



Dielectric relaxation analysis and Ac conductivity of polyvinyl alcohol/polyacrylonitrile film



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ABSTRACT

A film of 0.98 polyvinyl alcohol (PVA)/0.02 Polyacrylonitrile (PAN) has been prepared using casting method. The dielectric properties were measured as function of temperature and frequency. The dielectric permittivity of PVA is considerably enhanced by doping with PAN. Different relaxation processes have been recognized within the studied ranges of temperature and frequency. The frequency temperature superposition (FTS) is well verified. Frequency and temperature dependence of Ac conductivity, σ_{ac} , were studied. The conduction mechanism of pure PVA and PVA doped with PAN are discussed. The activation energy either for relaxation or conduction was calculated. Comparison with similar polymeric materials is discussed.

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1. Introduction

Polyvinyl alcohol (PVA) is a semi-crystalline polymer, with a high solubility in water, low cost, non-toxicity, and flexible hydrophilic network. It has a high dielectric permittivity and good charge storage capacity. These properties make PVA is an important and interesting polymer [1,2]. On the other hand, polyacrylonitrile (PAN), a synthetic vinyl homopolymer, offers quite good resistance [3], thermal stability [4], and mechanical strength [5]. It is regarded as the most preferable precursor material for the production of high strength, and high modulus carbon fibers. PAN fibers exhibit a high degree of molecular orientation, and higher melting point ($T_m \sim 317$ to 330°C) [6]. Moreover, PAN is completely non-toxic and suitable for biomedical applications [7–10].

Incorporation of conducting polymer into another forming a blend, composite, or inter penetrated bulk network may lead to combine electrical conductivity with desirable physical properties of both two polymers [11,12]. A treatment of polyaniline (PANI)/polyvinyl chloride (PVC) blend was examined [13]. The results of PANI/PVC blends showed an increase in conductivity at lower temperature.

knowing that the dielectric relaxation spectroscopy (DRS) is a useful method to throw light on the structure property relationships of polymers. Also, this method is sensitive to molecular

fluctuation of dipoles within the dielectrics. These fluctuations are related to the molecular mobility of branched groups, segments or wholly polymer chains which show different relaxation processes. Moreover, the dipole motions within the amorphous and crystalline phases have an effect on the semi-crystalline polymers [14,15]. Structural transitions in polymers are generally accompanied by changes in their relaxation properties. So, the relaxation properties are important for studying polymeric materials [16].

When an oscillatory electric field is applied to a polymeric material, several types of polarization are operative such as; electronic, ionic, orientational, or space charge. Orientational and space charge polarizations are particularly important when structural transitions are concerned. We reported previously on PVA/carboxymethyl cellulose (CMC) blends [17] as well as on 0.98 PVA/0.02 PANI film [18]. It become clear that the physical properties depend on the blend ratio of PVA and CMC. The physical properties of PVA are considerably affected by doping with PANI. Based on our knowledge, there is no previous report on the dielectric relaxation of PVA/PAN mixture. Therefore, we aimed in this work to throw light on the dielectric properties of (0.98/0.02) PVA/PAN film.

2. Experimental

PVA powder of molecular weight ($M_w \sim 17000$ g/mol), and Polyacrylonitrile powder ($M_w \sim 150,000$ g/mol) were obtained

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from (Polymer Laboratories, Essex, UK). (0.98/0.02) PVA/PAN film was prepared as follows: 0.98 g of the PVA and 0.2 g of PAN were dissolved separately each of them in 25 mL distilled water under stirring until clear solutions were obtained. The solutions were added to each other under ultrasonic stirring at room temperature (RT) for 2 h. The obtained mixture was then cast into Petri dishes and left to dry in air at RT for 24 h. Finally, the films were peeled off from the Petri dishes and care was taken to obtain homogenous samples with thickness (≈ 0.1 mm). Dielectric spectroscopy measurements were accomplished using a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR, with the accuracy of order $\pm 0.08\%$. The dielectric permittivity (ϵ'), and dielectric loss (ϵ'') were recorded at frequency and temperature ranging from 100 Hz to 4.4 MHz and from RT to 428 K, respectively. Both ϵ' and ϵ'' were calculated as follows:

$$\epsilon' = \frac{Cd}{\epsilon_0 A}, \quad \epsilon'' = \epsilon' \tan \delta \quad (1)$$

where C is the capacitance of the sample filled capacitor, d is the sample thickness, ϵ_0 is the vacuum permittivity, and A is the electrode area. The temperature was measured with a T -type thermocouple having an accuracy of ± 1 K.

3. Dielectric properties

3.1. Dielectric permittivity

Fig. 1 depicts the frequency dependence of ϵ' at different fixed temperatures. As seen, ϵ' decreases with increasing of frequencies. The decrease in ϵ' may be attributed to decreasing of the number of dipoles which contribute to polarization or the dipoles are no longer able to respond to the applied electric field. To emphasize the effect of PAN on the ϵ' PVA, the inset of **Fig. 1** shows the variation of ϵ' of pure PVA and 0.98PVA/0.02PAN versus frequency at some selected temperatures. It is clear that ϵ' of PVA is considerably enhanced by doping with PAN. The pronounced increase of ϵ' of PVA can be explained based on the chemical nature of PAN that has strong polar nitrile groups [19].

Fig. 2 displays the temperature dependence of ϵ' for PVA/PAN film at some selected frequencies. It is shown that ϵ' of PVA increased by adding PAN similar to that of PVA/PANI film [18]. The behavior of ϵ' with temperature can be explained as follows: at lower temperatures, the thermal energy that is absorbed by the

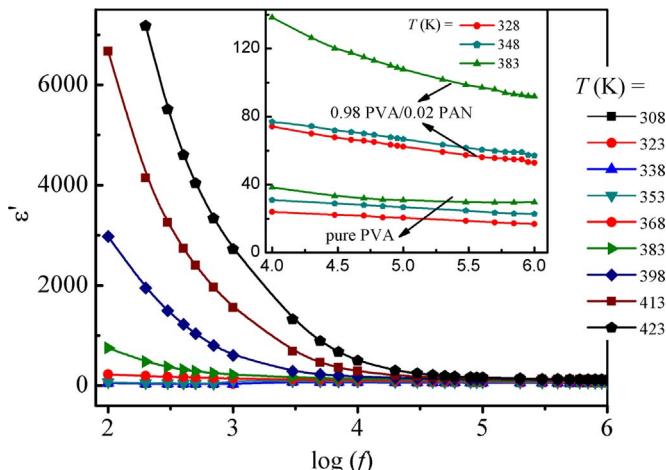


Fig. 1. The variation of dielectric permittivity, ϵ' , as a function of frequency for 0.98 PVA/0.02 PAN film at different temperatures. The inset shows the variation of ϵ' versus frequency for pure PVA and 0.98 PVA/0.02 films at some selected temperatures. The arrows point to the data of each sample.

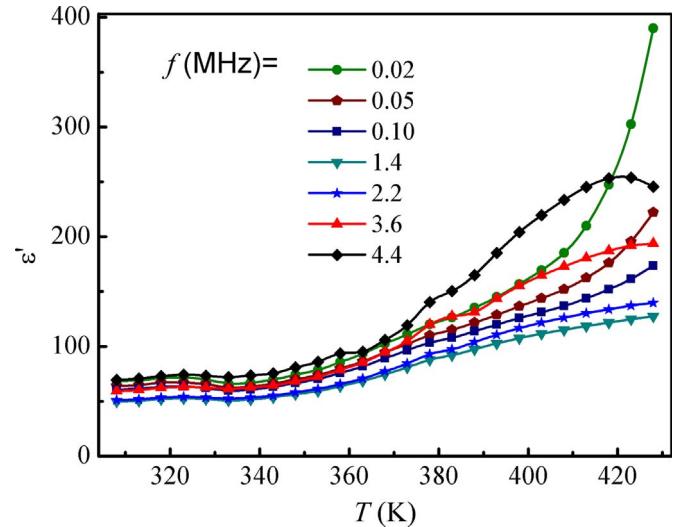


Fig. 2. The variation of dielectric permittivity as a function of temperature for 0.98PVA/0.02PAN film at different frequencies.

