Influence of Adding Silver Nanoparticles on Structural and Optical Characteristics of PMMA Nanopowders for Antibacterial Applications

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The study aimed to prepare a combination of polymethyl methacrylate/silver nanoparticles as an antimicrobial product. We achieved the formation of pure PMMA and PMMA/AgNPs samples using clove plants as a colloidal extract. The possible functional groups and surface morphology were examined. The surface plasmon resonance (SPR) was reported by the UV-visible absorption spectra. The antibacterial performance of the prepared samples was studied against Gram negative and Gram positive bacterial strains. The same functional groups were revealed with slight shifting to lower wavenumbers for PMMA/Ag sample. SEM analysis established that the preparation of PMMA by the extraction approach led to the creation of nano-to-micro-sized structures with significant grain aggregation when AgNPs were added. Finally, the antibacterial analysis presented an obvious influence by adding AgNPs to pure PMMA powder.

Keywords: PMMA; Silver nanoparticles; Colloidal extract; Antibacterial activity
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1. Introduction

Poly (methyl methacrylate) (PMMA) polymer has extensive demand in optical products, hard contact lenses, luminous surfaces, airplane glazing, and other applications [1]. Even though PMMA has particular features, it exhibits certain inherent disadvantages that restrict its use in applications such as temperature sensors and other optical, healthcare, and industrial sectors. These disadvantages include weak tensile strength, inadequate absorption of visible light, limited electrical conductivity, and a small positive thermal coefficient of resistance (with a change in resistivity by a factor of 1-3 [2-5]. PMMA characteristics are regularly enhanced by a variety of methods, including ion implantation, ion irradiation, and the embedding of nanofillers within the PMMA matrix [6].

In recent years, distinct mechanical and physical characteristics have been acquired by metal nanoparticles incorporated in polymer matrices [7]. The size, concentration, dispersion, and interaction of nanoparticles on the polymer matrix determine the characteristics of polymer composites [8]. These polymer nanocomposites with encapsulated metal nanoparticles have further uses in a variety of industries, including biosensors, electrical devices like nanowires, and super lenses [9]. Silver nanoparticles are preferred for polymer nanocomposites fabrication because of their optical absorption in the visible spectrum. [10]. In order to lower infections and stop germs from growing on plastic devices, polymer materials containing silver nanoparticles have been widely employed in biomedical items such as surgical gloves, catheters, vascular grafts, prostheses, and dental materials [11]. Strong antibacterial activity of silver nanoparticles against both Gram positive and Gram negative bacteria has been demonstrated [12]. Based on numerous literature studies [13-17], the interaction of the positive charge of silver ions with various negatively charged species such as thiol, carboxylate, phosphate, imidazole, indoles, and amines, has been hypothesized as one of the mechanisms for the antibacterial effect of silver ions. This type of interaction causes bacterial cell death by impeding microbial functions such as DNA replication, cell division, and the inactivation of enzymes that are necessary for cell energy (ATP) [18].

Nanomaterials can inhibit the development of germs. Many antibiotics can be encapsulated inside nanomaterials to prevent the development of bacterial resistance [19]. By using nanomaterials to enhance drug delivery to diseased cells, antibacterial drugs can be applied to infectious regions with minimal side effects to patients [20]. Various methods, including solution mixing, melt blending, in situ polymerization, and the sol-gel approach, have been utilized to encapsulate nanoparticles in polymeric matrixes [21]. Silver nanoparticles agglomerate quickly due to their significant activity; therefore, uniformly dispersing them into the matrix is a challenging approach. Modifying the particle surface with polymeric surfactants or another modifier is required to increase the stability of the dispersion and maintain regulated formation of nanoparticles. The aggregation of nanoparticles is decreased as a result of this surface alteration, which also lowers surface free energy [22, 23]. A suitable reduction agent can be employed to convert the metal salt into metal nanoparticles. The chemical reduction process is the most widely used technique for creating metal nanoparticles. Strong reducing agents often result in the creation of smaller particles than weak ones [24]. Using of reduction solvents can eliminate the harmful consumption of reducing chemicals. As a result, new "green" manufacturing techniques for nanoparticles must be developed. These techniques must be low energy and temperature, harmless, and environmentally friendly. Among other techniques, the biological approaches involve the production of nanomaterials from plant, bacterial, and fungal extracts [25,26].

