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Polymethylmethacrylate/Silver Nanocomposite Prepared by γ-Ray

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Abstract: Polymethylmethacrylate-silver (PMMA/Ag) nanocomposite is synthesized by irradiating the solution of silver ions in methylmethacrylate monomer by γ-ray. In this method, polymerization of the methylmethacrylate monomer and the silver ion reduction occurred simultaneously. Optical properties of the PMMA/Ag solutions are investigated using UV-Vis spectroscopy. The structural characterizations of the PMMA/Ag nanocomposite are determined by FTIR spectroscopy XRD, and SEM measurements. The SEM image shows that the Ag nanoparticles disperse in the PMMA matrix with a relatively uniform distribution. The antibacterial studies show that the PMMA/Ag nanocomposite is antibacterial against E. coli, as a model for gram-negative bacteria.

Keywords: ***Polymethylmethacrylate, Silver, Nanocomposite, γ-Ray***

1-Introduction

Metal-polymer nanocomposites have attracted considerable amount of interests in recent years. They have a wide range of applications in nonlinear optical materials [1], conductive composites [2] and nanoscale electronics [3]. In general, metal polymer nanocomposites are prepared by homogenizing polymer and nanometer metal powder [4], post-heating or calcining metal ion containing polymers [5 and 6], migrating the vapor of particles of noble metals into polymer matrices [7], and reducing metal ions in polymer gels [8].

PMMA/Ag nanocomposites are specially used in medical and dental devices for their antibacterial effects which are due to the presence of silver nanoparticles [9, 10]. It has been shown that morphology, particle size distribution, stability and properties of silver nanoparticles as well as corresponding nanocomposites are strongly dependent on the method of preparation and specific experimental conditions. Many routes have been reported to synthesis silver nanoparticles in PMMA [11, 12]. In these methods, the polymerization of organic monomer is performed initially and then the silver ions, dispersed in the polymer matrix, are reduced to zerovalent state by a reducing agent or by heat treatment. This, results in a wide distribution and poor dispersion of metal particles in the polymer matrix.

Recently, the radiochemical method has been reported to synthesize metal polymer nanocomposites due to its unique advantages. In this method the reduction of metal ions and polymerization of monomer can be carried out simultaneously under the normal pressure at room temperature without using excessive reduction of agents. This matter induces formation of homogenously dispersed metal nanoparticles in polymer matrix. Although several papers have been published on the radiation-induced synthesis of metal polymer nanocomposites [13, 14], to our knowledge, there is no any report on the use of γ-irradiation to produce PMMA/Ag nanocomposite. In this paper, we employed γ-irradiation to produce PMMA/Ag nanocomposite in which the reduction of silver ions and the polymerization of methyl- methacrylate monomer occur simultaneously at an appropriate applied dose of γ-ray.

2- Experimental

2-1 Materials and method

All chemicals were of analytical grade provided by Merck Company. Distilled water for sample preparation made by GFL Co. water purification system. Gamma irradiation was performed in ^{60}Co radiation facility, Gammacell-220, with a dose rate of 18.6Gy/min calibrated by Fricke dosimeter.

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2-2 Preparation and characterization

Methyl-methacrylate monomer was distilled under the vacuum to remove inhibitors. Then, the homogenous solution containing methyl-methacrylate monomer, isopropanol and $AgNO_3$ (0.1M) with 4:2:1 volume ratio was prepared in a glass vial with 20ml volume, purged with nitrogen for 20min to remove oxygen, and then exposed to 5kGy γ-ray (4hours and 48minutes, irradiation time) at room temperature. After the irradiation, a transparent, greenish, gel like material was obtained which was dried in the vacuumed oven and then characterized. A neat PMMA composite without Ag NPs was also prepared for the comparison. The FT-IR spectra of the samples, prepared in KBr pellets, were obtained using a Bruker IFS 45 spectrophotometer in the 400-4000cm^{-1} range. The X-ray diffraction (XRD) pattern of the sample was recorded by a Holland Philips Xpert X-ray diffractometer (CuKa). Scanning electron microscopy (SEM) image of product was taken on a Philips XL30 microscope. The UV–Vis spectrum of the diluted solution of PMMA/Ag was recorded using a Novaspec III Biochrom Ltd, spectrophotometer from 330 to 800nm.

