

Coating Silver Nanoparticles on Poly(methyl methacrylate) Chips and Spheres via Ultrasound Irradiation

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ABSTRACT: Ultrasound irradiation is used for anchoring silver nanoparticles with an average size of ~ 51 nm onto the surface of poly(methyl methacrylate) PMMA chips (2 mm diameter), and silver nanoparticles with an average size of ~ 20 nm onto the surface of the PMMA spheres (1–10 μm). The sonochemical reduction was carried out under argon atmosphere at room temperature. The silver nanoparticles were obtained by the irradiation of a mixture containing the PMMA, silver nitrate, ethylene glycol, ethanol, water, and 24% (wt) aqueous ammonia for 2 h, yielding a PMMA-silver composite. By controlling the atmosphere and

reaction conditions, we could achieve the deposition of silver nanoparticles onto the surface of poly(methyl methacrylate). The silver-deposited PMMA chips (loaded with 0.01–1.0 weight percent silver) were successfully homogenized in melt by extrusion and then injection molded into small, disc-shaped samples. These samples were analyzed with respect to their directional spectral optical properties in UV, VIS, and IR spectroscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2868–2876, 2007

Key words: sonochemistry; PMMA; silver nanoparticles

INTRODUCTION

New strategies for material fabrication are of fundamental importance in the advancement of science and technology. Nanomaterials form the building blocks for new bottom-up approaches to the assembly of materials for multipurpose use, and have received attention because of their intrinsic size-dependant properties and resulting applications.¹ The interest in nanocoatings relies mostly in the combination of the properties of the two (or more) materials involved, with emphasis on the fact that one of the materials (the shell) will determine the surface properties of the particles, while the other (the core) is completely encapsulated by the shell, so that although it does not contribute at all to the surface properties, it can be responsible for other (optical, catalytic, magnetic, etc.) properties of the system.² In view of the importance of the surface structure of nanoparticles on their properties, much effort has been invested to create new classes of materials through the modification of surface structure by anchoring metals/semiconductors (metal on semiconductor),³ semiconductors/semiconductors⁴ and semiconductors/metals.⁵ Recent achieve-

ments include the development of methods for the deposition of silver⁶ and gold⁷ nanoparticles on silica spheres, and for coating noble metal nanocrystals (Ag, Au, Pd, and Pt) on polystyrene spheres.⁸ The coated nanomaterials provide a very high surface area and possess chemical and physical properties that are distinct from those of both the bulk phase and individual molecules. More than 50 vol % of the atoms is associated with grain boundaries⁹ or interfacial boundaries when the grain is sufficiently small (~ 5 nm). The main benefit from coating nanoparticles on flat or spherical surfaces lies in preventing the spreading of the nanoparticles to the environment as powders. This is achieved by the bonding between the substrate and the coated nanoparticles. Thus, coated nanoparticles can become a safe way of moving nanomaterials across large distances. Supported catalysts are of special interest, because they allow for the fine dispersion and stabilization of small metallic particles,¹⁰ and provide access to a much larger number of catalytically active atoms¹¹ than those in the corresponding bulk metal.

A few methods have already been applied to prepare inorganic/poly(methyl methacrylate) (PMMA) composites. Singh et al.¹² used attritor milling followed by a hot pressing method for preparing Al/PMMA composites. Yang et al.¹³ reported on the preparation of nanocrystal and polymer composite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ /PMMA thin films by spin coating. The thin film of ion-conducting polymer electrolytes based on

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poly(methyl methacrylate) (PMMA) complexed with Li_2SO_4 were prepared using the solution casting technique, as reported by Uma et al.¹⁴

Sonochemical methods qualify for the deposition of nanomaterials on polymers because of their ability to combine the synthesis of various nanomaterials and their deposition on various substrates in a single operation. The additional advantage of this method is the ability to control the particle size of the product by varying the concentration of the precursors in the solution. Power ultrasound affects chemical changes as a result of cavitation phenomena involving the formation, growth, and implosive collapse of bubbles in liquid.¹⁵

Sonochemical phenomena have been exploited for the deposition of several different nanoparticles on a variety of substrates. Metallic (e.g., Ag, Au, Ni), metal oxides (e.g., MgO), and highly magnetic (air-stable Fe) nanoparticles were uniformly deposited on a variety of substrates.^{6,7,16,17} None of the previous reports used PMMA chips or spheres as a substrate.

The polyol reduction method has been used previously for the preparation of finely-dispersed silver nanoparticles. This process involves the reduction of soluble silver species by ethylene glycol or another polyol. When the reaction is carried out in the presence of the suitable protective agents (e.g., polyvinylalcohol, polyacrylate, PVP), the polymers can prevent the agglomeration of the silver nanoparticles at relatively low temperatures, 60–120°C.^{18,19}

The reason why we attempted to coat silver nanoparticles on PMMA is because PMMA is being used by the aviation industry for their windows. The possibility of coating PMMA with metallic silver nanoparticles might enable the transparency of the windows on the one hand, and the reflection of IR radiation on the other hand. Preventing the penetration of IR through the windows might keep the interior cooler than it would be without the nanosilver. In addition, the deposition of the nanosilver on the PMMA beads, and not on the finished window, allows the possibility of shaping the melted particles at a later stage into any desired structure.

