely arises the values of  $E_{\omega}$ , then it decrease gradually with increase coumarin content as depicted in Fig. 8 This decrease in  $E_{\omega}$  with decreasing coumarin is due to, that the increase in coumarin enhances more ions of Ag<sup>+</sup> to contribute in conduction.

Coumarine	Т	$\tau_m \times 10^{-5}$	$E_{\omega}$	$E_m$	ω
(wt. %)	(K)	(sec)	(eV)	(eV)	(Hz)
0	393	1.06	0.4	0.598	1.6 ×
	383	1.87			10 <sup>5</sup>
	363	17.7			
	343	26.5			
	323	45.5			
4	393	0.69	0.75	0.731	2.6 ×
	383	1.77			10 <sup>5</sup>
	363	15.9			
	343	31.8			
	323	79.5			
8	393	0.63	0.6	0.711	7.2 ×
	383	1.59			10 <sup>5</sup>
	363	6.36			
	343	22.7			
	323	63.6			
16	393	1.59	0.25	0.476	2.2 ×
	383	15.9			104
	363	31.8			
	343	31.8			
	323	79.5			
30	393	1.59	0.18	0.391	9.8 ×
	383	3.18			104
	363	15.9			
	343	31.8			
	323	53			

**Table 3.** The values of the relaxation time  $\tau_m$ , the energy of activation  $(E_{\omega}, E_m)$  and preexponential factor  $(\omega_0)$  of PVA-Ag/coumarin nanocomposites.



Fig. 7. Temperature dependence of the hopping rate  $\omega_p$  for PVA –Ag/ coumarin nanocomposites.



**Fig. 8.**  $E_{\omega}$  with coumarin content.

The variations of ac conductivity of PVA - Ag /coumarin nanocomposites as a function of temperature for different coumarin concentrations at different frequencies are depicted in Fig. 9. The ac electrical conductivity provided by Arrhenius formula as:

$$\sigma_{ac} = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right) \tag{7}$$

It can be seen that the ac conductivity increases with temperature at a specific constant frequency. The increase in  $\sigma_{ac}$  may be due to the increase in energy absorption, which leads to an increase in the charge carriers numbers that participate in the conduction process. This discloses that the conduction mechanism could be a hopping one. Also, this variation can be attributed to the common effect for the change of conductance with temperature and the trap distribution nature in the polymer networks. The values of activation energy at different frequencies have been calculated by using the least square fitting of equation (7). The values of  $E_a$  are depicted in Table 4. It can be noticed that the activation energy  $E_a$  decreases with both increasing frequency and coumarin content. This may be due to that the applied field supports the jumps of charge carriers among the localized states. Also the increase in coumarin content creat more traping sites which results in the observed decrease in activation energy values which leads to an increase in conductivity [40].

Concentration	0	4	8	12	16	30
( wt. %)						
Frequency	$E_a$	$E_a$	$E_a$	$E_a$	$E_a$	$E_a$
( Hz )	( eV )	( eV )	( eV )	( eV )	( eV )	( eV )
200	0.55	0.51	0.59	0.38	0.48	0.46
500	0.51	0.48	0.57	0.33	0.49	0.43
1000	0.5	0.48	0.54	0.31	0.55	0.42
5000	0.42	0.37	0.45	0.24	0.33	0.35
10000	0.35	0.28	0.37	0.21	0.3	0.31

**Table 4**. Activation energy  $(E_a)$  of PVA-Ag/coumarin nanocomposites at different frequency.



**Fig. 9.** The temperature dependence of  $\sigma_{ac}$  conductivity for PVA –Ag/ coumarin nanocomposites representative sample (16) wt.% coumarin.

Fig.10. depicted the variation of polarization current as a function of time for PVA -Ag/ coumarin nanocomposites to ensure that the main charge carriers in such nanocomposites are ions. It can be depicted that initially the current decreases with time and then it reaches a plateau value. The values of t ion were found to be varied between 0.7- 0.91. This indicates that the conduction in our samples is mainly ionic and this confirmed also in the calculation of frequency factor **s** in ac conductivity.



