

Influence of Rare Earth Ion Lanthanum on Physical Properties of Biodegradable Polymer Blend PVA/PVP

Sudha Kamath M. K.^{1*}, Chandramani R.² and Radhakrishna M. C.³

¹ Department of Physics, R V College of Engineering,
Bangalore-560059, Karnataka, India

²Department of Physics, Dayananda Sagar College of Engineering,
Bangalore, Karnataka, India

³Department of Physics, Bangalore University,
Bangalore, Karnataka, India

*Corresponding author's email: [sudhakamath \[AT\] rvce.edu.in](mailto:sudhakamath [AT] rvce.edu.in)

ABSTRACT--- *A biodegradable solid polymer blend films of PVA (50) /PVP (50) filled with La (NO₃)₃ were prepared by solution casting technique. The samples were subjected to Structural, Optical, Mechanical and Electrical investigations. The degree of amorphosity of the polymer blend composites was increased by the incorporation of filler into the polymer blend matrix which is shown by XRD. Decrease in the optical energy gap values was observed with the addition of filler which is illustrated by UV-vis studies, indicating the interaction of filler with polymer blend matrix. Temperature dependent broad band dielectric spectroscopic investigations have been carried out on all prepared samples in the frequency band 100 Hz to 1MHz. AC conductivity has been increased with increase in frequency which confirmed the possibility of higher concentration of charge carriers as well as their higher mobility. Dielectric behaviour was investigated using dielectric permittivity and dielectric loss tangent. With the temperature increase, value of dielectric constant was found to increase depicting the more polar nature of polymer matrix. The tangent loss spectra of the samples showed a broad peak which confirms the presence of relaxing dipoles in the polymer composites. Mechanical properties of the samples have been analysed employing nanoindentation technique which reveals the role of filler content in improving the elastic modulus and hardness of the samples.*

Keywords--- Polymer blend, XRD, UV-vis absorption spectroscopy, Dielectric properties, Nanoindentation

1. INTRODUCTION

The polymer blending technology turned out to be a brilliant means for modifying a polymer compound for specific uses/multifunctional device applications, often at much lower fabrication costs than the current available material. Very often precise properties are achieved by blending crystalline and amorphous polymers. Crystalline polymers have outstanding chemical resistance, good mechanical properties, low viscosity whereas amorphous polymers provide good dimensional stability [1]. Solution blending is one of the simple blending techniques which have control over the physical properties within the miscibility compositional regime.

Poly (vinyl alcohol) (PVA) is a semi crystalline, water soluble, nontoxic synthetic polymer which has highest application in polymer industry. PVA exhibits interesting physical properties due to the presence of OH groups which are responsible for hydrogen bond formation with other polymers [2]. Poly(vinylpyrrolidone) (PVP) is a low toxic amorphous vinyl polymer having outstanding physiological compatibility. PVP is soluble in water and most organic solvents [3]. The two polymers have polar side groups; PVA contains a hydroxyl proton and PVP contains a pyrrolidone ring, which has a proton-accepting carbonyl group [4]. It is therefore expected that a hydrogen bonding interaction occurs between PVA and PVP [5].

The superiority of polymeric materials is due to the aspects of their tremendous versatility and amazing degree of tailoring to bring them closer to the novel applications. Polymers in combination with transition metal/rare earth metal salts give complexes which find applications in high energy electrochemical devices. Dielectric properties of polymers play a dynamic role in device applications such as high performance capacitors, electrical cable insulation, electronic packaging to medical equipment etc., [6].

Rare earth ions filled polymer blend composites are extensively investigated because of their useful applications. The intention of this work is to explain the possibilities of fabrication of new polymer composites containing rare earth ions to make them useful in technological applications. Rare earth metal ion La^{3+} has shown significant effect on the crystallinity of the host matrix. Also, Optical, Mechanical and the Dielectric properties of pristine PVA (50) /PVP (50) polymer blend films are improved with the addition of La^{3+} metal ions.

2. EXPERIMENTAL WORK

Polyvinylalcohol (PVA) and (PVP) Polyvinylpyrrolidone (PVP) were purchased from Aldrich. Double distilled water was taken as a common solvent for both polymers and filler particles. Initially PVA(50)/PVP (50) stock solution was prepared according to the procedure explained by H. M. Ragab [7]. The uniform and homogeneous solution mixture of known quantities of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5, 15, and 25%) was added to the polymeric stock solution after ultrasonication at room temperature for 30 minutes. The mixture was stirred continuously for 6-8 hours and then kept for 24 hours to remove the bubbles. The mixture was then transferred into polypropylene plates and dried in oven for 4 days at 50°C to make the sample completely free from solvent traces[8].

