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Polymer/Noble Metal Nanocomposites

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Abstract

Recently, the polymeric materials have extensive uses because of their amazing combination of properties, durability, light weight and simplicity of processing. However, these materials face some problems like their weak thermal stability and also poor mechanical stability. Therefore, a large number of additives especially metal nanoparticles were added to polymeric matrix to overcome these problems and designed polymer matrix nanocomposite. A composite is defined as the combination between two individuals or more than one material by physical or mechanical method to get a new material with unique and elegant structure and properties and carrying the feature of the two separated materials and distinguishable interface. Many approaches are used to prepare the polymer nanocomposites such as *ex situ*, *in situ* and radiolytic methods. The nanocomposites have important features such as excellent mechanical properties like high stiffness, strength, toughness; good chemical properties like corrosion resistance; and high physical properties like high optical, mechanical, thermal, low density and specific antibacterial properties. The nanocomposite materials with these higher properties have a wonderful and different range of functional applications. The deep view on the synthesis strategies and physical properties of the polymer/noble metal nanocomposites is offered in this book and also their applications in many fields.

Keywords: polymer, noble metals, metal nanoparticles, nanocomposites, mechanical properties, optical properties, antibacteria

1. Introduction

Nanocomposite polymers are the composites where polymer matrix is doped with the particles and the particle size is in the nanoscale in at least one dimension. The main problems facing the nanocomposite are the aggregation and agglomeration. The metals of nanoscopic range doping into dielectric matrices represent a key to manipulation and stabilization

problems. For practical applications of the nanoparticles, they are embedded in the polymers to produce the nanocomposite polymers since these nanocomposite polymers may have optical, electrical and thermal insulators or conductor, mechanical and a variety of properties. The nanocomposites may have mechanically plastic behavior or elastic behavior and may have a water-loving or a water-hating nature. Finally, polymer doping with the metal nanoparticles is the easiest and widely convenient way for stabilization and handling the nanostructured metals [1]. The most interesting metals that were used in the nanocomposite materials are the noble metals. Noble metals lie in group 11 in the periodic tables and called (d-blocks). The most important thing that characterizes the noble metals in nanoscale is the surface plasmon resonance (SPR) and is formed due to the collective oscillations of the electrons that are located on the nanoparticles surface. This electron pulsation is proportionally related to the light electromagnetic field which fall on the electrons, that is, the conduction electrons symmetrically vibrate at its location when exposed to the light, as shown in **Figure 1**.

The simplest and normal shape of the produced composites is the films or powders, and also these are good for exploiting the desired properties. The combination between the metal nanoparticles and the polymer is very wonderful because its composite has good and promising physical and chemical properties. One of the most important things that make this combination to be excellent is the method that combines/connects them together (preparation method).

There are two general and principle approaches for preparation of the polymer/metal nanocomposite: the ex situ and in situ methods [1]. In the ex situ route, at first, the metal nanoparticles are synthesized, and the surface of the created particles is encapsulated and passivated with organic polymer materials. Then, the metal nanoparticle derivatives are dispersed into the liquid monomer of the polymer solution that is then polymerized. Contrarily, the metal ions are located on site with the monomer and the monomer occurred, where the metal ion reduced chemically, thermally, or by UV irradiation during the polymerization process to obtain the nanoparticles; this method is called the in situ methods. Illustration with more information and details of some of these key methods follows.

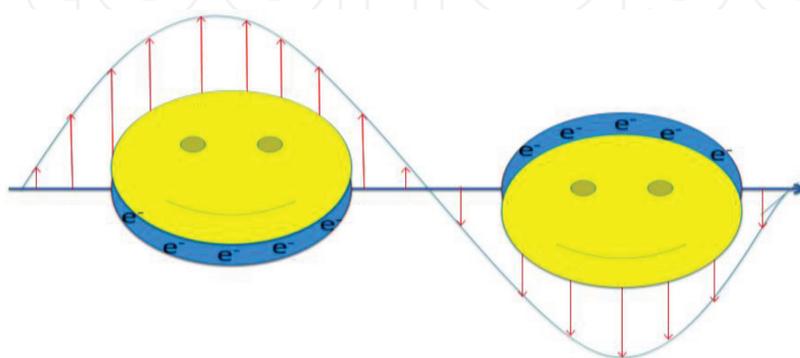


Figure 1. Cartoon showing the happy noble metal possessing the surface plasmon resonance.

2. Preparation methods

2.1. Ex situ technique

The metal nanoparticles are created in the ex situ method by any traditional method (chemical reduction, precipitation, laser ablation, etc.) and then the surface of the created particles is stabilized, capsulated and passivated by using stabilizing agent. This can be achieved by the reduction of the metal precursors which was dissolved in the appropriate selected solvent such as water or ethanol, which often contain a polymer as a stabilizing agent [2, 3]. Otherwise, it can be stabilized and be ready by controlling micelle, reverse micelle or micro-emulsion reactions [4–6]. Often, the surface of the obtained particles by the ex situ method is manipulated by covalent bonds, metal-thiol or ligand with other ions to inhibit the agglomeration and aggregation processes [7] or by encapsulating a polymer [8]. Then, the produced metal nanoparticles are inserted into the polymer matrix. This is achieved by combining the obtained nanoparticles with the polymer solution, or by interacting with the monomer, and then followed by the casting techniques, etc. to obtain the nanocomposite films [9, 10], as shown in **Figure 2**.

The ex situ technique was successfully used to prepare many metals in nanoscale such as Ag, Cu, Pt and Au with specific size and shape by using an external reducing agent (sodium borohydride NaBH_4 , tannic acid and sodium carbonate Na_2CO_3 , hydrazine hydrate), then added to the polymer matrix such as (polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polymethyl methacrylate (PMMA)) to produce the polymer/metal nanocomposites [11–13].