**Fig. 10.** Variation of polarization current as a function of time for PVA –Ag/ coumarin nanocomposites representative sample (30) wt.% coumarin.

Also, the Nyquist diagram for the faradic impedance was confirmed the charge carriers' conduction type, as shown in fig .11. It can be seen that in the high frequency region there is a broadened semicircle followed by a spikle in the lower frequency region. The spikle indicates that conduction in our prepared samples is ionic.



**Fig. 11.** Nyquist diagram for the faradic impedance for PVA –Ag/ coumarin nanocomposites representative sample (30) wt.% coumarin.

# 3. 5. Dielectric spectroscopy

Fig. 12. depicted the dependence of the real part of dielectric permittivity ( $\varepsilon$ ) for PVA-Ag/coumarin nanocomposites at different temperature and frequency. It can be seen that  $\varepsilon$ ' decreases rapidly with increasing frequency. But at higher frequencies, the dielectric constant attains constant behavior since beyond a certain frequency the dipole moments find it difficult to follow the quickly switching electrical field, which leads to the incompetence of the dipolar molecules in the polymer to respond with increasing the rates of the applied field. This behavior is similar to a number of reported polymers [41-43]. It is also observed that  $\varepsilon$ ' increases with temperature and coumarin concentration. The increases  $\varepsilon$ ' with temperature may be assigned to the increase in charge carrier density due to the increase in the dissociation of ion aggregates. On the other hand, as the temperature increased, the viscosity of polymeric films decreased and the dipoles have sufficient energy and can orient themselves easily in the direction of the applied electric field [44]. Also, the chain segments get sufficient thermal energy to speed up its rotational motion and consequently, the increase in polarization occurs [45,46].



**Fig. 12.** Variation of dielectric constant  $\varepsilon'$  with frequency for PVA –Ag/ coumarin nanocomposites representative sample (4) wt.% coumarin.

Fig.13. depicted the variation of  $\varepsilon'$  with coumarin concentration at room temperature. It is evident that  $\varepsilon'$  increases with increasing coumarin contents. This behavior is real at low content of coumarin concentration up to 12 wt.%. This increase may be attributed to the formation of some defects sites in the band gaps of a polymer as a result of the occurrence of chain clip. Generally, these defects may indicate a sign of the existence of charge carriers traps in the bandgap of the polymer; it may be capturing the charge carriers. Therefore, coumarin increases the ability of the polymer to store charge. At high concentrations of a coumarin dye, the number of dipoles increases, disrupting the movement of them and thus decreasing values of  $\varepsilon'$ . This behavior is extended to a concentration of 16 wt% coumarin. After that, the value of  $\varepsilon'$  returns to increases. In fact, at high content of coumarin the values of  $\varepsilon'$  results from a competition between the increasing of dipoles number, due to increasing the dye content, and the disrupting of their movement, which results in a decrease in the values of  $\varepsilon'$ . Thus we can say that at high content of coumarin the increasing number of dipoles is predominant.



Fig. 13. Variation of dielectric constant  $\varepsilon'$  with coumarin concentration at room temperature.

The imaginary parts of dielectric permittivity ( $\varepsilon$ ") as a function of the frequency of PVA - Ag/coumarin nanocomposites are shown in Fig. 14. It can be observed that the values of  $\varepsilon$ " decrease rapidly with increasing frequency. The high values of  $\varepsilon$ " at low frequency could be attributed to the mobile charges within the polymer matrix. At high frequency, periodic field relation is so fast that there is no excess ion diffusion in the direction of the electric field [47-48].





Fig. 14. Variation of dielectric loss  $\varepsilon''$  with frequency for PVA –Ag/ coumarin nanocomposites representative sample (8) wt.% coumarin.

