

Enhancement of the Optical Properties of Poly Vinyl Alcohol by Doping with Silver Nanoparticles

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ABSTRACT: Poly vinyl alcohol (PVA) incorporated with different weight percent of Silver nanoparticles (Ag NPs) were prepared. The enhancement factors for each band in the Raman spectra were calculated and the degree of enhancement were found to be increased as the percent of Ag NPs increases up to 0.3%, and thereafter it decreases. Some bands were red shifted while others were blue shifted. The overtones FTIR bands and photoacoustic spectra were recorded and show the same behavior as those bands. The X-ray diffraction pattern and Raman and photoacoustic

spectra showed that PVA has a high degree of crystallinity. The UV-vis spectra of the same samples were red shifted and increase in their intensities up to 0.3% Ag NPs, thereafter the band intensities of the peak corresponding to Ag NPs were diminished. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3608–3614, 2006

Key words: photoacoustic spectra; Raman spectra; PVA; silver nanoparticles

INTRODUCTION

Poly vinyl alcohol (PVA) has been used in many applications since its discovery in 1924.^{1–3} The optical applications of PVA are based on polarization and filtration of light and photograph.⁴ The medical applications are based on its use in contact lenses, drug-delivery systems, and artificial blood vessels.^{5,6} PVA is a crystalline polymer, highly soluble in water, and its dissolution requires breaking the molecular structure and requires elevated temperature.⁷

In 1984, Koon and coworkers prepared organic matrices like polymer doped with nanoparticles.^{8,9} The metal nanoparticles doped in polymer have unique applications, such as in optical filters and in magnetic and optical data storage.¹⁰

The optical properties of poly methyl methacrylate with implanted silver nanoparticles (Ag NPs) were measured.¹¹ The weak plasmon resonance absorption were observed. The nanoparticles doped in polymer matrices have long time stability and novel optical and electrical properties.^{12,13} It is aimed in this work to prepare PVA polymer doped with different amounts of Ag NPs. The effect of doping on the optical properties was monitored using FT-Raman and FTIR as well the UV-vis techniques, while the photoacoustic

technique is used to measure the spectra that are noisy in the IR spectra.

EXPERIMENT

Preparation of the samples

The PVA films doped with different amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42 wt %) were prepared using casting method,³ by mixing different amounts of solutions A and B, (0/50 mL), (5/45 mL), (10/40 mL), (15/35 mL), (20/30 mL), (30/20 mL), (40/10 mL), (50/0 mL).

Solution (A): 200 mL aqueous solution of Ag NO₃ (1.36 mM) was heated to boiling, then 50 mL aqueous solution of sodium citrate (19 mM) was added. The resulting solution was refluxed for 1 h and the process was completed using distilled water to a volume of 250 mL. PVA (10.7 g; 13,000 g/mol) was mixed with the Ag NPs solution and left for 24 h at room temperature to be swelled. The resulting solution was stirred at 60°C (200 rpm) for 4 h until a clear solution was obtained.

Solution (B): 8.69 g PVA (13,000 g/mol) was mixed with 200 mL distilled water and the same procedure for preparation of solution A was followed.

Instrumentation

The FT-Raman spectrometer (4 cm⁻¹ resolution; RFS 100/S) attached with FTIR spectrometer (2 cm⁻¹ resolution; Bruker IFS 66 VS) was used to measure the

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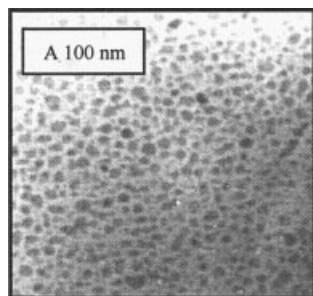


Figure 1 The transmission electron microscopy images for Ag NPs.

Raman scattering spectra (Nd : YAG laser, 1.4 W power) and the MIR spectra of PVA films. Moreover, a photoacoustic unit is attached to the same 2 cm^{-1} resolution (Bruker IFS 66 VS) spectrometer, while the UV-vis spectra were monitored using Bio Cary 50 Varian spectrophotometer in the range of 190–1100 nm.

