Silver- Polymer Blend Nanocomposite


Radiation Chemistry Dept., National Centre for Radiation Research and Technology (NCRRT), Cairo, Egypt
Chemistry Dept., Helwan University, Faculty of Science, Cairo, Egypt.

Ymn_darwish@live.com

Abstract: In this paper, silver polymer nanocomposites were synthesized using gamma irradiation and at the same time overcoming some of the disadvantages previously reported by other methods such as impurities, solvent toxicity, size and distribution control and difficulty in their preparation that limits their commercialization potential. Nanocomposite films have been reported from an aqueous solution of poly vinyl alcohol (PVA) poly vinyl pyrrolidone (PVP) and silver nitrate (AgNO₃). The silver nanoparticles have been generated in the PVA/PVP matrix by γ-irradiation method. The structure and morphology of the nanocomposite films have been studied as a function of either silver nitrate precursor concentration or irradiation dose. Ag nanoparticles were successfully prepared in one-step by γ-irradiation technique at room temperature and under ambient pressure. The as prepared films were characterized by UV-VIS spectroscopy and Transmission electron microscopy (TEM). The size of the as-prepared nano particles ranged from 7.9 to around 59.4 nm depending on the irradiation dose value, AgNO₃ concentration and PVP percentage change. The presence of PVP polymer was considered as an important reason that influenced the shape and distribution. On the other hand the transmission electron microscopy (TEM) showed the resultant particles were monodispersed and uniform particle size distribution.

Keywords: Ag/polymer nanocomposite, γ-rays irradiation, Poly (N-vinyl-2-pyrrolidone) (PVP), Poly vinyl alcohol (PVA), UV/VIS, TEM characterization.

1. Introduction:

Nanotechnology literally means any technology performed on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, science and technology research in nanotechnology promises breakthroughs in such areas as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next industrial revolution.

Radiation chemistry has proven to be a very effective method to construct three-dimensional polymer networks offering advantages over conventional physical or chemical methods of network formation: mild reaction conditions, negligible formation of by-products, fast gelation and no need for catalysts. Physicochemical properties of the radiation-crosslinked polymer network and the swelling ability of radiation-crosslinked hydrogels can be tailored by changing the irradiation time [2].

Gamma irradiation offers many advantages for the preparation of metal nanoparticles. Large number of hydrated electrons (e⁻₃₉) produced during γ-irradiation can reduce the metal ions to zero valiant metal particles [3]. A summation made by many authors suggested that irradiation cause a chemical change in polymers, including crosslinking, chain scission, formation of alkyenes groups, and depletion of hetero atoms (e.g. N, S or O) [4-5]. In recent years studies on the electrical and optical properties of polymers have attracted much attention in view of their application in optical devices. The optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix. Since AgNO₃ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation within a polymeric system may be expected to enhance its electrical and optical performance. The incorporation of inorganic/organic material is believed to remarkably improve a wide range of properties of the polymers due to nanosized dispersion [6]. Polymers have been frequently used as particle stabilizer and capping agent in irradiation synthesis of metal nanoparticles, since they prevent agglomeration and precipitation of the nanoparticles. The embedding of such particles in polymer matrix is also advantageous from point of view of film casting. PVA is known to
be a good stabilizer of metal nanoparticles, Moreover, it is a water soluble polymer, so it can react with metal salt via formation of chelate with metal cations in an aqueous solution and also act as a capping agent [7]. PVP is a potential material with very high dielectric strength. Furthermore, it has a good charge capacity and dopant-dependent optical properties.

PVA is a well-known biologically friendly polymer and has been developed for biomedical applications such as artificial pancreas [8-9], synthetic vitreous body [10], wound dressing, artificial skin, and cardiovascular device [11-12]. PVP is one of the most widely used polymers in medicine because of its solubility in water and its extremely low cytotoxicity [13]. Also there is a work described the application of PVP onto the skin for transdermal delivery of drugs [14]. Combination of the properties of PVA and PVP in their blends has led to the preparation of new biomaterials [15].

