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Characterization and Physical Properties of Silver/PVA nano- composite

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ABSTRACT

Silver nanoparticles filled polyvinyl alcohol (PVA) were prepared by casting method using water as a solvent. X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM) and ultraviolet-visible (UV-Vis.) were used to characterize the prepared nanocomposites. X-ray results indicated the formation of Ag-nanoparticles with FCC phase within the PVA polymeric matrix. Scanning electron microscopy shows that the prepared Ag-nanoparticles were dispersed and nearly uniform in diameter within the polymeric matrix. UV-Vis. absorption spectra were used to study the confined growth process of PVA-capped Ag-nanoparticles. The absorption showed a shift towards higher wavelength with increasing filler content.

Keywords: Silver nanoparticles – PVA – Spectroscopy –

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INTRODUCTION

Recently, the synthesis and characterization of nanostructured materials have attracted much attention not only because of their unconventional properties depending on dimensionality, but also due to their size-dependent properties and great potential for many technological applications such as solar cells for photoelectric conversation, optical switching, and transistors for electronic switch [1–6].

Polyvinylalcohol (PVA) is an important polymer, because of its unique physical and chemical properties and it continued to attract many researchers, over the years [1]. This polymer can be made in powder, film and fiber forms. It is a semi-crystalline polymer that arises from the role of OH group and the hydrogen bonds [2-4]. It is also recognized as one of the very few vinyl polymers soluble in water with a high transparency and a good flexibility. It is used industrially for emulsification, sizing and adhesives, in biomedical materials as drug-delivery system and membranes. PVA can also be used in medical applications such as artificial blood vessels, artificial intestines, and contact lenses. It had been noted as a medical material due to its compatibility to the living body [5, 6].

Silver nanoparticles are being used in numerous technologies and incorporated into a wide array of consumer products that take advantage of their desirable optical, conductive, and antibacterial properties. Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) [7, 8] and surface-enhanced Raman scattering (SERS) [9]

The aim of the present work is to introduce a new class of polymer filled nanoparticle with a simple method of preparation and unique optical properties suitable for sensing behavior.

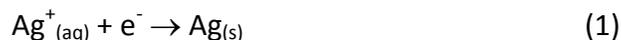
EXPERIMENTAL

Sample Preparation and composition

PVA (in the form of fine powder supplied by BDH molecular weight 14,000) was dissolved into distilled water in a glass beaker at constant temperature ranging from 60 - 70 °C. Pretreated silver nitrate solution was added drop by drop (one drop/second) using a burette while the temperature was maintained between 60 °C and 70 °C and with continuous stirring for about 6 hours. The mixture then casted on a glass dish and kept in a dry atmosphere at 333K. Nitric acid is evaporated and small particles of metal Ag is capped in PVA polymer molecules. Final color of the films obtained depends upon the concentration of silver added.

Synthesis of silver nanoparticles based on a wet chemical method will employed were silver nitrate (AgNO_3) is dissolved in aqueous media and splits up into a positive silver ion (Ag^+)

and a negative nitrate ion (NO^{-3}) and ions have to be reduced by receiving an electron from a donator according to the following equation 1;



Equation 2 illustrates the reduction of (Ag^+) in a solution of ethanol. After the silver germ has been formed it starts to grow and continue the growth until the equilibrium between the final nanoparticles and the (Ag^+) of the solution is reached.



Further control of the synthesis of silver nanoparticles can be obtained with the use of a stabilizer.

X-ray diffraction

X-ray diffraction (XRD) scans were obtained using PANalytical X'Pert PRO XRD system using $\text{Cu K}\alpha$ radiation (where, $\lambda = 1.540 \text{ \AA}$, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of $5\text{-}50^\circ$).

Scanning electron microscopy

Morphology and surface characteristics were studied using scanning electron microscope using (SEM Model Quanta 250 FEG FEI company, Netherlands) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun. 1n). Surface of the samples was coated with a thin layer of gold (3.5 nm) by the vacuum evaporation technique to minimize sample charging effects due to the electron beam.

Fourier Transform Infra-Red Spectroscopy

FT-IR absorption spectra were carried out using the single beam Fourier transform-infrared spectrometer (FTIR-Mattson 5000). FT-IR spectra of the samples were obtained in the spectral range of $4000 - 400 \text{ cm}^{-1}$.

Ultraviolet and visible Analysis (UV/Vis.)