The thickness of the prepared samples was around 100 micrometre. The XRD scans of the prepared samples were obtained using Cu-K_α radiation ($\lambda=1.5438\text{\AA}$), using Philips XRD 'X'PERT Pro diffractometer. UV-vis absorption spectra of the prepared samples were obtained in the wavelength range 190-500nm using Elico Spectrophotometer.

An investigation of the dielectric properties of prepared samples has been carried out using broad band dielectric spectrometer (BDS) (Make: NOVOCONTROL Technologies GmbH & Co. Germany Model: Concept 80). Various complex impedance parameters are measured. AC conductivity has been evaluated from dielectric data in accordance with the relation $\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan \delta$ where $\epsilon_r = C/C_0$ is the dielectric constant, $\tan \delta =$ tangent loss factor, $C_0 =$ capacitance of the cell. The real and imaginary part of dielectric constant was calculated from the following relations.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad \text{where } \epsilon'(\omega) = \frac{z''}{\omega C_0(z'^2 + z''^2)} \quad \text{----- (1)}$$

$$\epsilon''(\omega) = \frac{z'}{\omega C_0(z'^2 + z''^2)} \quad \text{----- (2)}$$

The tangent loss is expressed as $\text{Tan } \delta = \frac{\epsilon''}{\epsilon'}$

The mechanical behaviour of the polymer composites was evaluated by nanoindentation technique using Agilent made Nanoindenter Model G200. Indentation measurements were performed using a three side pyramid (Berkovich) diamond indenter and hardness and modulus values were calculated using Oliver Pharr method.

In an indentation measurement technique, hardness is the ratio of indentation load to the projected contact area, which is given in equation (1)

$$H = \frac{P_{\max}}{A} \quad \text{----- (1)}$$

The elastic modulus of the sample can be calculated according to the relationships developed by Sneddon as given in Eq. (2):

$$S = 2\beta \sqrt{\frac{A}{\pi}} E_r \quad \text{----- (2)}$$

Where A is the indenter projected contact area on the sample at the maximum load, P_{\max} ; S is the contact stiffness of the material; β is an indenter geometry dependent constant and E_r is the reduced elastic modulus which is calculated from Eq. (3);

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad \text{----- (3)}$$

Where E_i and ν_i are the elastic properties of the diamond indenter. E and ν are the elastic modulus and Poisson's ratio of the sample [9, 10]. The expected value of the ν of semi crystalline polymer is 0.35.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

Fig. 1 represents XRD scans on pristine PVA (50) /PVP (50) blend and PVA (50) /PVP (50) blend filled with various concentrations of La (NO₃)₃. In the XRD scan on pristine PVA (50)/PVP (50) blend the main peak centred at about $2\theta = 19.43^\circ$ reveals the semi crystalline nature of the blend which is in conformity with earlier reported data. This peak has been shifted slightly in PVA (50)/PVP (50)matrix filled with 5% and 15% filler to 19.72° and 20.46° respectively. Also the close observation of the scans suggests that there is a drop in peak intensity values in the case of 5% and 15% filler mixed blend composites. Absence of sharp peaks confirms the amorphous nature of the polymer blend composites. This may be due to the interaction between the blend and the filler which results in decrease in intermolecular interaction between the polymers blend chains [7,11]. This amorphous nature is responsible for ion diffusion in the matrix which can be obtained in the polymers that have flexible backbone[7].But in the case of 25% filler concentration, the peak reappears at 19.43° and the peak intensity again increases. This shows that lower filler concentration of rare earth metal ions is more effective as filler in creating an environment which is favourable for ion diffusion in the present chosen blend matrix.

