

SYNTHESIS AND CHARACTERIZATION OF PVA/AGNW COMPOSITES

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Abstract

The influence of silver nanowires and (AgNWs) on the structure, morphology and electrical properties of Polyvinyl Alcohol (PVA) has been studied in the present work. PVA/AgNW samples have been prepared by dissolving PVA in AgNW solution and the thin films has been prepared by solution casting method. Structural and morphological properties have been studied from XRD and FESEM. AgNWs affected the signature peak of PVA at 20° by breaking the hydrogen bonding and OH groups. All the fcc peaks of Ag are retained at same positions in all the composites. FESEM of the composites shows that AgNWs are well embedded in the PVA matrix. UV-Vis spectroscopy shows that the optical band gap of the composites is less than that of the PVA. DC conductivity results show that the conductivity of the composites has increased by nearly four orders than pure PVA. Best are obtained only till 15% of AgNW doping concentration. After 15% AgNWs got aggregated in the matrix and conductivity decreased in the composite containing 20% AgNWs.

1. INTRODUCTION:

Polymer based metal nanocomposites are attracting a considerable interest in the recent times as they blend the mechanical properties, processability, durability of polymers and the optical, thermal and electrical properties of metals [1-4]. It is a well known fact that the properties of nanostructures strongly depends on their size and shape and the polymers acts as best hosts for metal nanostructures. Opto-electrical properties of silver nanowires (AgNWs) are attracting the attention of the researchers towards the applications like liquid crystal displays, OLEDs, solar cells [5]. PVA is water soluble extensively investigated transparent polymer for nanofillers and behaves in different ways with different fillers. PVA is a material where its physicochemical properties are dependent on the degree of polymerization, hydrolysis, and distribution of its hydroxyl groups (OH) [6].

In the present work PVA/ AgNW (PVAW) composites has been prepared by adding AgNWs in to water solution containing PVA. Homogeneous film were then obtained by solution casting technique after evaporation of water. The samples were characterized by XRD, FESEM, UV- VIS spectroscopy for their Structure and morphology. DC conductivity of the samples has been done by two probe technique in the temperature range of 298K to 398K.

2. EXPERIMENTAL DETAILS:

Materials Used: Silver nitrate (AgNO₃), trisodium citrate, Polyvinyl alcohol (PVA) were obtained from SD Fine chem. Limited. Aniline, Sodium hydroxide (NaOH), Hydrochloric acid were purchased from Merc Specialities private limited

and Ammonium per sulphate from Fisher Scientific. All the chemicals were used as received.

Preparation of AgNWs: AgNWs were synthesized by Seedless, Surfactant less wet chemical method [7]. The synthesis involves two silver solutions A and B. Beaker A consisted of 100ml of deionised water, 2µl of 1M NaOH and 40µl 0.1M AgNO₃. This solution was brought to boil with rapid stirring and in this 5ml of 0.01M trisodium citrate was quickly added. Then the solution was allowed to boil for another 10min. Concomitantly, Solution B was prepared by adding 150ml deionised water, 2µl 1M NaOH and 20µl 0.1M AgNO₃ and bringing this to boil. Solution B was added to solution A and the mixture was allowed to evaporate till the solution becomes ~75 to 100ml.

Preparation of PVA/ AgNW (PVAW) composites: Appropriate amount of PVA has been dissolved in AgNW solution in deionised water. This mixture has been stirred vigorously for about 2hours for homogenous distribution of AgNWs into the matrix. Then uniform films of the composites have been formed by solution casting technique by evaporation of the solvent.

3. CHARACTERIZATION:

X-Ray diffraction (XRD) of the composites was done to know their crystal structure through Rigaku Smart lab X-ray diffractometer equipped with a Cu-Kα source. Morphologies of samples were determined with Carl Zeiss Ultra 55 Field Emission Scanning Electron Microscope. UV-Vis spectra of the aqueous dispersions were obtained from 1800 Shimadzu UV-Vis spectrophotometer. Electrical properties of PVA

and composites were investigated from lab set up two probe method.

Table: 1 Sample codes and optical band gaps of PVA and the composites.