UV/Vis. absorption spectra were measured in the wavelength region of 200-900 nm using spectrophotometer (T80+, UV/Vis. spectrometer, PG Instrument Ltd.) to retrace the structural changes due to different concentration of fillers and their optical properties.

RESULTS AND DISCUSSIONS

Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectroscopy has been proven to be a very powerful technique to study the internal structure of polymeric materials and intermolecular interaction between the polymeric material and filler.

Figure (1) shows FT-IR transmittance spectra of pure PVA and Ag-PVA nanocomposite films recorded at room temperature in the region $4000-400\text{ cm}^{-1}$.

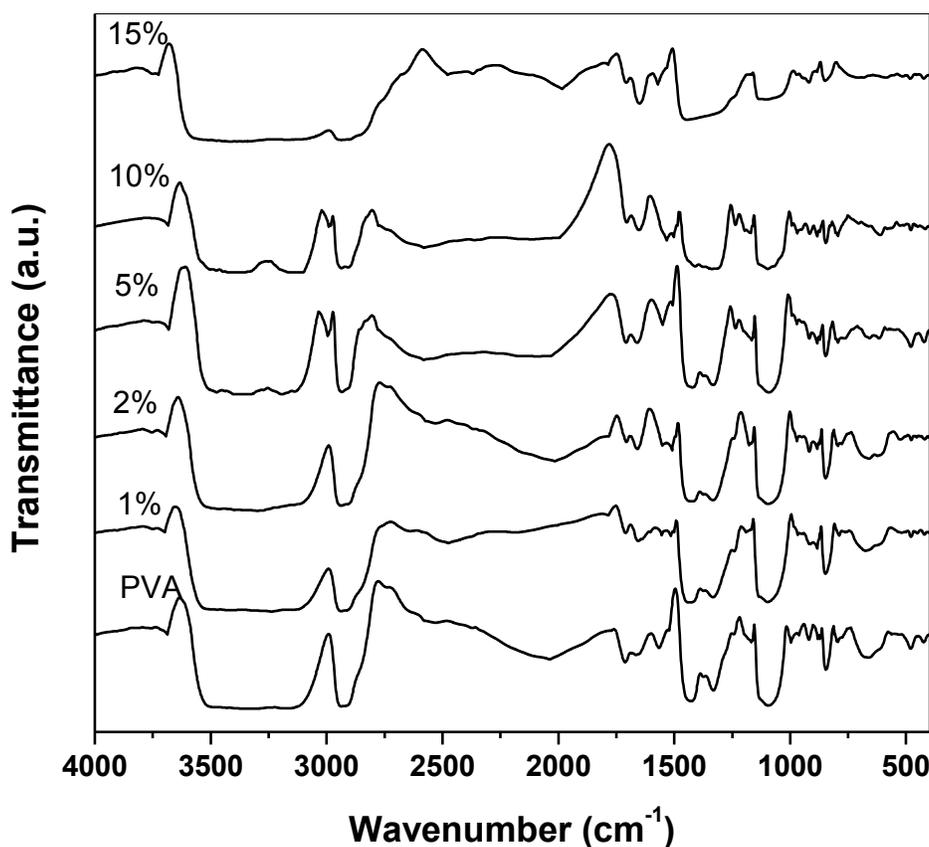


Fig 1: FTIR absorption spectra of pure undoped and silver nano-particle doped PVA films.

The spectra exhibited characteristic bands of stretching and bending vibrations of the functional groups formed in the prepared films. FT-IR absorption bands positions and their assignments of the prepared samples are listed in Table (1).

From the spectra, the broad band at about 3300 cm^{-1} is assigned to the stretching vibration of hydroxyl group (OH) of PVA, which may be due to the intermolecular or

intramolecular type of hydrogen bonding of the polymer and the nanoparticles. The band corresponding to CH₂ asymmetric stretching vibration occurs at about 2930 cm⁻¹.

The peaks at 1710 and 1652 cm⁻¹ have been attributed to the C=O, C=C stretching mode. It is remarkable that, the present double bonds segments are considered as suitable sites for polarons and/or bipolarons [10, 11]

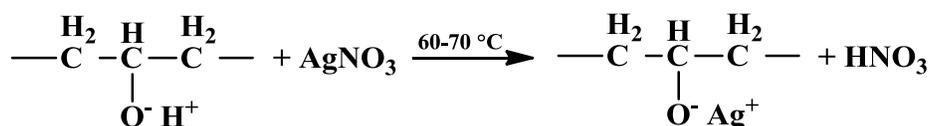
The absorption peak at 1240 cm⁻¹ has been assigned to the wagging (CH) group. The band at about 1105 cm⁻¹ corresponds to C–O stretching of carbonyl groups present on the PVA backbone. While The absorption band at about 962 cm⁻¹ is assigned to out-of-plane rings C–H bending.