The X-ray diffraction pattern was recorded using a pw1710 based Cu $K\alpha$ X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$); nickel was used as filter.

The shape and size distribution of the Ag NPs were estimated using the enlarged transmission electron microscopy Zeiss, 120 KV photography. The sample was prepared by spreading a drop of solution on a copper carbon grid and setting the drop to dry completely in a desiccator. Figure 1 shows a transmission microscopy image for the Ag NPs. The average particle size was calculated after counting 150 particles ($20 \pm 5 \text{ nm}$).

RESULTS AND DISCUSSION

X-ray diffraction of PVA

PVA results from the polymerizations of vinyl alcohol, and consequently, the structural repeat unit is $-\text{[CH}_2\text{-CH(OH)-]}_n\text{-}$. Moreover, hydrogen bonds may 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. It is well-known that PVA is a crystalline polymer and the degree of crystallinity was detected from the X-ray diffraction patterns. Figure 2 shows the X-ray diffraction patterns of PVA; two diffraction patterns at two θ ($19.1^\circ, 19.5^\circ$) values represent the crystalline phase,³ while the shoulder represents the noncrystalline (amorphous) part of the sample.

Ftir spectra of PVA doped with Ag NPs

PVA has no center of symmetry; therefore, most of the vibrational bands are IR and Raman active. The FTIR spectra of PVA and PVA incorporated with different

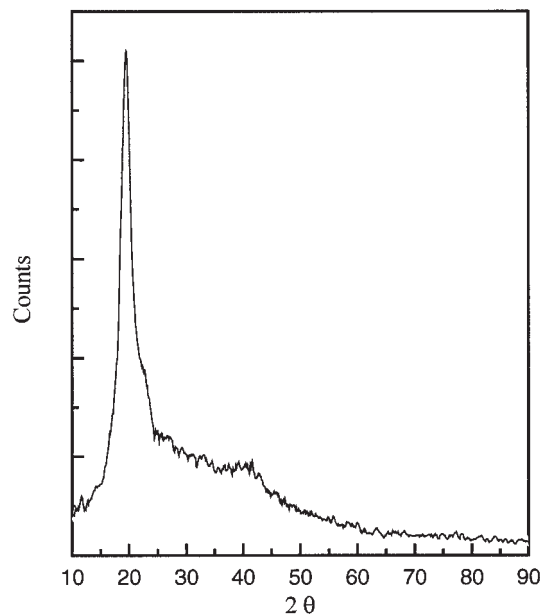


Figure 2 XRD patterns of PVA.

weight percents of Ag NPs are presented in Figure 3. On the other hand, the band assignments are presented in Table I. The vibration band at 5838 cm^{-1} was assigned to CH overtones stretching of CH_2 of PVA. This band was found to be enhanced as a result of doping with Ag NPs and the degree of enhancement was increased by increasing the percent of Ag NPs up to 0.3%, and then it starts to diminish on increasing the Ag NPs percent. While, the band at 5692 cm^{-1} , which is assigned to be CH overtones of CH, was found to be blue shifted after doping and the band intensities showed the same behavior as the CH stretching of the CH_2 . The residual acetate overtone stretching vibration band at 5138 cm^{-1} in PVA was

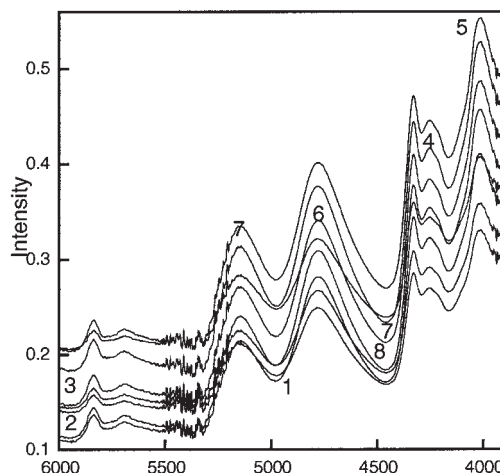


Figure 3 FTIR spectra for pure (1) PVA and (2–8) PVA doped with different amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%), respectively.