Sample Name	Sample code	Optical band gap (ev) Eg
Polyvinyl Alcohol	PVA	3.5
PVA/AgNW 5%	PVAW 5	2.1
PVA/AgNW 10%	PVAW10	2
PVA/AgNW 12%	PVAW12	3.25
PVA/AgNW 15%	PVAW15	2.1
PVA/AgNW 20%	PVAW20	3.5

4. RESULTS AND DISCUSSION:

XRD: From Figure 1 XRD of PVA shows a sharp peak at $2\theta=20^\circ$ indicating that most of PVA molecules are arranged in (101) plane.

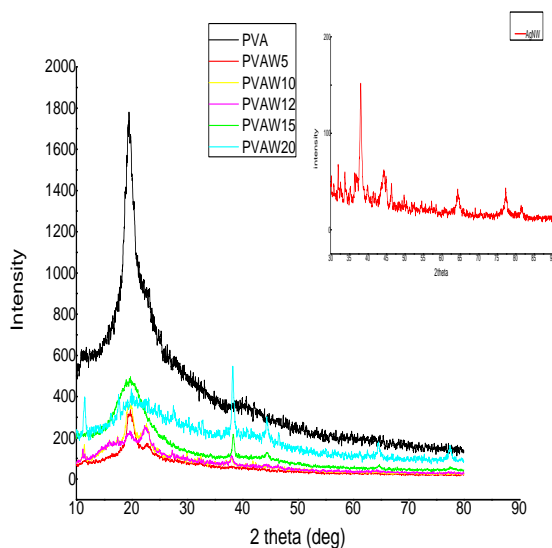


Figure: 1 XRD of PVA and PVAW samples with XRD of AgNW in the inset.

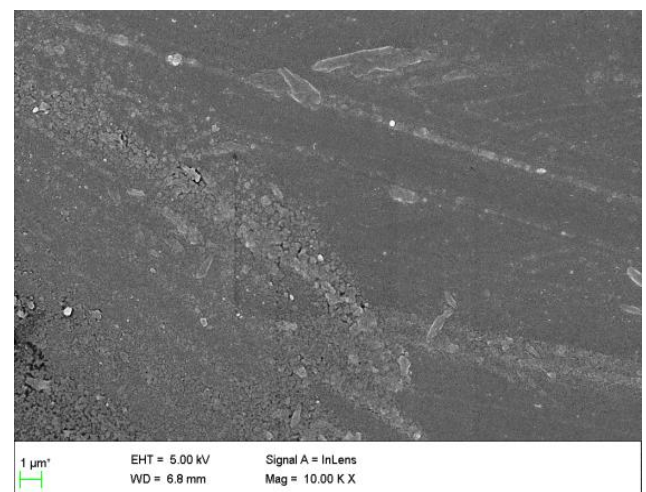
This peak shows the semi crystalline nature of PVA due to presence of strong inter-molecular and intra-molecular hydrogen bonding between the PVA chains [8]. Other minor peak at 23° might be due to minor crystallites or due to impurities. XRD of AgNW shows peaks at $2\theta=38^\circ, 45^\circ, 65^\circ$ and 78° corresponding to (111), (200), (220) and (311) planes respectively corresponding to fcc crystal structure (JCPDS, File No. 04-0783).

In the composites the intensity of characteristic peak of PVA at $2\theta=20^\circ$ has been reduced by increasing the concentration of AgNWs in to PVA matrix and the intensity of peak at

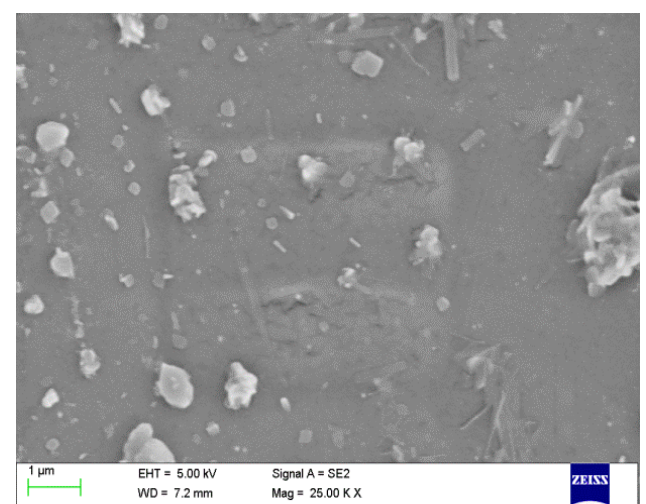
$2\theta=23^\circ$ has increased gradually. In PVAW20 both the peaks at $2\theta=20^\circ$ and 23° combined to a broad peak. The incorporation of AgNWs into the PVA matrix would have disturbed the hydrogen bonding and OH group of PVA, which resulted in the breakage of polymer chains. This might be the reason for the decrease in intensity of peak at 20° [9]. The breakage in the molecular chains lead the molecules free, so that they might rotate in the direction (200) because of which the intensity at 23° would have increased.