2-3 Antibacterial studies

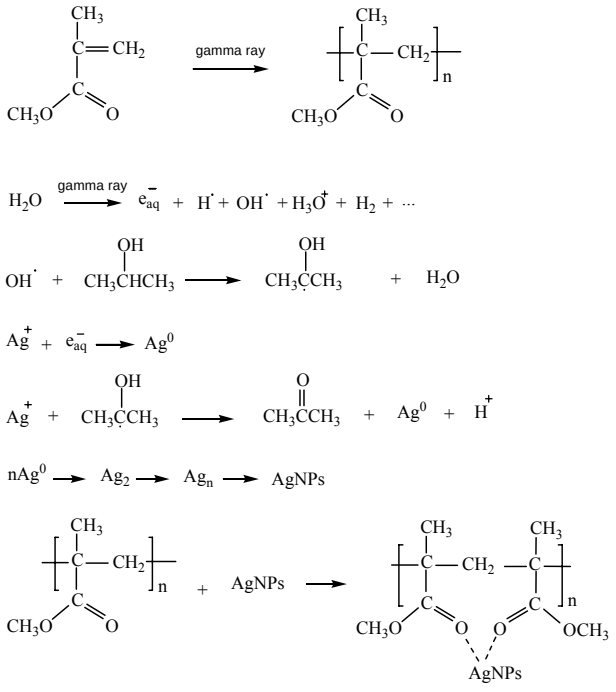
To examine the antibacterial effect of prepared PMMA/Ag nanocomposite on Gram negative bacteria, E.coli ATCC 25922 were cultured on LB agar plates supplemented with specimens, with a total surface area of 4cm^2. Sample free LB plates, cultured under the same conditions, were used as a controlling system control. The plates were incubated for 24hours at 37°C then the number of colonies was counted.

3- Results and Discussion

PMMA/Ag nanocomposite is simply prepared by irradiating the solution containing silver ions, isopropyl alcohol and methylmethacrylate monomer. The radiolysis of monomer solution results in the formation of radicals, which then initiate the polymerization of MMA to form polymer chains. On the other hand, the homodispersed silver ions are reduced to silver atoms by reductive particles such as solvated electrons and isopropyl radicals in the solution.

Then these silver atoms undergo further growing to progressively larger clusters leading to formation of nanometer silver particles [15]. As the polymerization of MMA is quicker than the reduction of silver ions the viscosity of the reaction system, resulting from the formation of polymer chains, increases. This effect as well as the availability of carboxylate functional groups of PMMA with a high affinity for the Ag^+ can limit the aggregation of silver particles and make them dispersed in polymer matrix homogeneously (scheme 1).

The possible physicochemical interaction between the silver nanoparticles and PMMA was tested by FT-IR. It is known that the shift of the peaks toward the lower wave numbers in the FT-IR spectrum is an indicator of the chemical bonding of surfactant onto the nanoparticle surface [16]. The spectra of the neat PMMA and the PMMA/Ag composite are shown in Fig. 1. As can be seen all the characteristic absorption peaks of standard PMMA including: the sharp absorption at 1728cm^{-1} (C=O groups), the peaks at 1147 and 1193cm^{-1} (C–H deformations), and 1244 and 1272cm^{-1} peaks (C–C–O stretch coupled with C–O stretch), are observed in neat and PMMA stabilized Ag nanoparticles indicating the occurrence of MMA polymerization by γ-ray.



Scheme 1. A proposal mechanism for the formation of PMMA/Ag nanocomposite.