Sharma et al. [14], used the ex situ method to synthesize the polyaniline/copper nanocomposites by using the NaBH_4 as a reducing agent to reduce the copper salt to copper nanoparticles. Also, Yao et al. [15] used the trisodium citrate to reduce the gold salt to gold nanoparticles and then embedded in the PVA to produce the PVA/Au nanocomposites. Feng et al. [16] obtained the PVA/Ag nanocomposite films via the ex -situ method. They used the tannic acid and

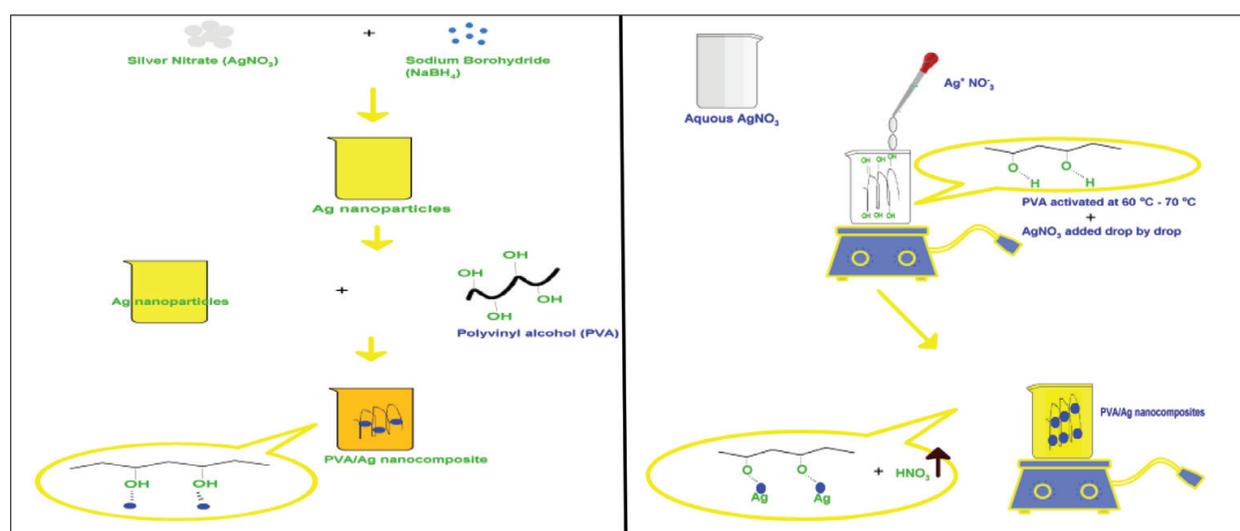


Figure 2. Scenario that depicts the ex situ technique (left side) and the in situ technique (right side).

Na_2CO_3 as a reducing and stabilizing agent to synthesize the silver nanoparticles. Then, the PVA solution was added to produce the nanocomposites. Another work by Campos et al. [17] was reported by the ex situ synthesis of the PVA/Ag nanocomposite films. The Ag nanoparticles powder with an average particle size of 25 nm was obtained and then mixed it with the PVA solution to produce the nanocomposite films.

However, this method has a shortcoming such as the aggregation, agglomeration and dispersion problems. It is necessary to manipulate and passivate the surface of the metal nanoparticles after the reduction process, in order to disperse them in the matrix. This surface manipulation led to changes in the properties of the nanoparticles. However, and after the surface manipulation process, it is very difficult to get well dispersion of nanoparticles in the composite. And also still a certain degree of agglomeration and aggregation is found in the composite. Also, the compatibility is another problem that facing the ex situ method, because of the difficulty of selecting the solvent which facilitates the compatibility between the particle-polymer- solvent systems. So, it was necessary to find a method (the in situ method) to overcome these problems.

2.2. In situ polymerization

The polymeric materials doped with metal nanofillers have been created by the in situ polymerization methods, which are composed of various techniques. The in situ methods have more benefits as compared to the ex situ methods such as its more simple, easy and straight-forward, and producing the class of nanocomposite materials with a higher feature and a higher quality, and more precise controlling. Firstly, the dispersion of metal nanofiller in a polymer monomer is utilized in this in situ method. Also, a technique similar to bulk polymerization is used to polymerize the resulting mixture. **Figure 2** shows a schematic diagram for the in situ technique.

In general, the in situ reduction mechanism in the PVA/Ag nanocomposite films is described as reported as example for the PVA/Ag nanocomposite as the following: the polymer PVA has a linear structure with the principle carbon backbone chains. Polyvinyl alcohol (PVA) molecules are hardly aggregate in dilute solution (water). Nevertheless, **Figure 3** shows the linear chains in a PVA planar structure, which interbridged by the H bonding coming from (or through) the OH groups. **Figure 3(a, b)** shows the PVA polymer in model configuration, where the PVA monomer is denoted by the symbol (R) and the PVA in part with an OH group. However, **Figure 3(c)** shows a cross section of the PVA structure. As apparent from the classical structure, especially when the PVA molecules dispersed in a dilute solution (water), the lateral or side growth to the backbone occurs. PVA structure contains weak hydrogen bonds, which extended to a little interbridging chain. In the coplanar PVA molecules structure, the hydrogen H-bond in a warm liquid at 60–70°C showed as floating and handling individually atoms and separately isolated with no much interaction with one another. The dispersion was facilitated by the thermo-mechanical stirring. It is possible that PVA molecular layers transform to a fibril structure or a favored structure, spiral in shape in linear polymer molecules (**Figure 3(d)**). Where the molecular layers of H-bonded monomers were interbridged from the OH groups, this is a compact structure, which takes place preferably in small island and dispersed molecules. At the surfaces, any type of the PVA molecular configurations has plenty of OH groups free from the H-bonding. There are electrons arranged in a definite localized

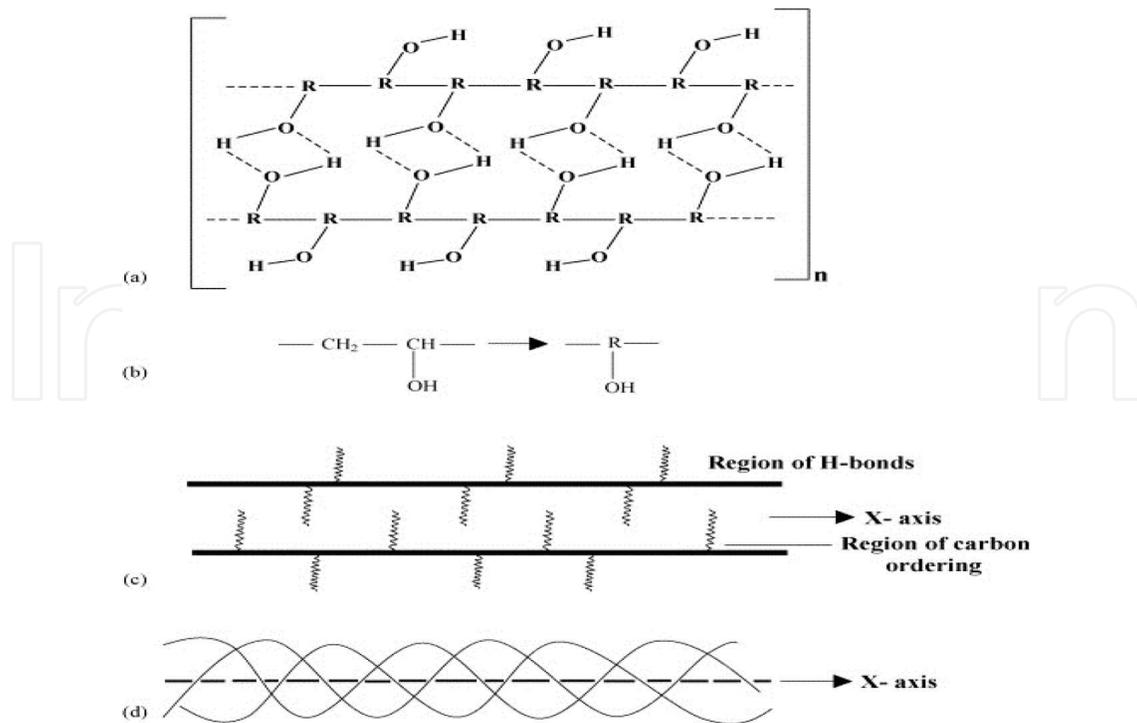
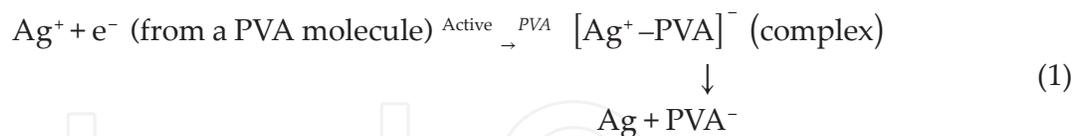
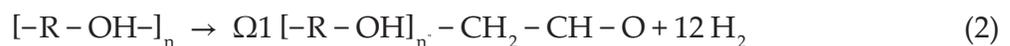