2. Materials and experimental techniques

Silver Nitrate (AgNO$_3$) was obtained from Nice chemicals PVT. LTD, India. Nitric acid (HNO$_3$) HEMAJET Assay=45% from Islamic International Establishment for Chemical and Lab Materials-Goumhouria. Iso propanol Nice chemicals PVT. LTD, India, Poly Vinyl Alcohol (PVA M.wt 125,000 gm/mol) and Poly vinyl pyrrolidone (PVP M. wt 40,000 gm/mol) in the powder form were obtained from laboratory J.T. Baker chemical co., Phillipsburg, N.J. 08865 and Sigma, USA, respectively. All chemicals were used without further purification.

2.1 Preparation of Ag/PVA Nanocomposite films

Firstly, PVA films were prepared by a casting technique. PVA solution was prepared by dissolving 3 gm PVA in 90 ml of deionized water. The PVA solution was then warmed and thoroughly stirred until the polymer become completely soluble. Secondly, 0.1 M of nitric acid solution was added to the PVA until the acidity of the solution pH=4 to prevent photo reduction of silver particles, thirdly, 10ml of freshly prepared AgNO$_3$ solution (different weights of AgNO$_3$ dissolved in 10 ml deionized water) was added to the above PVA solution with continuous stirring for 10 minutes (in dark). Finally, the solution was cast onto a glass plate. Homogenous film was obtained after drying at room temperature (in dark) for 3 days. All the investigated films were irradiated with irradiation dose of 25, 50, 75, 100 and 150 kGy, using Co-60-$\gamma$-cell-220 sources (manufactured by the Atomic Energy Authority of India with 3.48422 kGy/hr dose rate) installed at the National Center for Radiation Research and Technology, NCRRT, Egyptian Atomic Energy Authority (EAEA), Nasr City, Cairo. 

2.2 Preparation of Ag/PVA/PVP Nanocomposite films

PVA/PVP films were prepared by a casting technique. Different weights percentage of PVA/PVP dissolved in 90 ml deionized water Firstly, PVA solution was prepared by dissolving the different weights amount of PVA in 90 ml of deionized water. Secondly, the different weights amount of PVP was then added to the PVA solution with continuous stirring until homogenous solution obtained. Then the previous steps were completed until homogenous films were obtained and irradiated with the same dose.

2.3 Characterization Techniques

2.3.1 Ultraviolet/Visible Spectroscopy, (UV/VIS)

UV double beam Unicam Ultraviolet/Visible (UV/VIS) spectrophotometer made in England was used for scanning the absorption spectra in the range from 190 nm to 1000 nm wavelengths and measuring the optical density at $\lambda_{\text{max}}$ for unirradiated and irradiated samples.

2.3.2 Transmission Electron Microscope, (TEM) Measurements

Transmission electron microscopy (TEM) observation was performed with JEOL JSM – 100 CX, Shimadzu Co. electron microscope operated at an acceleration voltage of 80 KV. The sample for TEM analysis were prepared by deposition of a single drop of the nanocomposite dispersion on a 300 mech copper grid with a carbon film over a filter paper which absorbed excess solution. The copper grid was allowed to dry at room temperature.

3. Result and discussion

3.1 Optical properties of metal/polymer nanocomposites

When noble metal nanoparticles are excited by electromagnetic radiation, they exhibit collective oscillations of their conduction electrons that result in both absorption and scattering of the incident radiation. The excitation spectrum, which is the sum of the absorption and scattering spectra, of such nanoparticles in a vacuum solution, or supported on the surface of a substrates often, measured in transmission geometry using UV/VIS spectrophotometer. In a simple solution, such as that of nearly mono disperse spherical gold or silver nanoparticles in solution, the extinction spectrum exhibits a single peak known as the localized surface plasmon resonance (LSPR). The ability to manipulate and predict the LSPR of metal nanoparticle systems is desirable in several technological applications [16].
3.2 Effect of irradiation doses on the optical properties of Ag/PVA nanocomposite films.

Figure 1, shows the UV/VIS absorption spectra of unirradiated and irradiated Ag/PVA nanocomposite films. There is a weak band at $\lambda = 280$ nm that refer to PVA characteristics compound and assumed to be due to crystallinity loss of PVA by radiation [17]. Also, there is another weak and broad peak in the visible region at about (414 - 430 nm) which is referred to the surface plasmon resonance nature of free electrons in the conduction bands of Ag nanoparticles embedded in PVA matrix. The surface plasmon resonance absorption peak for Ag/PVA nanocomposite films increased as the irradiation dose increased up to 150 kGy. These results indicate the formation of more silver nanoparticles and more reduction of AgNO\textsubscript{3}. Similar results were observed by several authors [7-18]. Also, the effect of irradiation dose appear in a band shift (blue shift) from (430 – 406 nm). The blue shift indicates the formation of smaller sized metal nanoparticles [19].

