

Study on Structural Characterization and Dielectric Properties of PVA-TiO₂ Composite

S S MORE¹, R J Dhokane² and S V Mohril³

^{1*}RTMNU, Nagpur, MS, India

²Department of Physics, GHRIETW Nagpur, MS, India*

³RTMNU Nagpur, MS India

Abstract: In present study, the dielectric properties of PVA /TiO₂ composite films were estimated. PVA/ TiO₂ films were prepared by using the solvent casting technique and characterized by XRD, FTIR, and FESEM. XRD study reveals that polycrystalline nature of composite films. FESEM micrograph of thin films clearly confirms that the content of TiO₂ is rising with a concentration of it. The presence of hydroxyl group (O-H) of PVA structure and Ti-O bonding in thin films is verified by FTIR. An analysis of the frequency dependence of the AC conductivity is found to increase with increasing the TiO₂ concentration at room temperature. The highest conductivity observed is 2.48E-06 s/cm for PVTI-30. A usual power law dependency in the real part of the conductivity, at higher frequencies, of the form w^s is observed, with an exponent 's' that depends on the TiO₂ content. The frequency exponent factor was estimated, and it was found to vary between 0.87 and 0.55 with an increase of TiO₂ concentration. The dielectric properties such that, real and imaginary part of dielectric permittivity (ϵ' & ϵ''), dissipation factor ($\tan\delta$) of films were studied at higher frequencies. The dielectric permittivity and dissipation factor were found to decrease with frequency.

Keywords: PVA-TiO₂, Dielectric permittivity, dissipation factor, Ac conductivity.

I. Introduction

Thin films of polymer brought so many applications in technology due to its tremendous advancement in it; include sensors, electrochemical cells, coatings, lithography, and organic light emitting diodes. With variation in thickness of polymer thin films, varies different physical phenomenon, which occurs due to the effect of confinement and interfacial interaction. They have high conductivity; light in weight, inexpensive, flexible, etc. [1]. In industries doped and undoped polymers have good potential due to their remarkable properties such as high melting point & thermal conductivity, low coefficient of thermal expansion, high hardness, low density, etc. They are used in making a solar cell, optoelectronics device elements, laser diodes and light emitting diodes (LED) [2]. Polyvinyl Alcohol has such excellent properties usable in material science and technological applications. It is a semi-crystalline water soluble material exhibits certain physical properties resulting from crystal-amorphous interfacial effects [3, 4]. The considerable effect is observed on optical and electrical properties of PVA polymer due to the addition of inorganic additives such as transition metal salts. Dielectric properties of PEO-PVP-MMT nanocomposite hydrocolloids are studied by S Choudhary and R J Sengwa [5]. The dielectric properties of polymer thin films got much significance due to the discovery of memory phenomenon as well as large applications in thin film devices. Various ceramic filler, Al₂O₃, TiO₂ [6], SiO₂ [7] have been broadly studied for the growth of ionic conductivity in polymer matrix since the addition of them into polymer matrix allow to reduce the glass transition temperature and the crystallinity of the polymer, hence increases the amorphous phase. The ceramic particle filler creates some defects as well as the free volume at the interface of linking polymer chain, and the ceramic particle will be the reason for increasing ionic conductivity of the composite polymer. In the present work, we attempted to dope TiO₂ particles into the PVA matrix act as a solid plasticizer capable of improving mechanical, thermal and chemical stabilities of PVA- TiO₂ Composite.

II. Experimental Details

2.1 Materials and Methods:

PVA & TiO₂ (SD Fine Chemicals), were used as received without purification. Pure PVA films and PVA containing different amount of TiO₂ at 5%, 10%, 20% and 30% are used for the study. All samples were prepared from an aqueous solution of PVA. An aqueous solution of PVA is prepared by adding PVA in Double distilled water and stirring it at 70°C temperature for three hours on a magnetic stirrer. Then the solution was displayed on glass plates and kept it for 24 hours in the dark room to evaporate all water content. Pure PVA films are obtained from this solution. For PVA- TiO₂ films, desired TiO₂ concentration was introduced into an aqueous solution of PVA. The mixture was stirred on a magnetic stirrer for four hours and displayed on a glass

plate. The glass plates are kept in darkness for 24 hours at room temperature to evaporate all water content. The prepared films were kept in desiccators until use [8-10].