Figure 3. (1) A model coplanar structure of PVA molecules with interchain bridging via H-bonding between (2) the monomers forming (3) a molecular layer of extended surface. Such layers recombine further in different structures such as (4) an arbitrary spiral of three layers. [18]. Copyright 2007. Reused with permission from Elsevier Ltd.

distribution over the surface from the nonbonding hybrid electrons $2p^2(O)$ in such OH groups (the head groups) to interact with the metal ions to create a complex. Thermodynamically, the fugacity of the Ag surface is enhanced by Van der Waals interaction and facilitates a surface reaction of the $Ag^+ \rightarrow Ag$, which can be expressed as follows [18]:



The Ag metal, which passes in steps with temporary intermediate Ag oxidation states, creates via an intermediate product of a polymer PVA/ Ag^+ complex in this model reaction, reflecting a rapid transform in the mixture color. Where the Ag metal creates through a polymer PVA/ Ag^+ complex of an intermediate state Ag^q ($q < 1$), the PVA oxidation during this reaction interrupts the PVA/ Ag^+ complex structure. The Ag clusters formed from the Ag^q species convert to Ag atoms followed by coalescence, and then the Ag cluster forms and grows to achieve Ag particles. The Ag nanoparticles capsulated by the PVA molecules are stabilized from oxidative reactions. Where and simply, the PVA^- represents a partially oxidized state of PVA as follows:



that is, one hydroxyl group "OH" is substituted by oxygen 'O' group, with the number of monomers ($n = \Omega_{1n'}$) in the native polymer molecule. Where the produced hydrogen atoms drives the $Ag^+ \rightarrow Ag$ reduction,



The byproduct nitric acid (HNO_3) evaporates during the heating process, and the PVA polymer molecules capping the Ag metal results in small size particles (nanoparticles). To obtain the Ag metal of neat dispersed particles in the PVA matrix, the external heating is very important and a crucial process. Otherwise, the residual of (HNO_3) acid interacts with Ag metal back to AgNO_3 . The PVA has two functions in the reaction, first encapsulating the Ag particles and separating the $\text{Ag}^+ \rightarrow \text{Ag}$ reactions in small isolated groups. Second, the structure of the isolated Ag particles can be controlled by the PVA. Under a hot condition of 60–70°C and mechanical stirring, the PVA molecules dissolved in the water are difficult to agglomerate and aggregate. From the models shown in **Figure 3**, the surface energy of the planar structure is high because of the molecular stretching of the bonds. Also, the PVA molecules interacted with OH groups via the hydrogen bonds, which work as follows:

1. A matrix to $\text{Ag}^+ \rightarrow \text{Ag}$ reaction occurs over such surfaces;
2. A weak reducing agent, at moderate rate, to give $\text{Ag}^+ \rightarrow \text{Ag}$ reaction;
3. A surface stabilizer to maintain the Ag nanoparticles in the sample;
4. A protecting surface coating to inhibit the growth of the Ag nanoparticles and obtain a stable PVA/Ag surface-interface.

The nucleation and growth processes of the Ag particles start and depend on their morphology, the Ag size, and also on its template stability. A spiral structure stimulates a fibril of the PVA, whereas the different shapes (platelet or spheroids) grow by a PVA crystalline lamellar regions. The small spherical templates participate to evolve the spherical or near special shapes of the nanoparticles according to the reaction species interactions through the interface layer.

The reported mechanism of this reaction based on 'polyol route,' the PVA monomer, involves the secondary alcohol groups, R_2CHOH , on the polymer.



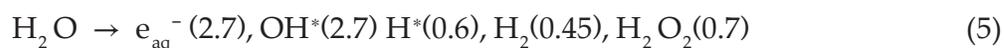
Here, R denotes a PVA monomer.

Recently, Deb and Sarkar [19] used the in situ method to prepare the PVA/Ag nanocomposite films and then followed the films by thermal annealing to obtain the PVA/Ag nanorods. In the same context, Llorens et al. [20] synthesized the cellulose/copper nanocomposite fibers by using in situ thermal treatment. Bogdanovic et al. [21] prepared the polyaniline/copper nanocomposites via the in situ method, wherein the Cu nanoparticles and polyaniline are created at the same instant. In this case, the reaction takes place at room temperature to obtain the nanocomposite. This route can be counted as a simple and inexpensive method of preparation. Also, Becerra et al. [22] prepared the poly(vinyl chloride)/copper nanocomposite films by the in situ method for antibacterial applications. Also, El-Shamy et al. [23] recently used the in situ method to produce the PVA/Ag nanocomposites, where they used the PVA polymer as a reducing agent by activation of the OH group in the PVA at 60°C to reduce the AgNO_3 to

Ag nanoparticles and obtained the nanocomposites. Ananth et al. [11] prepared the PVA/Ag nanocomposites by using the in situ method for the SPR-based protein sensors. Karthikeyan et al. [24] synthesized free-standing PVA/Pt nanocomposite films via in situ method for ultra-fast optical power-limiting applications.

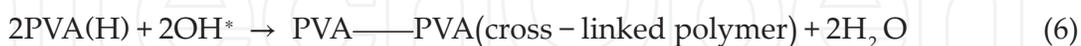
2.3. Radiolytic method

The radiolytic process means that the molecules separate to smaller atoms, radicals or ions by ionizing radiation like γ rays, UV irradiation. In fact, the gamma irradiation method is one of the most interested methods for preparing the polymer/metal nanocomposites. The desired highly reducing radicals generated free from any by-product are the main feature of gamma irradiation method for the creation of noble metallic nanoparticles. The primary and first radicals and upon gamma irradiation, the molecules produced in water are [25].



