One-Pot Preparation of Gold-Elastomer Nanocomposites Using PDMS-*graft*-PEO copolymer Micelles as Nanoreactors

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One of the greatest challenges to face regarding the design and synthesis of advanced nanocomposites is to avoid the typical nonuniform particle aggregation process that takes place when polymers and nanoparticles (NPs) are mixed.[1] An attractive way to overcome this problem is to synthesize the nanofiller inside the matrix or matrix precursor in such a way that the nanocomposite can be prepared following an one-pot strategy, which is simpler and less time and cost consuming than multi-step procedures. Additional advantages would be envisaged if size and shape of the NPs could be modified by simple changes of the reaction conditions. Siloxane amphiphilic copolymers consist of a methylated siloxane hydrophobe grafted with one or more polar chains. These copolymers are able to form micellar aggregates in nonaqueous media, which make them very attractive as potential nanoreactors and structured templates for the organization of nanocrystals.[2] Based on this potentiality, here we present our first results obtained by using poly(dimethylsiloxane)-*graft*-poly(ethylene oxide) (PDMS-*g*-PEO) micellar aggregates dispersed in a siloxane elastomer precursor as nanoreactors for the synthesis of gold nanocomposites.

The copolymer PDMS-*g*-PEO, traded under the name BYK-UV3510, was kindly supplied by BYK Chemie (Wesel, Germany). Molecular and structural characterization was carried out by size exclusion chromatography and ^{1}H NMR, respectively. BYK-UV3510 has an average molecular weight of 12,900 g/mol and a polydispersity index of 1.5, whereas the molar ratio of grafted to ungrafted DMS units, DMS_{g-PEO}/DMS is 3/97. In a first step, selected amounts of the copolymer and a hydroxyl-terminated poly(dimethylsiloxane) (Mn $\approx$ 550, Aldrich) were thoroughly mixed with a vortex. The resulting clear dispersion was loaded with an aqueous solution of $HAuCl_4.3H_2O$ and heated in an oven at a selected temperature between 50 and 80ºC. After this treatment, the dispersion developed a characteristic pink color associated to the plasmon resonance absorption of gold NPs. The absence of additional reducing agents in the system supports previous results that showed that ethylene oxide chains, facing the interior of micelles, could induce the reduction of metal salt to generate NPs. In a final step, an elastomeric siloxane network was formed by adding tetraethyl orthosilicate (TEOS) as a cross-linker and tin (II) 2-ethylhexanoate as a catalyst.

The evolution of the reaction was followed by monitoring the development of the plasmon band as a function of time by UV-Vis spectrophotometry (Figure 1). After an induction time of several minutes, the appearance of a characteristic single feature typical of spherical NPs was observed.[3] The reaction rate was very susceptible to the temperature in the 50-80ºC range (see inset in figure 1), although the position and shape of the band were hardly affected by this variable. It is worth noting that the optical characteristics of the samples (position and shape of the plasmon band) were not affected by the polymerization process.

Figure 2 shows photographs of monoliths and films of the modified elastomers obtained under different conditions. As can be observed, the copolymer/metal mass ratio (R) is a fundamental variable to be tuned in order to adjust the final colour and transparency of the nanocomposites. A decrease in R from 3060 to 2470 produced nanocomposites characterized by a wider and red-shifted band, probably due to an increase in size and degree of aggregation of the formed nanostructures. It seems possible that a decrease in R produced a drop in the

protection efficiency against growth and aggregation. On the other hand, a high R value was necessary but not sufficient to generate small, spherical nanoparticles with a narrow plasmon band. As an example, a sample prepared with a higher copolymer concentration and R = 3860 produced blue nanocomposites characterized by a wide absorption band in the visible region of the spectrum. The origin of this behaviour is still not clear, although it could be related with a shifting of the composition of the system to a different zone of the copolymer/PDMS-OH/HAuCl$_4$(aq) phase diagram.

In summary, in this work we demonstrated that elastomeric nanocomposites can be obtained in a one-pot process using micelles of a random graft amphiphilic copolymer as reducing nanoreactors. The possibility to produce anisotropic particles working in different regions of the copolymer/PDMS-OH/HAuCl$_4$(aq) phase diagram is currently under investigation.

References:

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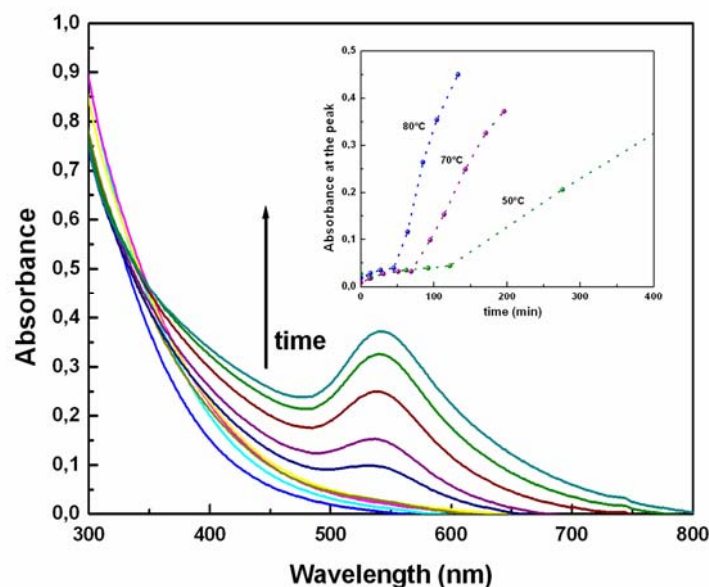[3] L. M. Liz-Marzán, Langmuir, **22** (2006) 32.

Figures:

Figure 1. Evolution of the plasmon band of a sample prepared with 10wt% of BYK-UV3510 and R=3060 at 70ºC. Inset: Temporal evolution at different reaction temperatures.

(a)   **(b)**

Figure 2. Photographs of nanocomposites prepared with (a) R=3060; (b) R=2470.