The dielectric properties of PVA-Ag/ coumarin nanocomposites are studied through the dipolar relaxation model with the assignment of relaxation time. Fig.15 depicted the frequency dependence of the dielectric loss tanδ of the PVA-Ag/ coumarin nanocomposites at different



temperatures. The tan $\delta$  behavior shown a peak that refers to a dielectric relaxation in these nanocomposites which, can be described as [39]

Tan 
$$\delta = (\varepsilon_0 - \varepsilon_\infty) \frac{\omega \tau}{\varepsilon_0 + \varepsilon_\infty(\omega \tau^2)}$$
 (8)

From Fig.15. It can be seen that by increasing the temperature the loss peak position is shifted to higher frequencies. This behavior may be due to the presence of a wide spectrum of times relaxation. The relaxation time ( $\tau_m = 1/\omega_m$ ) can be estimated from the position of the loss peak in the tan $\delta$  verse the frequency behavior. The relaxation time follows the Arrhenius law donate by[49]:

$$\omega_m = \omega_0 \exp\left(\frac{-E_m}{K_B T}\right) \tag{9}$$

The values of the energy of activation  $E_m$ , the pre-exponential factor  $\omega_0$  and the relaxation time  $\tau_m$ , have been calculated and tabulated in Table 4. It can be seen that  $\tau_m$  decreases with increasing temperature and concentration of coumarin. The decrease in  $\tau_m$  with temperature may be due to that the thermal energy of charge carriers increases, so they collide more frequently and hence the average relaxation time which is the average time between successive collisions are decreasing, the reduction in the relaxation time with increasing coumarin concentration may be attributed to the increase in amorphousty so the polymer chains are more flexible and are capable of orienting themselves relatively more easily and rapidly. On the other hand, the dipoles in the side chain of the polymer will orient themselves with certain frequencies governed by the elastic restoring force which binds the dipoles to their equilibrium positions and the rotational frictional forces exerted by neighboring dipoles. Also more and more free charges may accumulate on the interface resulting in a decrease of relaxation time as the concentration of coumarin increases.



**Fig. 15.** dissipation factor spectra with frequency for PVA –Ag/ coumarin nanocomposites representative sample (4) wt.% coumarin.

## 4. Conclusion

PVA-Ag / coumarin nanocomposites have been successfully prepared and characterized. Electric Conductivity and dielectric properties have been investigated. The dc conductivity of nanocomposites increased with increasing coumarin concentration. The dc electrical conductivity followed the Arrhenius law with activation energies between 0.54 and 0.3 eV for the different samples. The addition of coumarin increase the charge carrier mobility and the number of charge carrier concentration. The ac conductivity obeys the power law. The frequency exponent s decreases with the increase of dopant coumarin level. Such behavior of s has been interpreted by the CBH model. The existence of coumarin in the PVA matrix enhances the average polarization and then the dielectric constant  $\varepsilon'$ . The dielectric constant of the nanocomposites is very large and almost dependent on frequency. These studies indicate that PVA/Ag can be effectively doped with coumarin to enhance its electrical conductivity and alter its conduction behavior. Results show that PVA-Ag /30 wt.% coumarin sample is a potential candidate for photovoltaic devices and organic applications.

## Reference

[1] J.T. Kalathi, S.K. Kumar, M. Rubinstein, G.S. Grest, Rouse mode analysis of chain relaxation in polymer nanocomposites, Soft Matter. 20 (2015) 4123-4132. DOI: 10.1039/c5sm00754b.

[2] M.H. Makled, E. Sheha, T.S. Shanap, M.K. El-Mansy, Electrical conduction and dielectric relaxation in p-type PVA/CuI polymer composite. J. advan. Res. 4 (2013) 531-538. http://dx.doi.org/10.1016/j.jare.2012.09.007.

[3] A. Sorrentino, G. Gorrasi, V.Vittoria, Potential perspectives of bio-nanocomposites for food packaging applications. Trends in Food Sci. and Technol. 18 (2007) 84-95. Doi:10.1016/j.tifs.2006.09.004

[4] B. W.huynh, J. J.Dimttmer, W. C. Libby, G. L. Whiting, A.P.Alivisatos, Controlling the morphology of nanocrystal-polymer composites for solar cells. Adv.funct.Mater. 13 (2003) 73-79. 1616-301X/03/0101-0073\$17.50+50/0.

[5] D.Y. Godovsky, Device applications of polymer-nanocomposites. Biopolymers. PVA Hydrogels, Anionic Polymerisation Nanocomposites. Advan.Poly. Sci. 153 (2000) 163-205.

