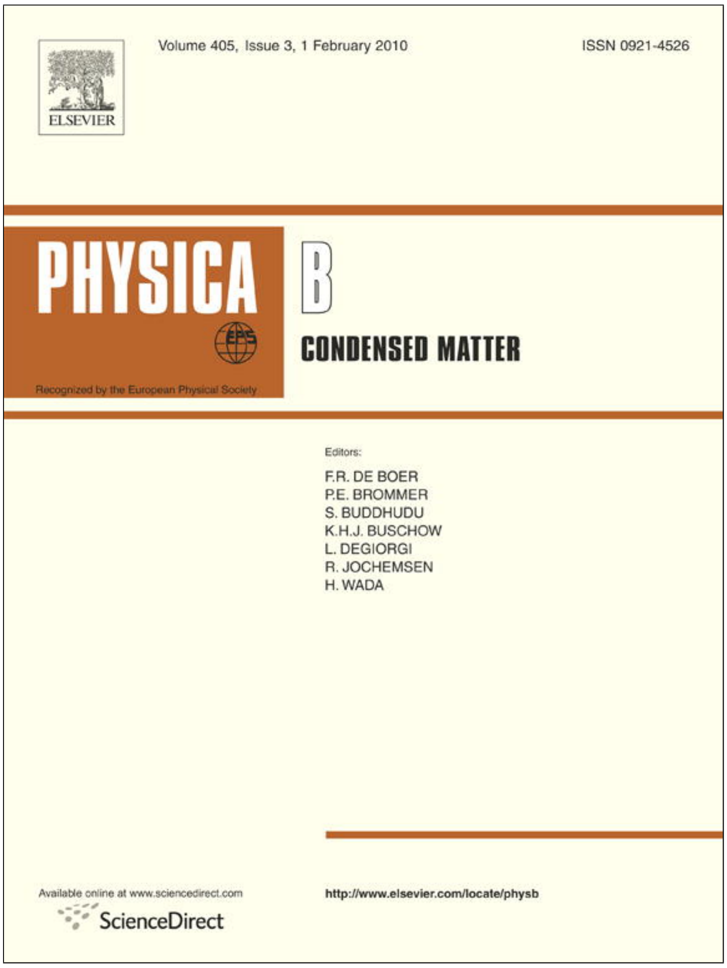

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Influence of titanium chloride addition on the optical and dielectric properties of PVA films

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ABSTRACT

Polymeric films based on polyvinyl alcohol (PVA) doped with titanium chloride ($TiCl_3$) at different weight percent ratios were prepared using the solvent cast technique. The structural properties of these polymeric films are examined by XRD and FTIR studies. The complexation of the dopant with the polymer was confirmed by FTIR studies. The XRD pattern reveals that the amorphous domains of PVA polymer matrix increased with raising the $TiCl_3$ content. The optical properties of these polymeric films were examined by optical absorption and emission spectroscopy. Electrical conductivity was measured at room temperature of pure PVA and PVA doped with different concentrations of $TiCl_3$ from 20 Hz to 3 MHz. The conductivity was found to increase with the increase in dopant concentration. The dielectric constant (ε') indicates a strong dielectric dispersion in the studied frequency range and increases as dopant content increases. This increase in both σ and ε' is attributed to the increase in the localized charges distribution. Moreover, a loss peak was identified in the dielectric loss spectra and it is attributed to the orientation of polar groups.

1. Introduction

Over recent years polyvinyl alcohol (PVA) polymers have attracted attention due to their variety of applications. PVA is a potential material having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It has carbon chain backbone with hydroxyl groups attached to methane carbons/these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer complexes [1]. On the other hand, titanium is interesting in terms of optical, electronic and UV-absorbing properties and shows promise for a variety of applications including self-cleaning, UV blocking, purification and antibacterial applications [2]. Therefore, titanium compounds have many scientific and industrial applications [1,3,4]. The study of dielectric relaxation in polymeric films is a powerful approach for obtaining information about the characteristics of ionic and molecular interactions. The dielectric parameters associated with relaxation processes are of particular significance in ion conducting polymers. The frequency-dependent conductivity and dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer. Many workers reported that the dielectric parameters are strongly influenced by the nature of additives and temperature. PVA doped with different types of elements was reported [5–7] but till now few physical studies on PVA doped with titanium complex have been available.