2.2 Structural Characterization:

X-Ray Diffraction pattern of PVA and TiO₂ doped thin films recorded at room temperature. XRD are obtained from advanced refraction system XRD. The intensity was recorded in scattering over the range angular angle (2θ) in between 5-20. Fourier Transform Infrared spectroscopy of samples is carried out by using spectrophotometer over the range of 400-4000cm⁻¹. The microstructural characterization was performed using Scanning Electron Microscope (FESEM).

2.3 Dielectric Measurement:

The dielectric properties ac conductivity (σ_{ac}), real and imaginary part of dielectric permittivity (ε' & ε''), dissipation factor (tanδ) were measured as a function of frequency (1 Hz to 1MHz) using a Novo control Broadband Dielectric Spectrometer. A sample was polished to make both the surfaces flat and coated with air drying conducting silver surfaces for better electrical contact.

III. Result and discussions

3.1 X-ray Diffraction:

The X-ray diffractogram is used to classify various crystalline phases or phase analysis of polycrystalline materials which shows the Bragg's diffraction peaks at a specific position depending on their natural crystalline structure. The X-ray Diffraction pattern has been done to investigate the structure and crystallinity of PVA/ TiO₂ polymer composites. Fig. 1 Shows diffraction peaks of pure PVA, pure TiO₂ of anatase type and PVA/ TiO₂ polymer composites, when diffracting angle is in the range of 2θ = 10-70°. Characteristic wide peak for an orthorhombic lattice at 2θ = 20° of pure PVA has seen and it contains the crystalline and amorphous region [11]. The peak occurs (2θ=35°) in PVA/ TiO₂ polymer composites at all loading percentage, which has not found in pure PVA and pure TiO₂. The appearance of this new peak may occur due to dissociation of particles during stirring process, and thereby interaction occurs between PVA and TiO₂ [12]. Semi-crystalline nature of PVA has been changed according to the percentage of loading of TiO₂. It has been found that certainly in doped films peak of PVA is increased in broadness and decreased in intensity, indicates that amorphous region is increasing with TiO₂ loading. The hydrogen bonds in PVA matrix are responsible for crystallization of it. Intermolecular interaction of PVA chains decreases due to the interaction between PVA chains and TiO₂ particles (via hydroxyl bonds), which decreases the crystalline degree of PVA on loading of TiO₂; further decrease the homogeneity of dispersion in the composite samples. The average crystallite size of PVA in the thin films is calculated by using Scherrer formula.

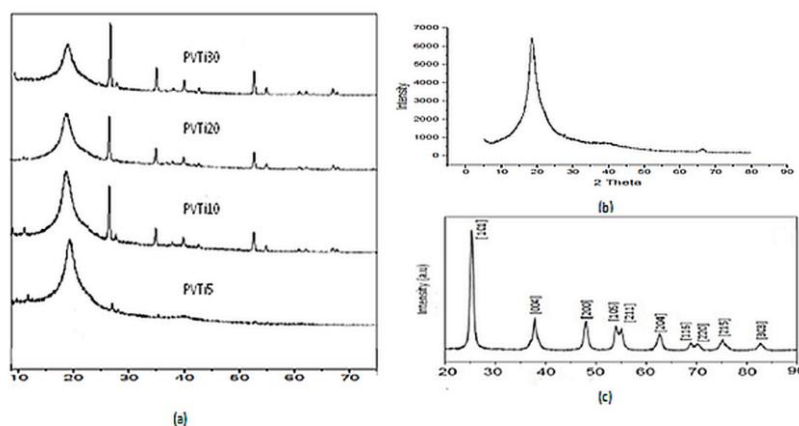


Fig. 1 XRD of a) PVA- TiO₂ composites PVTi5, PVTi10, PVTi20, PVTi30 b) Pure PVA c) Pure TiO₂

$$d = 0.9\lambda / \beta \cos\theta \quad (1)$$

Where λ is the wavelength of X-ray used (1.54Å), β is FWHM of the diffracted peak and θ is the Bragg's angle. The crystallite size is found to decrease with increase in TiO₂ loading.