Synthesis of an organic–inorganic combination exhibiting antimicrobial property is the goal of this research study. Synthesis of PMMA and PMMA/Ag powders was managed by using clove plants as colloidal extract. We investigated the structural and morphological properties, and studied the antibacterial behavior of both samples against different types of Gram negative and Gram positive pathogens. At the end of this study, integrating organic-inorganic materials could pave the way to discover green, cheap, nontoxic, environmental friendly, bioavailable combinations to be utilized in purification, fertilization, and sterilization sectors.

2. Experimental Part

Clove plants were first washed with tap water and then with distilled water several times to remove any dirt or dust, after which they were dried in an oven. The flowers were ground to yield a fine powder, and then 10 g was stirred intermittently for 24 hours with 100 ml of acetone for extraction. The prepared extract was filtered, it gained brown yellowish color, and finally was kept in an opaque bottle in the refrigerator till use, as demonstrated in Fig. (1).

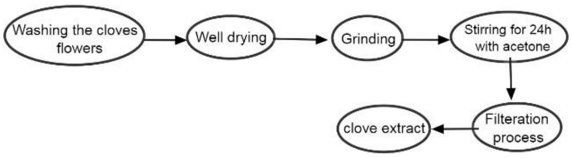

Fig. (1) Schematic sketch of the preparation process of clove extract

To prepare PMMA, we dissolved 1 g of standard MMA in 50 ml of acetone and then kept in two containers with 25 ml for each one. An aqueous solution of 0.1 g of sodium oleate was individually blended with the two MMA solutions. A solution of 1 mM silver nitrate ($AgNO_3$), which is used as silver ion source, was prepared by dissolving 0.2 g of $AgNO_3$ crystals in 20 ml of acetone and mixed well for 30 min to be finally added to one of the PMMA solutions. 5 ml of the cloves extract was poured into the PMMA/Ag solution only. Both solutions of pure PMMA solution (labeled as sample 1) and the mixture of PMMA/Ag (labeled as sample 2) were stirred thoroughly by a magnetic stirrer at 800 rpm to form a turbid slurry. The temperature was raised up to 60°C to evaporate the acetone and form silver nanoparticles in the PMMA/Ag mixture. The reaction proceeded for 1 hour to create PMMA and PMMA/Ag nanoparticles. Then the solutions were centrifuged at 10000 rpm for 10 min, afterward, the formed granules were washed carefully for several times and dried at 40°C for 24 hours. The prepared samples of pure PMMA (white nanostructured powder) and PMMA/Ag (pale yellow nanoparticles) were characterized. Additionally, the antibacterial activity of them was also investigated.

The antimicrobial efficiency of pure PMMA and PMMA/Ag nanoparticles was studied by Mueller Hinton agar well diffusion method against Gram negative pathogens (*Escherichia coli*, *Pseudomonas aeruginosa*, and *Salmonella typhi)*, and Gram positive bacteria (*staphylococcus mutans* and *Streptococcus pneumoniae*). The bacterial suspension was adjusted to match the tube of 0.5 McFarland turbid standard using spectrophotometry. The agar medium was organized, purified, consolidated and seeded with the bacterial suspension by pour plate method. We carefully placed 100 μg/mL of pure PMMA and PMMA/Ag powders in the agar plates. The plates were kept for incubation at 37°C for 24 hours. Afterward, the diameters of inhibition zones were measured.