In this paper an effort has been made to study the effect of addition of titanium chloride on dielectric behavior of polymeric films by measuring the dielectric parameters of the samples. The results obtained from these measurements have been analyzed and discussed.

2. Experimental work

2.1. Sample preparation

Polymeric films of PVA/$TiCl_3$ were prepared with weight percent ratio (100:0), (99:1), (95:5), (90:10), (85:15), (80:20) and (75:25) by the solvent casting technique using triple distilled water as a solvent. The desired concentrations were mixed and the solution was stirred thoroughly with a magnetic stirrer for 12 h to get a homogenous mixture and then cast onto Petri dishes and allowed to evaporate slowly at room temperature and peeled off from the Petri dishes after 48 h. The final films were vacuum dried. The thickness is in the range 20–50 μm.

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2.2. Measurements

X-ray diffraction (XRD) patterns were obtained using a Siemens type F diffractometer with CuK$_\alpha$ radiation and a LiF monochromator. A Perkin Elmer FT-IR spectrophotometer was used for recording the IR spectra of pure PVA and PVA doped with TiCl$_3$ samples in the region 400–1800 cm^{-1} with KBr pellet as IR transmitting materials. The fluorescence emission spectra of pure PVA and PVA doped with TiCl$_3$ were recorded at room temperature using FluroMax-2 spectroflourophotometer. The wavelength accuracy of emission was ± 1 nm. Optical absorption spectra of pure PVA and PVA samples doped with TiCl$_3$ were carried out at room temperature on a Perkin Elmer UV–Visible spectrophotometer in the wavelength range 200–900 nm. The dielectric constant, dielectric loss and relaxation time of the PVA complexes are determined by measuring capacitance C and loss tangent ($\tan\delta$) using an AC impedance bridge (WAYNE KERR precision component analyzer model 6440B) at room temperature in the frequency range from 20 Hz to 3 MHz. The dielectric constant (ε') is evaluated from the capacitance measurements using the following equation:

$$\varepsilon' = \frac{C}{C_0} \quad \text{and} \quad C_0 = \varepsilon_0 \frac{A}{d} \tag{1}$$

where C_0 is the vacuum capacitance of any configuration of electrodes and C is the capacitance with isotropic material filling the space. A is the cross section area of the sample and d is the thickness.

Relaxation times of the complexes are obtained from the study of $\tan\delta$ as a function of frequency. For maximum dielectric loss, the absorption peak is described by the relation $\tau\omega \approx 1$, where τ is the relaxation time and ω is the angular frequency of the applied signal.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Fig. 1 displays the comparison of the XRD scans of undoped PVA film with that of PVA/TiCl$_3$ films. The XRD pattern of pure PVA shows a characteristic peak for an orthorhombic lattice centered at 2θ=20° indicating its semicrystalline nature [8]. On the incorporation of titanium chloride into PVA, the intensity of this peak decreases gradually, suggesting a decrease in the degree of crystallinity of PVA. The crystalline nature of PVA results from the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bonding. These interactions between PVA and TiCl$_3$ lead to the decrease of the intermolecular interaction between the PVA chains and thus the crystalline degree. Hodge et al. [9] established a correlation between the intensity of the peak and the degree of crystallinity. They observed that the intensity of XRD pattern decreases as the amorphous nature increases with the addition of dopant. No sharp peaks were observed for higher concentration of TiCl$_3$ in the PVA films, suggesting the dominant presence of amorphous phase [10].

3.2. FT-IR spectroscopy

FT-IR spectroscopy is an important investigation of polymer structure that provides information about the complexation and interactions between the various constituents in the polymeric films. FTIR spectra of polyvinyl alcohol (PVA) and PVA/TiCl$_3$ are shown in Fig. 2. The infrared spectrum of pure PVA has been the subject of several investigations [11]. It is well known that the vibrational spectra of PVA are related to the stretching and bending vibrations of O–H, C–O, C=C and C–H groups. The complete assignments for the frequencies of different groups and vibrational modes of both PVA and PVA/TiCl$_3$ are presented in Table 1. From the infrared spectra, it can be noticed that the doping with TiCl$_3$ causes some observable changes in the spectrum of PVA in the range 1000–400 cm^{-1}. It induces some new absorption bands and slight changes in the intensities of some absorption bands. The new absorption bands may be correlated likewise to defects induced by the charge-transfer reaction between the polymer chain and the dopant [12]. The vibrational peaks found in the range 1000–400 cm^{-1} can be attributed to ν(C–Cl) and Ti–O which indicate that the dopant is complexed with the polymer matrix [13]. The absorption band at 1571 cm^{-1} is indicative of the formation of small conjugated polyene sequences which are presumably responsible for the color of the PVA/TiCl$_3$ complexes. These conjugated polyene sequences are suitable sites for the formation of some defects as polarons and bipolarons. The absorption band at 929 cm^{-1} was found to be characteristic of syndiotactic structure of the complex films.