polymeric material, is small and then a small number of dipoles can rotate along with applied electric field [20]. As the temperature increased, the viscosity of polymeric films is decreased and the dipoles gain sufficient energy and can orient themselves easily in the direction of the applied electric field, thus ϵ' increased with increasing temperatures. In addition, the specific volume of the polymer increases with further an increase in temperature, and hence ϵ' increased [21,22].

3.2. Electric modulus

At low frequencies and high temperatures, the observed values of dielectric permittivity do not refer to the bulk of the material. This is related to the so called “interfacial polarizations” that are dominant in composite polymeric materials [23]. To avoid the contribution of the interfacial polarization or electrode polarization, the modulus formalism can be used to analyze the dielectric behavior of PVA/PAN film. In this section, the recorded dielectric data are expressed in terms of the complex electric modulus (M^*), which is defined as the inverse of the complex permittivity (ϵ^*):

$$M^* = M' + iM'' = \frac{1}{\epsilon^*} \quad (2)$$

$$M^* = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (3)$$

where M' and M'' are the real and imaginary parts of the dielectric modulus, respectively.

The frequency dependence of the dielectric modulus M' at various temperatures is plotted in **Fig. 3**. It is clear that M' increases with increasing frequency and shows a peak around 1 MHz. The peak height decreases with increasing frequency and it can be attributed to ρ -relaxation [24]. Moreover, the values of M' tend to zero at low frequency indicating the removal of electrode polarization.

Fig. 4 shows the temperature dependence of M' for 0.98 PVA/0.02 PAN at different frequencies. It is observed that the values of M' decrease with increasing temperatures. A peak is observed around 340 K and it can be attributed to the glass transition, T_g , of the host polymeric material (PVA) [17]. It is called α_a -relaxation. Also, the values of M' decreased with the increase in temperature because of the thermally activated nature of the dielectric permittivity [23].

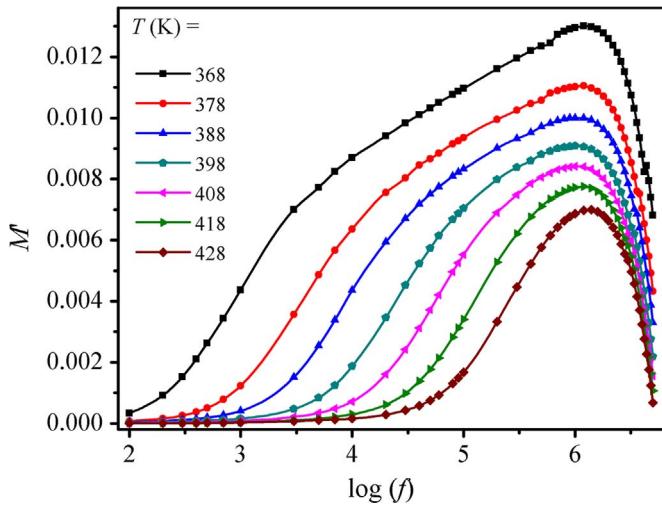


Fig. 3. The variation of the dielectric modulus, M' , as a function of frequency at some fixed temperatures.