To the best of our knowledge, this is the first report on the deposition of silver nanoparticles on poly(methyl methacrylate) chips and spheres using the polyol sonochemical method. The resulting sonochemically deposited silver–poly(methyl methacrylate) samples were characterized with X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, energy-dispersive X-ray analysis, high-resolution scanning electron microscopy, X-ray photoelectron spectroscopy, and the volumetric titration of the composite with KSCN according to the Foldgard method. In addition, the silver-deposited PMMA chips (loaded with 0.01–1.0 wt % silver) were successfully homogenized (homogenized means to achieve a uniform dis-

tribution of Ag nanoparticles) in melt by extrusion and then injection molded into small, disc-shaped samples. These samples were analyzed with respect to their directional spectral optical properties in UV, VIS, and IR spectroscopy.

EXPERIMENTAL

All reagents were of the highest commercially available purity, purchased from Aldrich and used without further purification. The poly(methyl methacrylate) chips of average grain size ~ 2 mm in diameter were supplied by the PALRAM Co., Ltd., Israel and used as obtained. The poly(methyl methacrylate) spheres of average size ~ 1 – 10 μm were purchased from G. Kisker GbR Produkte, Germany, and used as obtained.

In our first attempt, the reaction was conducted using the following starting materials: PMMA, water, ethylene glycol (EG), NH_4OH , and AgNO_3 . We could observe only a very small coating of the silver nanoparticles on the polymer (0.04 wt %). We attributed this failure to coat an appreciable amount of nanosilver on the PMMA to the hydrophobic nature of the PMMA surface,²⁰ which led to the rejection of the Ag^{+1} aqueous solution from approaching the PMMA surface. We therefore decided to add ethanol to the solution, so that it would bridge between the hydrophilic solution and the hydrophobic surface. Thus, the reaction mixture was composed of the following starting materials.

For silver deposition, 5 g of PMMA chips (or spheres), 0.02M solution of silver nitrate in 88 mL ethanol, 10 mL ethylene glycol (EG) and 2 mL water were added to a 100 mL sonication cell, which was attached to the sonicator horn. The sonication cell was wrapped by Al foil to avoid a photochemical reaction. The sonication was conducted under a flow of argon. Argon gas was also bubbled through the reaction mixture for 1 h prior to the sonication to expel dissolved oxygen/air. The sonication of the reaction mixture with high-intensity ultrasound radiation was carried out for 2 h by the direct immersion of the titanium horn (Sonics and Materials VCX600 sonifier, 20 kHz, 40 W/cm²) in a sonication cell under a flow of argon gas at 30°C. A 0.3 mL of 24 wt % aqueous ammonia was added drop wise to the reaction slurry during the first 10 min of sonication. The sonicator's intensity was determined calorimetrically. The temperature was controlled by a thermocouple and the constant addition of ice kept it at 30°C. The product was washed thoroughly (twice) with doubly distilled deoxygenated water and then dried in a vacuum for 12 h. The sonication lasted 2 h because the increasing the sonication time to 3 h did not add silver on the polymer surface. A control reaction in

which the same precursors were stirred at 30°C did not yield any product.

Characterization

The X-ray diffraction (XRD) patterns of the product were measured with a Bruker AXS D* Advance powder X-ray diffractometer (using Cu K α = 1.5418 Å radiation). The particle morphology and the nature of the noble metal nanoparticles' adherence to poly(methyl methacrylate) chips and spheres were studied with transmission electron microscopy (TEM) on a JEOL-JEM 100 SX microscope, working at 80 kV accelerating voltage. The poly(methyl methacrylate) chip sample was prepared by the epoxy embedding technique, ultramicrotome cutting. A small quantity of a sample of poly(methyl methacrylate) spheres was added to ethanol and sonicated for 20 min in a vial in a sonication bath. For TEM measurements, one or two drops of the nanoparticle solution were deposited on a carbon-coated copper grid. Keeping the grid on Whatman filter paper enabled the absorption of the droplet, dried for 5–10 min, and the evaporation of the excess solvent. The morphologies and nanostructure of the as-synthesized poly(methyl methacrylate) spheres were further characterized with a JEOL-2010 high-resolution transmission electron microscope (HR-TEM) using an accelerating voltage of 200 kV. SAEDS of one individual particle was conducted using a JEOL-2010 HRTEM model. The elemental composition of the material was analyzed by energy-dispersive X-ray analysis (EDX, JEOL-JSM 840 scanning electron microscope). The high-resolution scanning electron microscope (HR-SEM) images were obtained using a JEOL-JSN 7000F scanning electron microscope operating at 3-kV, 5-kV, and 15-kV accelerating voltage. The sample was placed on double-sided conducting carbon tape supported by a copper plate. The excess sample was removed by spraying air onto the sample holder. Poly(methyl methacrylate) sample surfaces were imaged by standard instrumentation and under standard conditions, with the exception that the samples were sputter-coated with gold prior to imaging. The energy state of the silver nanoparticles on poly(methyl methacrylate) chips and spheres was studied with X-ray photoelectron spectroscopy (XPS) on a KRATOS AXIS HS spectrometer using Al K α radiation. The C 1s (E_b = 285.0 eV) peak is chosen as a reference line for the calibration of the energy scale. The silver concentration on poly(methyl methacrylate) samples was determined by volumetric titration with KSCN according to the Foldgard method, after dissolving the samples in HNO₃ acid.²¹