3.2 Fourier Transform Infrared Spectroscopy:

The FTIR spectra for TiO₂ doped PVA thin films at different loading % of TiO₂ are shown in Fig. 2. The major peaks are associated with polyvinyl alcohol. For illustration, typical strong hydroxyl bands for free alcohol OH stretching band at 3580-3640 cm⁻¹, and strong OH stretching broadband at 3200-3600 cm⁻¹ are

observed. The strong, broad absorption bond of Ti-OH is observed around 3452 cm⁻¹, this bond arises due to bonding between the hydroxyl group of PVA and titanium ions, which allows forming the charge transfer complex which in turn the number of charges increases with increase in TiO₂. The changes in microstructural properties of the polymer are observed; depends on the interaction of filler with host polymer. The interaction between the PVA- TiO₂ shows the strong dependence of donor- acceptor mechanism between the metal ion and polymer since the filler serves as an electron acceptor (high electron affinity) while PVA act as an electron donor. Strong stretching C=O bond of the acetyl group of PVA chain observed at 1722 cm⁻¹. All the graphs show TiO₂

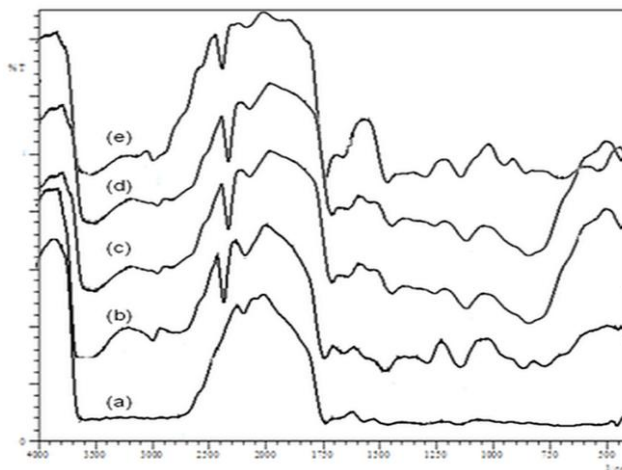


Fig.2. FTIR of (a) Pure PVA (b) PVTi5 (c) PVTi10 (d) PVTi20 (e) PVTi30

characteristics broadband in the region 450-575cm⁻¹. The medium OH bending (in plane) vibrations observed in the region 1250-1290cm⁻¹. C-O stretching vibrations of acetyl group observed in the region 1131-1138cm⁻¹. C-H asymmetric stretching vibrations occur at 2945-2967cm⁻¹ and symmetric stretching vibrations are occur at a vibrational frequency in the range 2805-2859cm⁻¹. Vibrating frequency of CH₂ stretching vibrations are observed to decrease with increase in doping concentrations. The medium C-H bending vibrations and strong C-H bending vibrations are occurred at 1457 cm⁻¹ and 620 cm⁻¹ respectively [13-15].

3.3 FESEM:

The Scanning electron microscopy of PVA- TiO₂ films was done to study the microstructure of the films shown in Fig.3. The morphology of the particles is seen to change with concentration of TiO₂ particles. At lower concentration, the dispersion of TiO₂ particles is nearly homogeneous, shows well the distribution of TiO₂ particles within the PVA matrix. With the increase in the concentration of TiO₂ irregular morphology seen, this could be an aggregation of TiO₂ particles.

3.4 Dielectric Properties:

Fig. 4(a) shows the dependence of real dielectric constant on the log of frequency at room temperature. It verifies that value of ε' is high at low frequencies since electric dipoles have enough relaxation time to support with the field; thus the high dielectric constant. But relaxation time decreases with increase in frequency as dipoles do not get sufficient time to support with the field and decreases the dielectric constant. The values of ε' rise with a dopant concentration of TiO₂. This rise in ε' values could be ascribed by Maxwell- Wagner interfacial polarization[16].