Table 1: Band assignment of IR vibrational modes

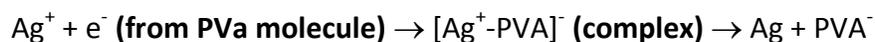
Wavenumber (cm ⁻¹)	Band assignment	Ref.
3300	OH stretching	18, 21
2930	CH ₂ asymmetric stretching	10, 17, 20, 21
1652	C=C stretching	21
1710	C=O stretching	10, 20, 21
1429	Symmetric bending of CH ₂	10, 19, 21, 23
1326	(CH+OH) bending	10, 19, 21
1241	wagging of (CH)	21, 23
1105	C–O stretching	10, 17, 18, 19, 21, 23
963	Out-of-plane rings C–H bending	17
845	CC stretching vibrations	10, 21
663	wagging mode of (OH) groups	21
481	bending mode of (CO)	21
421	Wagging of (CO)	21

The CC stretching vibrations of the moderate absorption planar zig zag carbon backbone is observed at 845 cm⁻¹. A broad moderate and weak band is observed at 663 cm⁻¹ which is assigned to the wagging mode of (OH) groups. The weak bands at 486 and 426 cm⁻¹ are assigned to the bending and wagging modes of CO group.

Change in the IR spectrum of the Ag-PVA nanocomposite was observed for the band peaking at 1326 (cm⁻¹). These changes are more pronounced for the Ag-PVA nanocomposites with higher content of inorganic phase. Therefore, the decrease in the ratio between the intensities of this band and the band at 1429 cm⁻¹ upon incorporation of the Ag nanofiller indicates decoupling between the corresponding vibrations due to interaction between Ag nanoparticles and the OH groups originating from the PVA chains. This result is in agreement with previously reported data [12-16]



All these data support the idea of complexation between Ag metal and polymer matrix via polymer complex of an intermediate state according to the following equation;



The result support the proposal of Longenberger and Mills [24] that Ag metal forms via a polymer complex of an intermediate state Ag^{q+} ($q < 1$). Oxidation of PVA through this reaction disrupts the $\text{Ag}^+ \text{-PVA}$ complex structure.

UV-Vis. absorption and optical studies

Fig.2 shows UV-Vis. absorption spectra of pure and silver filled thin polymeric film. The absorption spectra (Fig. 2) show tunability of surface plasmon resonance of Ag-nanoparticles films with (λ_{max} 420–460 nm) at different concentrations which caused by a collective excitation of the conduction band electrons of the nanoparticle.

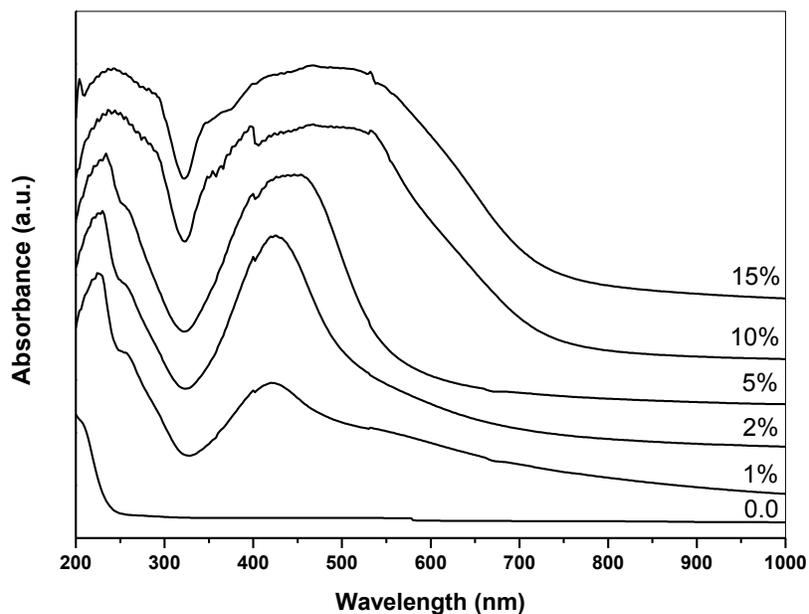


Fig 2: UV-Vis. spectra of pure and different concentration Ag-nanoparticle doped PVA.