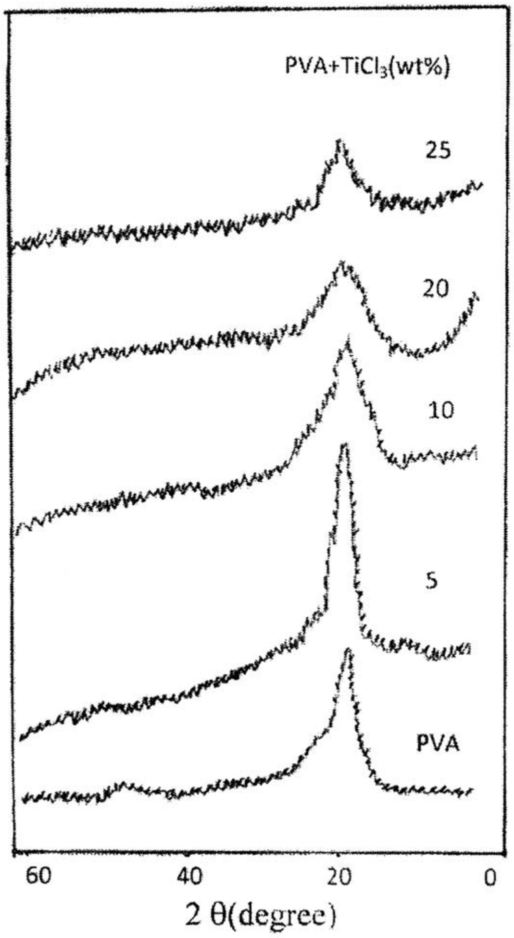

Fig. 1. X-ray diffraction patterns of PVA and PVA doped with different concentrations of TiCl$_3$.

The shift in frequency is correlated with force constant and bond length. The force constant values can be calculated from the expression [14]