TABLE I
The IR Band Vibration for Pure PVA and PVA doped with Different Amount of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%) and their Assignments

PVA	0.1	0.17	0.27	0.3	0.33	0.4	0.42	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)
4008v	4010v	4011v	4013v	4015v	4018v	4019v	4019v	γ_w (CH ₂), δ (OK)
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)

v, very sharp; s, sharp; m, medium; w, weak.

blue shifted by doping and the shift was found to be increasing with the percent of Ag NPs. The bands at 4331 and 4008 cm^{-1} , which are assigned to CH₂ and OH bending overtones mixture, were also blue shifted by doping with Ag NPs. Similar behavior was shown for the CO, CC overtone stretching vibration mixture at 4777 cm^{-1} and CO band at 4242 cm^{-1} .

Raman spectra of PVA doped with Ag NPs

The FT-Raman spectra of pure PVA and PVA doped with different amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%) are given in Figure 4 and the assignments of the vibrational modes are given in Table II.^{14–16} The band at 2910 cm^{-1} was assigned to

be the (CH) stretching vibration of the (CH₂) in the PVA spectrum and PVA doped with different amounts of Ag NPs spectra. These bands did not show any shift 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 increase up to 0.3% (sample), after which the intensities were found to diminish 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. The variations of intensities of the CH symmetric stretching of CH groups with different concentration of Ag NPs were found to

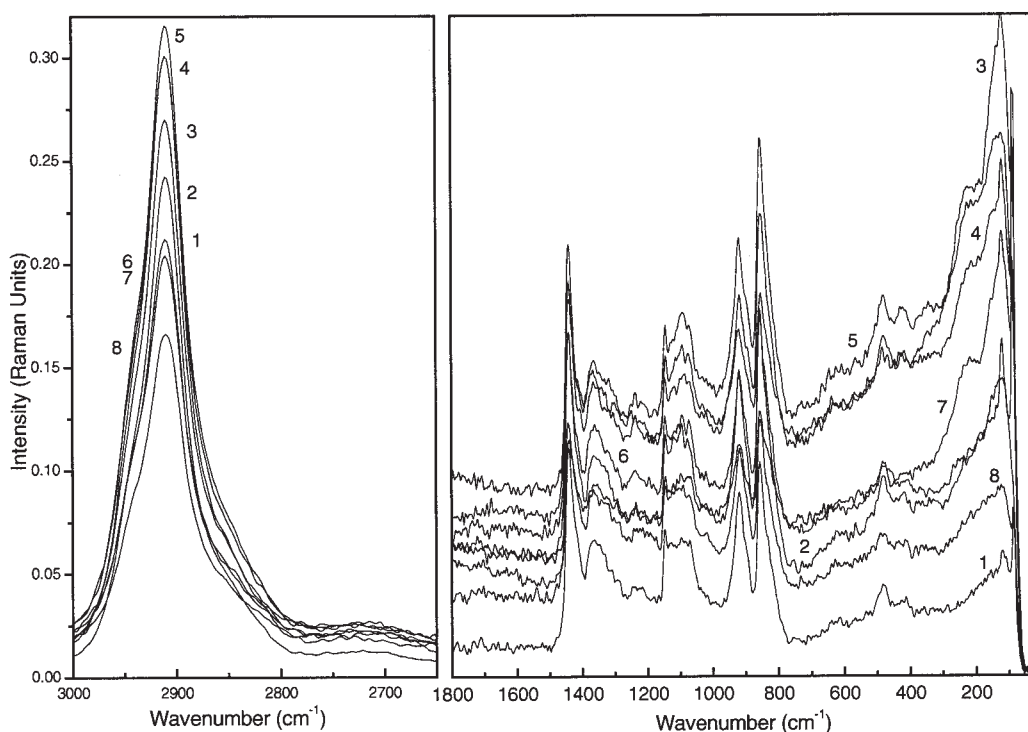


Figure 4 FT-Raman spectra for pure (1) PVA and (2–8) PVA doped with different amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%), respectively.

