# Synthesis and characterization of silver nanoparticle nanocomposite thin films with thermally induced surface morphology changes

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## ARTICLE INFO

## ABSTRACT

This work describes the preparation of thin film nanocomposites of silver nanoparticles (AgNPs) embedded in a copolymer matrix of poly(ethylene glycol) diacrylate (PEGDA) and triethylene glycol dimethacrylate (TEGDMA). The films were produced by UV-induced chemical reduction of $Ag^+$ ions using (1,5-cyclooctadiene)(hexafluoro-acetylacetonate)silver(I) as Ag precursor, together with the photopolymerization of PEGDA and TEGDMA using 2-hydroxy-2-methylpropiophenone as photoinitiator. The average size of AgNPs increased from ca. 6 nm to ca. 15 nm with 1 h heating at 180 °C because of the nanoparticle coalescence, which causes an important change on the surface morphology. Small details were observed on the nanocomposite surface and became more evident on the heated film, as demonstrated by SEM. The morphology change is the result of migration of AgNPs towards the surface and was very clear owing to thin thickness of the nanocomposite (ca. 30 μm). This nanoparticle relocation was also observed by TEM. This work offers a material that can provide important applications in which surface properties are relevant such as sensors and actuators.

## 1. Introduction

The development of nanoparticles (NPs) to prepare nanocomposites has been received considerable attention. Intrinsic properties of a nanoparticle are strongly dependent on the size, shape, composition, crystallinity, and morphology. Thus, the ideal method of nanoparticle synthesis would be one that allows designing a material with specific properties [1].

Nanocomposite materials consist of metal NPs embedded in a bulk such as ceramics, glasses, metals or polymers [2]. If compared with other substrates, the polymeric supports offer some advantages, such as flexibility and elasticity [3]. The formation of metallic films on polymeric substrates has great potential in the important fields of science and technology, such as, microelectronic, optical, biomedical, and space materials [4,5].

Films with nanometric-sized metallic particles can show excitation of surface plasmon resonance (SPR). Spectral features of SPR, such as, the resonance wavelength, and bandwidth are dependent on nanoparticle size [2,6]. For this reason, the control of this parameter is very important on obtaining metallized films. Traditional methods used to prepare metallized films include chemical vapor deposition, sputter technology, and lamination. However, metallization of polymeric films by these methods involves two or more stages [7]. Alternative approaches for synthesis of NPs may be based on ATRP [8] or photochemical reduction [5,9]. In order to have a control on the particle growth polymers, some stabilizing reagents based on copolymers can be efficiently used, such as poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), and polyglycerol-block-poly(acrylic acid) [4,10].

Silver nanoparticles (AgNPs) have been studied due to their optical, catalytic, electronic, antimicrobial and thermal properties [11,12]. Among the noble metals, AgNPs exhibit efficiency of plasmon excitation and can be synthesized by photochemical reduction [13,14].

This work aimed at preparing thin film nanocomposites of AgNPs. The nanoparticles were prepared by photochemical reduction of Ag using (1,5-cyclooctadiene)(hexafluoroacetylacetonato)silver(I) (Ag[(COD)(HFA)]) as metallic precursor. To control the nanoparticle size, the photochemical reduction was performed together with the photopolymerization of poly(ethylene glycol) diacrylate and triethylene glycol dimethacrylate, which were used as stabilizing agent.

## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA) $M_w = 600$ g mol$^{-1}$ and triethylene glycol dimethacrylate (TEGDMA) $M_w = 286$ g mol$^{-1}$ were purchased from Sartomer Company, Inc. (1,5-cyclooctadiene) (hexafluoro-acetylacetonate)silver(I) (Ag[(COD)(HFA)]) (Ag precursor) and 2-hydroxy-2-methylpropiophenone (photoinitiator) were purchased from Sigma-Aldrich. All materials were used without any further purification.

### 2.2. Synthesis of film and nanocomposites

The silver precursor solution was prepared by adding 2 mL of a 1:1 PEGDA/TEGDMA solution to Ag[(COD)(HFA)] precursor while stirring. The formed mixtures were added to 0.5% (v/v) 2-hydroxy-2-methylpropiophenone under stirring. The resulting solutions were brought between square glass plates separated by a rubber gasket and left to react under UV irradiation of a low-pressure Hg vapor lamp 250 W for 10 min. The distance from the lamp to the sample was 10 cm. After photopolymerization, the constructed films were heated at 80 °C for 1 h under ambient conditions. The film thickness was measured using a digital micrometer (Digimatic Micrometer Mitutoyo, model IP65, resolution of 1.0 μm). Each film thickness value was averaged from five measures. For all samples, the percentage error was lower than 5%. The average thickness of the films was 30 μm.

To identify the different compositions of the film and nanocomposites, the following notation was used to label the samples: film for PEGDA-co-TEGDMA film and (x)-nanocomposite for PEGDA-co-TEGDMA/Ag film; where x is concentration of Ag precursor. For example, nanocomposite with 1.75 mg mL$^{-1}$ is labeled as (1.75)-nanocomposite, and so on.