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{2}$$

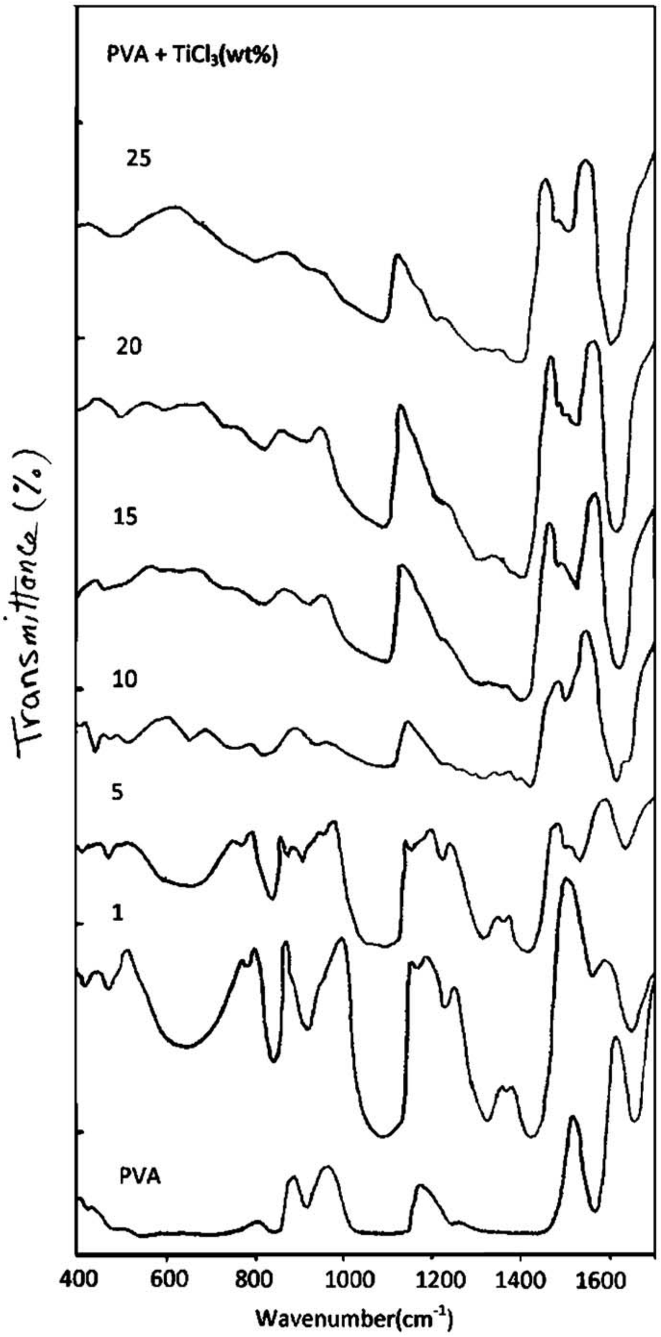

Fig. 2. FTIR spectra of PVA and PVA/$TiCl_3$ films.

Table 1
The characteristic infrared absorption frequencies of PVA/$TiCl_3$ films at room temperature.

Frequency (cm^{-1})	Assignment	Intensity
428	ν_w(CO)	Sharp and weak
491	δ (Co)	Sharp and weak
670	ν_w(OH)	Broad and strong
860	ν(CC)	Sharp and strong
929	$\nu_r(CH_2)$	Sharp and strong
1122	ν(CO)	Broad and very strong
1253	ν_w(CH)	Sharp and weak
1317	δ (CH–OH)	Sharp and very strong
1477	δ (CH_2)	Sharp and very strong
1571	ν(C=C)	Sharp and very strong
1662	ν(C=O)	Sharp and very strong

ν=stretching, δ=bending, ν_w=wagging, ν_r=rocking and ν_a=asymmetric.

where ν is the wavenumber, c the velocity of light, k the force constant and μ is the reduced mass. From Table 2, it is interesting to note that the force constant decreases for C–O stretching band with increase in $TiCl_3$ concentration. This decrease in force constant is due to titanium interaction with the polymeric matrix. These changes indicate the possibility of titanium ion to be attached to OH group in the side chain of PVA molecules. Similar results were confirmed by several authors [15].

3.3. *Fluorescence spectra*

In order to understand the PVA/$TiCl_3$ complex films, the fluorescence emission spectra of all the samples were recorded at room temperature and the spectra are shown in Fig. 3. The wavelength of excitation chosen for all samples is 250 nm. The emission spectra of the prepared films exhibit obvious main four peaks centered at 366, 398, 450 and 467 nm. Similar bands appear in the emission spectrum of PVA. It can be seen that the emission peaks are at the same spectral position. These bands may be assigned to the recombination of free charge carriers at the defects in PVA. The doping level dependence on the emission intensity of one of these bands is given in Table 3. It is found that, the fluorescence intensity of the doped films is higher than that of pure PVA except the doping level 10 wt%. The increase of the intensity of the emission peak may be due to the strong interaction between the dopant and the polymer. This observation is in agreement with pervious works [16–18]. The falling in the emission intensity may be because of an aggregation of dopant molecules [19].

3.4. *Optical absorption*

Fig. 4 shows the absorption spectrum of undoped PVA and doped PVA with $TiCl_3$.

3.4.1. *Spectrum characterization*

The UV–Visible absorption spectra of pure PVA as well as PVA doped with $TiCl_3$ are shown in Fig. 4. It is clear that the spectrum of pure PVA exhibits an absorption edge (AE) around 250 nm indicates the semicrystalline nature of PVA. This result is confirmed by XRD. Fig. 4 shows a shift in AE towards the higher wavelengths. These shifts in the AE indicate the formation of inter-/intra-molecular hydrogen bonding mainly between titanium ions with that of the adjacent OH groups. These bonds reflect the variation of the energy band gap which arises due to the variation in crystallinity within the polymeric matrix [20]. Jayasekaro et al. [21] have also reported such absorption bands for PVA and its blends. Table 3 shows the doping level dependence of the absorption edge (AE). It is clear that the AE increase dramatically with increasing titanium content. This may be due to a larger absorption increment associated with the charge-transfer transition $^2T_2$–^2E [3]. This can also be concluded from a simple visual inspection of the samples since their color gradually turns from white to brownish-red [15]. This means that the samples can absorb light in a quite broad spectral range up to the visible region [4]. Therefore, PVA/$TiCl_3$ films are an excellent UV absorber.

