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Manifestation of the silver nanoparticles incorporated into the poly vinyl alcohol matrices

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Electrical and optical properties of the silver nanoparticles (Ag NPs) incorporated into the polyvinyl alcohol (PVA) matrices were investigated as a function of Ag NPs. The intensities of FT-Raman bands have a maximum corresponding to the Ag NP amount about 3.6 mg.. The PVA doped with different amounts of Ag NPs shows UV-Visible peaks, were red shifted by Ag NPs increase, while their intensities according well with the FT-Raman spectra. The UV-Visible spectra for the 3.6 mg Ag NPs doped in PVA presented a small red shift and band intensity decrease by increasing temperature. © *2006 Springer Science + Business Media, Inc.*

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1. Introduction

Poly vinyl alcohol (PVA) has been used in many applications sine its discovery in 1924 [1–3]. The optical applications of PVA based on polarization and filtration of light and photograph [4]. While the medical applications depends on its use in contact lenses, drug-delivery systems, and artificial blood vessels [5, 6]. PVA is a crystalline polymer, highly soluble in water, its dissolution requires the breaking of the crystal structure and need to be carried out at elevated temperature [7]. One of the crucial features of the PVA consists in an existence of the promising acoustooptical effects determined by interaction of electron and phonon subsystems [8].

In 1984, Koon and coworkers have been prepared organic matrices like polymer doped with nanoparticles [9, 10]. The metal nanoparticles doped in polymer have a unique applications such as optical filters, magnetic and optical data storage [11].

The optical properties of poly methyl methacarylate with implanted silver nanoparticles (Ag NPs) were measured [12]; the weak plasmon resonance absorption were observed. The nanoparticles doped in polymer matrices have long time stability, novel optical, and electrical properties [13, 14]. It aimed here in this paper to prepare PVA polymer doped with different amount of Ag NPs. To monitor the effect of doping on the optical properties, the FT-Raman and FT-IR as well the UV-Visible spectrum were recorded. The electrical properties of these polymer sample were measured.

2. Experiment

2.1. Preparation of the samples

The Ag NPs solution was prepared by heating 200 mL an aqueous solution of Ag NO_3 (1.25 mM) to boiling, then 50 mL aqueous solution of sodium citrate (17.5 mM) was added. The resulted solution was refluxed for 1 h; a yellow colored Ag NPs colloidal was formed. The PVA films doped with different amounts of Ag NPs were prepared using a casting method; by mixing different volumes of the solutions (A and B) (see Table I) prepared by the following synthetic procedures.

Solution (A): 9.86 gm PVA (13000 gm/mol) was mixed with 230 mL of the Ag NPs solution and leaved 24 h at room temperature to be swelled. The resulting solution was stirred by a magnetic stirrer at 60°C for 4 h until obtaining clear solution indicating that the polymer became completely soluble.

Solution (B): 7.29 gm PVA (13000 gm/mol) was mixed with 170 mL distilled water and typical procedure in the preparation of solution A was followed.

2.2. Instrumentation

The FT-Raman spectrometer (RFS 100/S) attached with FT-IR spectrometer (Bruker IFS 66 VS) were used to measure the Raman scattering spectra (Nd:YAG laser, 1.4 W power) and the mid-IR spectra of PVA films, while the UV-Visible spectra were monitored using

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TABLE I The composition of Ag NPs doped with different amount of Ag NPs

Sample	PVA (mL)	Ag NPs and PVA (mL)
1	50	. . .
2	40	10
3	30	20
4	20	30
5	15	35
6	10	40
7	5	45
8	. . .	50

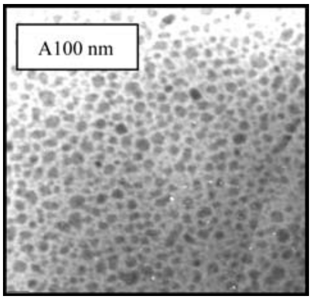

Figure 1 The transmission electron microscopy (TEM) images for Ag NPs

spectrophotometer (Bio Cary 50 Varian, USA) in the rang (190–1100 nm). The peltier cell was used for heating the PVA film during the recording of the UV-Visible spectra.