[6] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Hybrid Nanorod-Polymer Solar Cells. Sci. 295.5564 (2002) 2425-2427. DOI: 10.1126/science.1069156

[7] M. Delay, T. Dolt, A. Woellhaf, R. Sembritzki, F.H. Frimmel, Interactions and stability of silver nanoparticles in the aqueous phase: Influence of natural organic matter (NOM) and ionic strength. J. Chromatography A 1218 (2011) 4206-4212. Doi:10.1016/j.chroma.2011.02.074

[8] U. Schurmann, W. Hartung, H. Takele, V. Zaporojtchenko, F. Faupel, Controlled syntheses of Ag–polytetrafluoroethylene nanocomposite thin films by co-sputtering from two magnetron sources. Nanotechnol. 16 (2005) 1078. Doi:10.1088/0957-4484/16/8/014

[9] Y. Zhu, Y.Qian, X. Li, M. Zhang, γ-Radiation synthesis and characterization of polyacrylamide–silver nanocomposites. Chem.Communications 12 (1997) 1081-1082.

[10] S. A. Mohamed, A.A. Al-Ghamdi, G.D. Sharma, M.K. El Mansy, Effect of ethylene carbonate as a plasticizer on CuI/PVA nanocomposite: Structure, optical and electrical properties. J. advance. Res. 5 (2014) 79-86. http://dx.doi.org/10.1016/j.jare.2012.11.008

[11] Z. H. Mbhele, M. G. Salemane, C. G. C. E. van Sittert, J. M. Nedeljkovic, V. Djokovic, A. S. Luyt, Fabrication, and characterization of silver– polyvinyl alcohol nanocomposites. Chem. Mat. 15 (2003) 5019-5024. https://doi.org/10.1021/cm034505av.

[12] M.K. El-Mansy, E.M. Sheha, K.R. Patel, G.D. Sharm, Characterization of PVA/CuI polymer composites as an electron donor for photovoltaic application. Optik 124 (2013) 1624–1631. http://dx.doi.org/10.1016/j.ijleo.2012.05.009

[13] Z. I. Ali, H. M. Hosni, H. H. Saleh, O. A. Ghazy, Photoluminescence and electrical properties of polyvinyl alcohol films doped with CdS nanoparticles. Appl. Phy. A 122 (2016) 514. DOI 10.1007/s00339-016-0037-4.

[14] D. Basak, S. Karan, B. Mallik, Significant modifications in the electrical properties of poly (methyl methacrylate) thin films upon dispersion of silver nanoparticles. Solid state communications 141 (2007) 483-487. Doi:10.1016/j.ssc.2006.12.014

[15] S. Ram, A. Gautam, H. J. Fecht, J. Cai, J. Bansmann & R. J. Behm, A new allotropic structure of silver nanocrystals nucleated and grown over planar polymer molecules. Philos. Mag. let. 87 (2007) 361-372. DOI: 10.1080/09500830701191401

[16] A. Raouafi, M. Daoudi, K. Jouini, K. Charradi, A.H. Hamzaoui, P. Blaise, K. Farah, F. Hosni, Effect of gamma irradiation on the color, structure, and morphology of nickel-doped polyvinyl

alcohol films: alternative use as dosimeter or irradiation indicator. Nucl. Inst. and Meth. in Phy. Res. Sec. B 425 (2018) 4-10. https://doi.org/10.1016/j.nimb.2018.03.034.

[17] O. G., Abdullah1, Y.A.K. Salman, S. A. Saleem, In-situ synthesis of PVA/HgS nanocomposite films and tuning optical properties. Phy. and Mater. Chem. 3 (2015) 18-24. DOI:10.12691/pmc-3-2-1

[18] A.G. El-Shamy, W. Attia, K.M.A. El-Kader, the optical and mechanical properties of PVA-Ag nanocomposite films. J. Alloys. Compd. 590 (2014) 309–312. http://dx.doi.org/10.1016/j.jallcom.2013.11.203