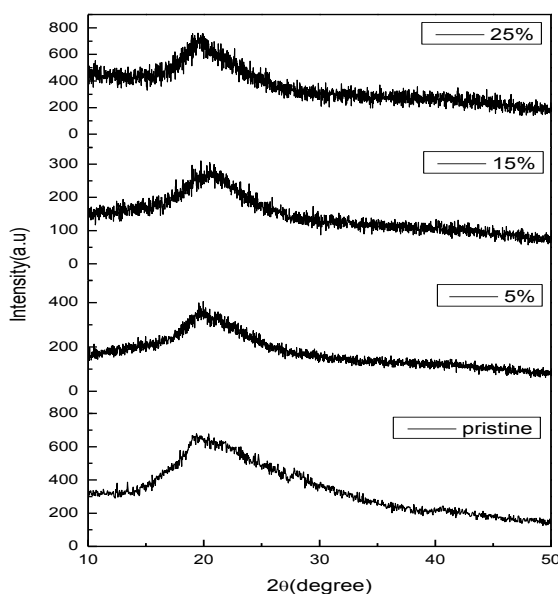


Figure1: XRD scans on pristine PVA (50)/ PVP (50) and PVA (50)/ PVP (50) filled with filler.

3.2 Ultra violet -visible analysis

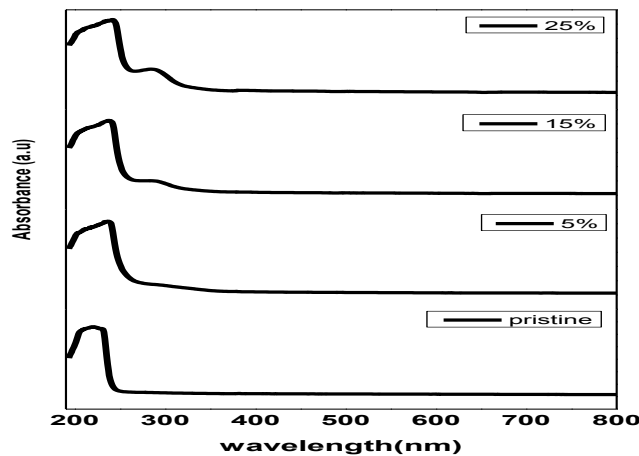


Figure 2: Absorbance Vs Wavelength spectra of pristine PVA (50)/ PVP (50) and PVA (50)/ PVP (50) with filler.

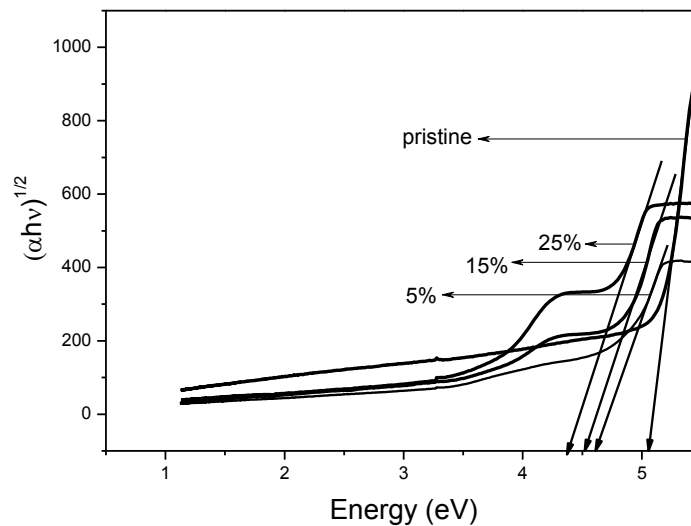


Figure 3: Plot of $(\alpha hv)^{1/2}$ v/s (hv) for pristine PVA (50)/PVP (50) and PVA (50)/PVP (50) with filler.

The band structure of materials is well understood by subjecting the materials to UV-vis analysis. Pristine blend showed absorption at 220nm. The filler mixed PVA (50)/PVP (50) blend demonstrated high absorption probability above 220nm and below 250nm which is shown in the Fig 2. This shows that there is a shift in the absorption wavelength compared to the pristine blend matrix. In the visible region, the samples were transparent. The absorption coefficient (α) is given by the relation [12] $\alpha hv = B(hv - E_g)^r$

Where hv - incident photon energy, B – constant. Exponent r is found out from the slope of the linear part of plot $(\alpha hv)^{1/2}$ v/s hv . Depending on the nature of the electronic transition that is taking place in the samples, r can take the value $1/2$, $3/2$, 2 & 3 . From the optical absorption spectra recorded for the samples, best straight line fit is obtained for $r = 2$, which indicates that an indirect transition is allowed near the fundamental band edge [12, 13]. The values of the band gap energies are estimated from the extrapolation of the straight line part of the plot of $(\alpha hv)^{1/2}$ v/s hv to the energy axis as shown in Figure 3. The estimated values of the E_g are given in Table 1. It can be observed from the table that the E_g of the pristine PVA (50) /PVP (50) and La (NO_3)₃ filled PVA (50) /PVP (50) polymer blend decreases with the increase in the concentration of filler. Also the values recorded in the table justify the change in the behaviour of polymer complexes tending towards semiconducting nature. This decrease in the energy band gap may be explained, that during polymer mixing, defects formation may occur, such as voids, which give rise to desirable localized states in the band gap of a material [14, 15].