The shape and size distribution of the Ag NPs were calculated using the enlarged transmission electron microscopy (TEM) (Ziess, 120 KV) photography, the sample was prepared by putting a drop of solution on a cupper carbon grid and setting the drop to dry completely in a desicrator. Fig. 1 shows the transmission microscopy for the Ag NPs, the particle size were calculated after counting 150 particle, it found to be 20 ± 5 nm.

The conductivity of PVA and PVA doped with different amounts of Ag NPs measured at 1 volt and different frequencies (10^5, 10^4, 10^3, 1.2×10^2, and 10^2) Hz using (Stanford bridge). Tow parallel edges of the polymer sheets were coated with silver pest after the measurement.

3. Results and discussion

3.1. Raman spectra of PVA doped with Ag NPs

PVA is a crystalline polymer with no centers of symmetry resulting from the polymerization of vinyl alcohol. Consequently; PVA containing the structural repeat unit $-[-CH_2-CH(OH)-]_n-$. Moreover; hydrogen bond might be formed among the hydroxyl groups and hydrogen atoms of the same chain or parallel ones leading to a low degree of structure ordering of PVA. The FT-Raman spectra of pure PVA and PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.66, 4.2, 4.8, and 5.3 mg) are given in Fig. 2 and the assignment of the vibrational modes are given in Table II according to [15–17]. The band at 2910.4 cm^{-1} assigned to be the (CH) stretching vibration of (CH_2) presented in the PVA spectrum and PVA doped with different amounts of Ag NPs spectra. These bands were un shifted but; their intensities were found to be highly dependent on the amount of doping material. As the amount of Ag NPs increases the band intensity was found to be increase up to 3.6 mg (sample), after which the intensities were found to be decreased less than that in the case of pure PVA. On the other hand the CH stretching vibration band of CH at 2721 cm^{-1} in the PVA was found to be blue shifted after addition of Ag NPs and the degree of blue shifts was found to increase as the amount of Ag NPs increases. Considering the variation of the intensities of the CH symmetric stretching of CH group with different concentration of Ag NPs was found to be similar to that observed above for the CH_2 group. A very weak band corresponding to the stretching vibration of the residual acetate carbonyl group in the PVA spectrum appeared at $\sim$ 1710 cm^{-1}.

The CH and OH bending bands at 1440 cm^{-1} of the PVA suffered a blue shift in the corresponding PVA spectra doped with Ag NPs. this blue shifts was found to increase by the increase the weight of Ag NPs. While the band intensities increases up to 3.6 mg Ag NPs there after is decrease again. By the same way; the CH_2 wagging and OH bending at 1356 cm^{-1} and CH wagging at 1236 cm^{-1} in the pure PVA showed blue shifts and band intensities enhancement similar to CH and OH bending bands; due to doping with Ag NPs. The bands at (1145 and 1095 cm^{-1}) in the pure PVA were assigned to be (C–C and C–O stretching vibration mixture) and (C–O stretching vibration and OH bending mixture) respectively. These bands were found to be red shifted with enhanced intensities in the PVA doped with Ag NPs increase up to 3.6 mg composition then decrease again as the amount of Ag NPs increased. Similar dependence of the band intensities was observed for the two (C–C) stretching vibration bands at 918 and 856 cm^{-1} in the pure PVA Raman spectrum as compared with PVA doped with Ag NPs. The band resulting from mixing of OH wagging and out-of-plane CH bending modes at 563 cm^{-1} in the pure PVA was blue shifted in the Raman spectra of PVA doped with Ag NPs. Similarly; the bands attributed to a mixture of CO bending and CH out-of-plane bending appeared at 477 cm^{-1} and the band at 410 cm^{-1} corresponding to the CO wagging in the Raman spectrum of pure PVA. In the other hand the C–C torsion appearing at 310 cm^{-1} in the pure PVA Raman spectrum was found to be blue shifted in PVA doped with Ag NPs. The bands at $\sim$200 cm^{-1} are assigned here to be the (Ag–O) bond vibration of the PVA doped with Ag NPs.