Surface plasmon resonance peak increase depends upon particle size, shape of the particle, refractive index of surrounding medium and dielectric properties. Also a peak at 210 nm appear, in undoped PVA due to $n \rightarrow \pi^*$ transitions [25], shifts gradually towards the higher wavelength side with increasing concentration of Ag-nanoparticles as dopant. This shift in the absorption edge can be correlated to the change in optical band gap [11], as an effect of dispersion of Ag-nanoparticles in PVA matrix.

It is clear that, the band gap energies (E_g) obtained in the present work are decreased with increasing Ag-nanoparticles content. This indicates that there are charge transfer complexes arose between the PVA and Ag-nanoparticles [12].

Measurement of the absorption spectrum is the most direct method to investigate the band structure of materials. In the absorption process an electron is excited from a lower to higher energy state by absorbing a photon of known energy. The changes in the transmitted radiation can decide the types of possible electron transitions. Fundamental absorption refers to band-to-band or exciton transition. The fundamental absorption shows a sudden rise in absorption, known as absorption edge, which can be used to determine the optical band gap ($E_g = h c/\lambda$). Absorption is expressed in terms of a coefficient α (absorption coefficient), which is defined as the relative rate of decrease in light intensity. The absorption coefficient α was calculated from the absorbance (A). Where $\alpha = 2.303 A/x$ and x is the sample thickness.

Absorption coefficient for amorphous materials can be related to the energy of the incident photon as follows [25]:

$$(\alpha h\nu) = \beta (h\nu - E_g)^r \quad \text{for } h\nu > E_g. \quad (1)$$

$$(\alpha h\nu) = 0 \quad \text{for } h\nu < E_g. \quad (2)$$

Where β is a constant, E_g is the optical energy gap and r the exponent that can takes the value 1, 2, 3, 1/2 and 3/2, depending on the nature of the electron transitions responsible for the optical absorption. It is well known that r takes the value of 1/2 in case of direct electronic transition across direct energy gap in the k space and 2 in case of indirect electronic transition across indirect energy gap. Davis and Shalliday [26, 27] reported that near fundamental band edge, both direct and indirect transitions occurs and can be observed by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus photon energy (h ν).

Fig. 3, 4 show Tacu's plot of the $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ as a function of photon energy (h ν), as an example for the base glass. The same procedure was used for the remaining doped glasses, to calculate its optical energy gap; these obtained values are listed in table 2.