Sample preparation

The directional optical properties of silver-loaded PMMA samples were investigated at EADS using an

FTIR-Analyzer (Perkin-Elmer, NIR/MIR) and an optical spectrometer using a graded mirror (Ocean Optics, UV-vis), covering a wavelength region from 200 nm up to 23 μ m. Preliminary tests revealed, that small quantities of silver nanoparticles loaded onto PMMA beads with 1, 0.5, 0.2, 0.03, and 0.02 wt % of Ag, must be homogenized in small processing equipment to achieve sufficiently good optical qualities.

The following steps were performed:

- Homogenizing the PMMA beads to get a homogeneous distribution of the silver in the PMMA using a high shear screw mixer.
- Injection molding the composite to obtain small plates (using a microinjector) for measuring the optical properties of coin-shaped plates of equal thickness.

The homogenizing procedure was conducted with about 8 g of the beads, which were placed in the mixer at 240°C. Filling time was about 3 min. The rotation speed of the screw was 60 rpm and the mixing time was about 3 min. The yield for homogenized PMMA was 80–90%. After each process the mixer was disassembled and cleaned. In a second step, the homogenized product was followed by the injection molding process combined with a microinjector: 1.5 g of the homogenized PMMA was melted in a cylinder at 225°C. After 4 min, the PMMA was injected into a mold at 70°C using a pneumatically-driven punch. After cooling for 10 min the PMMA disk-shaped samples were removed from the mold. The sample was prepared by diluting the PMMA containing 1 wt % silver nanoparticles with pure PMMA beads.

RESULTS AND DISCUSSION

X-ray diffraction (XRD)

(a) The XRD patterns (Fig. 1) of sonochemically deposited Ag nanoparticles on poly(methyl methacrylate) chips; (b) Ag nanoparticles on poly(methyl methacrylate) spheres that were measured to obtain information about the nature of the product, its crystal structure (the interatomic distance and angle), its purity, etc. The crystalline nature of the as-synthesized product, (a) Ag (PMMA chips), and (b) Ag (PMMA spheres) nanoparticles deposited sonochemically on poly(methyl methacrylate) is demonstrated by the diffraction peaks that match a face-centered cubic (fcc) phase of Ag (PDF: 4-783). The peaks at 2θ = 38.03, 44.23, 64.39, and 77.32° are assigned to the (111), (200), (220), and (311) reflection lines, respectively, of fcc Ag particles. The silver nanoparticles deposited on poly(methyl methacrylate) chips and spheres via ultrasound irradiation yielded nanocrystalline Ag particles on the surface of PMMA and will

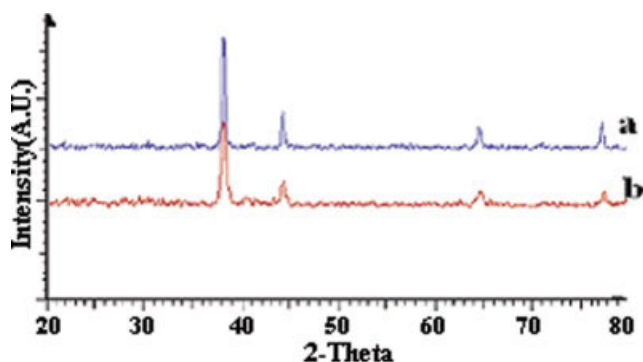


Figure 1 XRD patterns of (a) Ag (PMMA chips), (b) Ag (PMMA spheres) nanoparticles deposited on poly(methyl methacrylate) sonochemically. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

be referred to as as-synthesized materials. According to the Scherrer formula, silver nanoparticles with an average size of ~ 51 nm were deposited onto the surface of PMMA chips. The size of the particles anchored onto the surface of PMMA spheres were ~ 20 nm, which is in good agreement with the HR-SEM measurements. No peaks characteristic of any impurities were detected.