To allow a better understanding of the Raman band intensities enhancement for PVA doped with Ag NPs; the enhancement factor (EF) was calculated for each band after normalization to the (CC) stretching vibration band appearing at $\sim$918 cm^{-1}. where EF = Normalized ($I_{\text{doped PVA}}/I_{\text{pure PVA}}$). Fig. 3 shows the relation between the enhancement factor for each Raman band vibration in PVA doped with different amounts of Ag NPs.

PVA molecules consists of parallel chains connected by hydrogen bonds. Consequently; doping PVA with Ag

TABLE II The Raman band vibrations for pure PVA and PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.6, 4.2, 4.8, and 5.4 mg) and their assignments

PVA	1.14 (mg)	2.1 (mg)	3.2 (mg)	3.6 (mg)	4.2 (mg)	4.8 (mg)	5.4 (mg)	Assignments
2910s	2910s	2910s	2910s	2910s	2910s	2910s	2910s	ν(CH) of (CH_2)
2721w	2722w	2723w	2734w	2735w	2735w	2744w	2769w	ν(CH)
1710v	1715v	1718v	1720v	1723v	1717v	1715v	1722v	ν(C=O) residual acetate
1440s	1442s	1442s	1443s	1443s	1444s	1444s	1445s	δ (CH_2),δ (OH)
1356m	1358m	1361m	1362m	1363m	1364m	1364	1365m	γ_w (CH_2),δ (OH)
1232m	1236m	1237m	1237m	1238m	1238m	1239m	1240m	γ_w (CH)
1145m	1144m	1143m	1142m	1140m	1139m	1138m	1135m	ν(C–O),ν(C–C)
1095m	1094m	1093m	1093m	1093m	1092m	1091m	1090m	ν(C–O)
918s	918s	918s	918s	918s	918s	918s	918s	ν(C–C)
856s	856s	855s	856s	855s	856s	856s	856s	ν(C–C)
563w	565w	565w	566w	568w	568w	569w	569w	γ_w (O–H), CH out-of-plane
477m	478m	478m	478m	482m	484m	486m	482m	δ (C–O), CH out-of-plane
410w	416w	414w	414w	415w	416w	418w	415w	γ_w (C–O)
310w	312w	310w	313w	314w	315w	318w	318m	C–C torsion and bending
...	234m	233m	226m	222m	221m	219m	216m	ν (Ag-polymer)
117.9	117.9	117.9	117.9	116.0	119.9	121.8	116.0	...

NPs have great effect on the hydrogen bonds as well as the ordering of their chains. Hence, the Raman spectra were found to be varied after doping. Vibration modes at (2721, 1440, 1356, 1256, 1236, 563, 477, 410, and 310 cm^{-1}) in the pure PVA Raman spectrum corresponding to (CH stretching vibration, CH and OH bending mixture, CH wagging and OH bending mixture, CH wagging, CH and OH bending mixture, CO and CH bending, CO and CC torsion) were found to be blue shifted in the Raman spectra of PVA doped with Ag NPs. The blue shifts increase as the amount of Ag NPs increase. The Ag NPs make polymer chains far apart, consequently; leading to weakening of the hydrogen bonds and blue shifting of the CH and OH mode of vibrations and bending takes place. While; the blue shift of the CC vibrational modes might be attributed to the decrease of the streak among the carbon skeleton chains. The band assumed to be corresponding to polymer-Ag NPs bond vibration was found to be red shifted as the amount of Ag NPs increases due to adsorption of polymer on the surface of Ag NPs.