The numbers in parentheses represents the G values. The G value for a given irradiated system is the absolute chemical yield expressed as the number of individual chemical events occurring per 100 eV of absorbed energy. Thus the G (e_{aq}^-), G (OH^\bullet), etc. are the number of solvated electrons, hydroxyl radicals, etc., formed per 100 eV of absorbed energy. The alcohol radical is produced when the radicals (OH^* and H^*) are able to capture hydrogen from the alcohol group. This way, oxidizing OH^* radicals are transformed into reducing alcohol radicals. The scavenger material was used to make the reaction free from the OH^* radicals. The e_{aq}^- and OH^* radicals possess the electron transfer reaction between the PVA and Ag^+ , and then the reduction of Ag^+ ions to Ag particles takes place. The color of the composite solution is converted from colorless to pale yellow color as a result of the Ag^+ ions reduction in PVA solution by the radiolytic method.

It is well known that the OH^* radicals induce the cross-linking of PVA molecules in aqueous medium by/through the gamma radiation (with the G value of the intermolecular cross-linking induced via the gamma irradiation is 0.48).



The Ag^+ ions are reduced, under the given conditions of the experiment, with highly reducing hydrated electrons, reducing agent and the PVA radicals created by the H atom, which is abstracted from the (OH^*) radicals in the PVA chains.



The hydroxyl radicals formed by the hydrated electrons during the gamma irradiation of N_2O -saturated aqueous solution are as follows:



According to the reaction in Eq. (6), the PVA interacts with the hydroxyl (OH^*) radicals and is lost in the reaction to obtain the polymeric PVA^* radicals. After the gamma irradiation of the (PVA/Ag^+) hydrogel, the color of the hydrogel is changed to pale yellow color due to the electron transfer interaction between the PVA and Ag^+ . Reduction of the silver ions in PVA/Ag^+ hydrogel induced the creation of Ag nanoparticles with a characteristic fingerprint surface plasmon resonance (SPR) band.

The advantage of the gamma irradiation method comes from the gamma rays and is as follows: (1) hydrated electron resulted from the gamma radiolysis can reduce metal ions to metal nanoparticles. (2) Escaping from the use of external reducing agent and the resultant side reactions like oxidation reactions in UV irradiations and other byproducts produced in the reducing agent methods. (3) The gamma rays used to control the reduction reaction by controlling the doses of the irradiation and also the amount of the reduced nanoparticles nuclei by controlling the amount of radicals. (4) The gamma radiation used to reduce the AgNO_3 to Ag seeds point which serves as nuclei or nucleation sites for Ag atoms formation, to start the Ag nanoparticles growing directly on the PVA backbone. Also, this method has the ability to produce the metal nanoparticles in different shape and size.

Recently, El-Shamy and his group [26] reported a promising route for the creation of the PVA/Ag and the $(\text{PVA}/\text{Ag}$ nanorods) nanocomposites by using the gamma rays. After producing the PVA/Ag nanocomposite films via the chemical reduction in situ route, the films were directed to gamma rays with different irradiation doses from 25 to 100 K Gy with steps 25 K Gy, and at special case, the Ag nano-rods were produced at 125 K Gy, and the Ag nanoparticles appeared on the back surface (the surface not facing the gamma source) as nanorods, as shown in **Figure 4**.

In the real reaction, two processes may occur simultaneously. At first, Ag nanoparticles are created through homogeneous nucleation process and then grow along the direction of the lowest energy $\{111\}$ plane. The Ag nanoparticles were firstly created by the homogeneous nucleation process, through the silver nitrate reduction by gamma rays. The nucleation process was done by the Ag seeds which was a source of the formation of Ag atoms. The rod-like PVA micelles were created through the gamma irradiation, and this is strongly related to the $\text{PVA}:\text{Ag}^+$ molar ratio. The backbone chain of PVA contains oxygen atoms from the $(-\text{OH})$ groups in the PVA. This oxygen atoms coordinate with the Ag to form complexes (PVA/Ag^+) as an intermediate state in the reaction via the covalent bonds. The second step includes merging and fusing of the Ag nanoparticles to create Ag nanorods in the matrix via the photo-thermal effect of gamma irradiation.

Here, the PVA polymer has two functions in the reaction: (1) the first function is the PVA forming a complex (PVA/Ag^+) with Ag^+ through the coordination reaction and (2) the second function is the PVA used to adsorb on the Ag nanoparticles facets. From the PVA structure, the binding capacity of PVA to the Ag surface increases, because of the PVA containing the $-\text{C}=\text{O}$ groups. So, the adsorption of the PVA on the Ag nanoparticles surface increases. From this fact, the Ag crystals interact with the PVA groups $(-\text{C}=\text{O})$, leading to a decrease in the crystal growth of the $\{100\}$ plane as compared to the $\{111\}$ plane. The plane $\{100\}$ has energy lower than the plane $\{111\}$, so there is a high energy difference between the two surfaces. According