The increase in the absorption intensity of surface plasmon resonance (SPR) peak with increasing the irradiation dose give an indication of the highly amount of the as-prepared Ag nanoparticles. The calculated particles sizes of the as-prepared Ag nanoparticles are listed in Table (1). It can be seen that the particle size of Ag nanoparticles decrease due to either increasing irradiation dose or decreasing AgNO\textsubscript{3} molar concentration. In other words, the particle size is probably depends on the irradiation dose, the concentration of AgNO\textsubscript{3} and the amount of the stabilizing polymer’s chain. The $\gamma$-irradiation causes crosslinking of PVA and the macromolecules of the polymer are giving rise to three dimensional networks, as the crosslinking of polymer increase, the molecular mass of the polymer chains around the nanoparticles will increase [20]. In addition, the increase of irradiation dose will increase the extent rate of Ag$^+$ reduction and the nucleation rate resulting in formation of Ag nanoparticles. At low irradiation dose, the surface plasmon peak gets weak and broad, then become narrower and sharper and also increases intensity with increasing the irradiation dose (see Figure 1).

A possible reaction mechanism can be suggested based on the present experimental observations and the previous work in literature. Silver nitrate and PVA were chosen as starting materials due to their molecular structure and chain polarity, both the metal salt and polymer exhibit high water solubility. AgNO\textsubscript{3} is soluble in PVA to such an extent that a complete dissolution is observed as the first step of the reaction. This property allows administration of uniform concentration of the precursors within the polymer matrix. Silver nitrate (AgNO\textsubscript{3}) dissociates into Ag$^+$ ions and NO$_3^-$ ions in aqueous solution of PVA according to the following reaction:

$$\text{AgNO}_3 \rightleftharpoons \text{Ag}^{+} + \text{NO}_3^- \quad (1)$$

The addition of the HNO\textsubscript{3} acid to the AgNO\textsubscript{3}/PVA mixture shifts the above equilibrium to the left side, i.e. it prevents the dissociation of the silver nitrate. Therefore, the role of the nitric acid is to prevent the photo reduction of silver nitrate which in turn causes the formation of a highly homogeneous film of PVA/AgNO\textsubscript{3} after removal of solvent. Upon exposure to gamma irradiation, the hydrated electrons ($e_\text{aq}^-$) can reduce Ag$^+$ to Ag$^-$ and silver clusters are then formed.

$$\text{Ag}^+ + e_\text{aq}^- \rightarrow \text{Ag}^- \quad (2)$$

The growth of silver nanoparticles by reduction of Ag$^-$ to Ag is step wise [21]. Silver atom primarily reduced by hydrated electron is rapidly complexes with a silver ion to form dimmer cluster, and the dimmer then combines with another dimmer cluster to be tetramer cluster [22-23]. The atoms formed dimerize when encountering or associate with excess Ag$^-$ ions by a cascade of coalescence processes, these species progressively coalesce into larger clusters (reaction 2-5).

$$\text{Ag}^+ + e_\text{aq}^- \rightarrow \text{Ag}^+ \quad (2)$$
$$\text{Ag}^- + \text{Ag}^- \rightarrow \text{Ag}_2 \quad (3)$$
$$\text{Ag}_n^- + \text{Ag}^+ \rightarrow \text{Ag}_n^+ \quad (4)$$
$$\text{Ag}_{n+1}^- + e_\text{aq}^- \rightarrow \text{Ag}_{n+1}^- \quad (5)$$

The fast reactions (3) and (4) are an ion association with atoms or cluster growth mechanism. The competition between the reduction of free silver ions and absorbed ones is controlled by the rate of reducing radical formation therefore, the cluster formation by direct reduction followed by coalescence is predominant at high irradiation dose and the final cluster size is smaller [24].