The bands corresponding to (CC and CO stretching vibration mixture) and (CO stretching vibration and OH bending mixture) were found to be sensitive to the degree of crystalinity in the PVA. While; the band at 1124 cm^{-1} if

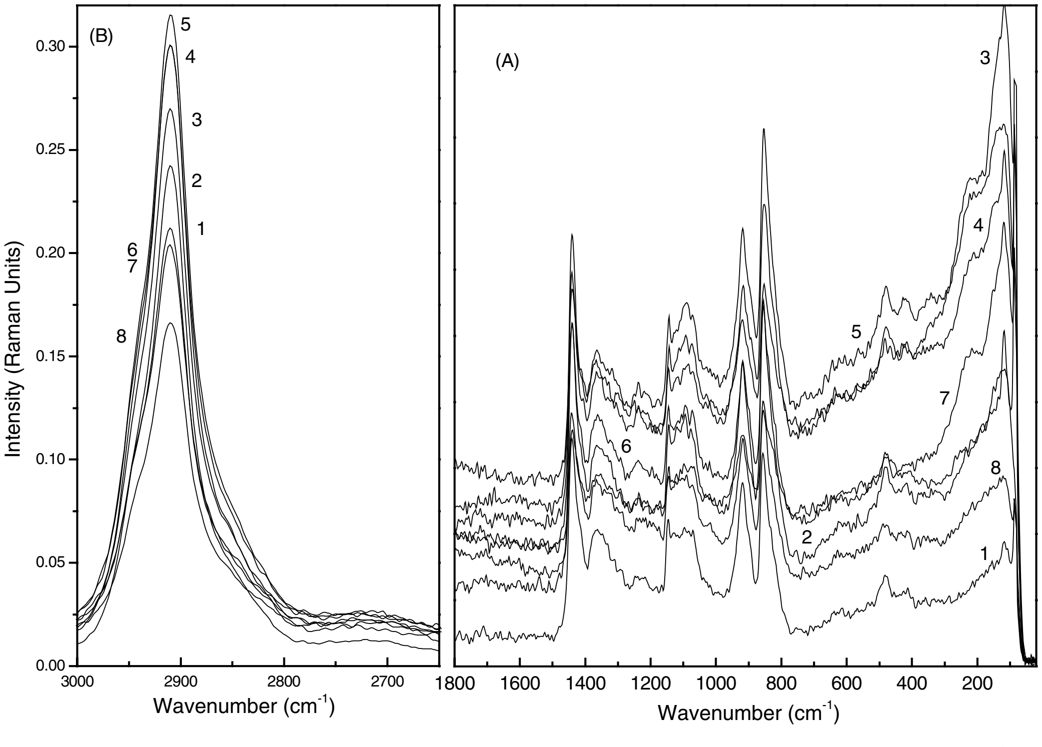

Figure 2 FT-Raman spectra for pure (1) PVA and (2–8) PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.6, 4.2, 4.8, and 5.4 mg); respectively.