All the composites shows the peaks corresponding to the fcc crystal structure of Ag and the peak intensities increased with the increase in Ag percentage in the composites. As there is no chemical reaction between PVA and AgNWs, the peaks of cubic structure of Ag are at the same positions. This can be observed from the FESEM images.

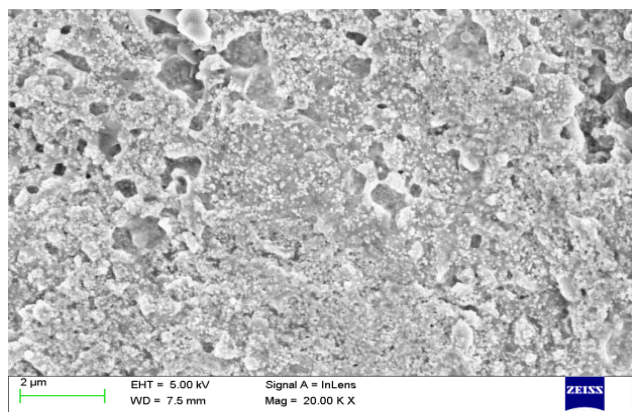
FESEM: Figure 2b) shows the FESEM image of PVAW10 in which a well embedded AgNW network is seen clearly. The nanowires are well dispersed in the matrix of PVA. Some wires even deeply immersed in the matrix with a small portion of the wire protruded out, which shows the random nature of dispersion.



(a) FESEM of PVA



(b) FESEM of PVAW 10

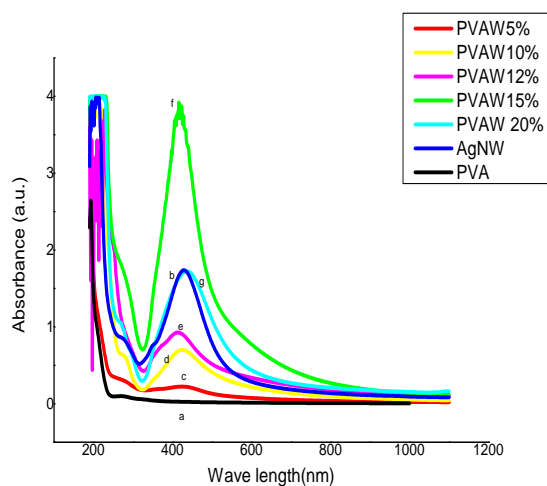


(c) FESEM of PVAW 20

Figure: 2 FESEM images of PVA and the composites

In the image of PVAW 20 there is a lot of Ag cluster formation because of which the wires are not seen. The dispersion of nanowires is also not seen.

UV-Vis Spectroscopy:

**Figure: 2** UV-Vis Spectroscopy of PVA, AgNW and the composites

UV-Visible spectroscopy of PVA, AgNW and the composites is given in the figure: 2. PVA (curve 'a') has a peak at 273nm which may be due to the $n \rightarrow \pi^*$ transitions of the C=O group of PVA [9]. There is no other peak in the entire visible region. AgNWs ('b' curve) in this figure shows an absorption band at 427nm which is due to surface plasmon resonance of silver ions that collectively oscillates due to resonance with the incident electromagnetic radiation (visible light). There is a shoulder peak at 352nm in the same curves of AgNW, which is due to the transverse plasmon resonance of nanowires of Ag[10].

In the composites, absorption peak at 273nm is due to PVA matrix and the shoulder peak at 352nm is sustained in all the composites. The SPR peak due to Ag ions has been shifted to lower wavelength from 427nm in PVAW5 to 412nm in PVAW15 again shifted to the same position 427nm in PVAW20. Shifting of the peak to lower wavelength may be due to decrease in the diameter of AgNWs after doping into

the matrix [11]. Good dispersion of wires has observed in the composites till PVAW15. This can be confirmed with the increase in intensity of absorption peak up to PVAW15. However it is well known fact that the absorption of nanostructures depends mainly on their size. As the diameter of the wires is reduced, the intensity of the absorption peak increased and a corresponding shift towards the lower wavelengths has been observed.