Transmission electron microscopy (TEM)

The TEM micrographs depict: (a) Ag nanoparticles penetrating PMMA chips with the aid of power ultrasound and prepared for the measurements by the ultramicrotome cutting technique, (b) Ag nanoparticles deposited on a PMMA substrate by anchoring to the surface of 1–10 μm spheres. Both images are shown in Figure 2. Figure 2(a) shows the transmission electron micrograph of the silver nanoparticles with an average size of ~ 20 nm and a spherical nature,

penetrating the PMMA chips. Figure 2(b) shows the transmission electron micrograph of the silver nanoparticles with an average size of ~ 20 nm and a spherical shape, anchored to the surface of the PMMA spheres with the aid of power ultrasound. This leads to the conclusion that ultrasonic radiation facilitates the penetration of spherical nanosilver particles into PMMA chip substrates and brings about the deposition of spherical nanosilver particles on the surface of 1–10 μm size PMMA spheres.

High-resolution transmission electron microscopy (HR-TEM)

Additional evidence for the crystalline nature of the as-synthesized silver nanoparticles on a poly(methyl methacrylate) sphere sample is provided by conducting HR-TEM measurements. Indeed, the coated Ag particles showed interlayer spacing and an electron diffraction (ED) pattern that was evidence of the crystalline nature of the particles. The image [Fig. 3(a)] is recorded along the [111] zone. It illustrates the perfect arrangement of the atomic layers and the lack of defects. The measured distance between these (111) lattice planes is 0.2386 nm, which is very close to the distance between the planes reported in the literature (0.2359 nm) for the fcc phase (PDF: 4-783) of Ag. Figure 3(b) demonstrates the fast Fourier transform (FFT) image of the coated Ag particle, evidence of the crystalline nature of coated silver nanoparticles. The selected area ED [Fig. 3(c)] was measured for the Ag particle depicted in Figure 3(a). The obtained ED pattern is assigned to the respective planes of Ag. The SAEDS results related to the silver nanoparticles on poly(methyl methacrylate) spheres are presented in Figure 4, which depicts the SAEDS of the sample imaged in Figure 3(a). It shows the presence of carbon and Ag and the absence of any impurity. The origin

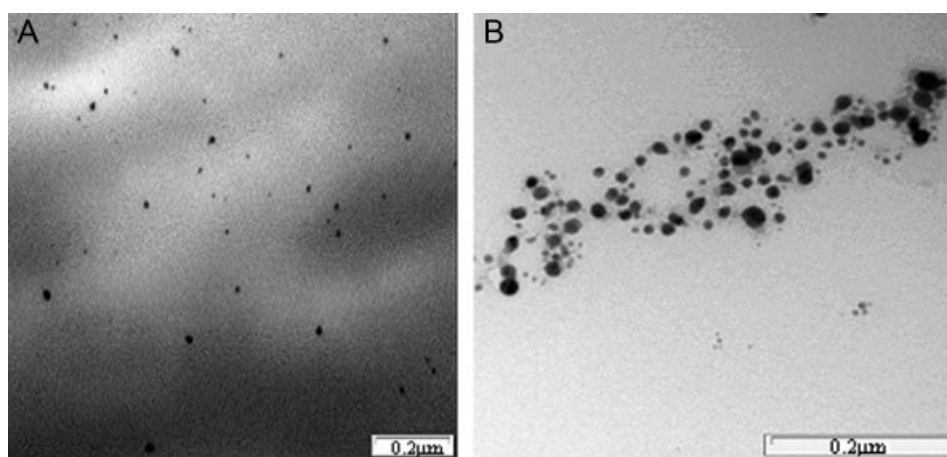


Figure 2 Low-resolution transmission electron micrographs of (a) Ag (inserted into PMMA chips), (b) Ag (deposited on PMMA spheres) nanoparticles.

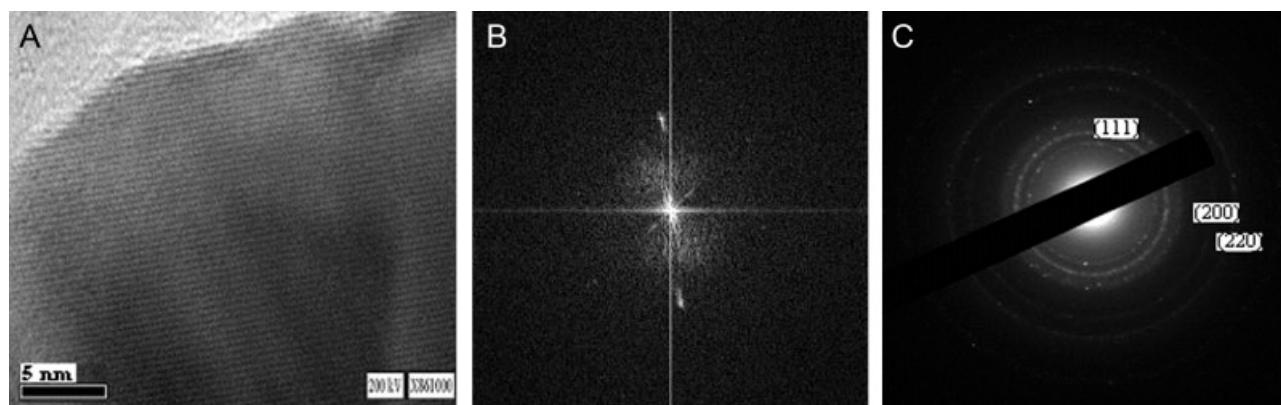


Figure 3 HR-TEM of (a) the crystalline nature and interlayer spacing between the Ag planes, (111) (b) the crystalline nature of an Ag nanoparticle on the surface of PMMA spheres, and (c) the ED obtained from the silver nanoparticles.

of the Cu peak is from the Cu grid used for HR-TEM measurements. These results also confirm the presence of coated pure Ag particles.