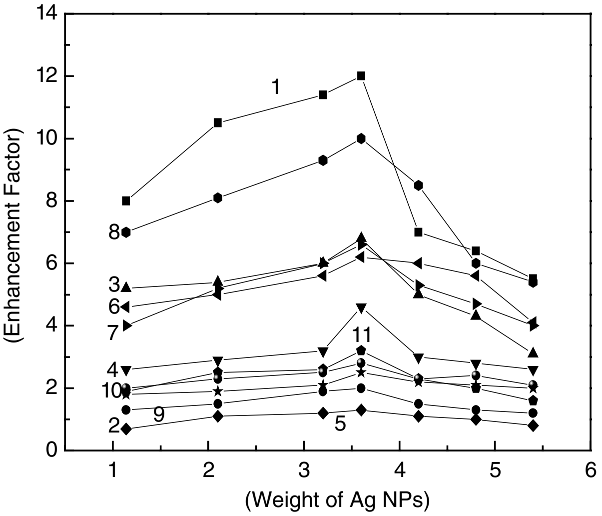

Figure 3 The enhancement factors for the PVA (doped with different amounts of Ag NPs) band vibration intensities after normalization to the (CC) stretching vibration band appearing at ~918 cm^{-1}. (1,2) CH stretching vibration of CH_2 and CH groups, (3) CH and OH bending mixture, (4) CH wagging and OH bending mixture, (5) CH wagging, (6,7) CO and CC stretching, (8) OH wagging and CH bending mixture, (9) CH and CO bending mixture, (10) CO wagging, (11) CO and CC torsion.

appeared attributed to be due to the presence of amorphous polymer [18–20]. The other hand no band is appeared at 1124 cm^{-1}.

Irradiation of PVA doped with Ag NPs with laser during Raman measurement causes excitation of collective oscillations of the surface charges of Ag NPs. This oscillations lead to the formation of a strong localized magnetic flied near the particle surface. The enhancement of the PVA Raman spectra were assumed to be a result from of resonance between the Surface plasmon of Ag NPs and Raman spectra of PVA which reinforce the Raman intensity. The relative enhancement factors were found to increase by increasing the amount of Ag NPs up to 3.6 mg, as a result of the mentioned above localized surface plasmon. When the multiple scattering of the created particle plasmon becomes significant a damping of the particle plasmon may then occur [21] leading to the observed here reduction in the enhancement factor above 3.6 mg Ag NPs. For the metallic NP incorporated into the PVA matrices substantial role may play also nanoconfined effects and electron-phonon anharmonic interactions.[22].

3.2. FT-IR spectra of PVA doped with Ag NPs

The PVA polymer has no center of symmetry, therefore it is IR active, great similarities among the Raman modes of vibration and the corresponding IR were observed in the rang of (400–3000 cm^{-1}). Fig. 4 represent the FT-IR spectra of PVA and PVA doped with different amounts of Ag NPs while Table III present their assignments. The bands at 5838 and 5692 cm^{-1} were assigned to be CH overtone stretching vibration of (CH_2 and CH groups), respectively. the residual acetate overtone stretching vibration appeared at 5138 cm^{-1}. while, the (CO, CC) overtone stretching vibration mixture is at 4777 cm^{-1}. the bands at 4331 and 4008 cm^{-1} assigned to be (CH_2 and OH bending mixture) and (CH_2 wagging and OH bending mixture), respectively. on the other hand the band at 4242 cm^{-1} is the CO overtone bond vibration. All the overtones of PVA and PVA doped with Ag NPs have the same behavior as the normal vibration Raman and IR bands in terms of band shifting and enhancement.

3.3. The UV-Visible spectra of PVA doped with Ag NPs

The UV-Visible spectra of PVA and PVA implanted with different amounts of Ag NPs are shown in Fig. 5. The absorption peak maxima of the UV-Visible spectra of PVA

