



Enhanced degree of polymerization of methacrylate and epoxy resins by plasmonic heating of embedded silver nanoparticles



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ARTICLE INFO

Article history:

Received 4 September 2014

Received in revised form 9 March 2015

Accepted 27 June 2015

Available online 25 July 2015

Keywords:

Silver nanoparticles

Plasmonic heating

Post-curing

Photopolymerization

ABSTRACT

Silver nanoparticles (Ag NPs) were synthesized in situ in light-cured methacrylate and epoxy resins. The UV–vis spectra of the colloidal suspensions displayed an intense surface plasmon resonance band in the wavelength range 350–550 nm with an absorption peak at 415 nm. Suspensions containing different amounts of Ag NPs were photopolymerized by UV irradiation. Cylindrical specimens of the resulting nanocomposites (10-mm diameter × 1-mm thickness) were irradiated with a 420-nm LED source while the temperature evolution was monitored. The heat released by the Ag NPs under irradiation at the plasmon-resonant wavelength increases the temperature of the surrounding medium. The temperature reached in a methacrylate-based nanocomposite containing 0.03 wt% Ag NPs was 100 °C after 250 s irradiation. This increases the mobility of the reaction environment and, consequently, induces the polymerization of the unreacted monomer. Moreover, the degree of polymerization of films prepared from an epoxy resin containing 0.02 wt% Ag NPs was 35%, and then increased up to 75% after 10 min irradiation at 420 nm. In practice, the post-curing of partially cured polymers is commonly carried out by thermal treatments. Results obtained in this study show that the use of a small amount of Ag NPs, as controlled sources of heat under light irradiation, is an attractive strategy to post cure methacrylate and epoxy resins in the absence of external heating.

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1. Introduction

Noble metal nanoparticles (NPs) can efficiently release heat under light irradiation [1–5]. The electromagnetic field strongly drives mobile carriers inside the NPs and the energy gained by these carriers is turned into heat. The heat then diffuses away from the NPs and leads to an elevated temperature of the surrounding medium. Heat generation in noble metal NPs induced by light absorption has long been considered only as a side effect, which had to be minimized. However, in the emerging field of thermo-plasmonics the focus has shifted toward the design of optically induced nanoscale thermal sources. This opens up a new set of applications in nanotechnology and gives rise to the new promising field of plasmonic heating [4,5]. The number of potential applications of plasmonic heating is becoming increasingly important in areas of nanotechnology such as chemical catalysis [6], photo thermal cancer therapy [7], and materials processing [8–10]. Most of the research on plasmonic heating of noble NPs has been carried out on gold nanoparticles under laser irradiation. However, recent studies

have shown that silver nanoparticles irradiated by light-emitting diodes (LEDs) are an interesting alternative [8,9]. Silver NPs have the advantages of possessing a stronger plasmonic heating effect [11], being cheaper than gold nanoparticles. In addition, the surface plasmon resonance of the Ag NPs can be controlled by changing the shape of the particles. Ag NPs with different shapes, such as spheres, pentagons, triangles, etc. can be easily synthesized [12]. Spherical Ag NPs have a surface plasmon wavelength range between 400 and 450 nm, while the pentagon ones a 500–550 nm range and the triangular ones 650–700 nm [12]. As light with a longer wavelength generally has a lower price, longer wavelength LED lights should be considered from the economical point of view.

It is well known that the polymerization of methacrylate [13] and acrylate [14] monomers in the absence of external heating leads to glassy polymers in which only some of the available double bonds are reacted. As the polymerization proceeds, vitrification effects begin to limit the mobility of even small molecules such as the monomer or primary initiator radicals. Before completion of conversion, the vitrification phenomenon decelerates the reaction to a hardly perceptible rate. As shown by Kloosterboer and Lijten [15] the room temperature polymerization of the unreacted monomer proceed slowly for a long period. The presence of non-reacted monomer has a plasticizing effect on the polymer, thereby

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altering its physical and mechanical properties. In practice, the plasticizing effect of the non-reacted monomer on the mechanical behavior of the polymer is reduced by post-curing treatments. Heating the partially cured polymer increases the mobility of the reaction environment (i.e. monomer, radical and polymer) and consequently increases the degree of polymerization. The post-curing of incompletely cured polymers is commonly performed by thermal treatments. This study was carried out in order to explore the possibility of post-curing methacrylate and epoxy resins via plasmonic heating of embedded Ag NPs. This treatment has the advantages that require less equipment space and has lower energy consumption with respect to thermally-driven processes carried out in ovens. Thus, it can be considered more environmental friendly than other post-curing methods.

2. Experimental

2.1. Materials

Silver nitrate (AgNO_3 , $\geq 99\%$, Aldrich) and absolute ethanol (Merck) were employed as received. The iodonium salt *p*-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) (OMAN 071, 96%) was from Gelest Inc., Philadelphia, USA. Benzoyl peroxide (BPO, $\geq 97\%$), 1-phenyl-1,2-propanedione (PPD, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), ethyl-4-dimethylaminobenzoate (EDMAB, 99%) and 2,6-di-*tert*-butyl-*p*-cresol (BHT, $\geq 99\%$) were from Sigma Aldrich, USA.