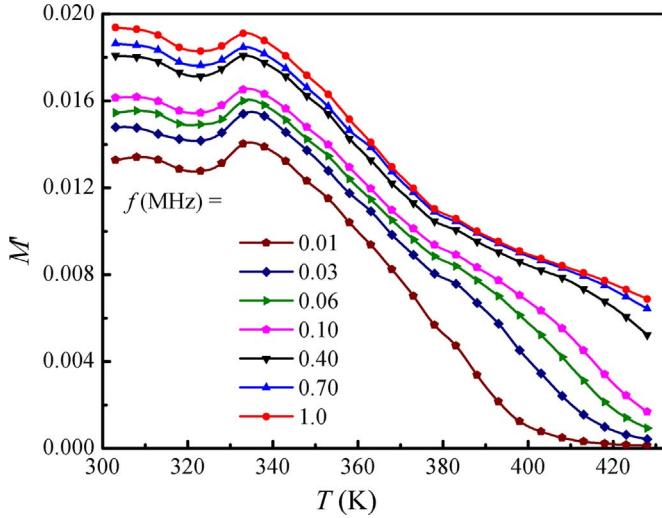


Fig. 4. The variation of dielectric modulus, M' , as a function of temperature at some fixed frequencies.

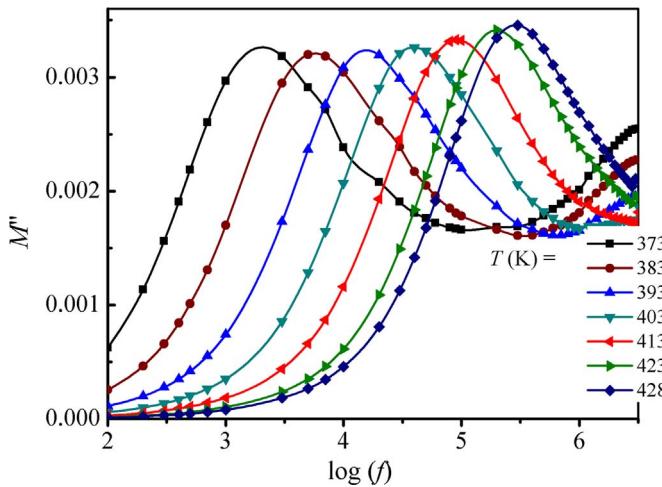


Fig. 5. The variation of dielectric modulus, M'' , with frequency at different temperatures.

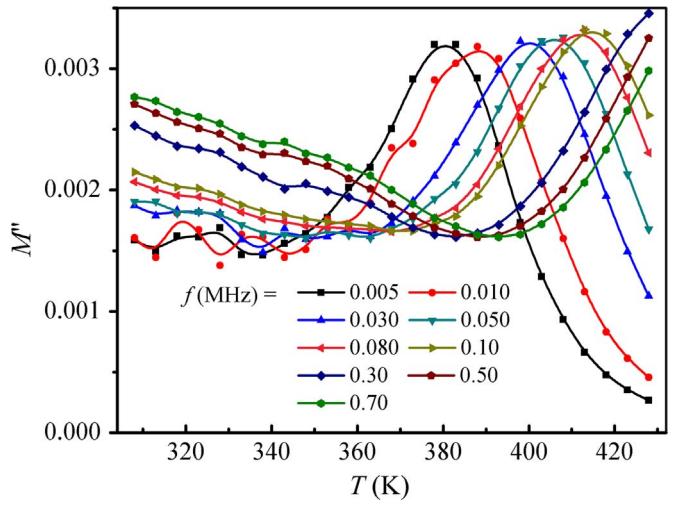


Fig. 6. The variation of dielectric modulus, M'' , with temperature at some selected frequencies.

The frequency dependence of M'' for 0.98 PVA/0.02 PAN film at different temperatures is shown in Fig. 5. The M'' spectrum shows asymmetric peak that corresponds to α_c -relaxation. This relaxation process can be attributed to the segmental relaxation in the crystalline phase of the host PVA matrix [25]. One also noted that the M'' peak shifts toward higher temperatures with increasing frequency because more dipoles released with temperatures. By other words, the density of dipoles contributing to the relaxation process increases with increasing temperature.