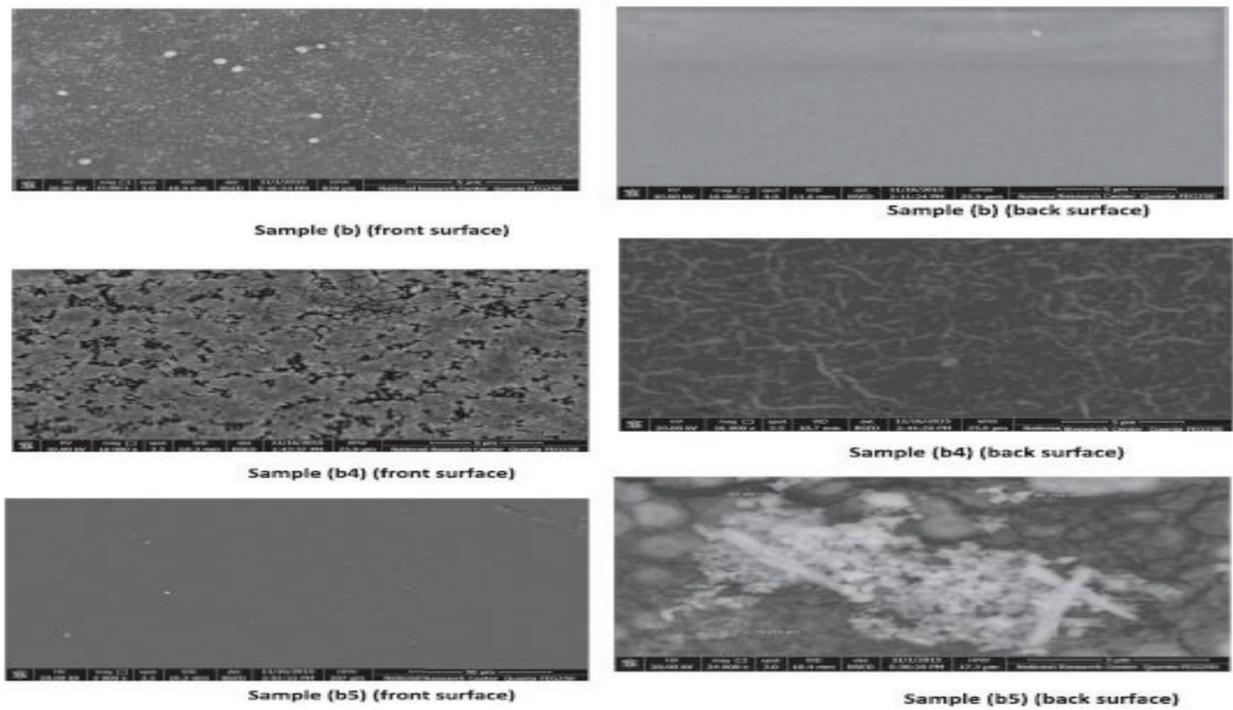


Figure 4. SEM images of front and back surfaces for samples 0 (b1), 100 (b4) and 125 KGy (b5) [26]. Copyright 2018. Reused with permission from Elsevier Ltd.

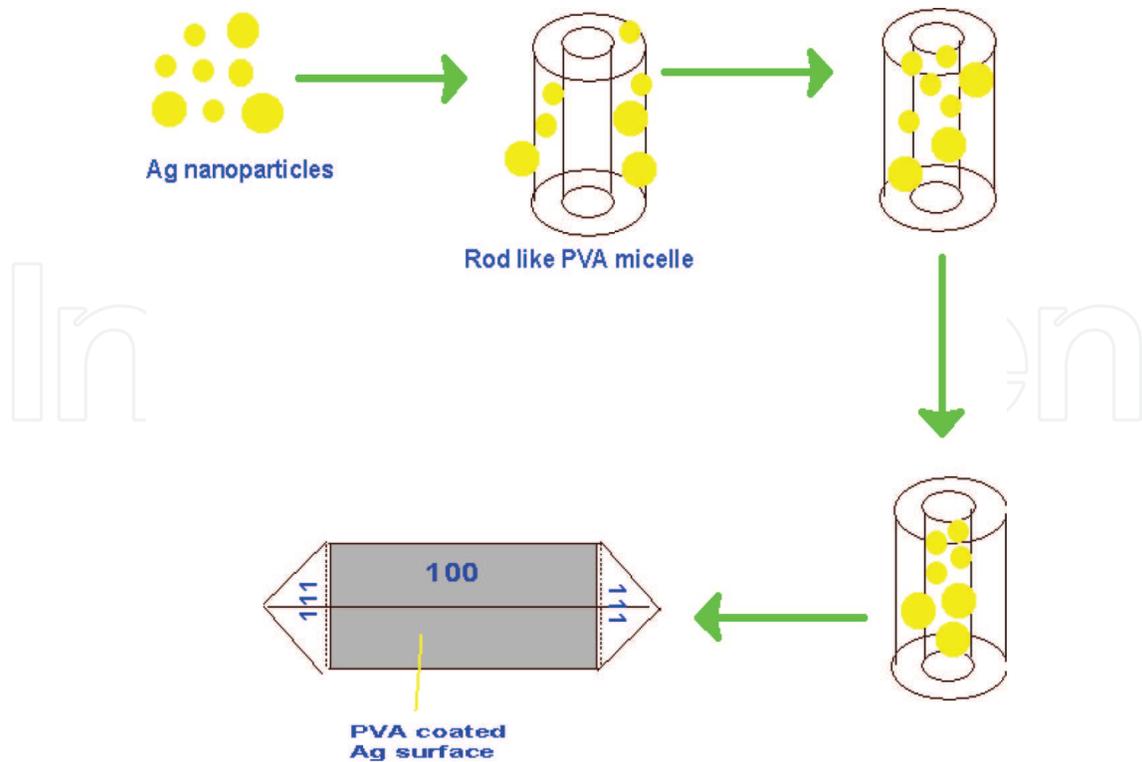


Figure 5. Schematic illustration of the formation of the Ag nanorods in the PVA matrix.

to this fact, the reactivity of the plane {100} to interact with PVA is larger than the reactivity of the plane {111} with PVA. So, there is a large difference in reactivity between the two surfaces of Ag nanorods. Consequently, the PVA coated the plane {100} of the Ag nanorods and completely blocked Ag nanorods from growing. On the other hand, the PVA partially coated the plane {111} of the Ag and also PVA partially blocked the Ag nanorods from growing along this direction as shown in **Figure 5**. This investigation confirms that the PVA macromolecule interacts with the Ag plane {100}, which is stronger than the Ag plane {111}.

Yonghong et al. [27] successfully prepared the polyacrylamide/gold (PAM/Au) nanocomposites by γ (gamma)-irradiation in an ethanol system. In a similar way, Krkljes et al. [28] prepared the PVA/gold nanocomposites via the gamma irradiation, in situ method. Also, Ali et al. [29] recently used the gamma irradiation to prepare the PVA/copper nanocomposites, with the obtained copper size ranging from 13.9 to around 19 nm. Graeser et al. [30] used gamma irradiation to reduce Ag⁺ ions in the presence of polyvinylpyrrolidone (PVP) to produce the PVP/Ag nanocomposites.

3. Properties of PVA/Ag nanocomposites

3.1. Mechanical properties

From the experimental and theoretical approaches that deal and explain the behavior of the nanocomposites, the insertion of the nanoparticles into polymer matrices is the direct reason to obtain nanocomposite materials with higher mechanical properties. There are many techniques to determine the mechanical parameters of the polymer/metal nanocomposites such as tensile, compression and shear stress techniques. From the stress-strain curve, the mechanical parameters including Young's modulus, elongation at break, stress yield, tensile strength and compressive strength were determined. The interfaces between the nanoparticles surface and polymer matrix (called the interfacial or boundary region) exhibit the nanocomposites local properties different than that of the bulk or traditional composites.

One of the most important and major factors that affect the mechanical behavior of the polymer/metal nanocomposite is the concentration of the metal nanoparticles and the preparation method. Experiments showed that the mechanical parameters of the polymer/metal nanocomposites are strongly altered by these two parameters. Given facts showed that Young's modulus was found to be 2.2 [31] and 4.6 GPa [23] at approximately the same concentration of Ag nanoparticles 1 wt.% for the PVA/Ag nanocomposites, but with different experimental procedures. Also, it increased with raising the Ag nanoparticles content by using the same experimental procedures for the same nanocomposite. We believed that this increment in Young's modulus and the reduction in the elongation at break is assigned to the growth in the intra- and intermolecular hydrogen bonding due to the increase in the content of the Ag nanoparticles and then higher the cross-linking level in the nanocomposite. So, the increasing Young's modulus behavior and the decrease in the behavior of the elongation at break take place.