3. Results and Discussion

The possible functional groups and the physicochemical interactions within the pure PMMA and PMMA/Ag nanopowders were investigated by Fourier-transform infrared (FTIR) spectra shown in Fig. (2). Both spectra showed similar functional groups with slight shifts to lower wavenumbers for the PMMA/Ag curve, which indicates a weak physical force rather than strong chemical bonding between the AgNPs and the PMMA polymer. However, the shift to higher wavelengths suggests that the mass of the created molecules has increased. Because the mass of a vibrating molecule is inversely proportional to its frequency of vibration. As a result, the lighter the molecule, the higher the vibration frequency and wavenumber [27,28]. Both spectra presented sharp absorption peaks at about 2800 and 2900 cm^{-1} which were assigned to saturated C–H stretching vibrations. The characteristic absorption peak at about 1730 cm^{-1} refers to C=O carboxyl groups. C–H bending peak can be distinguished at about 1450 cm^{-1}. Peaks that appeared around 1190-1240 cm^{-1} are fingerprints of C–C and C–O stretching vibration, respectively [29,30].

The peak at about 1560 cm^{-1} indicates the presence of C=C stretching bond which could be related to residuals of the main substance MMA remaining without polymerization. The most important difference between the two curves can be obviously seen at 700 and 750 cm^{-1} in PMMA/Ag curve which points out to the presence of silver particles that physically interacted with PMMA powder.

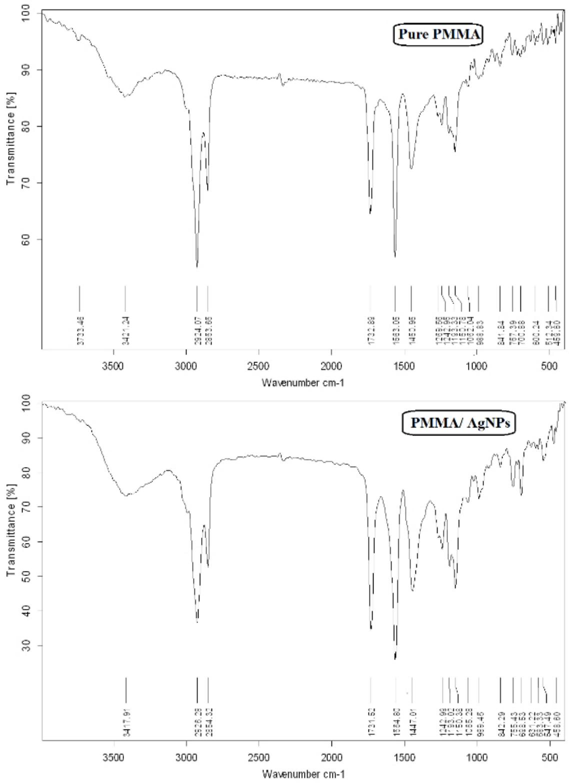

Fig. (2) FTIR spectra for pure PMMA and PMMA/AgNPs

The surface morphology of pure PMMA and PMMA/Ag samples was further examined using scanning electron microscopy (SEM), as noticed in Fig. (3). It can be seen that the preparation of PMMA by extraction approach led to the creation of nano/micro structured particles. These fine particles combined together forming groups of aggregates separated by grooves and pores. The Ag nanoparticles have almost spherical shape, non-uniform size distribution, and uniformly dispersed through PMMA nanopowder. As obviously shown in the figure, Ag particles entirely filled the resulting vacancies created in the pure PMMA sample.

UV-visible spectroscopy was utilized to examine the optical properties of the synthesized PMMA and PMMA/AgNPs, as displayed in Fig. (4). The spectra showed identical curves with slightly shifting towards the right side (longer wavelengths) for the sample of PMMA embedded AgNPs. The sharpest absorption peaks appeared at 196 and 199 nm which might be an indicator to granules aggregation through the preparation process as clearly presented by the SEM analysis.