Fig. 6 represents the frequency dependence of M'' at various temperatures. The α_c -relaxation peak is observed and shifted to higher temperature with increasing frequency. This is another evidence to observe α_c -relaxation in the studied film. Based on Fig. 6, the maximum frequency, f_{max} , was determined to throw light on the activation energy of the α_c -relaxation. Therefore, Fig. 7 depicts the change of f_{max} for 0.98PVA/0.02PAN film versus $1000/T$. The behavior of f_{max} was described by Arrhenius equation [24]:

$$f_{max} = f_0 \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

where f_0 is a characteristic constant parameter for a particular relaxation process, k is Boltzmann's constant, and E_a is the

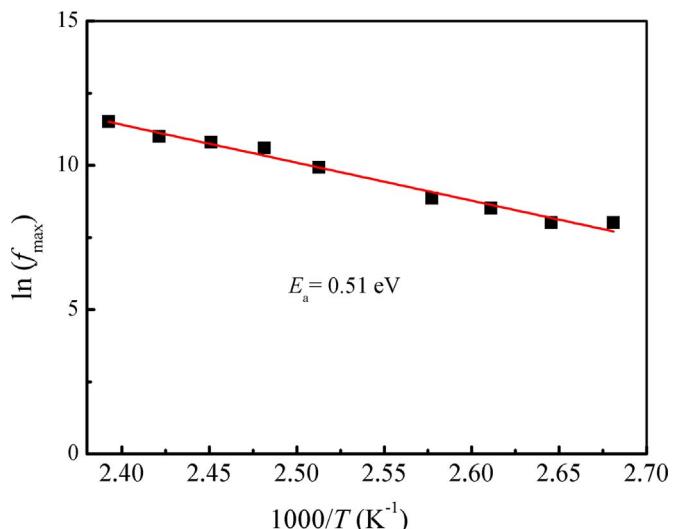


Fig. 7. The variation of $\ln(f_{max})$ versus $1000/T$ for 0.98 PVA/0.02 PAN film. The solid line displays the fitting according to Eq. (4).

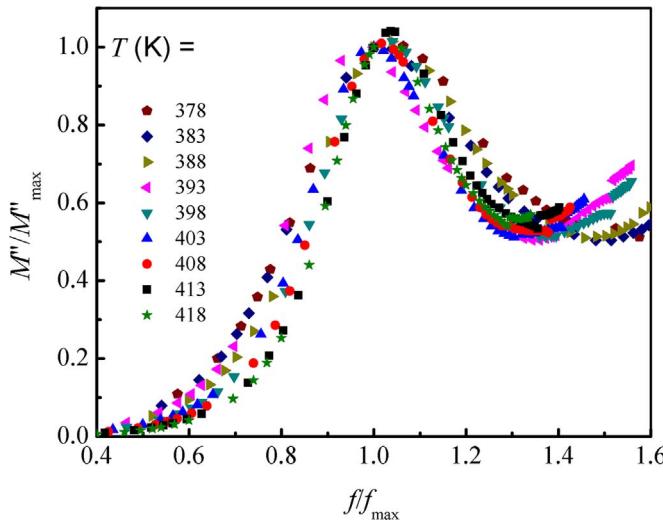


Fig. 8. Master curve for 0.98 PVA/0.02 PAN film at different temperatures.

activation energy. Based on Eq. (4), the calculated value of E_a is 0.51 eV.