Energy-dispersive X-ray analysis (EDX)

The presence of silver in the coated poly(methyl methacrylate) chips and spheres was examined by EDX measurements. The EDX spectrum (Fig. 5) was also used to obtain a quantitative estimate of the Ag. The silver content on poly(methyl methacrylate) chips and spheres was about 1 wt %. No evidence for the involvement of the Ti sonotrode in a so called “electrochemical-like” reaction was found in the SEM-EDX or the SAEDS spectra.

High-resolution scanning electron microscopy (HR-SEM)

The HR-SEM micrograph of the Ag nanoparticles on poly(methyl methacrylate) chips (a), and the Ag nanoparticles on poly(methyl methacrylate) spheres

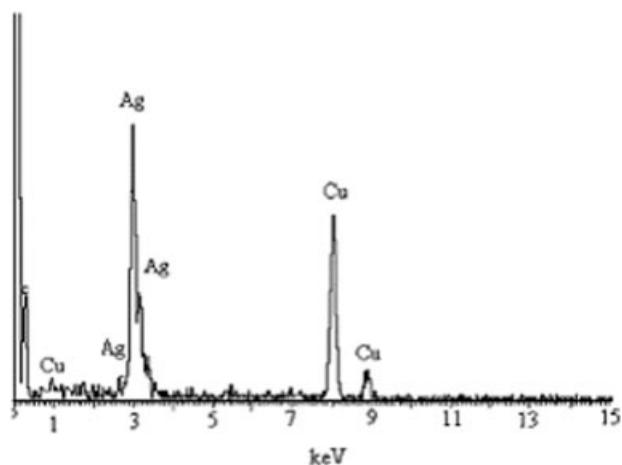


Figure 4 SAEDS results of Ag on PMMA spheres.

(b,c), are shown in Figure 6. Figure 6(a) shows the HR-SEM micrograph of the silver nanoparticles with an average size of ~ 51 nm deposited on the surface of poly(methyl methacrylate) chips with the aid of power ultrasound. Figures 6(b,c) show the HR-SEM micrographs of the silver nanoparticles with an average size of ~ 20 nm deposited on the surface of the poly(methyl methacrylate) spheres. This result is in good agreement with the TEM measurements of Ag nanoparticles on PMMA spheres.

X-ray photoelectron spectroscopy (XPS)

The energy state of the silver nanoparticles on poly(methyl methacrylate) chips and spheres was studied with XPS (Fig. 7). The XPS spectrum of the Ag nanoparticles on poly(methyl methacrylate) chips (a), and Ag nanoparticles on poly(methyl methacrylate) spheres (b), shows that silver on poly(methyl methacrylate) samples is in a zero oxidation state. The peak observed in the energy region of Ag 3d transition is symmetric, and centered at 368.6 eV that corresponds to Ag^0 . No evidence for the existence of silver + 1 ions is obtained.

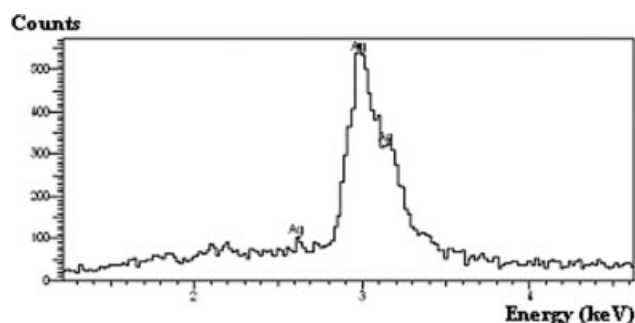


Figure 5 EDX patterns of Ag (PMMA chips) and Ag (PMMA spheres) nanoparticles deposited on poly(methyl methacrylate) sonochemically.