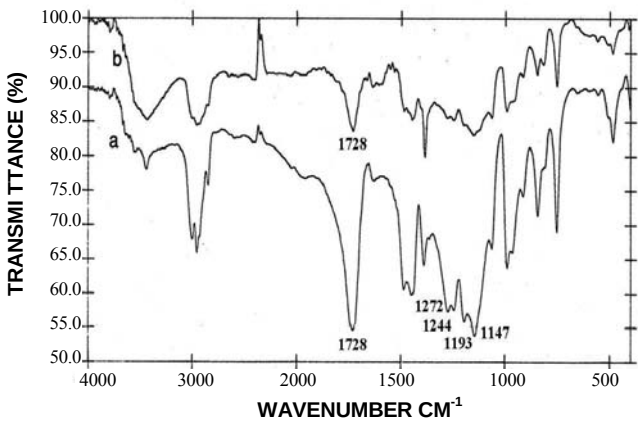


Fig. 1. FT-IR spectrum of the a) neat PMMA b) PMMA/Ag nanocomposite.

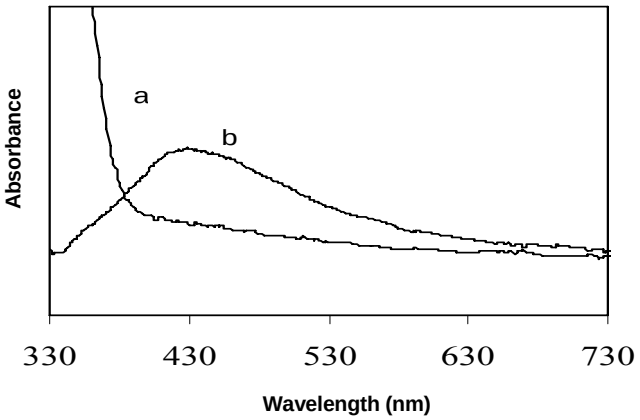


Fig. 2. UV-Vis absorption spectra of neat PMMA and PMMA/Ag nanocomposite.

In addition, there are no noticeable shifts in the peaks (in terms of wave numbers) between the neat PMMA and the PMMA stabilized Ag nanoparticles, demonstrating that the interaction between the Ag nanoparticles and the PMMA probably occurs through a weak physical force rather than a strong chemical bonding [16]. This observation may also indicate that most of the PMMA molecules are either physically linked to the nanoparticles or are present without any contact with the nanoparticles. Further information is needed to probe the essence of the physicochemical interaction between PMMA and silver nanoparticles.

UV-Vis absorption spectra are quite sensitive to the formation of Ag NPs because the position of the surface plasmon absorption peak depends on their particle diameters and shapes [17]. Therefore UV-Vis absorption spectra of the neat PMMA and PMMA/Ag were obtained (Fig. 2). In comparison to neat PMMA, the PMMA/Ag composite shows an absorption band at about 428nm, which is consistent with the established absorbance wavelength of silver nanoparticles [9].

To determine the size and distribution of the silver nanoparticles, scanning electron microscopy was performed. The SEM micrograph of PMMA/Ag composite (Fig. 3) indicates that Ag particles with mean size of 90±14.4nm disperse in the PMMA matrix with a relatively uniform distribution. This confirms that when reduction of silver ions and the polymerization of monomer take place simultaneously during irradiation, the silver nanoparticles are homogeneously dispersed in the polymer matrix.