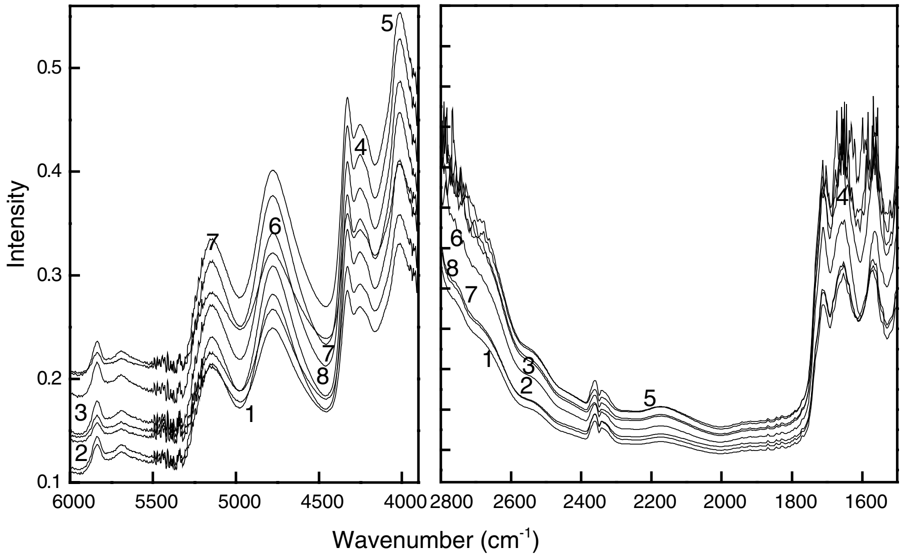

Figure 4 FT-IR spectra for pure (1) PVA and (2–8) PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.6, 4.2, 4.8, and 5.4 mg); respectively.

TABLE III The IR band vibrations for pure PVA and PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.6, 4.2, 4.8, and 5.4 mg) and their assignments

PVA	1.14 (mg)	2.1 (mg)	3.2 (mg)	3.6 (mg)	4.2 (mg)	4.8 (mg)	5.4 (mg)	Assignments
5838m	5837m	5838m	5838m	5838m	5838m	5838m	5838m	ν(CH) of (CH_2)
5692w	5694w	5696w	5695w	5699w	5702w	5705w	5706w	ν(CH) of (CH)
5138s	5139s	5140s	5139s	5142s	5142s	5143s	5144s	ν(C=O) residual acetate
4331s	4334s	4336s	4337s	4339s	4341s	4344s	4344s	δ (CH_2),δ (OH)
4008vs	4010vs	4011vs	4013vs	4015vs	4018vs	4019vs	4019vs	γ_w (CH_2),δ (OH)
4777s	4778s	4779s	4779s	4780s	4782s	4783s	4783s	ν(C–O),ν(C–C)
4242s	4243s	4242s	4243s	4243s	4244s	4244s	4244s	ν(C–O)
2906s	2906s	2906s	2906s	2907s	2906s	2907s	2908s	ν(CH) of (CH_2)
2736s	2737s	2737s	2738s	2739s	2739s	2742s	2746s	ν(CH)
1710m	1712m	1711m	1712m	1713m	1713m	1714m	1716m	ν(C=O) residual acetate
1448m	1450m	1451m	1452m	1453m	1454m	1454m	1456m	δ (CH_2),δ (OH)
1388m	1389m	1391m	1393m	1395m	1396m	1396m	1398m	γ_w (CH_2),δ (OH)
1295m	1294m	1293m	1292m	1291m	1289m	1288m	1286m	γ_w (CH)
1141m	1139m	1138m	1137m	1137m	1136m	1135m	1135m	ν(C-O),ν(C–C)
1097m	1095m	1094m	1095m	1094m	1094m	1092m	1091m	ν(C–O)
910m	910m	910m	911m	910m	911m	910m	910m	ν(C–C)
889m	889m	889m	889m	889m	889m	889m	889m	ν(C–C)
858m	858m	858m	858m	858m	859m	858m	858m	γ_r(CH)
582m	583m	584m	585m	586m	588m	588m	589m	γ_w (O–H),out-of-plane
474m	478m	478m	478m	479m	479m	482m	484m	δ (C–O), CH out-of-plane
412m	414m	416m	416m	418m	419m	420m	421m	γ_w (C–O)