The methacrylate resins used for this study were 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxo)phenyl]-propane (BisGMA, 90%, from Esstech, Essington, PA), 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (BisEMA, 98%, from Esstech, Essington, PA), and triethylene glycol dimethacrylate (TEGDMA, 95%, from Aldrich, USA). BisTEG stands for a blend 70:30 BisGMA/TEGDMA. The epoxy resin was 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (UVR) (UVR-6110, 95%, Dow Chemical Co., Midland Michigan, USA). The resins were used without further purification. The methacrylate resins contain hydroquinone (HQ), hydroquinone methyl ether (MEHQ) and 2,6-di-*tert*-butyl-*p*-cresol (BHT) as inhibitors to prevent premature polymerization during storage. BisEMA contains 300 ppm MEHQ and 200 ppm BHT. BisTEG contains 400 ppm MEHQ, 5 ppm HQ, and 200 ppm BHT. Different amounts of each inhibitor are added to the methacrylate resins by the manufacturer in order to optimize the inhibition during storage and to minimize the increase in color produced by the inhibitors (yellowing). In all cases the Ag^+ /reducer mol ratio equal to 1 was maintained by adding the required amount of BHT. Similarly, BHT at a mol fraction Ag^+ /BHT equal to 1 was added to formulations prepared from UVR. All materials were used as received. The structures of the resins and photoinitiators used are shown in Fig. 1.

The methacrylate resins were activated for UV light (365 nm) polymerization by the addition of 0.5 wt% DMPA. The epoxy resin containing 2 wt% iodonium salt (Ph_2ISbF_6) was activated for visible light (420 nm) polymerization by the addition of 1 wt% PPD and 1 wt% EDMAB. The light sources used were assembled from light emitting diodes (LED) with its irradiance centered at 365 nm (OTLH-0480-UV, Optotech) or 420 nm (LHUV-0420-0650, Luxeon-Philips). The intensity of the 365-nm LED was 175 mW. The intensity of the 420-nm LED was set at two different values by varying the electrical voltage through the semiconductor: 200 and 1000 mW.

2.2. Preparation of suspensions of Ag NPs

Dispersions of colloidal silver particles were obtained by reduction of silver nitrate in methacrylate (BisEMA and BisTEG) and

epoxy (UVR) resins in the absence of protective agents. AgNO_3 (0.126 g) was dissolved in 10 ml of absolute ethanol (solution A). The solution was stirred at room temperature until complete dissolution of the silver nitrate was achieved. Solution A was diluted with ethanol to volume ratio 1:5 (solution B) or 1:20 (solution C). Suspensions having different silver content were prepared by mixing 1 ml of the corresponding solution of AgNO_3 (A, B or C) with the appropriate amount of methacrylate or epoxy resin. The silver proportion in the resins was varied in the ranges: 3000–5000 ppm using solution A, 400–2000 ppm using solution B, and 50–300 ppm using solution C. In all cases, the required amount of ethanol was added in order to have a resin/ethanol mass ratio equal to 2. The reaction was carried out in glass tubes placed in a thermostat held at 70 °C allowing continuous evaporation of volatiles. The reaction was allowed to proceed for ~24 h in order to ensure complete evaporation of the ethanol. Silver cations were reduced by HQ, MEHQ and BHT present in the methacrylate resins.

2.3. Methods of characterization

The absorption spectra of dispersions of silver nanoparticles in methacrylate and epoxy resins were measured with an UV-vis spectrophotometer 1601 PC Shimadzu at room temperature (20 ± 2 °C). The dispersions were contained in thin cells (~0.5 mm) constructed from two quartz microscope slides separated by a PTFE gasket. An identical cell containing the resin was used as the reference.

The size distribution of silver NPs was determined using a Philips CM-12 transmission electron microscope (TEM) operated at an accelerating voltage of 100 kV. In order to obtain good quality images, the suspensions of silver nanoparticles in the resins were diluted with ethanol (1 drop of the resin in 600 μl de ethanol). Samples for TEM images were prepared by dropping 6 μl of the diluted dispersion of the particles on a copper grid coated with Formvar and a carbon film.

2.4. Photopolymerization studies

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific. Measurements of C=C conversion in BisEMA and BisTEG methacrylate resins were carried out at room temperature (20 ± 2 °C) using near infrared spectroscopy (NIR). The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. The resins were contained in a 10 mm diameter well constructed from a rubber gasket material sandwiched between two glass plates. The thickness of the samples was 2 mm. With the assembly positioned in a vertical position, the light source was placed in contact with the glass surface. The samples were irradiated at regular time intervals and the spectra were collected immediately after each exposure interval. These spectra were corrected with the background spectrum collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1} . Two replicates were used in the measurement of conversion.

The conversion at the surface of 2 mm thick specimens of methacrylate resins was assessed by attenuated total reflectance using a diamond crystal. The conversion was evaluated from the decay of the band at 1637 cm^{-1} assigned to the methacrylate double bond. Spectra were obtained from 64 scans at 4 cm^{-1} resolution. Measurements of conversion of epoxy groups in UVR resin were carried out at room temperature (20 ± 2 °C) using mid-infrared spectroscopy (MIR). Spectra were acquired over the range 700–1200 cm^{-1} from 32 co-added scans at 2 cm^{-1} resolution. The resins were coated onto a polyethylene film and covered with another polyethylene film. The assembly was sandwiched between two NaCl plates and was tightly attached to the sample holder

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