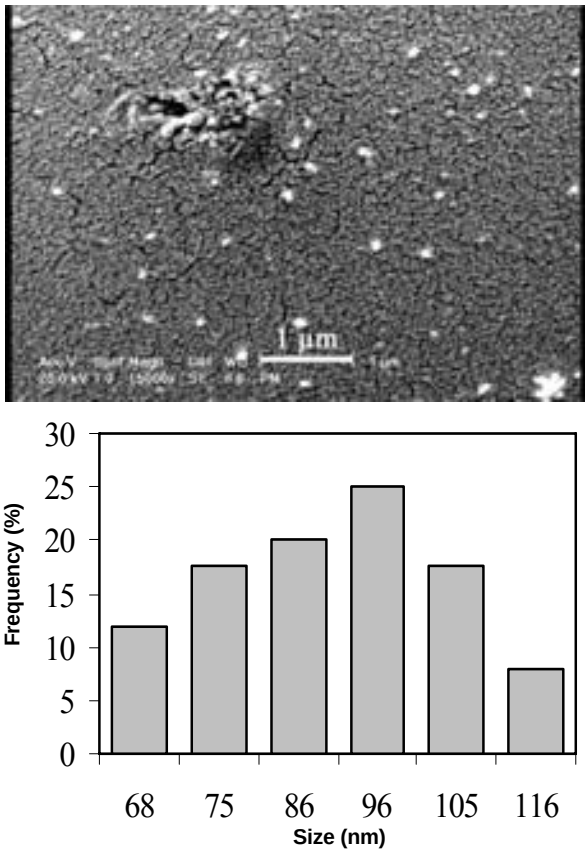


Fig. 3. SEM micrograph of PMMA/Ag nanocomposite and size distribution of the Ag nanoparticles.

To carry out further investigation of the size and structure of the silver nanoparticles in PMMA matrix, the XRD patterns of the PMMA and the PMMA/Ag composite are also obtained (Fig. 4). The PMMA/Ag composite displays a typical amorphous PMMA pattern and does not show any diffraction peak relating to crystal structure of Ag. This may be

attributed to the fact that the silver particles are relatively in low concentration to be detected with our instrument and are also embedded in the polymer matrix.

We have also evaluated the antibacterial effect of PMMA loaded with silver nanoparticles. The antibacterial tests were performed against 4.5×10^4 CFU of E.coli ATCC 25922 on LB agar plates containing PMMA/Ag composite. While the bacterial growth is observed for control plates, the presence of the Ag in the plates containing composite, inhibits bacterial growth completely (Fig. 5). Therefore PMMA/Ag nanocomposites can be considered to have a satisfactory antibacterial activity against E.coli.

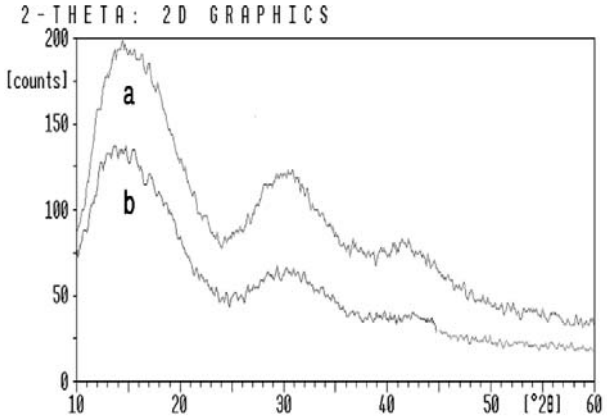


Fig. 4. XRD pattern of the a) pure PMMA and b) PMMA/Ag nanocomposite.

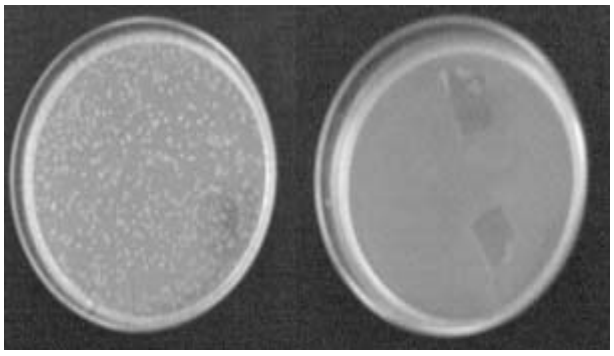


Fig. 5. Number of E. coli colonies grown on control plates without PMMA/Ag (left) and on PMMA/Ag nanocomposite containing plate (right).

4- Conclusion

PMMA/Ag nanocomposite was synthesized by γ-radiation reduction of Ag^+ ions and polymerization of methylmethacrylate monomer in one step at ambient temperature. The UV-Vis spectroscopy as well as the structural characterizations of the PMMA/Ag nanocomposite by FTIR and SEM measurements showed that the Ag nanoparticles with less than 100 nm are dispersed in PMMA matrix with a relatively uniform distribution. The antibacterial studies showed that the prepared PMMA/Ag nanocomposite has antibacterial effect against E. coli, which render medical applications. The results revealed that the radiolytic method can be taken into account as a capable method to prepare PMMA/Ag nanocomposite.

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