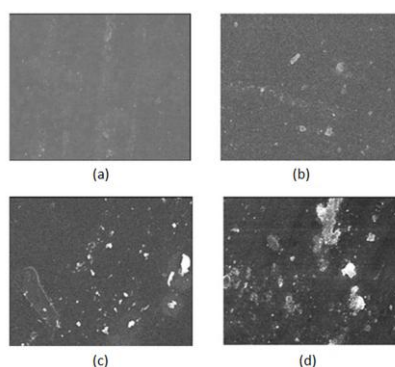


Fig 3 SEM of PVA-TiO₂ composites at (a) PVTi5 (b) PVTi10(c) PVTi20 (d) PVTi30

The variation of dielectric loss with frequency for PVA- TiO₂ at different concentrations is shown in Fig 4(b). It is clear from the graph that loss decreases with frequency. The higher value of the dielectric loss at the higher concentration of TiO₂ can be understood regarding electrical conductivity, which is related to the dielectric loss. Moreover, PVA is a polar polymer with polar bonds and shows flexible polar groups since the bond rotating has an intense dielectric α -transition.

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^\gamma} \quad (2)$$

Where, ϵ_s and ϵ_∞ are the static and infinite dielectric permittivity, τ is the relaxation time and ω is the angular frequency.

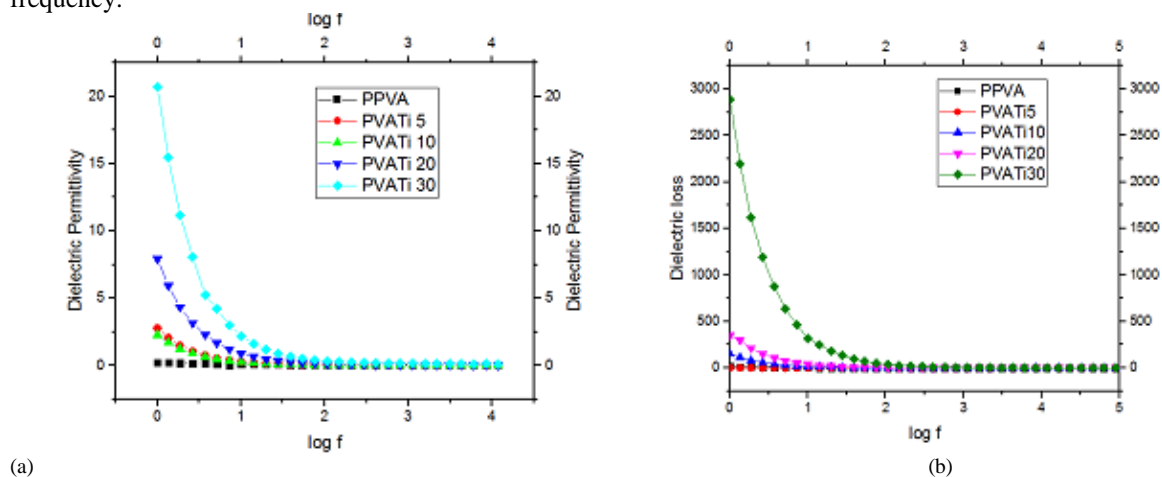


Fig 4 variation of (a) Real (ϵ') and (b) imaginary part (ϵ'') of dielectric permittivity

The flexibility of polymer chain is due to change in chemical composition of repeated units of polymer due to configuration of hydrogen bonds with hydroxyl groups during polymerization process and hence increases the electrical conductivity [17-18]. Variation of dissipation factor ($\tan\delta$) with $\log f$ is shown in Fig.5. It is found that $\tan\delta$ values decrease with increase in frequency although increase with increase in wt% of TiO₂. This behavior occurs due to interfacial polarization in PVA- TiO₂ composite. At lower frequencies, dielectric loss is high but at higher frequencies, loss decreases due to smaller relaxation time, then increases the conductivity. The AC conductivity for pure PVA and PVA- TiO₂ composite films obtained at ambient temperature is shown in Fig.6. By incorporating a good inorganic material like TiO₂ in traditional PVA, structural and electrical properties are found to be improved [19]. Fig.5 depicts that ionic conductivity rises by