Table 1: Band gap energy (Eg) for pristine PVA (50)/PVP (50) and filler incorporated PVA (50)/PVP (50) blend films.

Samples	Pristine PVA(50)/PVP(50)	PVA(50)/PVP(50) +5% filler	PVA(50)/PVP(50) +15% filler	PVA(50)/PVP(50) +25% filler
Energy band gap (eV)	5.02	4.5	4.46	4.31

3.3 Dielectric studies

3.3.a Energy storage ϵ' and Energy loss ϵ'' measurement

The dielectric response is generally explained by the complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$, where ϵ' and ϵ'' are energy storage and energy loss in each cycle of applied electric field. The variation of ϵ' and ϵ'' as a function of logarithmic frequency at room temperature for pristine and filler incorporated films are as shown in the fig 4a & 4b. It is observed from the graphs that ϵ' and ϵ'' values are high at low frequency, followed by decrease of ϵ' and ϵ'' values with the increase in frequency and then relatively constant with frequency above 10 kHz. This may be due to the interfacial effects and the electrode effects within the bulk of the sample [6].

It is also observed that the variation of ϵ' and ϵ'' with $\log f$ for 5% and 15% is almost same except in the low frequency region. Whereas variation of ϵ' and ϵ'' with $\log f$ for 25% filler concentration is losing its dopant role and the curve is overlapping with the pristine blend curve. This is in agreement with the XRD results for 25% filler concentration. This may be due to the decrease in number of mobile ions resulting by the recombination of anion with cations leading to neutral ion pairs [16].

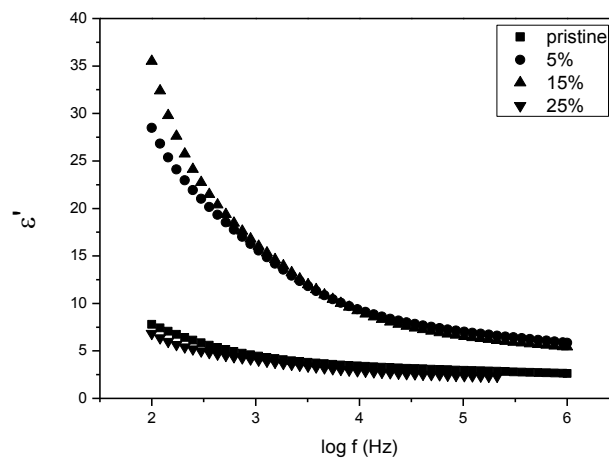


Figure 4 (a): Frequency dependence of dielectric constant ϵ' for pristine PVA (50)/PVP (50) with filler at room temperature.

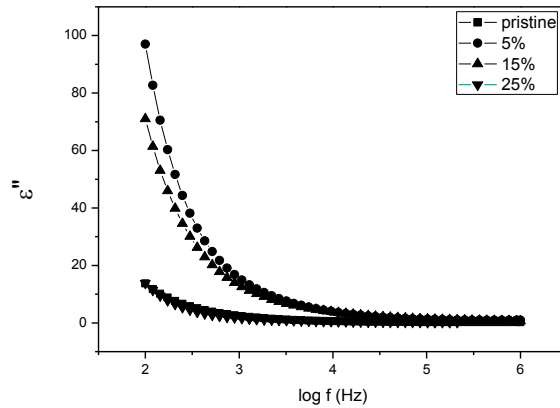


Figure 4 (b): Frequency dependence of dielectric loss ϵ'' for pristine PVA (50)/PVP (50) with filler at room temperature.

At low frequency as the field reversals are slow there is time for charges to build up at the interface before the applied field changes its direction. The filler addition may result in more localization of charge carriers along with mobile ions causing higher ionic conductivity[17]. At high temperature, dipoles show greater tendency to orient in the direction of the applied field. Hence total polarization increases in the polymer composites, which is revealed by higher value of the dielectric constant [18]. Frequency dependence of ϵ' and ϵ'' for PVA (50)/PVP (50) incorporated with 5% & 15% filler at varying temperatures is shown in Fig 5a & 5b.

