

Control on the dispersion of gold nanoparticles in an epoxy network

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Available online 6 March 2007

Abstract

Poly (*N*-vinyl-2-pyrrolidone) (PVP)-protected gold nanoparticles (NPs) were used as modifiers of epoxy/PVP systems to obtain well dispersed, homogeneous nanocomposites. The presence of the homopolymer significantly enhanced the NPs dispersion grade, probably due to the double role of PVP as complexing agent of the metallic cores and soluble modifier of the epoxy network. Tuning of the optical properties could be attained through the use of nanoparticles with variable shapes and sizes. The homogeneity of the colors and the absence of scattering in the final nanocomposites could found practical applications in the development of new optical devices.

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PACS: 81.05.Qk; 82.35.Np; 81.07.Pr

Keywords: Nanocomposites; Nanocrystals; Nanoparticles; Absorption

1. Introduction

In the last time, metal nanoparticles (NPs) have attracted considerable attention, especially due to their unique catalytic [1], electronic [2] and optical properties [3]. Many applications based on these special properties require dispersion of the nanostructures in solid matrices, while avoiding or controlling aggregation phenomena. Main efforts in this sense have been directed to the use of techniques based on the in situ generation of NPs in the matrix [4,5]. However, these techniques generally present important disadvantages as poor shape and size tuning and limited control on concentration. Hence, development of new techniques to allow the dispersion of pre-formed NPs is highly desirable. The excellent mechanical, dielectric and chemical properties of epoxy networks [6] make them a good choice for the development of advanced nanocomposites. However, the dispersion of NPs in these resins is not a trivial task and aggregates are commonly formed

[7]. In order to overcome this problem, we propose a new approach based on the use of a homopolymer that can act simultaneously as a compatible modifier of the epoxy network and a very efficient stabilizing of metal NPs. Poly (*N*-vinyl-2-pyrrolidone) (PVP) has been extensively used to stabilize colloidal particles of different materials in water and many non-aqueous solvents [8]. We have recently found that PVP can form homogeneous solutions with the epoxy system enabling the synthesis of single-phase transparent crosslinked networks (unpublished results). Thus, we propose to use PVP-protected gold NPs as modifiers of epoxy/PVP systems to obtain homogeneous nanocomposites with tuneable optical properties.

2. Experimental

PVP, $M_w = 10\,000$, and tetrachloroauric acid ($\text{HCl}_4\text{Au} \cdot 3\text{H}_2\text{O}$) were purchased from Aldrich and used as received. An epoxy/amine system based on diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow) and *meta*-xylylenediamine (*m*-XDA, Aldrich) was used. Gold nanoparticles were synthesized by direct reduction of an aqueous

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Table 1
Characteristics of NPs samples used for the synthesis of the nanocomposites

Sample	Mean Size (nm)	Rm	Morphology	Color
I	5.8	800	Spherical	Pink
II	6.9	600	Spherical ($\approx 80\%$)	Purple
III	14.1	400	Polyhedral ($\approx 70\%$)	Blue

solution of the metal salt with PVP, according to the method previously developed in our laboratory [9]. In a typical experiment, 5 ml of the AuCl_4^- aqueous solution (0.02 M) was added onto 50 ml of PVP solution (0.027 M) and heated at 70 °C. PVP/ HAuCl_4 mass ratio was varied to obtain NPs with different optical features (see Rm column in Table 1) [9]. After completion of the reaction, acetone was added to precipitate the particles. The solid was separated and dried at 70 °C. Selected amounts of PVP, DGEBA and PVP-coated NPs were dissolved in chloroform (CHCl_3) in order to obtain a homogeneous dispersion. The amount of modifier (PVP + PVP-coated NPs) was kept at 10 wt% based on previous results that showed that optically transparent materials are obtained by modifying the epoxy system with this amount of PVP (unpublished results). After removing the solvent and cooling to room temperature, a stoichiometric amount of amine was added and the mixture was poured in polystyrene or polypropylene moulds. Curing was carried out in an oven at different selected temperatures. Final concentrations of NPs were of the order of 0.5–1.0 mM.

Transmission electron microscopy (TEM) was performed at an accelerating voltage of 100 kV. Samples were prepared by dropping an aqueous dispersion of the NPs on copper grid supported Formvar films. UV-Visible spectra of gold hydrosols and epoxy nanocomposites cured at room temperature (1 cm thick), were measured with a diode-array spectrophotometer.

3. Results and discussion

Nanoparticles with different sizes and shapes were incorporated in epoxy-PVP reactive blends to obtain the nanocomposites (samples I, II and III in Table 1).