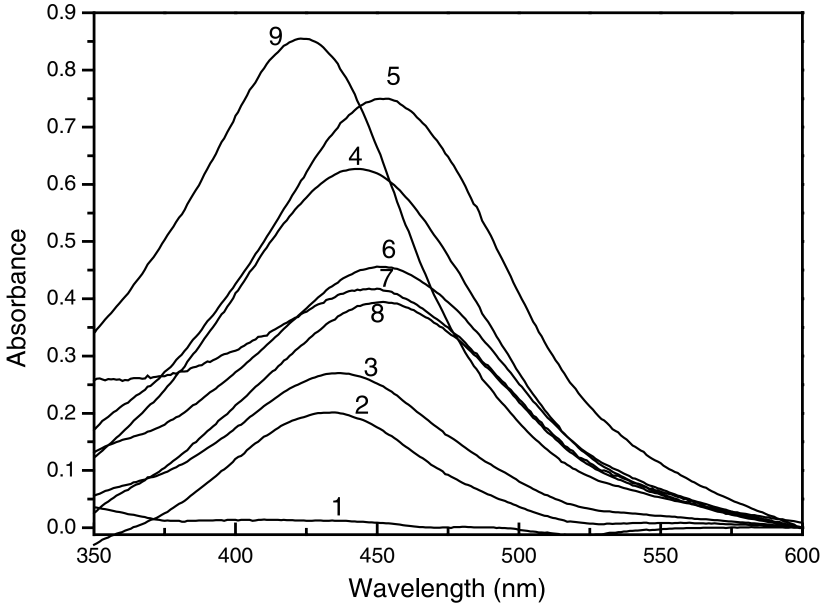

Figure 5 The UV-visible spectra of pure(1) PVA and (2–8) PVA doped with different amounts of Ag NPs (1.14, 2.1, 3.2, 3.6, 4.2, 4.8, and 5.4 mg); respectively and (9) pure Ag NPs solution

doped with Ag NPs were found to be red shifted as the weight of Ag NPs increases see Table IV. However, the intensities of these peaks were increased by increasing the amount of Ag NPs reaching its maximum value at 3.6 mg. Then; the values were found to decrease as the amount of Ag NPs increased. While; the pure Ag NPs solution has maximum absorption peak at 423 nm. The pure PVA show no bands in the rang of measurement. The UV-Visible spectra of PVA doped with 3.6 mg Ag NPs at different temperatures (20, 40, 60, and 80°C) are given in Fig. 6. The maximum absorption peaks were found to be directly proportional to the heating temperature, while; the peak intensities decreased as the temperature increased (Table V).

The width and frequency of the surface plasmon absorption depends on the size, shape, and size distribution

TABLE IV The absorption spectra of PVA and PVA doped with different weights of Ag NPs

Weight of Ag NPs	Sample number	Maximum absorption (nm)
PVA	1	0
Ag NPs	9	423
1.1	2	433
2.1	3	436
3.2	4	442
3.6	5	451
4.2	6	452.5
4.8	7	453
5.3	8	454.6

TABLE V The absorption spectra of PVA doped with 3.6 mg Ag NPs

Temperature	Maximum absorption (nm)
20	441
40	442
60	442.5
80	444

and shape of the metal nanoparticle as well as on the dielectic constant of the metal and the surrounding medium [23–25]. According to the Mie theory which can applied in case of low concentrations of nanoparticles in a solvent and solid matrix [26]. There is no interaction among the electric fields created around each particle by the excitation of surface plasmon resonance. On the other hand;