As electric field changes its direction very rapidly at high frequencies, the switching action of molecular dipoles cannot keep in step with that of the changing field, the polarization due to the charge accumulation decreases leading to the decrease in the values of ϵ' and ϵ'' and also the number of ions flowing in the direction of the field[6].

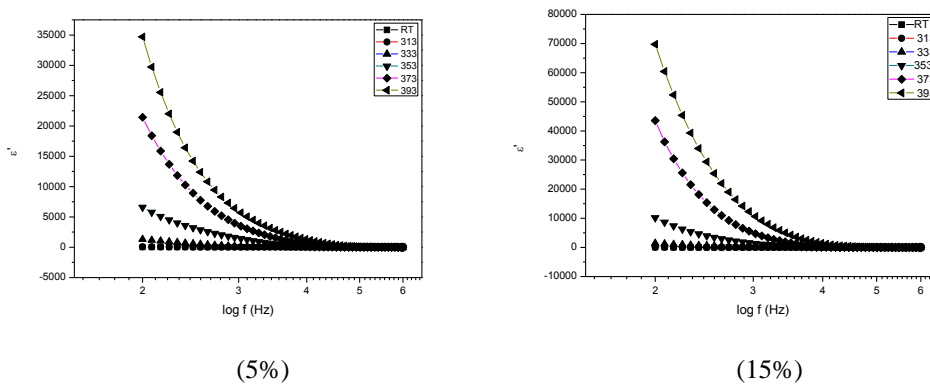


Figure 5 (a): Frequency dependence of ϵ' for PVA (50)/PVP (50) filled with 5% & 15% filler at varying temperatures.

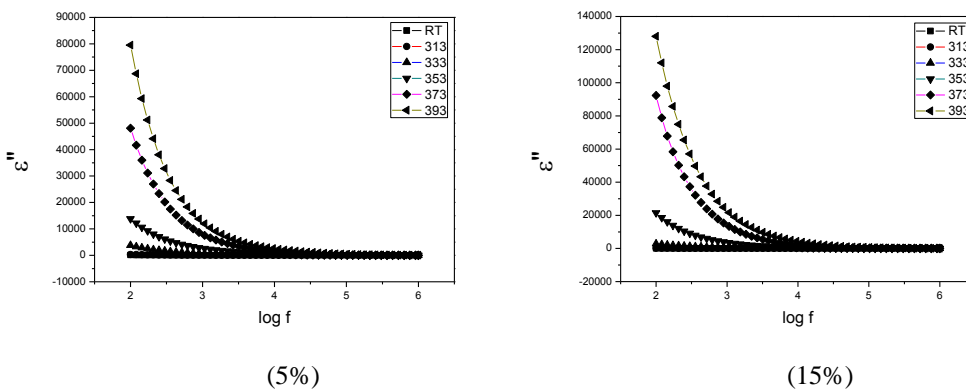


Figure 5 (b): Frequency dependence of ϵ'' for PVA (50)/PVP (50) filled with 5% & 15% filler at varying temperatures.

3.3b AC Conductivity measurement

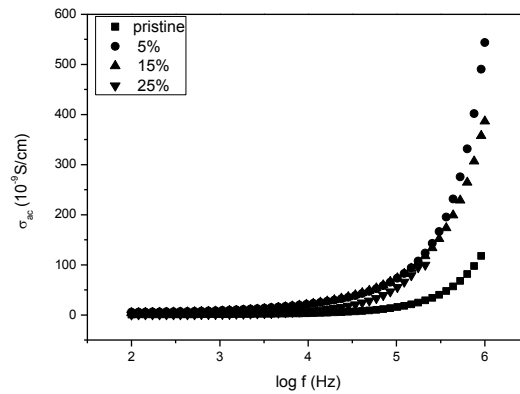


Figure 6 (a): Frequency dependence of the AC conductivity of PVA (50)/PVP (50) filled with filler at room temperature.