In PVAW20, because of increased Ag concentration the wire structure has been damaged after doping into the matrix and the nanostructures not dispersed well in the matrix which is also confirmed in FESEM of PVAW20. The absorption peak may have shifted again to the higher wavelength side with a less intensified absorption due to this reason.

Optical energy band gap of Pure PVA and the composites has been obtained using Tauc relation. The values of optical band gaps has determined by extrapolating the lines fitted in the plots of $h\nu$ versus $(\alpha h\nu)^2$ where α is the absorption coefficient and $h\nu$ is the energy of incident photon[12]. The values are tabulated in the Table no. 1

Optical band gap has decreased from 3.5ev in PVA to 2.1ev in the composites. This reduction in value of optical band gap may be due to the formation of chemical bonds between PVA chains and AgNWs responsible for generation of localized states between HOMO and LUMO energy bands in PVA. The AgNWs has formed connecting networks in the PVA matrix which is evident from the FESEM of PVAW10. Embedding of AgNWs in the PVA matrix would have generated new energy levels between the HOMO and LUMO which made the energy transitions possible at the lower energies. In PVAW20 such networks are absent and the AgNWs has agglomerated in the matrix. This might be the reason for the increment of E_g to 3.5ev in PVAW20.

DC conductivity:

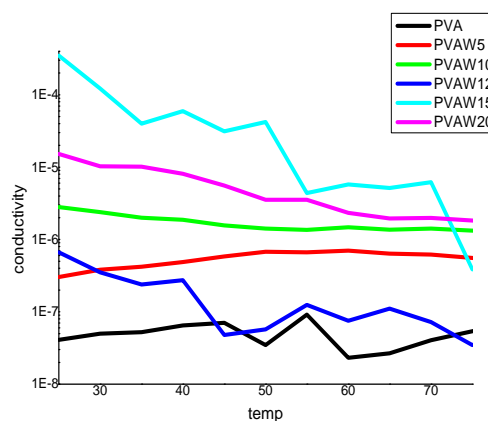
**Figure: 4** DC conductivity of PVA and the composites

Figure:4 shows the variation of conductivity of the samples with respect to temperature. Pure PVA has conductivity of 4.10549×10^{-8} S/cm at 298K. By introducing AgNWs in to PVA matrix conductivity has increased by two orders

minimum in PVAW5. With the increase in AgNW concentration in the matrix the conductivity has improved and PVAW15 shows maximum conductance of approximately $3.5E-4$ S/cm. That is conductivity has improved by 4 orders magnitude when compared to pure PVA.

Increase in conductivity in the composites may be due to the formation of charge transfer complexes in the polymer networks with the introduction of AgNWs in the matrix. With the formation of charge transfer complexes in semi crystalline polymers like PVA, the barrier height between the trapping sites reduces which in turn provides a connecting path in the amorphous regions of PVA and hence the conductivity enhances [13]. The Ag ions fill the free volume holes and occupy free interstitial places between the polymer chains in the amorphous phase and link these chains by charge exchange process between the nanowires and the PVA chains. Further this complex formation increases with the doping concentrations of AgNWs. Because of this reason conductivity has increased with the increase in AgNWs percentage in PVA

Conductivity of PVAW 20 is less compared to PVAW 15, which might be due to aggregation of Ag in the matrix. Because of cluster formation AgNWs could not provide the connecting path in the amorphous PVA matrix which resulted in low conductivity. Aggregation of AgNWs in PVAW20 is evident from FESEM images. Also, the optical band gap of PVAW 20 supports these results.

CONCLUSION

PVA/AgNW composites have been synthesized and characterized for their structural, morphological and electrical properties. Addition of AgNWs into PVA has affected its structure which is evident from reduction of intensity of signature peak of PVA at 20° . FESEM image of PVAW 10 shows the well dispersion of AgNWs in the polymer matrix. UV-Vis spectroscopy of the samples shows a blue shift in the SPR absorption peak of Ag ions, which may be due to reduction of diameter of AgNWs. There is a reduction in optical band gap till PVAW15 which also supports the conductivity of the samples. Conductivity in the composites has improved nearly by 4 orders magnitude by the introduction of 15% AgNWs in to PVA.

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