TABLE II
The Raman Band Vibration for Pure PVA and PVA Doped with Different Amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%) and their Assignments

PVA	0.1	0.17	0.27	0.3	0.33	0.4	0.42	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	1091w	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	318w	C—C torsion and bending
—	234m	233m	226m	222m	221m	219m	216m	ν (Ag-polymer)
117v	117v	117v	118v	116v	119v	121v	116v	—

v, very sharp; s, sharp; m, medium; w, weak.

be similar to those observed earlier for the CH₂ group. A very weak band corresponding to the stretching vibration of the residual acetate carbonyl group in the PVA spectrum appeared at ~ 1710 cm⁻¹.

The CH and OH bending bands at 1440 cm⁻¹ of the PVA blue shifted in the corresponding PVA spectra doped with Ag NPs. This blue shift was found to increase on increasing the weight of Ag NPs. The band intensities increase up to 0.3% of Ag NPs and then decrease on increasing the Ag NPs percent. Similarly, the CH₂ wagging and OH bending at 1356 cm⁻¹ and CH wagging at 1236 cm⁻¹ in the pure PVA showed blue shift and band intensities enhancement similar to CH and OH bending bands because of doping with Ag NPs. The bands at 1145 and 1095 cm⁻¹ in the pure PVA were assigned to 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 up to 0.3% 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 the mixture of CO bending and out-of-plane CH bending appeared at 477 cm⁻¹, and the band at 410 cm⁻¹ was corresponding to the CO wagging in the Raman spectrum of pure PVA. On 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 ~ 200 cm⁻¹ are

assigned to the Ag—O bond vibration of the PVA doped with Ag NPs.

To better understand the Raman band intensity enhancement in PVA doped with Ag NPs, the enhancement factor (*EF*) was calculated for each band after normalization to the (CC) stretching vibration band appearing at ~ 918 cm⁻¹, where $EF = \text{Normalized } (I_{\text{doped PVA}}/I_{\text{pure PVA}})$. Figure 5 shows the relation between the enhancement factor for each Raman band vibration in PVA doped with different amounts of Ag NPs.

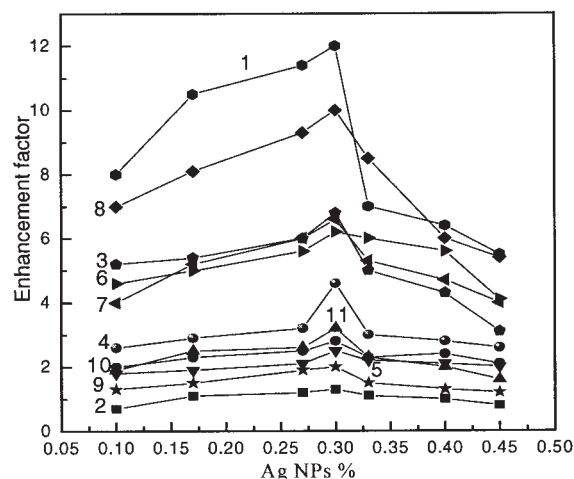


Figure 5 The enhancement factors for the PVA (doped with different amounts of Ag NPs) band vibration intensities after normalization to the (CC) stretching vibration band appearing at ~ 918 cm⁻¹. (1,2) CH stretching vibration of CH₂ and CH groups, (3) CH and OH bending mixture, (4) CH wagging and OH 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, and (11) CO and CC torsion.

PVA molecules consist of parallel chains connected by hydrogen bonds. Consequently, doping PVA with Ag NPs has a great effect on the hydrogen bonds, as well as on the order of their chains. Hence, the Raman spectra were found to be varying with doping. Vibration of 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, and CO and CC torsion were found to be blue shifted in the Raman spectra of PVA doped with Ag NPs. The blue shift increases as the amount of Ag NPs increases. The Ag NPs make polymer chains far apart; consequently leading to the weakening of hydrogen bonds and a blue shift of the CH and OH mode of vibrations and bending. 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 because of 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 crystallinity in the PVA. Although the band at 1124 cm^{-1} is believed to be due to the presence of amorphous polymer,^{17–19} this band did not exist in our investigation and this is supported by the X-ray diffraction pattern analysis.