3.3. Frequency temperature superposition (FTS)

The frequency temperature superposition (FTS) principle is useful to describe the microscopic mechanisms of many systems. From FTS spectral shapes, it is possible to force the data corresponding to different temperatures to fall on a single master curve, which indicates some similarity in the physical mechanisms that underlie various materials. This behavior also demonstrates that the microscopic mechanisms of various systems are independent of temperature [26]. For examples, inorganic solids, glasses, semiconductors, and polymers have been found to follow FTS [27,28]. Fig. 8 displays the dielectric spectra of the normalized imaginary part of the electric modulus, M''/M''_{max} , as a function of the normalized frequency f/f_m , at different temperatures. It is noted that both low-frequency ($f/f_m < 1$) and high-frequency sides ($f/f_m > 1$) of the relaxation peak follow FTS. It can be concluded that the distribution function for the relaxation time (τ) has a mild temperature dependent.

3.4. Ac conductivity

A common feature of dielectric materials is the frequency dependence of the Ac conductivity, $\sigma_{\text{ac}}(f)$. It was found, $\sigma_{\text{ac}}(f)$ of 0.98 PVA/0.02 PAN film can be described by the well known universal dynamic response [23,29]:

$$\sigma_{\text{ac}}(\omega) = \sigma_t - \sigma_{dc} = B\omega^s \quad (5)$$

where σ_{dc} is the dc (or low frequency) conductivity, σ_t is the total conductivity, s is the universal frequency exponent, and B is a pre-exponential factor. A linear behavior was observed between $\log(\sigma_{\text{ac}})$ versus $\log(f)$ as shown in Fig. 9. The fitting of the ac conductivity yields the values of s . The inset of Fig. 9 presents the variation of σ_{ac} of pure PVA versus frequency at different temperatures to compare between the ac conductivity of pure PVA film and that of 0.98 PVA/0.02 PAN. Doping PVA by PAN increased its ac conductivity. The values of s for both pure PVA and PVA/PAN films are given in Table 1. The values of s for pure PVA are less than 1.0 and decreased with increasing temperature. This means that the conduction mechanism of pure PVA film could be correlated barrier hopping (CBH) [30]. On the contrary, the s values of 0.98PVA/0.02PAN are larger than 1.0 and increased with increasing

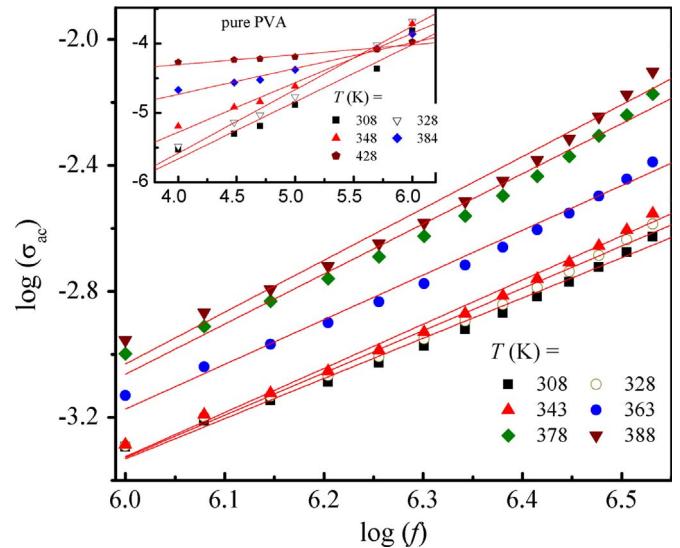


Fig. 9. Frequency dependence of σ_{ac} for 0.98 PVA/0.02 PAN at different temperatures. The inset displays the frequency dependence of σ_{ac} for pure PVA film. The solid red lines in the main frame and inset of the figure are the fitting according to Eq. (5). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

The values of the frequency exponent, s , for pure PVA and 0.98PVA/0.02PAN films at different temperatures according to the fitting of Eq. (5).