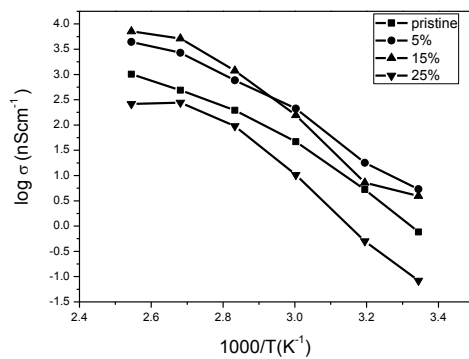
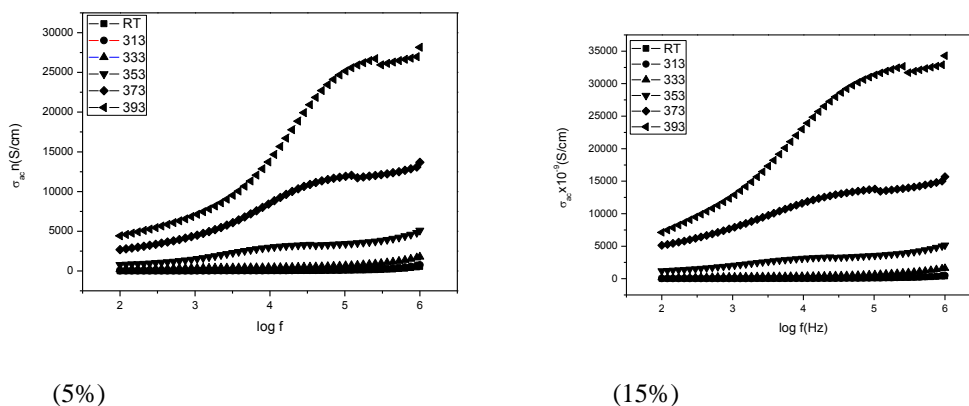


Figure 6 (b): $\log \sigma$ (nScm⁻¹) Vs $1000/T$ (K⁻¹) for PVA (50)/PVP (50) and PVA (50)/PVP (50) filled with filler at room temperature.

Fig. 6a & 6b shows the frequency-dependent AC conductivity spectra of PVA (50)/PVP (50) filled with La (NO₃)₃ at room temperature and $\log \sigma$ (nScm⁻¹) Vs $1000/T$ (K⁻¹) for PVA (50)/PVP (50) and PVA (50)/PVP (50) filled with La (NO₃)₃ at room temperature. Low conductivity is observed in low frequency region as number of charge carriers having high relaxation time with higher energy barrier are less in low frequency region. However, with the increase in the frequency more number of the charge carriers with low barrier heights responds easily, hence increase in the conductivity



is observed [7].

Figure 7: Frequency dependence of the AC conductivity of PVA (50)/PVP (50) filled with (a) 5%, (b) 15% filler at varying temperatures.

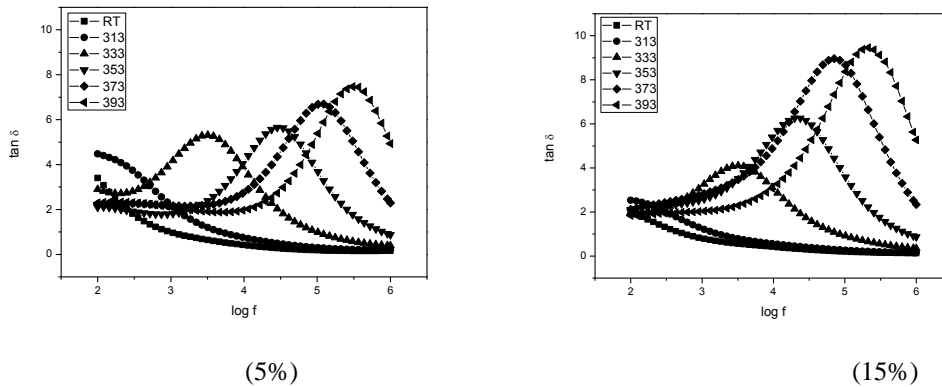


Figure 8: Frequency dependence of $\tan\delta$ for PVA (50)/PVP (50) filled with 5% & 15% $\text{La}(\text{NO}_3)_3$ at varying temperatures.

3.3c Measurement of tangent loss

Variations of tangent loss with frequency for PVA (50)/PVP (50) filled with 5% and 15% filler at varying temperatures are shown in Fig.8. The loss spectra of the samples showed a broad peak at a specific frequency which confirms the existence of relaxing dipoles in the polymer composites. The shift in peak position observed at higher temperatures and at specific frequency may be attributed to rapid segmental motion coupled with the mobile ions thereby increasing the ionic conductivity resulting due to appropriate concentration of dopant ions[17].