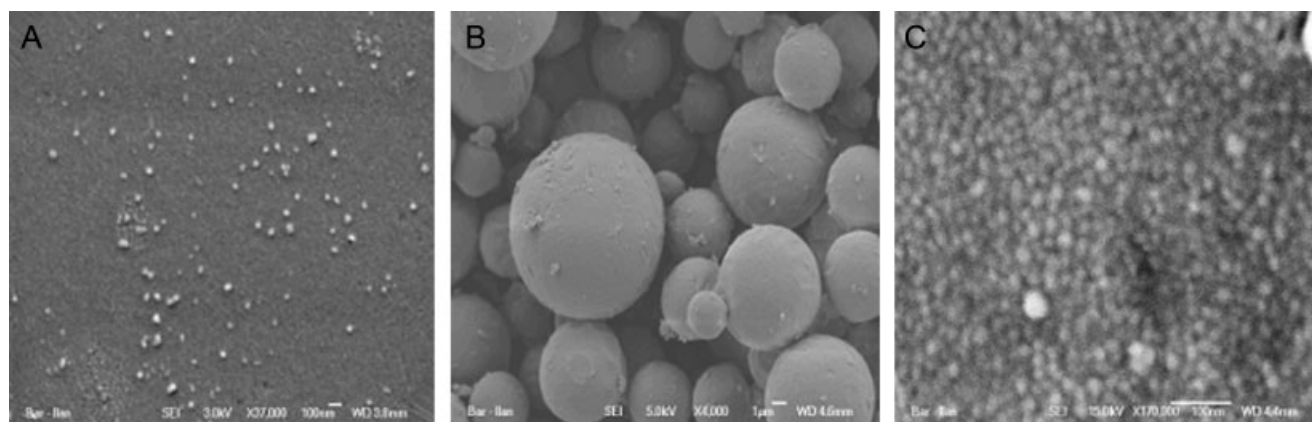


Figure 6 Scanning electron micrographs of (a) Ag nanoparticles on poly(methyl methacrylate) chips, (b, c) Ag nanoparticles on poly(methyl methacrylate) spheres.

Volumetric titration with KSCN according to the Foldgard method

Volumetric titration with KSCN according to the Foldgard method, after dissolving the samples in HNO₃ acid, was used to obtain a quantitative estimate of the Ag concentration on poly(methyl methacrylate) chips and spheres. The silver content on poly(methyl methacrylate) chips and spheres was about 1 wt %.

OPTICAL PROPERTIES OF PMMA DOPED WITH SILVER NANOPARTICLES

Spectral transmittance in the VIS/NIR/MIR

A decrease in the transmittance, with an increase in the silver content, was observed in the visible region as well as in the NIR, as shown in Figure 8. It is remarkable that 0.03% of the silver nanoparticles was sufficient to reduce the spectral transmittance of PMMA by about 10%. This can be rationalized based

on the large surface area of the absorbing silver nanoparticles. Scattering effects can be excluded due to the much smaller size of the silver nanoparticles, in comparison with the wavelengths of the radiated spectra from UV/VIS/NIR and MIR sources.

Spectral transmittance of PMMA in the UV-vis

The spectral transmittance of the sample with 0% Ag presents the pure PMMA, with high transmittance in the VIS and NIR range and high absorption between 250 and 370 nm (Fig. 9). The functional relationship between transmittance and the silver nanoparticle concentration is the same in the NIR and MIR regions (Fig. 8).

As in the NIR/MIR, the sample containing 0.02% Ag reveals exceptional behavior as its transmittance is below that of the sample with 0.04% Ag (see discussion in the Sample Preparation section). With a filling of 0.5% and above, the sensitivity of the equipment

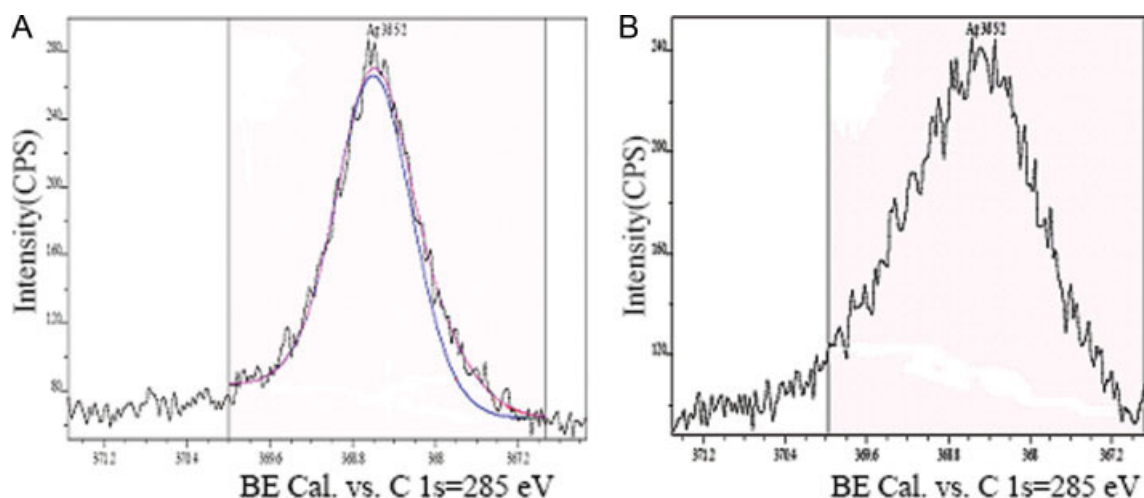


Figure 7 XPS spectrum of (a) Ag nanoparticles on poly(methyl methacrylate) chips, (b) Ag nanoparticles on poly(methyl methacrylate) spheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