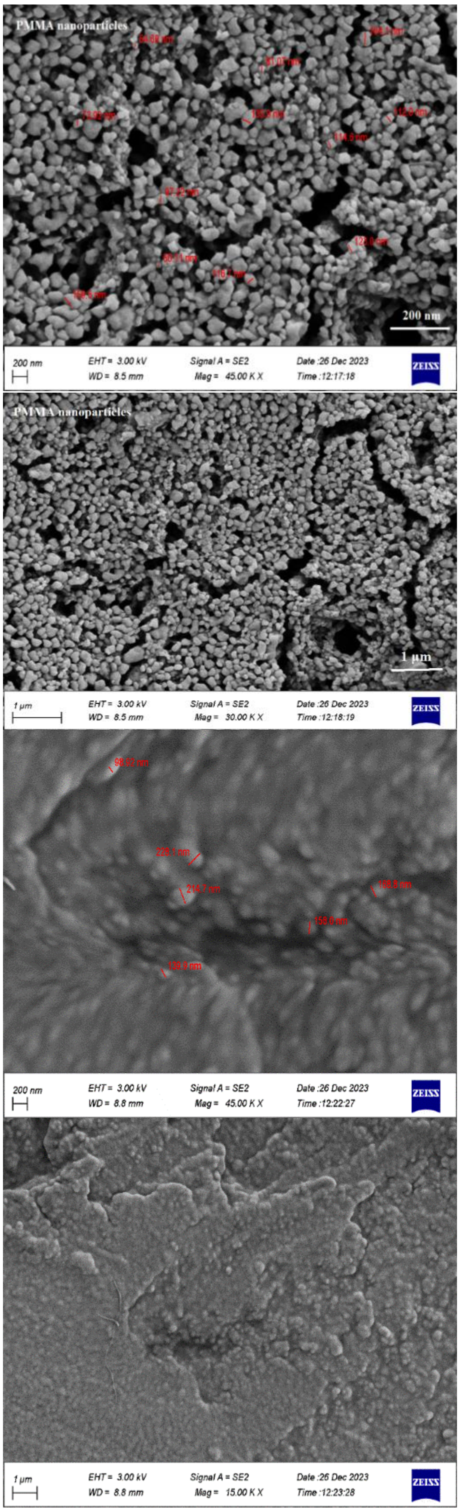

Fig. (3) SEM images of pure PMMA and PMMA/AgNPs with two magnification powers

The peaks at 231 and 280 nm are characteristic peaks for PMMA structural bonds according to surface plasmon resonance (SPR) for π- π^* and n–π^* transitions

[28]. The effect of AgNPs incorporation into PMMA was primarily observed in band shifts to the right without an obvious peak at the region between 300-500 nm that refers to AgNPs formation. This could be attributed to insufficient amount of AgNPs added to produce the combination. This confirms that the PMMA/Ag solution turned a pale yellow color instead of brown.

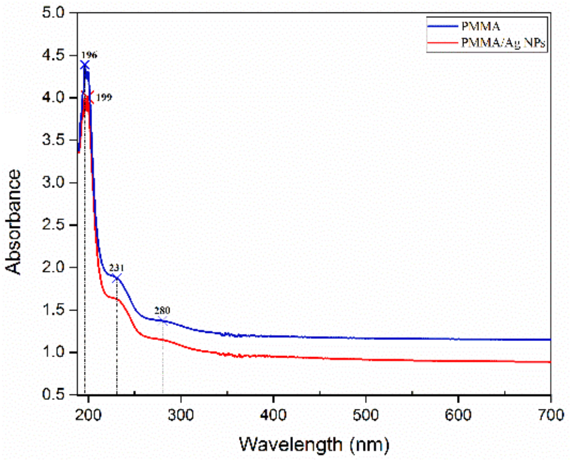

Fig. (4) UV-visible spectra of the prepared PMMA and PMMA/Ag samples

Figure (5) shows the antibacterial activity of the prepared samples and also figure (6) displays the results by using a bars chart for further clarification, while the radius of inhibition zones were presented in table (1). The *in vitro* findings showed that the antibacterial activity of pure PMMA was somewhat ineffective when applied to either type of microorganism (Gram negative and Gram positive). However, embedding AgNPs with PMMA exhibited a substantial antibacterial efficiency than pure PMMA. High antibacterial activity of AgNPs against bacteria has been explained in several studies with different strategies. The interaction between the negatively charged microbial cell membranes and positively charged molecules can dissolve the cell wall, allowing intracellular components to diffuse away. Additionally, it is hypothesized that cations may lead outside solutes to penetrate inside the cell and interact with DNA and RNA structures [31,32].