[19] S. Mahendia, A.K. Tomar, S. Kumar, Electrical conductivity and dielectric spectroscopic studies of PVA–Ag nanocomposite films. J. Alloys and Compd 508 (2010) 406-411. Doi:10.1016/j.jallcom.2010.08.075

[20] R. P. chahal, S. Chahal, A.K.Tomar, S. Kumar, UV irradiated PVA–Ag nanocomposites for optical applications, Appl. Sur. Sci. 343 (2015) 160-165.
https://doi.org/10.1016/j.apsusc.2015.03.074

[21] P. S. Jogi, J.Meshram, J. Sheikh, T. B. Hadd, Synthesis biopharmaceutical characterization, and antimicrobial study of novel azo dye of 7-hydroxy-4-methyl coumarin. Medicinal Chem. Res. 22 (2013) 4202-4210. DOI 10.1007/s00044-012-0421-3

[22] P. K. Jain, H. Joshi, Coumarin: Chemical and Pharmacological Profile. J. Appl. Pharma. Sci. 6 (2012) 236-240. DOI: 10.7324/JAPS.2012.2643

[23] Y. yang, J. Zou, H. Rong, G.D. Qian, Z.y. wang, M.q. wang, Influence of various coumarin dye on the laser performance of laser dye co-doped into ORMOSILs. Appl. Phys. B 86 (2007) 309–313. DOI: 10.1007/s00340-006-2462-0

[24] K.-G. Weng, Y.L. Yuan, Synthesis and evaluation of coumarin derivatives against human lung cancer cell lines. J. Med. Bio. Res. 50 (2017) 1-6. http://dx.doi.org/10.1590/1414-431X20176455

[25] R. Bisen, J. Tripathi, A. Sharma, A. Khare, Y. Kumar, S. Tripathi, Optical behavior of coumarin dye in PVA and PMMA film matrices. Vacuum 104 (2018) 3059–3078. https://doi.org/10.1016/j.vacuum.2018.03.004 [26] A. El-Shamy, Composite (PVA/Cu nano) films: Two yield points, embedding mechanism and thermal properties, Progress in Organic Coating 127 (2019) 252- 259. https://doi.org/10.1016/j.porgcoat.2018.11.024.

[27] H. Zidan, Effect of AgNO<sub>3</sub> filling and UV-irradiation on the structure and morphology of PVA films. Polym. Test. 18 (1999) 449–461. https://doi.org/10.1016/S0142-9418(98)00049-X.

[28] I. Saini, J.Rozra, N. Chandak, S.Aggarwal, P. Sharma, A.Sharma, Tailoring of electrical, optical and structural properties of PVA by addition of Ag nanoparticles. Mater. Chem. Phys. 139 (2013) 802–810. http://dx.doi.org/10.1016/j.matchemphys.2013.02.035.

[29] S. Chandrana , V. Ravichandranab , S. Chanvranb , J. Chemmandab, B. Chandarshekar, Biosynthesises of PVA encapsulated silver nanoparticles. J.Appl. Res. and Techn 14 (2016) 319-324.\_http://dx.doi.org/10.1016/j.jart.2016.07.001.

[30] A. M. Meftah, E. Gharibshahi, N. Soltani, W. Mahmoud Mat Yunus, Elias Saion, Structural, optical and electrical properties of PVA/PANI/Nickel nanocomposites synthesized by gamma radiolytic method. Poly. 6 (2014) 2435-2450. doi:10.3390/polym6092435

[31] A. Dey, S. De, A. De, S. K. De, Characterization and dielectric properties of polyaniline– TiO2 nanocomposites. Nanotechnol. 15 (2004) 1277-1283. Doi:10.1088/0957-4484/15/9/028.

[32] S. M. Reda, S. M. Al-Ghannam, Synthesis and electrical properties of polyaniline composite with silver nanoparticles. Adva. Mater.s Phy. Chem. 2 (2012) 75-81. http://dx.doi.org/10.4236/ampc.2012.22013.

[33] D.A. Seanor, Electrical properties of polymers, Academic Press, New York 1982.