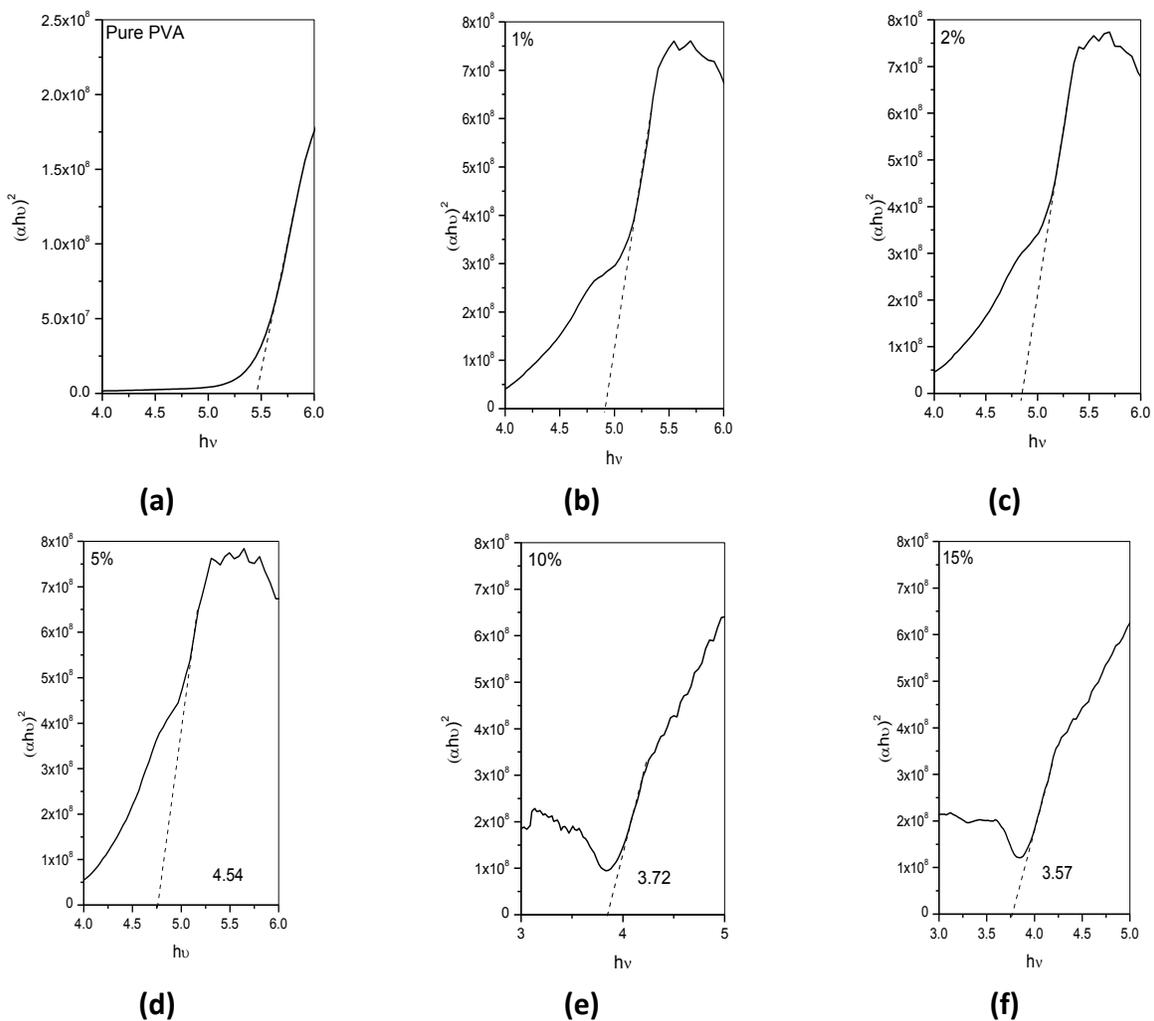


Fig 3: Tacu's plot of the $(\alpha hv)^2$ as a function of photon energy ($h\nu$)

Table 2: Relation between doping level and optical energy gap for pristine and filled PVA

Doping level (wt%)	Optical energy gap (eV)	
	Direct	Indirect
0.00	5.45	5.50
1.00	5.40	4.60
2.00	5.35	4.38
5.00	5.25	3.55
10.0	3.80	3.50
15.0	3.75	3.42