Irradiation of PVA doped with Ag NPs with laser during Raman measurement causes excitation of collective oscillations of the surface charges of Ag NPs. These oscillations lead to the formation of a strong localized magnetic field near the particle surface. The enhancement of the PVA Raman spectra was assumed to result from a 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 0.3%, as a result of the aforementioned localized Surface plasmon. When the multiple scattering of the created particle plasmon becomes significant, a damping of the particle plasmon may then occur,²⁰ leading to the observed reduction in the enhancement factor above 0.3% Ag NPs.

Photoacoustic spectra of PVA doped with Ag NPs

The Photoacoustic spectra of PVA and PVA doped with different percent of Ag NPs might be more useful than the IR spectra, because the MIR spectra were found to suffer some set of noise, especially in the range below 1500 cm^{-1} . Consequently, we use the Photoacoustic spectra instead of FTIR spectra. The Photoacoustic spectra of PVA and PVA doped with

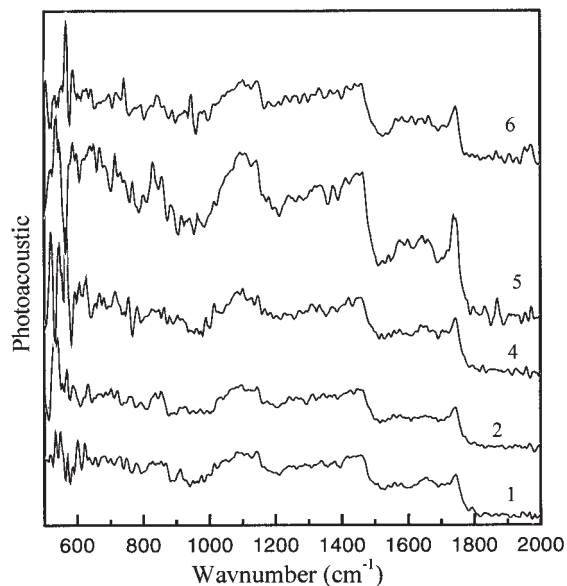


Figure 6 Photoacoustic spectra for pure (1) PVA and (2, 4, 5, and 6) PVA doped with different amounts of Ag NPs (0.1, 0.27, 0.3, and 0.33%), respectively.

different amounts of Ag NPs are shown in Figure 6, while Table III gives the corresponding band assignments. The Photoacoustic bands at 1746, 1469, 1381, and 571 cm^{-1} corresponding to stretching vibration of the residual acetate carbonyl groups in PVA, CH and OH bending mixture, CH wagging and OH bending mixture, and out-of-plane wagging of OH group were found to be blue shifted and enhanced in its intensity because of doping up to 0.3% and then the intensities started to diminish. While the bands at 1280, 1152, and 1098 cm^{-1} , which are assigned to be CH wagging, CO and CC stretching mixture, CO stretching, respectively, were red shifted and their intensities were found to show similar behavior as those before. On the other hand, some bands were enhanced but unshifted, and these bands corresponded to CC stretching vibration at 937, 867 cm^{-1} and the band at 833 cm^{-1} corresponding to the CH rocking.

The UV–vis spectra of PVA doped with Ag NPs

The UV–vis absorption spectra of PVA, Ag NPs, and PVA doped with different weight percent of Ag NPs are shown in Figure 7. The pure PVA has peak maximum at 274 nm while the Ag NPs colloidal solution with particle size 20 ± 5 nm has peak maximum at 423 nm. The PVA samples doped with amounts of AgNPs have two absorption peak maxima corresponding to the Ag NPs and PVA matrix.

The width and frequency of the surface plasmon absorption depend on the size, shape, and size distribution and shape of the metal nanoparticle, as well as

TABLE III
The Photoacoustic Band Vibrations for Pure PVA and PVA Doped with Different Amounts of Ag NPs (0.1, 0.27, 0.3, 0.33%) and their Assignments