Table (1) The inhibition zone results measured by Mueller-Hinton agar approach against Gram negative and Gram positive bacteria

Bacteria	Inhibition zone (mm)	
	PMMA (1)	**PMMA/Ag (2)**
E coli (-)	8	12
Pseudomonas aeruginosa (-)	12	26
Salmonella typhi (-)	8	22
staphylococous mutans (+)	7	21
Sterptococous pnemani (+)	10	20

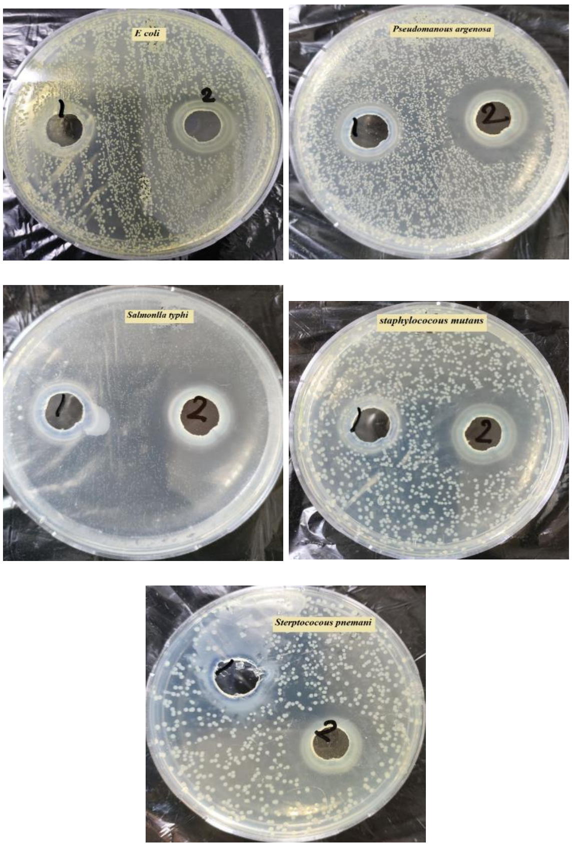

Fig. (5) Antibacterial efficiency of pure PMMA and PMMA/AgNPs depending on the diameter of inhibition zones for both types of pathogens

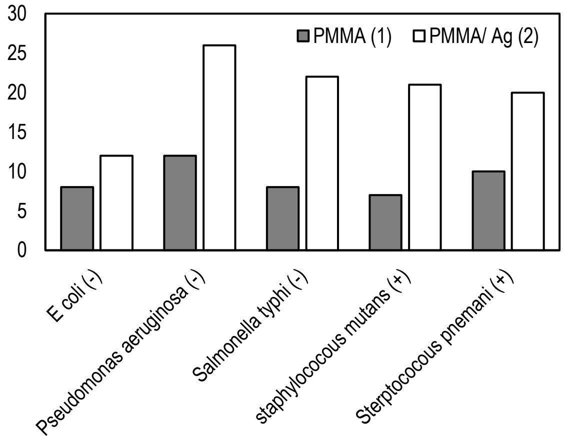

Fig. (6) Variation in the antibacterial efficiency of the prepared samples against Gram negative and Gram positive bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*, and *Salmonella typhi)* & (*staphylococcus mutans* and *Streptococcus pneumoniae*), respectively

4. Conclusion

Results revealed that only physical reactions between PMMA and AgNPs had occurred. Pure PMMA morphology presented groups of aggregates, while AgNPs were uniformly dispersed through PMMA powder. The absorption spectra are identical with slight shifts to the longer wavelengths for the sample of PMMA embedded AgNPs. Moreover, adding AgNPs to the pure PMMA sample demonstrated significant antibacterial activity against both Gram-negative and Gram-positive bacteria.

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