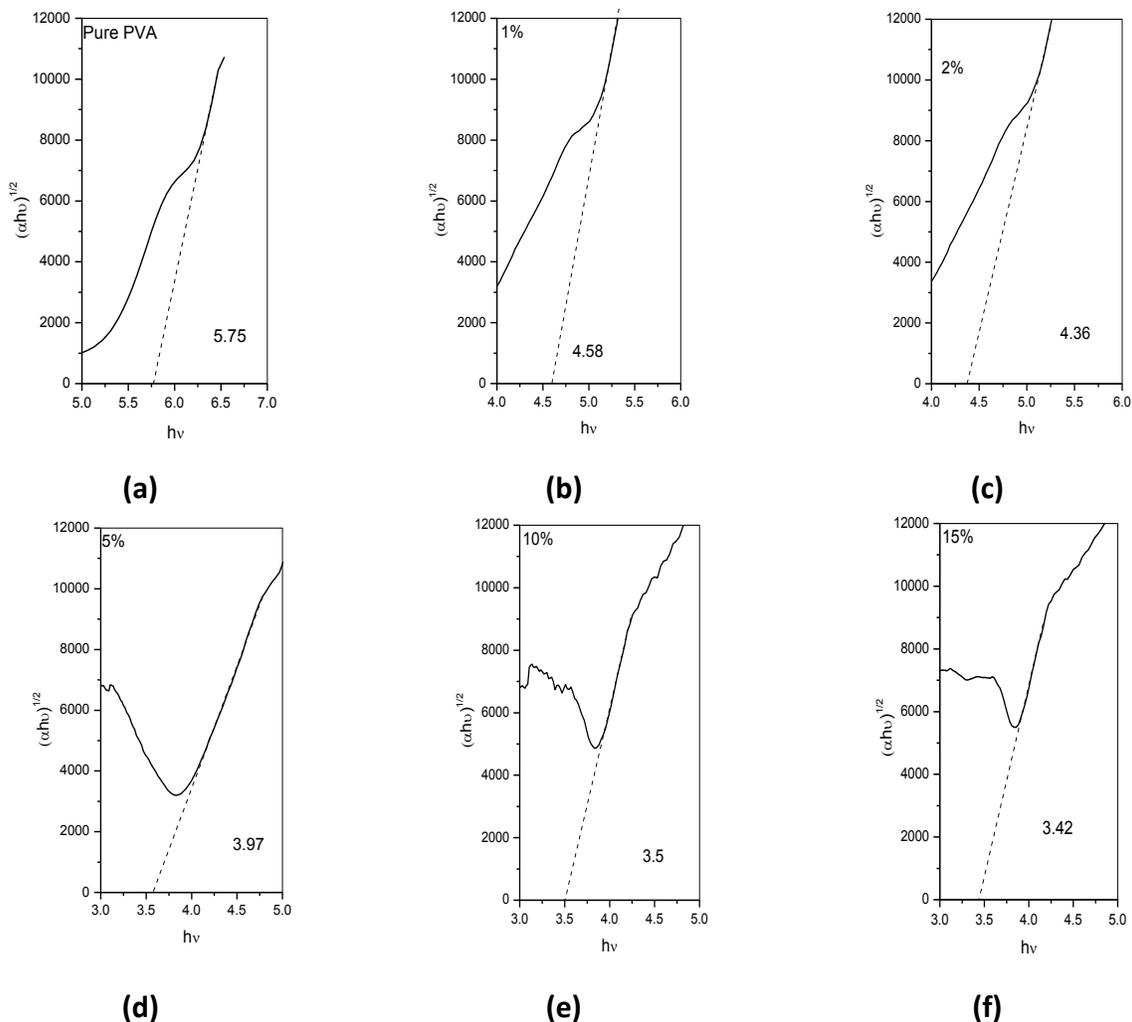


Fig 4: Tacu's plot of the $(\alpha hv)^{1/2}$ as a function of photon energy ($h\nu$)

The values of direct band gap and indirect band gap are listed in Table 2. It is clear from Table 2 that the direct band gap and indirect band gap values showed a decrease with increase in doping level. This decrease may be attributed to the formation of defects in the polymeric matrix. These defects produce the localized states in the optical band gap. These overlaps are responsible for decreasing energy band gap when FL is increased in the polymer matrix [18]. In other words, the decrease in the optical gap results in an increase in the degree of disorder in the films. These results are supported by the data obtained from XRD studies in the present work.

X-ray diffraction (XRD)

Fig.5 shows the XRD of pristine PVA films and films that doped with Ag-nano particle with different filling level (FL) namely 1, 2, 5, 10, and % by wt. The diffraction pattern of undoped PVA indicates a diffraction peak at $2\theta = 19.4^\circ$, as is clearly depicted in Fig. 4. This band

can be assigned to the partially crystalline nature of PVA polymer molecules, which may be as a result of strong inter-molecular and intramolecular hydrogen bonding between the PVA chains [23]. Further, it is evident from the same figure that new peaks at nearly 32 and 46 are generated after doping, which may be assigned to the Face-centred-cubic (fcc) structure of embedded Ag metal particles corresponding to h k l parameters (111) and (200).