T (K)	Pure PVA	T (K)	0.98PVA/0.02PAN
328	0.92	308	1.28
348	0.86	328	1.34
368	0.79	343	1.40
388	0.43	363	1.42
408	0.24	378	1.59
428	0.16	388	1.65

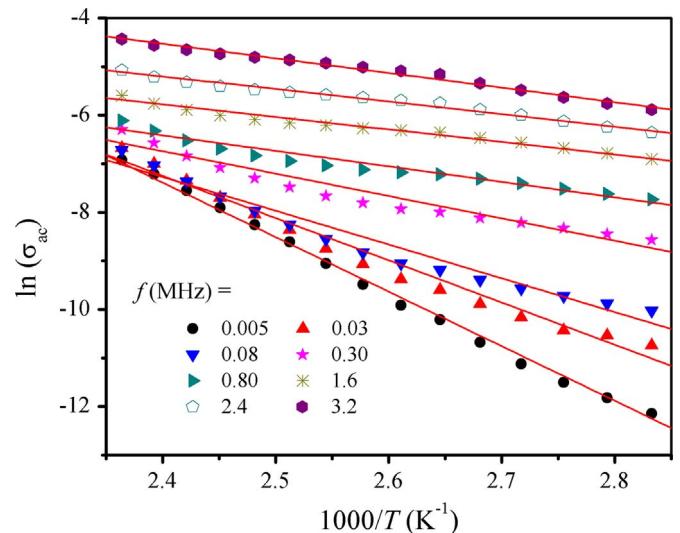


Fig. 10. The variation of $\ln(\sigma_{\text{ac}})$ against $1000/T$ for 0.98 PVA/0.02PAN film at different frequencies. The solid lines represent the fitting according to Eq. (6).

temperature. The conduction mechanism for this case may be attributed to localized/reorientational processes [31,32].

Fig. 10 shows the temperature dependence of the ac conductivity, $\sigma_{\text{ac}}(T)$. It is clear that σ_{ac} increased with increasing temperature and applied frequency. This may be due to the increase of the absorbed energy which leads to increase the number

Table 2

The activation energy E for 0.98 PVA/0.02 PAN film at different frequencies.

$f = E$ (eV)	5 kHz	30 kHz	80 kHz	0.3 MHz	0.8 MHz	1.6 MHz	2.4 MHz	3.2 MHz
	0.9	0.778	0.615	0.407	0.283	0.228	0.229	0.265

of the charge carriers that contribute to the conduction process. The σ_{ac} (T) obeys Arrhenius relation within the temperature ($330 \text{ K} \leq T \leq 420 \text{ K}$) range:

$$\sigma_{ac} = \sigma_0 \exp\left(-\frac{E}{kT}\right) \quad (6)$$

where σ_0 is pre-exponential factor and k and T have their usual meaning. The activation energy within the thermally activated region of the ac conductivity was calculated at different frequencies and listed in Table 2. It is noticed that the values of E vary from 0.9 to 0.22 eV with increasing frequency.

4. Conclusions

The dielectric properties of 0.98 PVA/0.02 PAN film as a function of temperature and frequency were studied. The dielectric permittivity of PVA considerably increased by adding 0.02 wt% PAN. Different relaxation processes have been recognized. The first is ρ -relaxation due to space charge formation or Maxwell-Wagner polarization. The others are α_a - and α_c - relaxations that can be attributed to micro- Brownian motion of chain segments in amorphous and crystalline part of host PVA matrix, respectively. FTS principle is verified over wide ranges of temperature and frequency. According to the frequency dependence of ac conductivity, the conduction mechanism of 0.98 PVA/0.02PAN film could be localized hopping and/or reorientational motion but it is CBH for pure PVA. $\sigma_{ac}(T)$ of the studied composition is thermally activated in the temperature range ($330 \text{ K} \leq T \leq 420 \text{ K}$), where the activation energy E decreased with increasing frequency. The pronounced change in the dielectric properties of PVA by doing with PAN can be ascribed to the strong polar nitrile groups of polyacrylonitrile matrix. These results may reflect the importance of 0.98 PVA/0.02 PAN film in dielectric applications.

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