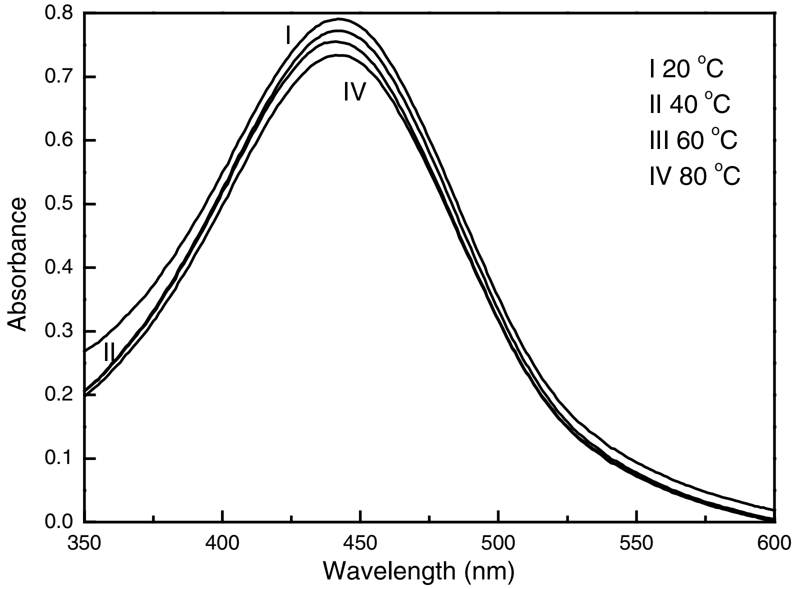

Figure 6 The UV-Visible of PVA doped with 3.6 mg Ag NPs at different temperature (20, 40, 60, and 80°C)

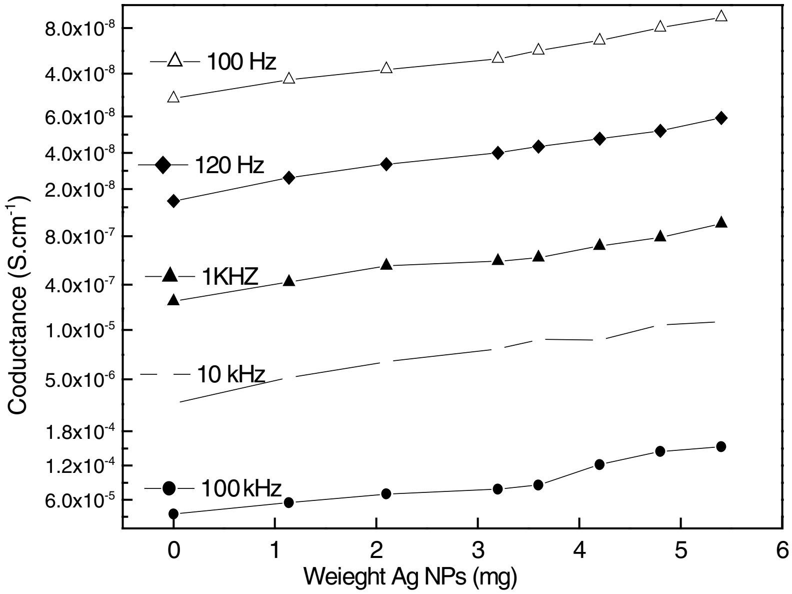

Figure 7 The conductivity of PVA and PVA doped with different amounts of Ag NPs measured at 1 volt and different frequencies (10^5, 10^4, 10^3, 1.2 × 10^2, and 10^2) Hz

when the inter-particle distance become smaller than the particle size or when the particles undergo aggregation, the plasmon resonance was found to red shifted [27, 28].

3.4. Conductivity of PVA and PVA doped with Ag NPs

The conductivity of PVA composite doped with Ag NPs of different concentration was found to be drastically enhanced compared with pure PVA (see Fig. 7). This might attributed to the presence of electron rich Ag NPs which permitting charges to pass through them as well as the creation of free radicals resulting from the polymer Ag NPs interaction, which was assumed from the PVA Raman assignments.

4. Conclusion

The Raman and IR spectra of PVA doped with different amounts of Ag NPs were recorded. The vibrational band intensities were found to be enhanced up to 3.6 mg Ag NPs then decreased. While; some bands were red shifted due to the interaction of polymer with Ag NPs. The UV-Visible spectra of PVA doped with Ag NPs show a peak maxima were found to be red shifted as the amount of Ag NPs increase, while; the maximum peak intensities were increased up to 3.6 mg Ag NPs then decreased. The conductivity of PVA was found to be increased due to doping with Ag NPs.

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