3.4.2. *Determination of the optical energy band gap (* $\boldsymbol{E_g}$ *)*

The optical absorption spectrum is an important tool to obtain optical energy band gap of crystalline and amorphous materials.

Table 2
FTIR modes of C=C and C–O band variations in PVA/$TiCl_3$ complexes.

$TiCl_3$ (wt%)	C=C band variations		C–O band variations	
	Wavenumber (cm^{-1})	Force constant (N/cm)	Wavenumber (cm^{-1})	Force constant (N/cm)
Pure	1571	8.72	1147	5.37
1	1571	8.72	1141	5.26
5	1556	8.56	1143	5.28
10	1535	8.33	1141	5.26
15	1527	8.245	1139	5.24
20	1529	8.26	1139	524
25	1527	8.24	1143	5.28

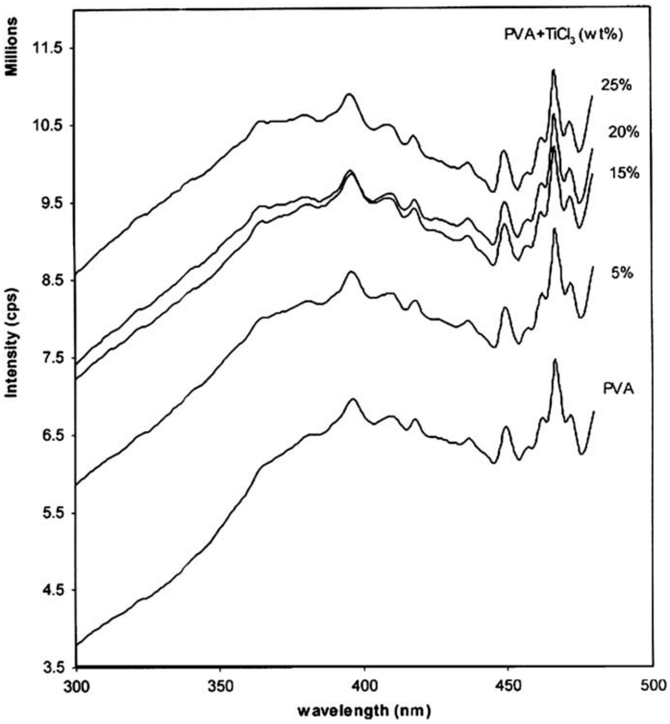

Fig. 3. The emission spectra of PVA and PVA doped with different concentrations of $TiCl_3$ recorded at room temperature.

Table 3
The filling level dependence of AC conductivity (σ_{AC}), dielectric constant (ε'), impedance (Z), relaxation time (τ), optical energy gap (E_g), intensity of the emission peak at 467 nm and absorption edge (AE).

$TiCl_3$ (wt%)	Conductivity parameters at 1 kHz				Optical parameters		
	σ_{AC} (MΩ)	ε'	Z (MΩ)	τ (μs)	E_g (eV)	I_F (million cps)	AE (nm)
Pure	0.05	11.3	17.3	106.11	5.2	7.4	235
1	2.12	220	5.1	3.18	4.2	10.2	284
5	0.44	160	4.0	1.98	3.8	9.2	316
10	0.08	183	6.9	–	3.5	6.2	332
15	0.15	396	3.3	–	3.5	10	336
20	0.10	381	2.14	–	3.5	10.6	338
25	0.30	157	3.8	–	3.5	11.2	344

In order to determine optical energy band gap of the films, the absorption coefficient was determined from the spectra using the formula:

$$\alpha = \frac{\ln \frac{1}{T}}{d} \tag{3}$$

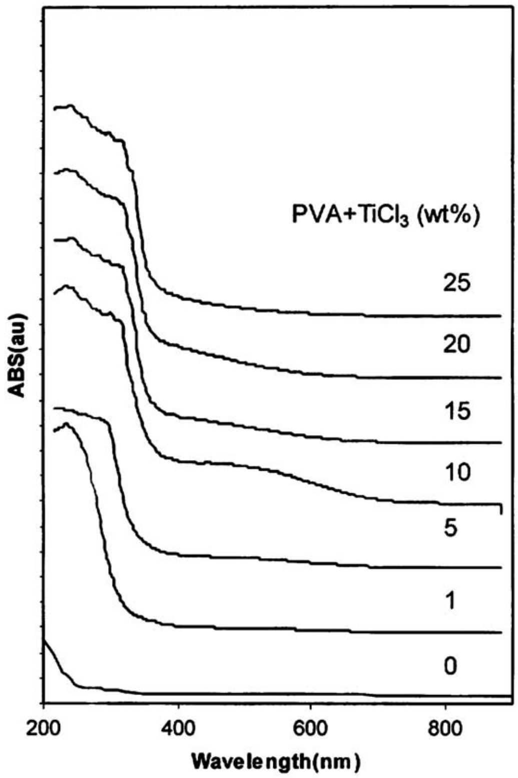

Fig. 4. The variation of the absorption with the wavelength for different concentrations of $TiCl_3$.

where T is the transmittance and d is the film thickness. The optical energy band gap of the films was determined from the absorption spectra near the absorption edge. The absorption coefficient dependence on photon energy is expressed as [22]

$$\alpha(\upsilon) = B\frac{(h\upsilon - E_g)^r}{h\upsilon} \tag{4}$$

where B is a constant, $h\nu$ is the photon energy and E_g is the optical energy band gap, r is an exponent which can take values of 1, 2, 3, 1/2, 3/2 depending on the nature of the electronic transitions responsible for the optical absorption. The best straight line can be determined from the slope of the linear part of $(\alpha h\nu)^2$ versus $h\nu$. This suggests that the transition energy for electrons may account for direct allowed transition. So the direct optical energy band gap (E_g) were evaluated from $(\alpha h\nu)^2$ versus $h\nu$ plots from the linear parts of these curves as shown in Fig. 5. The optical energy band gap of the prepared samples is observed in Table 3. It is evident from Table 3 that the values of the optical band gap firstly decreases with increasing $TiCl_3$ content and goes on a constant value for doping levels more that 10 wt%. Titanium chloride

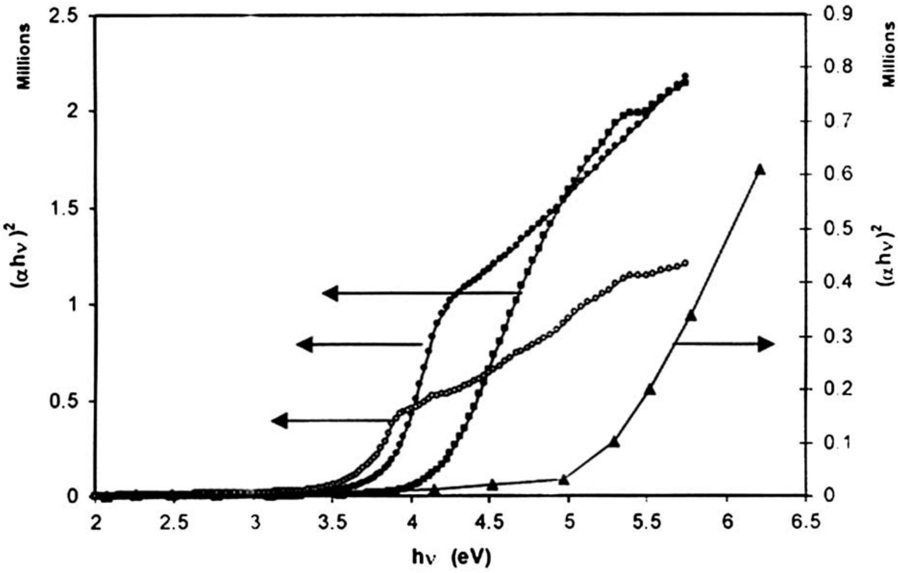

Fig. 5. $(\alpha h\nu)^2$ versus photon energy $h\nu$ for pure PVA (▲), PVA doped with 1%(■), 5% (•) and 10%(◦).

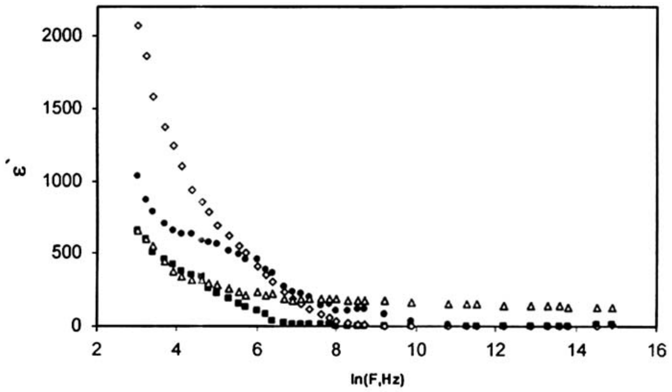

Fig. 6. Frequency dependence of the dielectric constant ε' for PVA (■), 1 wt% (•), 10 wt% (•) and 25 wt % (◇).