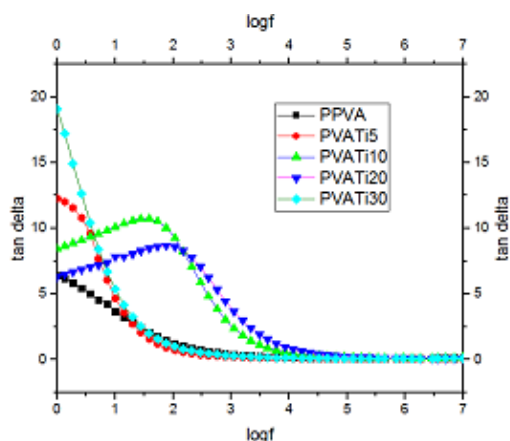


Fig.5 Variation of $\tan \delta$ with $\log f$

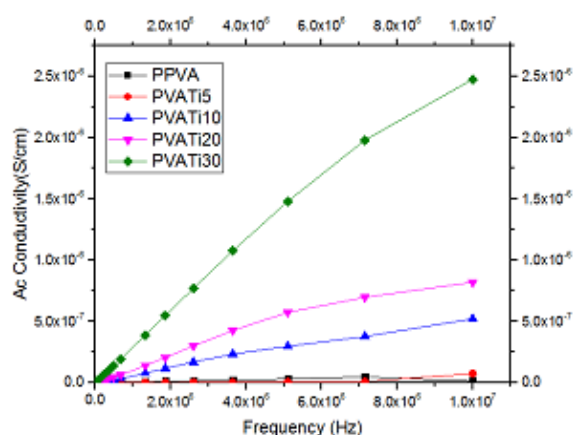


Fig. 6 Variation of conductivity with frequency

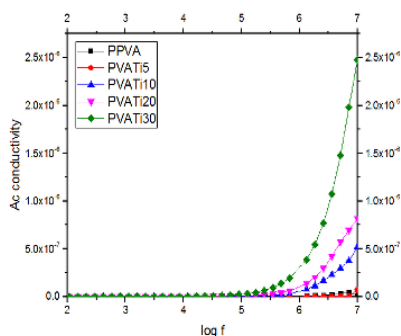
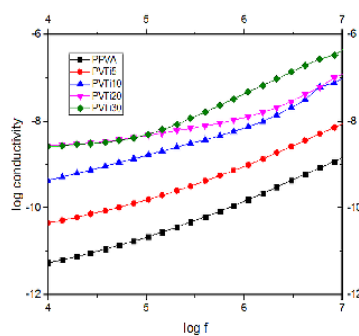


Fig.7. Variation of conductivity with log f


 Fig.8 Variation of log σ with log f

frequency; is frequent for all polymeric and semiconductor samples. Since the gradual increase in the amorphous region, polymer chain gains faster internal modes; produces segmental motion due to bond rotations, causes hopping interchain and intra-chain ion movements, this in turn conductivity of samples becomes high [20]. XRD studies could confirm the increase in conductivity of samples with TiO₂ concentration. It shows that crystallinity decreases and amorphicity increases with the concentration of TiO₂.

From Fig 7 it is depicted that ac conductivity remains almost independent of frequency in the low-frequency region and reveals dispersion at high frequencies. This behavior confirms the universal power law,

$$\sigma_{ac} = \sigma_{dc} + A\omega^s \quad (3)$$

Where, σ_{dc} is the dc conductivity, A is a pre-exponential factor, s is the frequency exponent which lies between 0 and 1. It is the universal character of the frequency dependent conductivity preserved for a wide range of amorphous materials, among which are polymeric materials. The values of s for different TiO₂ concentration are evaluated from linear slope of log σ_{ac} against log f as illustrated in Fig.8. The values frequency exponent's' for PVA- TiO₂ composites given in Table 1. Its values decrease with increasing concentration of TiO₂ at room temperature. It confirmed that σ_{ac} obeys a power law, and the values of s are within $0 < s < 1$.

Table 1: Values of frequency Exponent factor (s) for PVA-TiO₂ composites

Samples	PPVA	PVTi5	PVTi10	PVTi20	PVTi30
Exponent factor (s)	0.87	0.72	0.67	0.56	0.55

IV. Conclusions

PVA- TiO₂ composites films were prepared by solvent casting technique. Composite films characterized by XRD, FTIR, and FESEM. The dielectric properties of composites were studied; the results show that Ac conductivity of PVA increases by increasing TiO₂ concentrations. It confirms the universal power law and the frequency exponent (s) decline with the increase of doping content and it lies between $0 < s < 1$. The values of dielectric permittivity and loss factor decrease with increase in frequency and increases by the addition of TiO₂ concentrations. The addition of semiconducting fillers in the insulating polymers could lead to innovation in a synthetic method for better-conducting films.

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