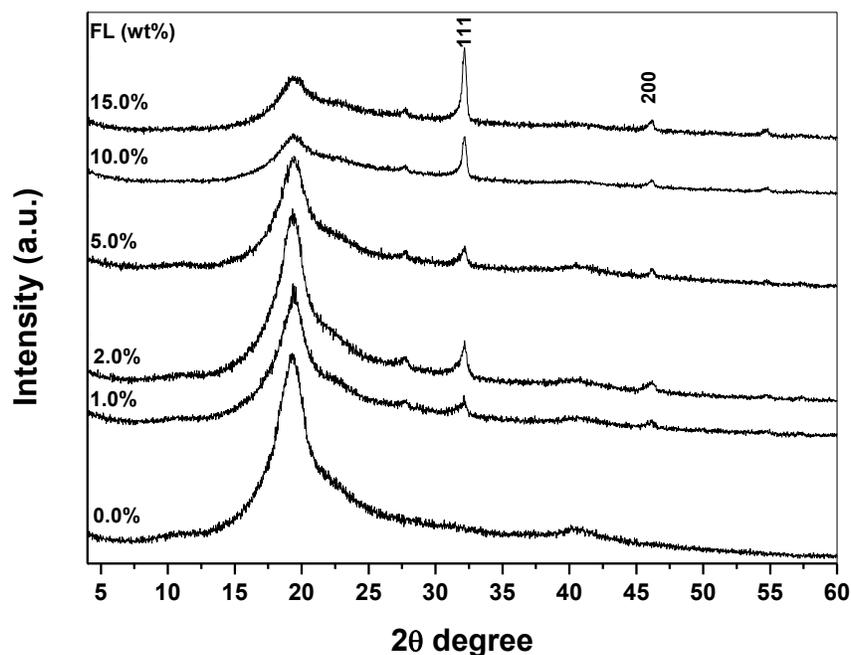


Fig 5: x-ray diffraction pattern for pristine and Ag-nano filled PVA films.

Scanning electron microscopy (SEM).

Scanning electron microscopy (SEM) was utilized to study the morphological property of polymeric films before and after doping with silver nanoparticles with different filling levels. Fig. 6.a shows the morphology and surface nature of base PVA film prepared by casting technique. The surface of pristine samples was smooth and there is no evidence for any texture without any texture. Fig. 6(b-f) shows SEM images of filled PVA films, the nanoparticles from all formulations displayed nearly spherical shapes and did not show any aggregations except in the highest concentration (15%).

There was no obviously difference amongst different formulations of nanoparticles. The distinct spherical nanoparticles could be observed, both single nanoparticle and multi-nanoparticles. The particles were closed and sorted out well from each other without adhesion or cohesion. The surface was relatively smooth. The result showed that the difference in FL had no significant influence on the nanoparticles morphology.

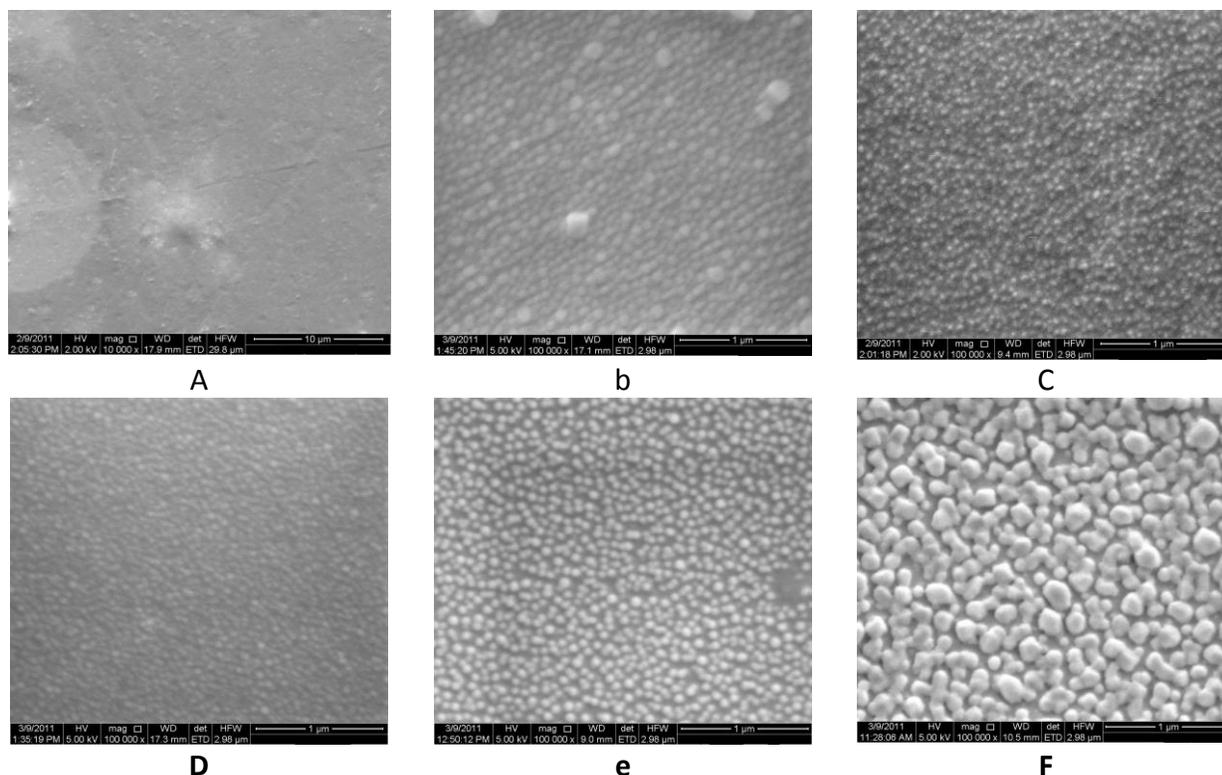


Fig 6: (a-f) scanning electron micrograph of pristine and Ag-nanoparticles filled PVA films.