3.3 Effect of AgNO\textsubscript{3} concentration on the UV/VIS spectrum of Ag/PVA nanocomposite.

The interaction between different concentration of AgNO\textsubscript{3} ($10^{-3}$, $5\times10^{-3}$ and $10^{-2}$ M), and PVA was further traced by the UV-visible absorption method. Figure 2, shows the AgNO\textsubscript{3} concentration dependent absorption spectra of the PVA collected at 100% PVA and 100 kGy. It can be seen that for the lowest molar concentration of AgNO\textsubscript{3} ($10^{-3}$), a very weak and broad absorption shoulder is appeared at about (394 nm). The absorption of this band is gradually increases in intensity with increasing the molar concentration of AgNO\textsubscript{3}. In addition, the absorption band because narrows and shifts continuously to larger wave length i.e. the absorption band shift to (408) nm for the highest content of AgNO\textsubscript{3}. It can be investigated that the optical absorption spectrum of metal nanoparticles is dominated by the SPR which exhibits
a shift towards the red end or blue end depending upon the particles size, shape, state of aggregation and the surrounding dielectric medium [25]. In this study, the plasmon band of Ag nanoparticles was noted at (394 - 403 nm). Hence, the appearance of this very weak band at low concentration of AgNO₃ may be related to the formation of small quantity of reduced silver nanoparticles. The spontaneous formation of silver nanoparticles can be attributed to the direct redox between PVA and Ag⁺ and using γ-irradiation dose (100 kGy), where there is no other reducing agent in the system. Moreover, the increased intensity as well as the red shift of the SPR band may be attributed to considerable increase in the amount of reduced silver and growth of silver nanoparticles. In particular, silver nitrate is soluble in PVA to such an extent that a complete dissolution is observed as the first step of the reaction. In the next step, the 'OH groups of PVA molecule anchor the Ag⁺ ion at the cluster surface which efficiently reduces the precursor metal ions Ag⁺ to Ag nanoparticles, while the polymeric chain protects the cluster from fusion with the next silver molecule. The final size of silver clusters stabilized by the polymer is of few tens of nanometers. The presence of very weak and broad classical surface absorption band at (394) nm for low AgNO₃ concentration means that PVA is weak reducing agent for silver salt.

3.4 UV/VIS characterization of Ag/ PVA/PVP nanocomposite films

Reduction of silver ions present in the polymeric blends of different PVA/PVP percentages using γ-irradiation doses was routinely monitored by visual inspection of the prepared samples as well as by measuring the UV/VIS spectra. It is noticed that, the color of polymeric blend films started to change from transparent to yellowish brown. The color of films is intensified as the PVP % increased (5, 10, and 20% PVP). PVA/PVP are water polymeric blends consist of a hydrophilic polymer that forms a three dimensional network, which contains a lot of water. They are one of the most promising materials for biomedical applications and have several advantages.

The Ag⁺ concentration variation from 5x10⁻³ M to 10⁻² M and γ-ray irradiation are shown in Figures 3-5, respectively. The λ_max of the observed SPR is red shifted with increase in Ag⁺ concentration, whereas it is blue shifted with irradiation dose. This shows that the Ag nanoparticle size increases with increasing Ag⁺ concentration. But the decrease in size with irradiation dose due to the polymer crosslinking behavior which prevent Ag nanoparticle agglomeration. In order to investigate the role of PVP in stabilization of the as-prepared Ag nanoparticles, the Ag nanoparticles were synthesized at different PVP content. The PVP content was varied from 5, 10, and 20 wt % (see Figures 3-5). On the other hand, PVP act as stabilizing and/or reducing agent and the extent of this effect increases with increasing PVP content. In other words, the function of PVP in the blend composition is not only as a binder but it also prevents the process of agglomeration of Ag nanoparticles and limits the size of the nanoparticles formed. The increase of the intensity of peaks indicates that the concentration of silver nanoparticles increases [26]. In other words, the formation rate of silver nanoparticles is faster for higher irradiation dose and/or concentration of PVP under the same condition. The symmetric and narrow absorption peak implies the narrow size distribution of silver nanoparticles at higher PVP percentages (see Figure 5).

The role of PVP in the formation of Ag nanoparticles can be recognized as follow: The PVP is a homo-polymer whose individual unit contains an amide group. The N and O atoms of this polar group probably have a strong affinity for the silver ions and metallic silver. PVP macromolecule in the solution may take part in some form of association with the Ag⁺ and reduces these ions into metallic nanoparticles which in turn increase the probability of nucleus formation. In addition the resultant metallic silver particles are faster capped by PVP molecules of higher concentration than by that of lower concentration. The PVP molecules are regarded as the stabilizing agents, which form a steric hindrance around the silver particles to prevent them from aggregation greatly by electrostatic interactions [27]. Because of the PVP presence, the rate of spontaneous nucleation increases, and a higher number of final particles increases, and the mean particle size therefore decreases (from 38 - 23nm, see Table 1) [28].