Figure 6 explains as follows: the true stress-strain curve is changed after the addition of Ag nanoparticles in the PVA that show a transformation from a rubber-like of the PVA polymer

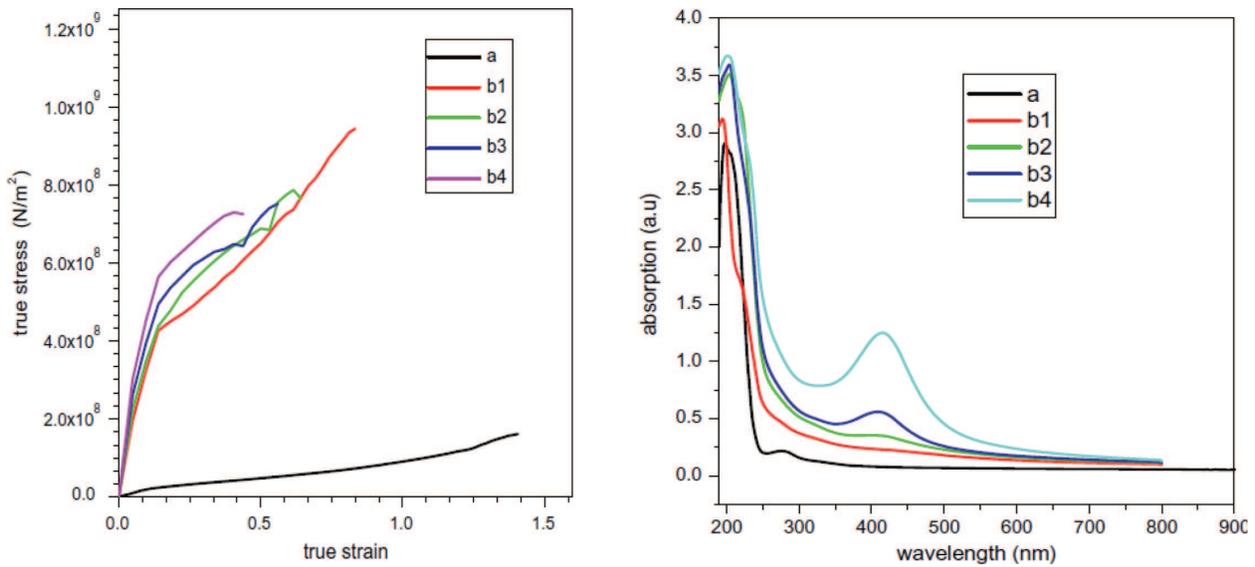


Figure 6. (left side) the stress-strain behaviors, (right side) the optical absorption spectra for prepared samples (pure PVA (a) and 0.2, 0.4, 0.8 and 1.5 wt.% of Ag nanoparticles take a label (b1–b4)) [23]. Copyright 2014. Reused with permission from Elsevier Ltd.

to a semi-crystalline state. The behavior of true stress-strain curve can be divided into three distinct lines. The first stage is the linear part and called the elastic strain following Hooke's law. The increase in the slope of this stage is attributed to the increase in the density of Ag nanoparticles. The second stage shows the starting of the neck formation. The length of this stage decreases with raising the content of Ag nanoparticles. Accordingly, the crystals of the isotropic PVA begin to be oriented in this deformation stage under the tensile stress. Also, it is clear that Young's modulus raises as the amount of Ag nanoparticles increases. This may be illustrated on the assumption that the introduction of metals in the polymer chain increases the density of the materials which leads to a decrease in lattice strain under external mechanical stress (where the introduction of silver nanoparticles in the PVA leads to the increase in the intra-molecular forces, creating a charge transfer complex which inhibits the molecules of PVA from sliding over each other. This may describe the raise of Young's modulus). The increase in the concentration of Ag nanoparticles causes shifts in the neck region to low strain side and the neck formation appears by increasing the concentration of Ag nanoparticles. These results can be explained by the fact that the increase of silver nanoparticles concentration causes an increase in the intra-intermolecular forces inside the polymer. This increase demonstrates itself by the shift of the formed neck to low strain appearance on its gradual side.

Chatterjee et al. [32] doped the PMMA/block copolymer with the Ag (from 0.16 to 0.65 wt.%) and then studied the storage moduli for this nanocomposite film. They documented the increment in both the storage and loss moduli of nanocomposite as the Ag concentration raise. This behavior was explained on the basis of the attraction forces (van der Waals forces) between the PVA and the Ag nanoparticles, and huge surface area to volume ratio of the Ag nanoparticles. Also, Deka et al. [33] recorded enhancement in the mechanical parameters such as Young's modulus, tensile strength, elongation at break, impact resistance and Shore A hardness of the

polyurethane PU/Ag nanocomposites with the Ag nanoparticles concentration from 2.5 to 5 wt.%. Moreover, Young's and storage moduli of PVP/PU blend were enhanced by introducing the Ag nanowires in the matrix. However, the elongation at break decreased from 536% for neat PVP/PU to 304% for 1.5 vol.% of Ag-doped PVA/PU in the PVA/PU blend, and also the ultimate strength decreased from 12.7 for PVA/PU to 9.8 MPa for 1.5 vol.% of Ag [34]. Also, Papageorgiou et al. [35] determined the tensile mechanical parameters (Young's modulus, strain) and impact strength of the same polymer polystyrene (PS) doping with 3 wt.% of different nanofillers such as PS/Ag nanoparticles, PS/Cu nanofiber, PS/nano-diamond and PS/MWCNT nanocomposites (**Table 1**). By comparing the obtained data, it is shown that Young's modulus, elongation and impact strength in PS matrix containing the metal nanoparticles are better than the other nanocomposites containing the multiwall carbon nanotube MWCNT, and nanodiamond. The improvement and enhancement of the mechanical parameters by embedding metal nanoparticles was also reported in chitosan/Ag [36] and PVA/Ag [37] nanocomposites. As a result, the mechanical behavior of polymer matrices can be improved by dispersing the metal nanoparticles through the polymer and giving many benefits.