CONCLUSION

Ag-PVA nanocomposites with different filling level were prepared using casting technique. XRD and SEM micrographs revealed uniform dispersion within the PVA matrix and that Ag particles are in nanometer size domain. XRD pattern shows also a decrease of the content of crystalline PVA phase with the increase of the content of inorganic phase. FTIR measurements indicated interaction between Ag nanoparticles and PVA chain over OH groups and support x-ray results for the decrease of crystalline PVA phase with the increase inorganic filler content.

The optical band gap as a result of doping has been found to be reduced significantly. The doping of silver nanoparticles forms the trap levels, rich in charge carriers. All these data support the idea of complexation between Ag metal and polymer matrix.

REFERENCES

- [1] Zhao H, Douglas EP. Chem Mater 2003; 14: 1418.
- [2] Chen L, Zhu J, Li Q, Chen S, Wang Y. Eur Polym J 2007; 106: 443.
- [3] Kim JY, Kim HM, Shin DH, Ihn KJ. Macromol Chem Phys 2006; 207: 925.
- [4] Pardhan B, Sharma AK, Ray AK. J Cryst Growth 2007; 304: 388.
- [5] Pattabi M, Amma BS, Manzoor K, Sanjeev G. Sol Eng Mater Sol Cell 2007; 91:1403.

- [6] Wang H, Fang P, Chen Z, Wang S. *Appl Surf Sci* 2007; 253: 8495.
- [7] Bondre N, Zhang Y, Geddes CD. *Sensors and Actuators B: Chemical* 2011; 152:82-87.
- [8] Pribik R, Dragan AI, Zhang Y, Gaydos C, Geddes CD. *Chemical Physics Letters* 2009; 478: 70-74.
- [9] Zhu Y, Dluhy RA, Zhao Y. *Sensors and Actuators B: Chemical* 2011; 157:42-50.
- [10] Tawansi A, Oraby AH, Zidan HM, Dorgham ME. *Physica B* 1998; 254:126-133.
- [11] Tawansi A, El-Khodary A, Abdelnaby MM. *Current Appl Phys* 2005; 5:572.
- [12] Paul DR, Robeson LM. *Polymer* 2008; 49:3187–3204.
- [13] Karthikeyan B. *Physica B* 2005; 364: 328–332.
- [14] Mbhele ZH, Salemane MG, van Sittert CGCE, Nedeljkovic JM, Djokovic V, Luyt AS. *Chem Mater* 2003; 15:5019–5024.
- [15] Krkljes A, Nedeljkovic JM, Kacarevic-Popovic ZM. *Polym Bull* 2007; 58:271–279.
- [16] Aleksandra NK, Milena TM, Zorica MK, Nedeljkovic JM. *European Polymer Journal* 2007; 43: 2171–2176.
- [17] Abdelrazek EM, Elashmswi IS, Elkhodary A, Yassin A. *Current Applied Physics* 2010; 10: 607–613.
- [18] Abdelrazek EM, ElDamrawi G, Al-Shahawy A. *Physica B* 2010; 405: 808–816.
- [19] Abdelaziz M, Abdelrazek EM. *Physica B* 2007; 390: 1–9.
- [20] Rajendran S, Sivakumar M, Subadevi R, Nirmala M. *Physica B* 2004; 348:73-78.
- [21] Omkaram I, Sreekanth Chakradhar RP, Lakshmana Rao J. *Physica B* 2007; 388: 318–325.
- [22] Abdelrazek EM. *Physica B* 2008; 403:2137–2142.
- [23] Gautam A, Ramb S. *Mater Chem Phys* 2010; 119: 266–271.
- [24] Longenberger L and Mills G. *J Phys Chem B* 1995; 99:475.
- [25] Thutupalli GKM, Tomlin SG. *J Phys D Appl Phys* 1976; 9:1639-1646.
- [26] Davis PW, Shilliday TS. *Phys Rev* 1960; 118:1020-1022.
- [27] Abdelghany AM, ElBatal HA, MariL. *Radiation Effects and Defects in Solids* 2012; 167(1):49-58.