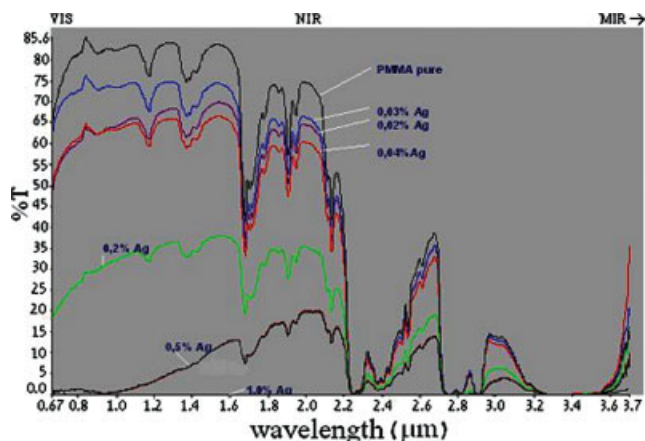


Figure 8 Spectral transmittance of PMMA in the VIS/NIR loaded with silver nanoparticles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was too low to detect a transmittance signal in the UV/VIS.

Spectral reflectance of silver doped PMMA

To probe whether the above results are related to the surface or to the bulk properties, the reflectance was measured in the VIS/NIR (Figs. 10 and 11). As expected, the reflection degree of the samples is low, below 10% (Fig. 10).

Figure 10 illustrates that the reflection degree of the sample ranges between 1.5 and 8% with no significant dependence on the silver nanoparticles' weight. The difference between the samples is between 3.5 and 5%.

Differences of this order of magnitude can be attributed to the roughness of the sample surface (scattering) or to the adjustment of the samples because the FTIR systems used measures the directional spectral properties.

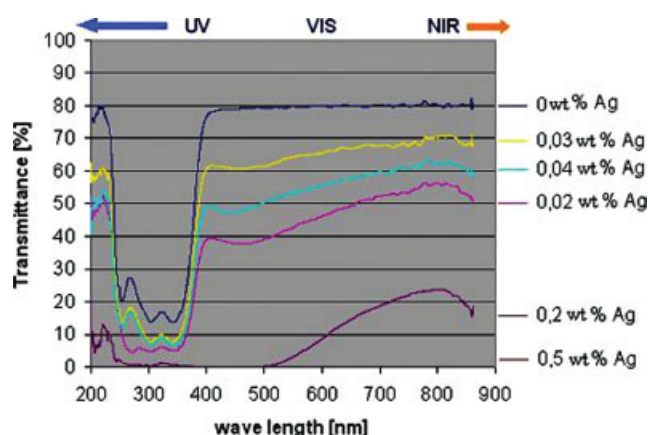


Figure 9 Spectral transmittance of PMMA samples filled with silver nanoparticles in the UV-vis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

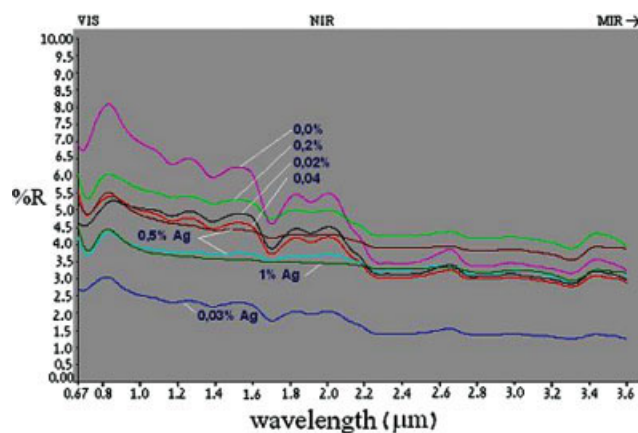


Figure 10 Spectral reflectance of PMMA, filled with silver nanoparticles in the VIS, NIR, and MIR, 0.7–3.6 μm . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the UV-vis, (200–800 nm), the reflectance is on the average about 5% (Fig. 11). The transmittance of pristine PMMA in the 400–800 nm range (VIS) is 80% and less than 80% for the silver-doped samples (Fig. 9). This means that there is an increase in the absorbance upon the adding of silver nanoparticles. The same tendencies will be found in the NIR/MIR, (cf. Figs. 8 and 10).