3.4 Mechanical studies.

Fig 9 shows the load vs displacement curves for pristine PVA (50)/PVP (50) and PVA (50) /PVP (50) filled with filler as a function of different filler concentration. With the increase in the filler concentration, the upward shift of the curves observed indicating that the filler filled polymer blend composites resist indentation. This suggests the requirement of lesser loads to induce comparable indenter penetration in the case of softer materials [10]. The penetration depth is due to both the elastic and plastic displacements. The peak loads are kept constant for a period of 60s before unloading. Load versus displacement profiles illustrate the decrease in the penetration depth with increase in the filler content which confirms the improvement of hardness of the sample[10]. When load is decreased at the same rate as in the loading cycle elastic displacement is regained. Initial unloading stiffness S in Eq. (2) is estimated from the slope of the unloading curve which is found to increase with increasing filler content, thus leading to the increase of elastic modulus. The hardness and modulus profiles of the pristine and filler incorporated samples calculated from the load-displacement curves as shown in Fig 10(a) & 01(b) respectively.

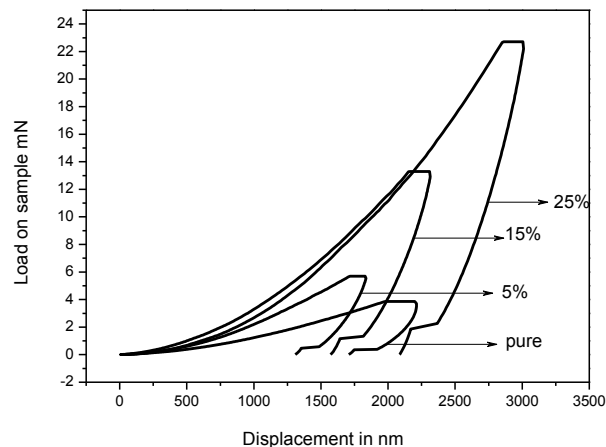


Figure 9: Load vs displacement graphs for pristine PVA (50)/PVP (50) and PVA (50) /PVP (50) with filler.

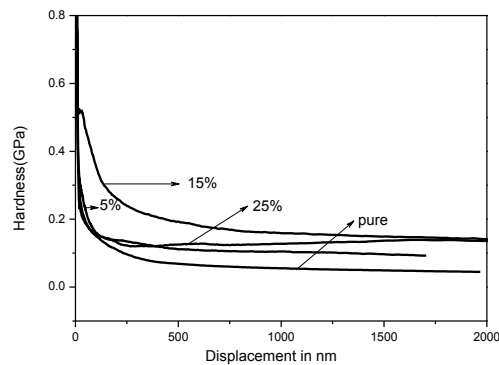


Figure 10(a): Hardness vs displacement graphs for pristine PVA (50)/PVP (50) and PVA (50) /PVP (50) with filler.

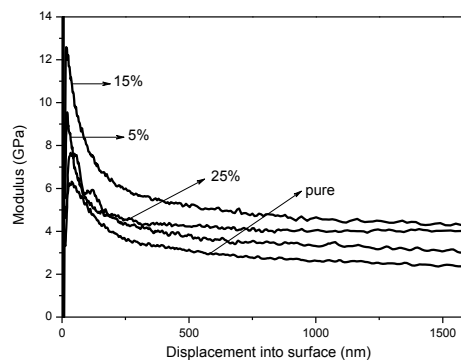


Figure 10(b): Modulus vs displacement graphs for pristine PVA (50)/PVP (50) and PVA (50) /PVP (50) with filler.

It is also observed that from the surface to 500nm of the depth for all the samples both the hardness and modulus decrease, followed by almost constant values along the indentation depth. This behaviour i.e., decrease at lower depth is exhibited by many polymeric materials and could be attributed to indentation size effects as well as imperfection of the indenter used[10]. Both the elastic modulus and hardness increase with increasing filler content. Significant improvement in elastic modulus and hardness are seen with the addition of 15% filler content when compared with pristine polymer blend as well as other filler concentrations. The hardness and modulus values found by nanoindentation measurements are summarized in Table 1.

Table 1:

Mechanical properties of pure PVA (50)/ PVP (50) and PVA (50)/ PVP (50) filled with different concentrations of La (NO₃)₃.