3.2. Optical properties

For centuries, the polymer/metal nanocomposite is one of the most important classes of functional materials due to its useful optical properties, including light absorption, photoluminescence spectra and refractive index, and its applications. The size of metal particles and their allocation inside the polymer matrix are the two strongest parameters that the optical properties of these polymer/metal nanocomposites depend on them. Polymer/metal nanocomposites that consist of inorganic UV-absorbers and polymer have been of interest in many fields. The fingerprint behavior for all the noble metal nanoparticles is the unique absorption peak in the visible spectrum (**Figure 6**). This band called surface plasmon resonance (SPR) band is attributed to the excitation of the collective modes of motion of the electron cloud (plasmon excitation) at the boundary of the particle under the effect of the light electrical field. When the light falls with a definite frequency, the resonance takes place and results in an optical absorption, surface plasmon, plasma resonance absorption, plasmons or localized surface. Some factors exerted on this band position, width and intensity, are as follows:

Polymer/metal nanocomposites	Young's modulus (Gpa)	Elongation (%)	Impact strength (J/m)
Ps	2.59	1.93	11.1
Ps/Ag	2.81	2.65	12.5
PS/Cu nanofibers	2.79	1.8	14.6
Ps/MWCNT	2.92	2.06	13.9
Ps/nanodiamond	3.1	2.34	11.7

Table 1. Mechanical properties of PS nanocomposites, data were collected from [35]. Copyright 2014. Elsevier Ltd. Reused with permission from Elsevier Ltd.

1. The dielectric constants for both the metal and its surrounding matrix;
2. Size, dimensions and shape of the particle;
3. The interface area, crossing point or the boundary between the particle and the surrounding matrix;
4. The particles distribution in the surrounding matrix.

Metals in the nanoscale range allow to control the refractive index (RI) and the dispersion behavior of polymeric nanocomposites when inserted into the polymer matrix. The higher refractive index of nanocomposite materials obey these materials to a functional application in many fields such as optical and optoelectronic lab (lenses, optical filters, optical waveguides), and advanced technology such as solar cells, photodiodes, optical adhesives or antireflection films [38]. A large number of the metal nanoparticles can be inserted into the polymer matrix for boosting the refractive index of polymer nanocomposites. The refractive index of polymer/metal nanocomposites has a linear function with the density of the metal nanoparticles and the absorption coefficient. Either the increase in the refractive index or a decrease makes the polymer/metal nanocomposites very useful in many applications such as chemical and biosensors. Another important parameter, which very much influences the refractive index of the nanocomposites, is the isotropy or anisotropy of the metal nanoparticles in the polymer matrix. The anisotropy of the metal nanoparticles in the polymer matrix produces birefringence behavior; this means that the nanocomposites have two refractive indexes [39].

3.3. Antibacterial properties

In recent years, the race to develop polymer/metal nanocomposite materials with microorganisms' resistance properties had been of a very significant value and considered an important key factor for inhibiting foodborne diseases and preventing or controlling bacteria and infections originating in a hospital (nosocomial infections) from growth. Marketing, the polymer/metal nanocomposite product with the antibacterial properties is extremely used. The mechanism of the interaction between the polymer/metal nanocomposite and the bacteria is subsequently summarized and is shown in **Figure 7**.

3.4. Antibacterial mechanism of metal/polymer nanocomposites

The antimicrobial effects showed in polymer/metal nanocomposites depend on three phenomena:

1. Metal ions that can release from the nanocomposites,
2. Nanocomposites can release metal nanoparticles from it.
3. The inhibition was done by biofilms.

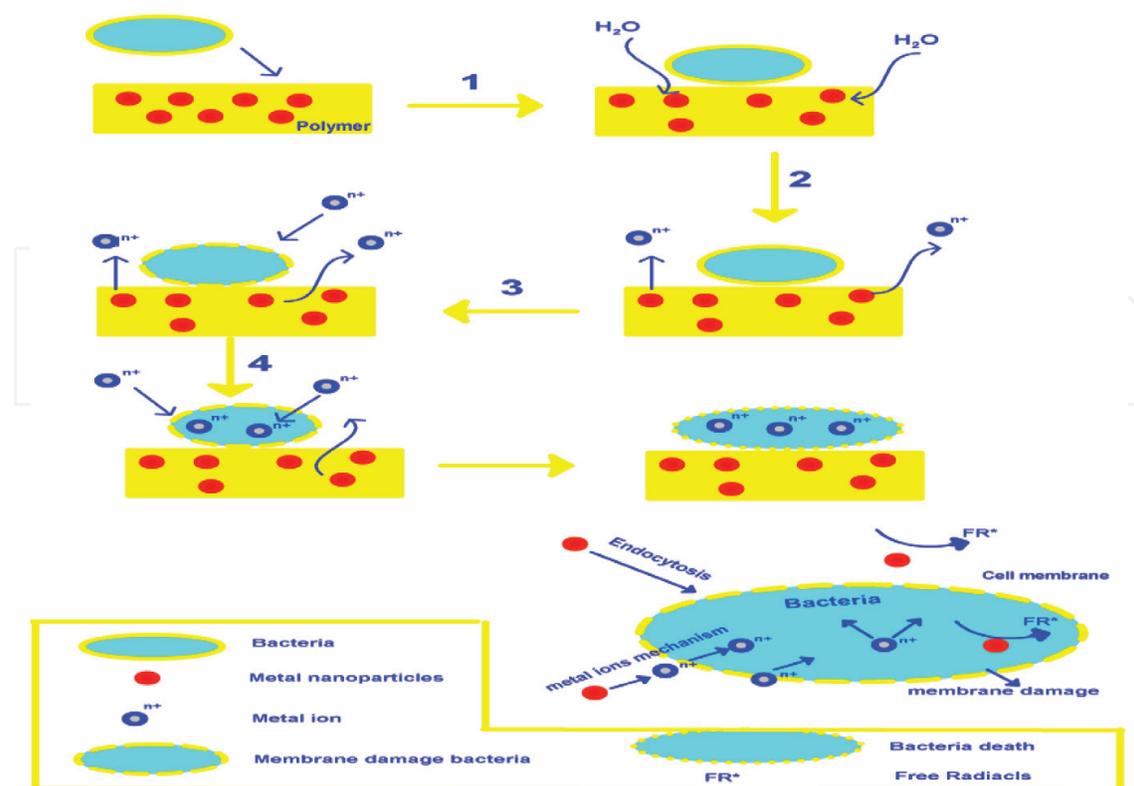


Figure 7. Mechanisms for the antibacterial behavior of polymer/metal nanocomposites: (1) adsorption of bacteria on the polymer surface triggering the diffusion of water through the polymer matrix due to the medium surrounding the bacteria; (2) water with dissolved oxygen reaches the surface of embedded metal nanoparticles allowing dissolution or corrosion processes, and this way metal ions are realized; (3) metal ions reach the nanocomposite surface damaging the bacteria membrane; (4) afterward, metal ions can diffuse into the bacteria.