Proposed sonochemical mechanism for the deposition of Ag on poly(methyl methacrylate) chips and spheres

The sonochemical reactions leading to the formation of silver nanoparticles are the manifestation of the polyol-assisted reduction method. It is known that silver salts are easily reducible by any polyol solvent, for example, ethylene glycol, by regular heating for a few hours.²²

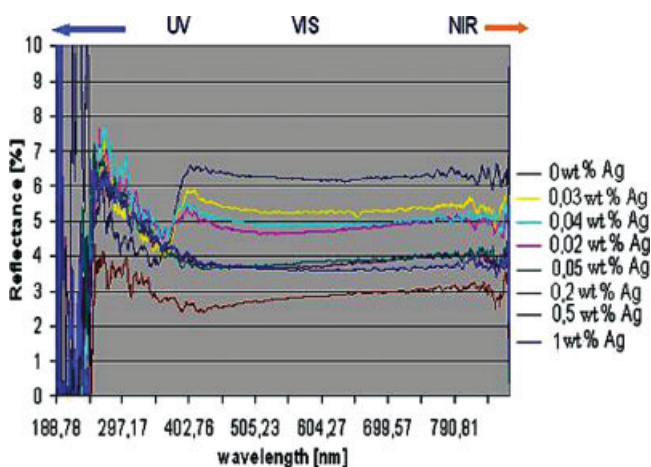


Figure 11 Spectral reflectance of PMMA filled with silver nanoparticles in the UV-vis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The mechanism by which the Ag nanoparticles are bonded to the poly(methyl methacrylate) surface is related to the microjets and shock waves created near solid surfaces after the collapse of the bubble.²³ These jets, which cause the sintering of micrometer-sized metallic particles,²⁴ push the nanoparticles toward the poly(methyl methacrylate) surface at very high speeds. When nanoparticles hit the poly(methyl methacrylate) surface, sintering of the particles and/or interparticle collision between PMMA and Ag particles changes the surface morphology and reactivity, resulting finally in the coating of these particles. It is interesting to note that the products of many sonochemical reactions are in the form of amorphous nanoparticles. The reason for the amorphicity of the products is related to the high cooling rates ($>10^{11}$ K/s) obtained during the collapse of the bubble, which does not allow the products to organize and crystallize. These high cooling rates result from the fast collapse that takes place in less than 1 ns.²⁵ The mechanism of coating Ag nanoparticles on poly(methyl methacrylate) chips and spheres might be different, because it leads to the formation of crystalline products, as in the case of coating silver nanoparticles on polystyrene spheres.⁸ We believe that this is due to differences in the surfaces and the chemical interactions between the particles. As was mentioned previously,^{6,7} chemical interactions between silica and Ag lead to the formation of a chemical bond between SiO₂ and Ag due to the reactive surface silanols, which led to the production of an amorphous product after sonication. On the other hand, when we used the poly(methyl methacrylate) chips and spheres as substrates, chemical interactions between Ag and poly(methyl methacrylate) are different. During the sonochemical reaction, poly(methyl methacrylate) does not form chemical bonds with the silver but rather is coated due to the melting or softening of the polymer surface as a result of the particles and/or interparticle collisions between the poly(methyl methacrylate) surface and Ag. The strong collision of the particle with the polymeric surface pushes the particles into the polymer body, and thus, the particle "diffuse" partially in the polymer. Indeed, 20 nm silver particles were found at the center of the polymer upon its microtoming. These collisions also led to a better heat exchange between the polymer and the metallic particle. Thus, the local temperature is raised and reaches the crystallization temperature. In the coating of the ceramics, as with silica,⁶ there is no softening of the outer ceramic layers. The contact time in the silica coating is shorter, which does not allow the local temperature to rise to that of the crystallization temperature. Another two possible explanations for the formation of crystalline products are as follows: (1) poly(methyl methacrylate), unlike silica, is capable of plastic deformation at the impact site. This deforma-

tion carries away sufficient heat so that the cooling rate is not so high and, consequently, crystallization can occur. The formation of amorphous products in sonochemistry is due to the fast cooling rates. In the current case this situation does not occur.

(2) Another possibility is that the poly(methyl methacrylate) surface functions, through chemical interaction as a kind of templating site for the initial deposition of Ag particles. Energy loss into the polymer matrix would allow for nanocrystalline formation. The remaining Ag atoms in the impact site during the relatively short cooling time then use the templating interaction as a nucleating site for further growth.⁸

CONCLUSIONS

Silver nanoparticles were deposited (with an average size of ~ 51) nm and penetrated (with an average size of ~ 20 nm) by ultrasound onto the surface of poly(methyl methacrylate) chips. Moreover, silver nanoparticles with an average size of ~ 20 nm were deposited by ultrasound onto the surface of poly(methyl methacrylate) spheres. The presence of silver nanoparticles on the poly(methyl methacrylate) was evidenced by X-ray diffraction, high-resolution transmission electron microscopy, energy-dispersive X-ray analysis, and X-ray photoelectron spectroscopy. The morphology and the nature of adherence of the silver coated on poly(methyl methacrylate) were studied with transmission electron microscopy and high-resolution scanning electron microscopy. The advantage of the process described in this report is that it is a simple, efficient, one-step synthesis that produces a uniform coating of silver nanoparticles on poly(methyl methacrylate) chips and spheres. The period of sonication is only 120 min. As far as we know, this is first complete study of the coating of poly(methyl methacrylate) chips and spheres with silver nanoparticles. The results of the spectral optical characteristics, particularly evident in the UV/VIS, show an increasing absorption with an increase in the filling degree of silver nanoparticles at a very low weight percent.

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