PVA	0.1	0.27	0.3	0.33	Assignments
1746s	1747s	1748s	1749s	1751s	ν (C=O) residual acetate
1469s	1471v	1473v	1475v	1476v	δ (CH ₂), δ (OH)
1381m	1383m	1383m	1385m	1387m	γ_w (CH ₂), δ (OH)
1280m	1279m	1274m	1275m	1274m	γ_w (CH)
1152s	1150s	1149s	1147s	1147s	ν (C—O), ν (C—C)
1098v	1095v	1094v	1093v	1092v	ν (C—O)
937m	937m	937m	937m	937m	ν (C—C)
867m	867m	867m	867m	867m	ν (C—C)
833m	833m	833m	833m	833m	γ_r (CH)
517s	517s	518s	519s	520s	γ_w (O—H), out-of-plane

v, very sharp; s, sharp; m, medium.

on the dielectric constant of the metal and the surrounding media.^{21–23}

The absorption peaks corresponding to the PVA matrix were found to be sensitive to the doping percent in such a way that the peak intensities increased by increasing the percent of Ag NPs, which might be attributed to the decrease of transparency of the PVA.

The absorption maxima of the UV–vis spectra of PVA 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 0.3%. Then the values were found to decrease as the amount of Ag NPs increased.

According to the Mie theory, which can be applied in the case of low concentrations of nanoparticles in a solvent and solid matrix,²⁴ there is no interaction among the electric fields created around each particle by the excitation of surface plasmon resonance. On the other hand, when the interparticle distances become smaller than the particle size or when the particles undergo aggregation, the plasmon resonance was found to be red shifted.^{25,26}

CONCLUSIONS

The X-ray diffraction pattern confirmed that PVA is a crystalline polymer. The Raman and photoacoustic spectra of PVA were found to be changed after incorporation with different percent of Ag NPs. The Raman and photoacoustic bands were enhanced up to 0.3% of Ag NPs and then diminished. Some bands undergo blue shift while others suffer red shift due to doping. The overtones IR spectra were recorded and accorded well with the photoacoustic and Raman spectra. The UV–vis spectra of PVA doped with Ag

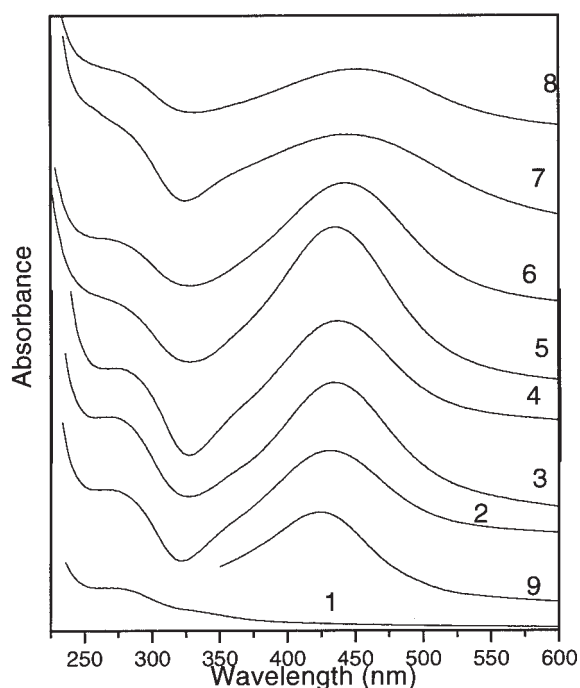


Figure 7 The UV–vis spectra of pure (1) PVA and (2–8) PVA doped with different amounts of Ag NPs (0.1, 0.17, 0.27, 0.3, 0.33, 0.4, and 0.42%), respectively, and (9) pure Ag NPs solution.

TABLE IV
The Absorption Wavelengths of PVA and PVA Doped with Different Weights of Ag NPs

Percent of Ag NPs	Maximum absorption wavelengths of PVA (nm)	Maximum absorption wavelengths of Ag Nps (nm)
PVA	274	0
Ag NPs	—	423
0.1	279	433
0.17	280	436
0.27	283	442
0.3	284	451
0.33	286	453
0.4	287	453
0.42	289	455

NPs show a peak maxima, which were found to be red shifted as the amount of Ag NPs increases. The maximum peak intensities were found to increase up to 0.3% Ag NPs and then decreased. While the peaks corresponding to the PVA absorption were found to be red shifted due to doping with Ag NPs, the absorption intensities increased on increasing the percent of Ag NPs.

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