3.4.1. Release of metal ions

1. The metal ions are released from the polymer/metal nanocomposites and reach the bacteria cell wall (the outer membrane) and denaturation of proteins in the bacterial membrane by their interaction with the sulfhydryl groups and amines and carboxyl groups in the peptidoglycan layer that found in N-acetylglucosamine and N-acetylmuramic acid.
2. The cell wall and membrane of the bacteria are destabilized or broken and subsequently disintegrated by these interactions, which is known as the bacteriolytic effect.
3. The released ions bind to DNA in the bacteria resulting in disorganized helical structures involved in cross-linking within and between nucleic acid strands; this leads to the cell not capable of reproducing. Also, the reactive oxygen species, lipid peroxidation and protein oxidation are generated by the metal ions.

3.4.2. Release of metal nanoparticles

1. The metal nanoparticles via molecular interactions adhere to the bacteria surface and with the electrostatic forces.

2. By one of two ways (endocytosis or direct diffusion), the bacteria cell wall penetrates by the metal nanoparticles.
3. There are three steps for the metal nanoparticles within (10 and 100 nm) to penetrate the bacteria cell wall by endocytosis: sticking to the membrane, the metal nanoparticles warped by the membrane and finally the particle-lipid complex separates from the membrane.
4. The hydrophobic or hydrophilic nature of the metal nanoparticles at 10 nm plays an important role. The metal nanoparticle penetrates the membrane of the bacteria cell wall, if the interaction is strong, driven by its preference for the lipid head group or tail.
5. Side by side and at the same time with these above mechanisms, the ions were freed and released from the nanoparticles and also concurrently excite the effects linked with the ions release.

3.4.3. Biofilm inhibition

1. The metal nanoparticles move through the nanocomposite matrix toward the surface, so the outer layer of the nanocomposite becomes much more active.
2. The attachment of bacteria is altered, by reducing the cell surface hydrophobicity (CSH) via the surface of the metal nanoparticles. Also, the extracellular polymeric substances (EPSs) are reduced by the surface of the metal nanoparticles, which also take a role in biofilm creation and growth.

Recently, Fatema et al. [40] prepared the PVA/Ag nanocomposites by two methods: first, by water in oil (w/o) microemulsion and the second by the in situ method. The antibacterial efficiency was done against G- bacteria '*E. coli*' and G+ bacteria '*S. aureus*,' respectively, for the above nanocomposites. They observed that the (w/o) microemulsion films have antibacterial activity higher than the in situ films under the same test condition. Also, Espana-Sanchez et al. reported the treatment of polypropylene PP/Ag and PP/Cu nanocomposites surface by using the argon plasma [41]. They showed that the nanocomposites have a higher quality in the antibacterial efficiency versus, pathogenic, the human disease bacteria, because of the larger surface area of the metal nanoparticles and the raising of the hydrophilicity and the roughness of film surface. Also, the in situ route was used to prepare the polyethylene PE/Ag nanocomposites for antibacterial applications [42]. They recorded that the Ag ions were released from the PE/Ag nanocomposites with larger Ag concentration higher than the neat PE.

4. Applications of polymer-metal nanocomposites

The embedding of noble metal nanoparticles as filler into organic polymer matrices gives superior thermal, electronic, optical and mechanical properties for the resulting polymer/metal nanocomposite materials. The improvements and enhancement of the physical properties go with these materials to be used in different technical applications in many various

Metal/polymer nanocomposite	Microorganism	Application	Refs.
Hydroxypropyl Methylcellulose/ Cu	<i>S. epidermis</i> , <i>B. cereus</i> , <i>E. faecalis</i> , <i>Salmonella</i> , <i>P. aeruginosa</i> , <i>Staphylococcus aureus</i>	Food packaging	[43]
Polymers based on acrylic/ Cu	<i>Chlamydomonas</i> CD1 Red, <i>Synechocystis</i> PCC 6803, <i>Phaeodactylum tricornutum</i> CCMP 1327	Marine antifouling coatings	[44]
Cellulose acetate/Ag nanofibers	G- bacteria (<i>E. coli</i> and <i>Pseudomonas aeruginosa</i>); G+ bacteria such as (<i>S. aureus</i> and <i>Bacillus subtilis</i>)	wound dressing	[33]
Polyurethane/Ag nanocomposites	G- bacteria (<i>E. coli</i> and <i>Pseudomonas aeruginosa</i>); G+ bacteria such as (<i>S. aureus</i> and <i>Bacillus subtilis</i>)	Marine antifouling coatings	[45]

Table 2. Main application of polymer/metal nanocomposites in antibacteria.

Polymer/metal nanocomposites	Application/Refs.
Polyaniline/gold	Sensor [46]
Natural rubber/Ag	Latex gloves [47]
Polysulfone/Pt	Sensor [48]
Polypyrrole/Pt	Fuel cell [49]

Table 3. Application of polymer/metal nanocomposites.

fields, such as energy, environment, mechanics, optics, electronics, optical transformation technology, engineering, biology and medicine. Many applications like catalysts, membranes military equipment and separation devices, and solar cells, aerospace, fuel sensors, automobiles, antimicrobial, have been reported for the polymer/noble metal nanocomposites. Nanocomposite materials are used for this purpose, as shown in **Table 2**: tissue engineering, textiles and functional smart coatings, paints and drug carriers. Furthermore, the superior and high-quality mechanical and thermal properties of these nanocomposites allow them to be used in many various industrial applications, such as filters for irradiation protection, life power equipment, electronic devices, conductors and insulators in daily electrical tools, and pagers for the manufacturing of pressure molds in the ceramic industry. More details about the application of polymer/metal nanocomposites are shown in **Table 3**.

5. Conclusions

From the previous discussion and clear different examples and principal strategies of the polymer/noble nanocomposites preparation mentioned in this chapter, it can be concluded that the radiolytic route for the synthesis of the nanocomposites is a smart way and a very easy method with a large possibility to solve the problems of the nanocomposite synthesis in the future. For polymer/metal nanocomposite synthesis, one main problem is the nanoparticles agglomeration and it must be solved: once obtained, and how to inhibit this

problem. The synthesis methods have to be tuned in such a way that gamma irradiation is used that avoids the agglomeration of nanoparticles. The mechanical parameters, Young's modulus, of the polymer/metal nanocomposites are highly dependent on the cross-linking density of the polymer, the morphology of the nanoparticles and the molecular interaction (intra- and intertype) between the metal nanoparticles and the polymer matrix. The optical properties of polymer/metal nanocomposites, such as the SPR intensity and position and the refractive index, are strongly dependent on the dimensions and shape of the metal nanoparticles, the dielectric functions of the metal and the surrounding material, the boundary between the particle and the surrounding, and the particle distribution in the surrounding matrix. The polymer/metal nanocomposites have a strong resistance toward the bacteria or antibacterial activity. The polymer capping metal nanocomposite materials have many various and important functional potential applications. Finally, it can be concluded that the main advantage of polymer/metal nanocomposites is the possibility to obtain the needed desired properties with higher quality than that from the conventional microcomposites by using very small volume of filler that can be low in magnitude by one or even two orders.

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