3.5 Estimation of silver nanoparticles size

Assuming that Ag nanoparticles have spherical shape, Mie theory [29] was applied for the evaluation of silver nanoparticles size in Ag/PVA/PVP nanocomposite. Correlation between SPR peak position and particle size experimentally established by Evanoff and Chumnov [30] was used for the calculation of silver nanoparticles in PVA/PVP polymer blends using experimental data:

\[ D = 0.715 \lambda_{\text{max}} - 258 \]  

Where \( D \) = particle diameter (nm), and \( \lambda_{\text{max}} \) is the SPR peak position in UV-Vis absorbance spectrum. The calculated Ag nanoparticles size was listed in Table (1).
4. Transmission electron microscope (TEM) of Ag/PVA and Ag/PVA/PVP nanocomposites

TEM is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. TEM approach would provide a quick way to obtain particle size, shape and size distribution. Direct imaging provides a fast automated image analysis solution, capturing several tens of particle images in a few seconds with an electron microscope and a high-resolution camera.

Table 1: The absorption of the SPR peak and the estimated particle size diameter from UV-VIS data

<table>
<thead>
<tr>
<th>PVP %</th>
<th>AgNO₃ concentration</th>
<th>Irradiation dose (Gy)</th>
<th>λ_max (nm)</th>
<th>D nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>5x10⁻³ M</td>
<td>25</td>
<td>412</td>
<td>36.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>412</td>
<td>36.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>408</td>
<td>33.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>406</td>
<td>32.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>404</td>
<td>30.86</td>
</tr>
<tr>
<td></td>
<td>1x10⁻² M</td>
<td>25</td>
<td>430</td>
<td>49.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>418</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>424</td>
<td>45.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>408</td>
<td>33.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>406</td>
<td>32.29</td>
</tr>
<tr>
<td>5%</td>
<td>5x10⁻³ M</td>
<td>25</td>
<td>430</td>
<td>49.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>420</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>420</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>412</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>404</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td>1x10⁻² M</td>
<td>25</td>
<td>444</td>
<td>59.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>438</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>434</td>
<td>52.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>428</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>412</td>
<td>36.5</td>
</tr>
<tr>
<td>10%</td>
<td>5x10⁻³ M</td>
<td>25</td>
<td>434</td>
<td>52.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>430</td>
<td>49.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>426</td>
<td>46.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>422</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>422</td>
<td>43.7</td>
</tr>
<tr>
<td>20%</td>
<td>5x10⁻³ M</td>
<td>25</td>
<td>426</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>424</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>424</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>418</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>418</td>
<td>40.8</td>
</tr>
</tbody>
</table>

4.1 TEM of irradiated PVA/Ag nanocomposite

Figure 6 (a) represents TEM images of Ag nanoparticles prepared in PVA matrix. The Gaussian fit to the particle size histogram is performed and is shown as a solid line in Figure 6 (b). A number of well-dispersed nanoparticles can clearly be seen in the TEM picture with external spherical shape and are to a large extent well separated from one another. The average diameter of the nanoparticles is indicated as the peak position of the Gaussian curve of the histogram to be 11.7 nm. Regarding to histogram the particle size distribution of the Ag nanoparticles prepared in the PVA under 50 kGy γ-irradiation doses; exhibit a uniform shape and a very narrow size distribution. This result means that, the size of the prepared particles gets smaller and the particle size distribution is well at 50 kGy irradiation dose.

1.2 TEM irradiated Ag/PVA/PVP nanocomposite

Transmission electron microscope was used to obtain direct information about the structure and
phase morphology of unirradiated and irradiated Ag/PVA/PVP nanocomposite.