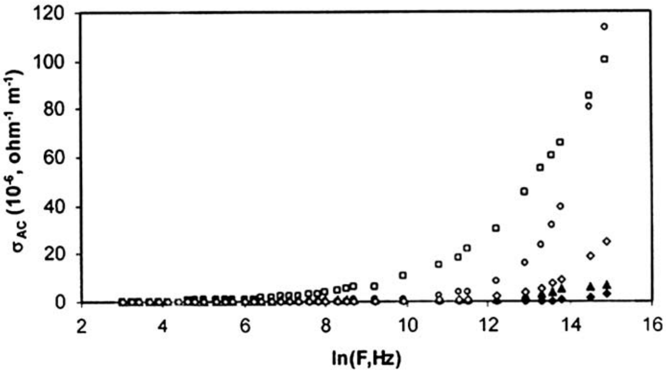

Fig. 7. Frequency dependence of the AC conductivity for PVA (♦), 1% (□), 5% (▲), 10% (◇) and 20% (◦).

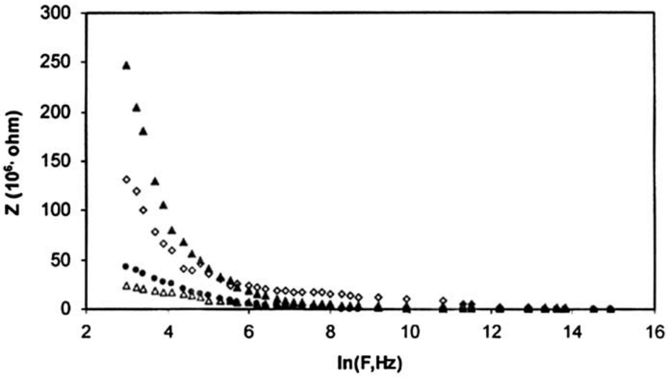

Fig. 8. Impedance dependence on frequency for PVA (◇), 5% (△), 10% (▲) and 20% (•).

content is responsible for the formation of some defects in the films. These defects produce the localized states in the optical band gap and overlap. These overlaps give an evidence for decreasing energy band gap when the $TiCl_3$ content is increased in the polymeric matrix. In other words the decrease in the optical gap reflects the increase in the degree of disorder in the films. These results are in agreement with that obtained from XRD. Yakuphanoglu and co-workers [23] observed similar results.

3.5. Dielectric studies

The dielectric behavior of pure PVA and its complexes have been studied and the results are analyzed in terms of different parameters. It was noticed that the phase angle was always negative, indicating that the complexes were capacitive and could be represented by parallel RC networks connected in series. Fig. 6 shows the variation of dielectric constant ε' with frequency at room temperature for pure PVA and PVA doped with $TiCl_3$. It is observed from the figure that the dielectric constant continuously decreases with increasing frequency and reaches a constant value at high frequency. A rapid decrease in dielectric constant may be noticed over the frequency range 1–10 kHz. This may be attributed to the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field in the low-frequency range. However, in the high-frequency range the dipoles will hardly be able to orient themselves in the direction of the applied field and hence the value of the dielectric constant is nearly constant [24].