Samples	Hardness (GPa)	Modulus (GPa)
pristine PVA (50)/ PVP (50)	0.07	3.0
pristine PVA (50)/ PVP (50)+ 5% filler	0.10	3.4
pristine PVA (50)/ PVP (50)+ 15% filler	0.13	4.4
pristine PVA (50)/ PVP (50)+25% filler	0.13	4.0

4. CONCLUSIONS

La (NO₃)₃ incorporated PVA (50)/PVP (50) polymer blend films have been prepared using solution casting technique. X-ray diffraction scans have shown an increase in the amorphosity of composites which is a favourable condition for ion diffusion. Optical studies have confirmed the decrease in E_g with the increase of La (NO₃)₃ making the material semiconducting in nature. AC conductivity has increased with increase in frequency revealing higher stability of the films. The values of ε' and ε'' have decreased with increase in frequency due to space charge arising from the electrodes. With the increase in temperature the value of dielectric constant was found to increase depicting the more polar nature of polymer matrix. Appearance of loss tangent peaks at characterise frequencies confirmed the presence of relaxing dipoles. Shift in the peak position towards higher frequency justified the fast segmental motion coupled with mobile ions. The indentation results disclose that the hardness and modulus of the polymer composites increase with increasing filler concentration. All these significant results are obtained for 5% and 15% filler concentration where as higher concentration 25% is losing its role as effective filler. From the above investigations of physical properties the results confirm that 15% is the optimized filler concentration showing significant improvement in many properties. Hence based on these results it could be recommended that these rare earth ion Lanthanum filled PVA (50)/PVP (50) polymer composite films are found to be potential novel multifunctional materials for various opto-electronic and electro-mechanical devices.

5. REFERENCES

- [1] Franck A, Introduction to Polymer blends and Alloys; T A instruments Germany.
- [2] Abdelrazek E M, Elashmawi I S, Labeeb S. *Physica B* 405 (2010) 2021-2027.
- [3] Yuwei Jin, Xiaofeng Lu, Ce Wang. *Journal of applied Polymer Science*, (2006), Volume 102, Issue 6, 6017-6022.
- [4] Rajeswari N, Selvasekarapandian S, Karthikeya C, Sanjeeviraja Y, Iwai, J. Kawamura. *Ionics* (2013) 19.1105-1113.
- [5] Hatta F F, Yahya M Z A, Ali A M M, Subban R H Y, Harun M K, and Mohamad A A. *Ionics* 11 (2005).
- [6] Subba Reddy Ch, Xia Ha, Quan-Yao Zhu, Li-Qiang Mai, Wen Chen. *Microelectronic Engineering* 83(2006) 281-285.
- [7] Ragab H M, *Physica B* 406 (2011) 3759.
- [8] Elashmawi I S, Abdelrazek E M, Ragab H M, Hakeem N A, *Physica B* (2010), Volume 405, and Issue 1, p. 94- 98.
- [9] Miguel Manzano Æ, Antonio ., Salinas Æ, Francisco J, Gil Æ Mari´a Vallet-Regi. *J Mater Sci: Mater Med* (2009) 20:1795–1801.
- [10] Yucai Hu, Lu Shen, Hai Yang, Min Wang, Tianxi Liu, Tao Liang, Jiang Zhang. *Polymer Testing* 25 (2006) 492-497.
- [11] El-Houssiny A S, Ward A A M, Mansour S H, Abd- El- Messieh S L, *Journal of Applied Polymer Science*. (2012), Vol. 124, Issue 5, pages, 3879-3891.
- [12] Harish Kumar H G, Mathada R D, *Radiation effects and defects in solids*, Volume 166, Issue 3, (2011), 198- 207.
- [13] Harish Kumar H G, Mathad R D, Ganesh S, Sarma K S S, Haramghatti C R. *Brazilian Journal of Physics* 2011, 41 (1).
- [14] Armand M B, Chabagno J M, Duclot In M, Vashistha P, Murthy JN, Shenoy GK (eds.), *Fast ion transport in solids*. North Holland, Amsterdam (1979).
- [15] M. A. El-Shahawy, *Polym.Int.* 52 (2003) 1919.
- [16] Shyly P M, Karuppasamy K, Linda T, Paitip Thiravetyan, Balakumar S, Sahaya Shajan, *IOSR Journal of Applied Physics* Volume 1, Issue 4 (July-Aug. 2012). PP 47-51.
- [17] Pradhan D K, Choudhary R N P, Samantaray B K, *Int. J. Electrochem. Sci*, 3 (2008) 597-608.
- [18] Jayanthi S, Sundaresan B, *Ionics* DOI 10.1007/s11581-014-1230-0 Springer-(2014).