Under the conditions above described, initial reactive dispersions were completely homogeneous to the naked eye. Nevertheless, in a test carried out with a carefully washed NPs sample (with a very low amount of PVP), it was found that dispersion was not efficient and aggregates could be observed. This could be reverted by addition of pure PVP followed by stirring, which provoked the total homogenization of both components. This indicates that PVP efficiently acts as a compatibilizer between gold NPs and the epoxy reactive system, which is probably due to the double role of the lactame ring in the dispersion process. The polarity of this group provides high affinity by the epoxy/amine network, whereas carbonyl acts as stabilizer of the NPs through the formation of metallic complexes.

The effect of the cure procedure on the homogeneity of the nanocomposites was also analyzed. It is expected that the use of a high reaction temperature would favor the development of homogeneous nanocomposites because shorter gel times would decrease the time for coalescence and aggregation of the NPs [10]. However, an increase in temperature also would produce an initial decrease in the viscosity of the reactive sample and an enhancement of the probability of aggregation. Interestingly, analysis of samples cured at 70, 40 and 25 °C showed that, in all the cases, optical quality of the samples was reasonably preserved and aggregation prevented. This is probably due to the stabilization and viscosity increase provoked by the presence of the homopolymer. Final samples showed uniform characteristic pink, purple and blue colors associated to the strong plasmon resonance bands of the NPs located at 521, 543 and 597 nm. Moreover, they remained transparent after polymerization even at the highest thicknesses, indicating absence of large NPs aggregates that would produce opacity of the samples (photographs in colour are available on request).

Fig. 1 shows the visible spectra of NPs hydrosols and those corresponding to the 1 cm thick nanocomposites monoliths cured at 25 °C. The high similarity between the spectra confirms the low aggregation degree in the final samples and the low contribution of scattering processes arising from the matrix, even at these high thicknesses.

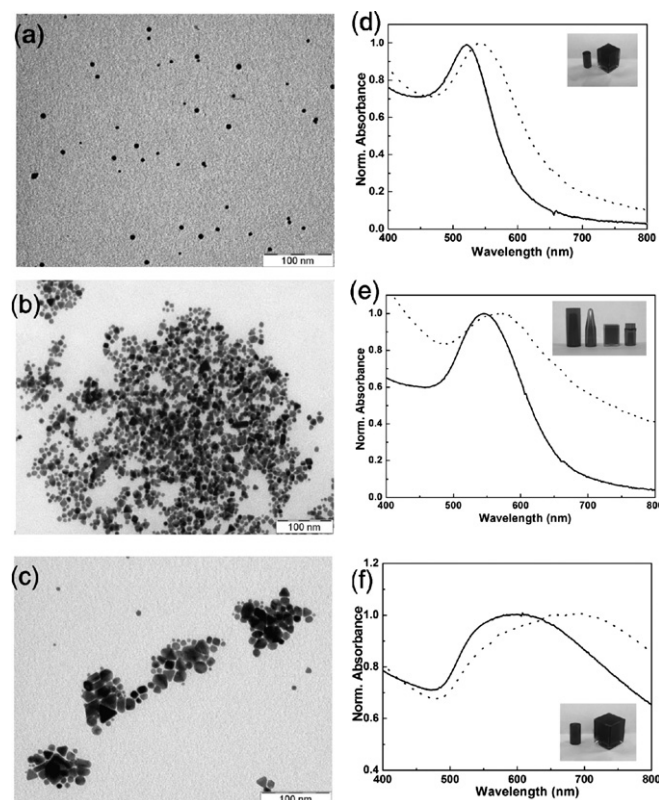


Fig. 1. TEM micrographs of I (a), II (b) and III (c) gold NPs samples used for the synthesis of nanocomposites, scale bar: 100 nm; (d–f) normalized visible spectra of gold hydrosols (solid lines) and nanocomposites cured at 25 °C (dotted lines) obtained with I (d), II (e) and III (f) gold NPs samples. Insets show photographs of the as synthesized nanocomposites.

The slight red-shift in the peak positions is related to the different refractive indexes of water ($n = 1.33$) and the fully cured epoxy ($n \approx 1.59$).

4. Conclusions

PVP-coated gold NPs could be homogeneously dispersed in epoxy/m-XDA reactive systems modified with PVP. Tuning of the optical properties of these nanocomposites could be easily attained through the use of NPs with variable shapes and sizes. The high optical quality of the samples (homogeneous colors and absence of scattering) could be useful in the development of coatings, filters and other kind of optical devices. Since stabilization with PVP can be applied to other materials the approach shows a high potential as general method for the development of epoxy-based nanocomposites.

Acknowledgments

The authors thank the financial support of the ‘Ministerio de Ciencia y Tecnología’, (Spain) under the project

MAT2005-07554-C02-01. C.E. Hoppe thanks 2006-IIF Marie Curie Grant (Proposal number 021689, AnaPhaSeS).

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