[34] A. Mostafaei, A.Zolriasatein, Synthesis, and characterization of conducting polyaniline nanocomposites containing ZnO nanorods. Prog. Nat. Sci. Mater.International 22 (2012) 273-280. http://dx.doi.org/10.1016/j.pnsc.2012.07.002

[35] F. M. Fowkes, D. O. Tischler, J. A. Wolfe, L. A. Lannigan, C. M. Ademu-John, M. J. Halliwell, Acid–base complexes of polymers. J. Poly. Sci.: Polymer Chemistry Edition 22 (1984) 547-566. https://doi.org/10.1002/pol.1984.170220304

[36] N.M. Shash, Influence of Cobalt Chloride Addition on the Electrical and Optical Properties of Poly(vinyl alcohol). J. Appl. Poly. Sci. (2008) 1-27.

[37] A.K.Jonscher, s The universal dielectric response. Nat. 267 (1977).

[38] M. H. I. El Eraki, A. M. Y. El Lawindy, H. H. Hassan, W. E. Mahmoud, The Effect of Heating– Cooling Cycles on PTCC andNTCC Made of FEF/NBR Composites. J. Appl. Poly. Sci. 103 (2007) 2837–2842. DOI 10.1002/app.24504.

[39] N.Shash, Effect of vanadium pentoxide on the electrical, dielectric, and optical properties of poly(vinyl alcohol)/vanadiumpentoxide nanocomposites . Ionics 1-10 (2013) . DOI 10.1007/s11581-013-0923-0.

[40] V. P. Anju, S.K. Narayanankutty, Polyaniline coated cellulose fiber/polyvinyl alcohol composites with high dielectric permittivity and low percolation threshold. AIP. Adv. 6 (2016) 015109. http://dx.doi.org/10.1063/1.4940664

[41] K. Wadhwani, S. Srivastava, S. Mathur, Dielectric studies of (x) NiFe<sub>2</sub>O<sub>4</sub>+(1-x) BaTi  $_{0.9}$  Zr  $_{0.1}O_3$  (where x= 0, 0.25, 0.50, 0.75 and 1). AIP. Conference Proceedings 1953 (2018). https://doi.org/10.1063/1.5032709

[42] T. Abdel-Baset, M. Elzayat, S.Mahrous, Characterization and Optical and Dielectric Properties of Polyvinyl chloride/Silica Nanocomposites Films, Int. J. Poly. Sci.( 2016) 1-13.http://dx.doi.org/10.1155/2016/1707018

[43] F.S. Shokr, S.A. Al-Gahtany, Dielectric properties of conductive polypyrrole/ethylene vinyl acetate copolymer blends. J. Elastom. Plastics 46 (2014) 470-480. DOI: 10.1177/0095244312469960

[44] A. Hassen, A. M. El Sayed, W. M. Morsi, S. El-Sayed, Influence of Cr<sub>2</sub>O<sub>3</sub> nanoparticles on the physical properties of polyvinyl alcohol. J. Appl. Phy. 112 (2012) 093525. Doi: 10.1063/1.4764864

[45] T. A. Hanafy, Dielectric relaxation and alternating-current conductivity of gadolinium-doped poly (vinyl alcohol). J.App. poly. Sci. 108 (2008) 2540-2549. DOI 10.1002/app.27567

[46] S. Das, N. Lalla, G.S. Okram, Synthesis, characterization and dielectric properties of nanocrystalline nickel. Indian J. Pure Appl. Phy. 52 (2014) 386-390.

[47] A. G. El-Shamy, W. M. Attia, K. M. Abd El Kader, Enhancement of the conductivity and dielectric properties of PVA/Ag nanocomposite films using γ irradiation. Mater. Chem. Phy. 191 (2017) 225-229. DOI 10.1016/j.matchemphys.2017.01.026

[48] P. B. Bhargav, B. A. Sarada, A. K. Sharma, V. V. R. N. Rao, Electrical conduction and dielectric relaxation phenomena of PVA based polymer electrolyte films. J. Macromol. Sci. Part A 47 (2009): 131-137. http://dx.doi.org/10.1080/10601320903458564

[49] M.K. E1-Mansy, Electrical conduction and dielectric relaxation in vanadium phosphate glasses, J.Mater.chem.phy. 56 (1998) 236-242