A primary purpose of the introducing PVP was to protect the silver nanoparticles from growing and agglomerating. Figure 7 shows the TEM photograph of 50 kGy irradiated PVA/PVP composite (with ratio 90–10%) with the same concentration of AgNO₃ (5×10⁻³ M). The Gaussian fit to the particle size histogram is performed and is shown as a solid line in the Figures. The micrograph depicts a number of agglomerates but generally the nanoparticles are well dispersed in the TEM images. The average particle size was 22 nm. Regarding to Figure 7, larger size for Ag nanoparticles of can be recognized and the particle size distribution was broadened after blending. The particle size is probably related to either the irradiation dose or the amount of the stabilizing polymer’s chains. With increasing irradiation dose, the individual macromolecules of PVA are assumed to be crosslinked, giving rise to a three dimensional network. The crosslinking of polymer molecules results in a significant increase in molecular mass; this in turn will increase the amount of polymer chains surrounding the nanoparticle [31]. The more polymer chains there are, the more they inhibit the aggregation and/or the growth of the silver nanoparticles [32]. In addition, the increase of irradiation dose will increase the extent, rate of Ag⁺ reduction and the nucleation rate which results in formation of metal nanoparticles [33]. But at higher irradiation doses, (50 kGy for PVP) gamma-rays induce chain scissions in the polymer matrix. The polymer chains acquire mobility on the experimental times scale. This causes Ag nanoparticles to move again; allowing crystals to aggregate and/or agglomerate. This may be also attributed to after addition of PVP, it would coordinate with Ag⁺ and H⁺, and the complex compounds, Ag(PVP)⁺ and H(PVP)⁺ were generated, Ag⁺ and H⁺ were stabilized. The stabilization of Ag⁺ restrained the reaction, but the stabilization of H⁺ facilitated it. The latter affection may be stronger than the former one, and the reaction was accelerated which lead to more reduction of Ag⁺ to Ag nanoparticles which facilitate the aggregation process. After PVP was introduced, it would react following formula [34].

\[
\begin{align*}
H_2O \rightarrow \gamma_{\text{radiation}} & \rightarrow e_{\text{aq}} + H_3O^+ + H^+ + H_2 + OH^- \quad (7) \\
Ag^+ + PVP & \rightarrow Ag(PVP)^+ \quad (8) \\
H^+ PVP & \rightarrow H(PVP)^+ \quad (9) \\
2[Ag(PVP)]^+ + 2e^- & \rightarrow 2Ag(PVP)_\downarrow \quad (10)
\end{align*}
\]

![Figure 1. UV/VIS spectra of Ag/PVA nanocomposite films at different irradiation doses (5×10⁻³ M AgNO₃, 100% PVA)](image-url)
Figure 2. UV/VIS spectra of Ag/PVA nanocomposite films irradiated at 100 kGy with different AgNO₃ concentration.

Figure 3. UV/VIS spectra of Ag/PVA/PVP nanocomposite films at different irradiation doses (5x10⁻³M AgNO₃, 95%PVA/5%PVP)

Figure 4. UV/VIS spectra of Ag/PVA/PVP nanocomposite films at different irradiation doses (5x10⁻³M AgNO₃, 90%PVA, 10%PVP)
Figure 5. UV/VIS spectra of Ag/PVA/PVP nanocomposite films at different irradiation doses (5x10⁻³ M AgNO₃, 80% PVA/20%PVP)

Figure 6 (a) TEM image of Ag nanoparticles and (b) the histogram of the particle size distribution with Gaussian fitting for 5x10⁻³ M, 50 kGy irradiated Ag/PVA nanocomposite
Conclusion
Radiolytic methods have proved to play an important role in the development and modification of metal nanostructures; γ-irradiation is an effective technique for preparing inorganic/organic nanocomposites. In this study the Ag-PVA and Ag-PVA/PVP nanocomposites were synthesized using highly reducing radicals generated by steady state gamma irradiation. Silver nanoparticles (AgNPs) were synthesized by γ-irradiation, using different dispersant agent poly(N-vinyl-2-pyrrolidone)(PVP), (Poly vinyl Alcohol)(PVA) blends as a capping agent. TEM results have shown spherical AgNPs with narrow size distribution were obtained at higher PVP content. UV/VIS spectroscopy results shown that all Ag/PVA, Ag/PVA/PVP, investigated systems exhibited absorption band peaking at the wavelength value around 400nm confirming the formation of AgNPs. The absorption peak in all films increased as the irradiation dose increased up to 150 kGy, indicating the formation of more silver nanoparticles and more reduction of AgNO₃. On the other hand UV/VIS spectroscopy shows a slight red shift of maximum absorption wavelength due to increasing the size of silver particles with increasing PVP content.
References