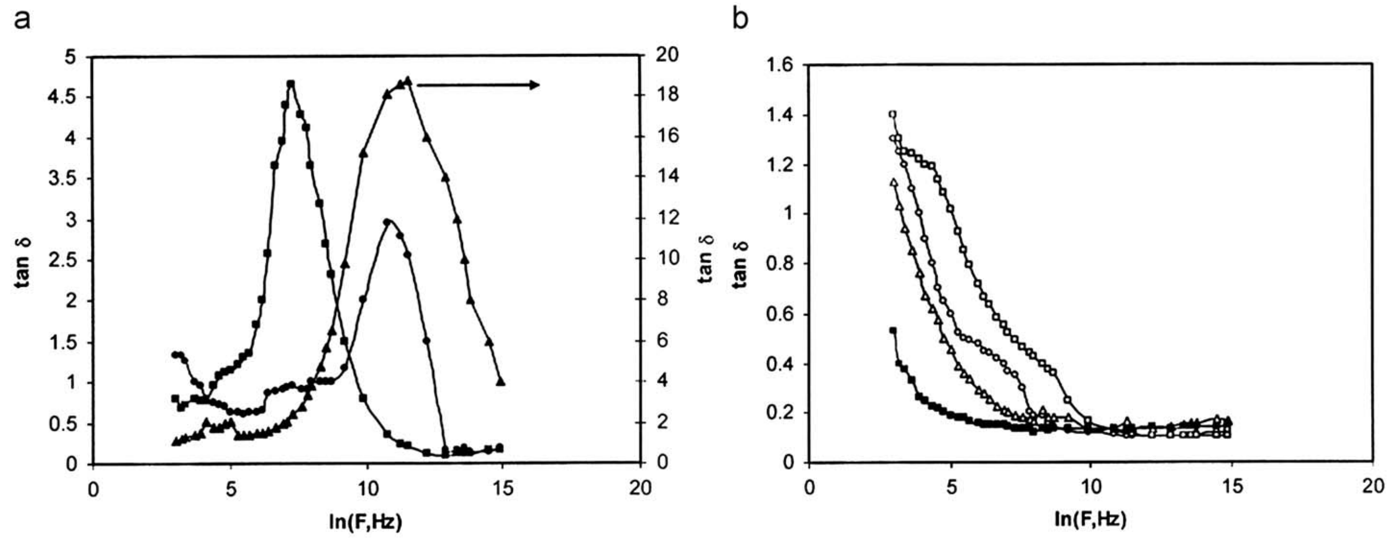

Fig. 9. (a, b) Variation of dielectric loss (tan δ) with frequency for (a) PVA (■), 1% (•) and 5% (▲) and (b) 10% (◦), 15% (□), 20% (△) and 25% (■).

At a particular frequency $f=1$ kHz, the doping levels dependence of the values of the dielectric constant for the PVA–TiCl$_3$ complexes are determined and summarized in Table 3. It is clear that the dielectric constant value, for undoped PVA, has a higher value than that observed for doped PVA films. The increasing of dielectric constant values is due to the formation of newer complexes.

The AC conductivity, σ_{AC}, for the polymeric films is calculated from the following equation [25]:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \qquad (5)$$

where f is the applied field frequency, ε_0 is the permittivity of free space and ε'' is the dielectric loss. The dependence of the calculated AC-conductivity on frequency is shown in Fig. 7. At high frequency, the conductivity increased rapidly. This increase arose from the movement of free ions. The doping level dependence of the σ_{AC}, at $f=1$ kHz, is given in Table 3. It is clear that all doped samples show higher values than the undoped sample due to the introduction of localized states.

Fig. 8 shows the frequency dependence of impedance. Impedance values decrease with increasing frequency and increasing titanium chloride. The observed decrease in impedance with TiCl$_3$ content is due to ionic migration existing in the dopant. This motion also leads to higher electrical conduction in the doped samples.

The variation of loss tangent (tan δ) as a function of frequency for pure PVA and PVA complexes with titanium chloride is shown in Fig. 9a. It is clear that pure PVA and doping levels 1, and 5 wt% show a relaxation process. For higher doped samples the values of tan δ decrease as frequency increases as shown in Fig. 9b. Relaxation times were found to decrease with the increase of titanium content. The doping level dependence of relaxation time is tabulated in Table 3. The decrease in relaxation time may be attributed to the increase in mobility of ions in the polymer matrix [26].

4. Conclusion

The examinations of PVA/TiCl$_3$ films conclude:

1. The spectroscopic investigations revealed that the spectra of the doped films show some observable changes in peak intensity and position with the doping levels and this may be due to the link between the metal ions and the polymer OH group.
2. The optical energy gap decreases dramatically as TiCl$_3$ increases up to doping level 10% and then remains a constant.
3. The decrease in the impedance as the doping level increases may be mainly attributed to the high degree of amorphization in the structures. The decrease in relaxation time as doping levels increase may be attributed to the increase in mobility of ions in the polymeric matrix.
4. The increase in both σ and ε'' are implied an increase in the localized charges distribution within the polymeric matrix.

Finally titanium chloride plays an important role in modification of the optical and dielectric properties of PVA to make it more applicable.

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