### 2.3. Characterizations

Surface Plasmon Resonance (SPR) was obtained using UV–vis spectrophotometer Biochrom model Libra S12. FTIR spectra were recorded in a Bomen FT-IR model MB100 spectrometer. Powdered samples were prepared into pellets with KBr. A total of 128 scans were run for each spectrum to reach the resolution of 4 cm$^{-1}$. Thermogravimetric analysis (TGA) was made in a Shimadzu model TGA-50. Samples of approximately 6 mg were weighed into open platinum pans. The nitrogen flow was 50 mL min$^{-1}$ at a heating rate of 10 °C min$^{-1}$, starting from room temperature up to 600 °C.

Morphological characteristics on surface of the obtained films were analyzed by a scanning electron microscope (SEM, Shimadzu, model SS 550 Superscan). Transmission electron microscope (TEM) images were made on a ZEISS model CEM-902. Changes on the crystallinity degree were identified by XRD using a Shimadzu D6000. The diffractograms were obtained in the following conditions: copper tube with Kα radiation of 1.5406 Å, $2\theta = 30$–$80°$, voltage 40 kV, and current of 30 mA.

## 3. Results and discussions

Fig. 1(I) shows the FTIR spectra of photoinitiator, PEGDA and TEGDMA (above on the left). This spectrum was obtained in order to track the progress of the photopolymerization. Both of the monomers show a strong absorption band in the carbonyl region, owing to the C=O stretching vibration (1717 cm$^{-1}$), and the same vibration of photoinitiator (C=O stretching) was observed at 1670 cm$^{-1}$. The absorption bands of vinyl groups (C=C) of the monomers were observed at 1636 cm$^{-1}$ [15]. Moreover, in the
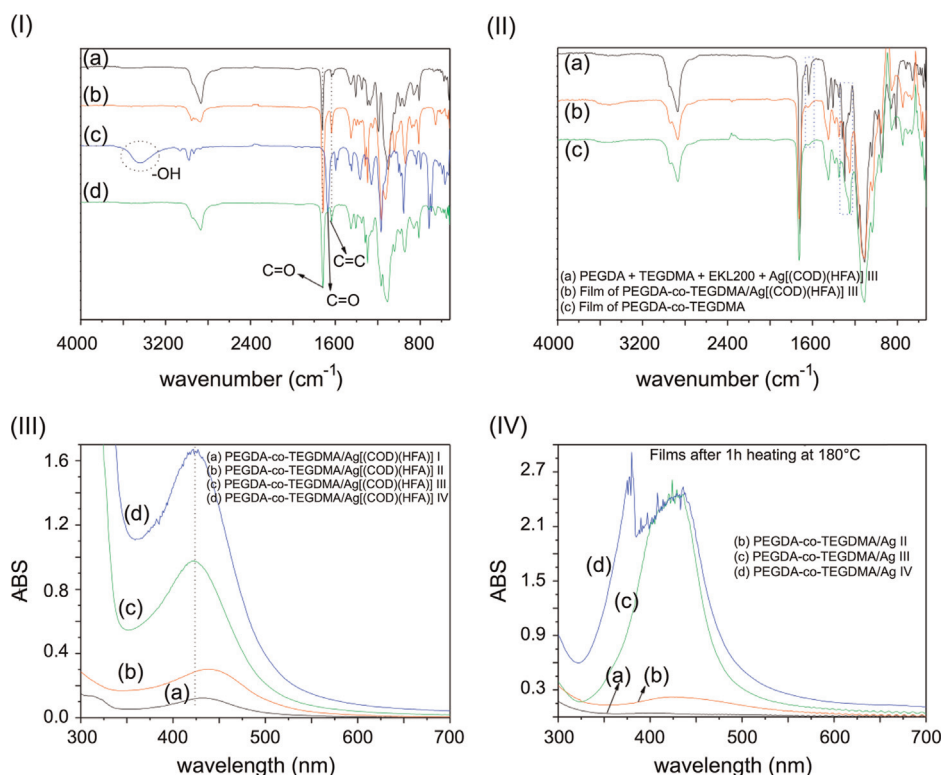


**Fig. 1.** (I) FTIR spectra of monomer PEGDA (a), TEGDMA (b), photoinitiatior (c) and mixture of PEGDA+TEGDMA+photoinitiator (d). (II) FTIR spectra of mixture PEGDA+TEGDMA+photoinitiator with 30 mg mL$^{-1}$ Ag precursor (a), nanocomposite with 60 mg mL$^{-1}$ Ag precursor (b) and film (c). (III, IV) UV–vis spectra of nanocomposites with different amounts of Ag precursor. (III) Before heating: 1.75 mg mL$^{-1}$ (a), 7.5 mg mL$^{-1}$ (b), 30 g mL$^{-1}$ (c) and 60 g mL$^{-1}$(d). (IV) After 1 h heating at 180 °C heating: (a) 1.75 mg mL$^{-1}$, (b) 7.5 mg mL$^{-1}$, (c) 30 mg mL$^{-1}$ and (d) 60 g mL$^{-1}$.