Silver and Poly(*tert*-butyl)acrylate Nanocomposites for Molecular Detection by SERS

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Abstract — Nanocomposites of poly(*tert*-butyl)acrylate have been prepared via in situ miniemulsion polymerization in the presence of Ag nanoparticles (NPs) that have been previously prepared by the polyol method. Electron microscopy (SEM/TEM) showed sub-micron polymer composite particles loaded with the metal phase. The nanocomposites were characterized by infrared spectroscopy and thermal analysis, and these results will be discussed. The Ag based nanocomposites were then investigated as new substrates for surface enhanced Raman scattering (SERS) aiming to develop new platforms for (bio)sensing. In this context, the performance of the composite substrates for SERS of distinct analytes (e.g. thiosalycilic acid) will be discussed.

Introduction

Nanotechnology based on novel systems composed by metal particles encapsulated in a polymer matrix open a broad range of new applications for biomedical material [1], optoelectronics and photonics areas [2], as well as biosensors [3].

Following our studies on the effects of inorganic nanoparticles (NPs) on the properties of diverse polymers, this work aims to investigate the influence of Ag NPs in poly(*t*-butylacrylate) (P*t*BA), used here as dispersing medium. Furthermore, the Ag/P*t*BA nanocomposites were investigated in more detail as new SERS substrates using the thiosalicylic acid as model analyte (Figure 1).

Experimental

Silver nanoparticles (NPs) were firstly prepared by an adaptation of the polyol method and employed as fillers to load P*t*BA prepared *in situ*, based on a similar methodology described by us for Au nanocomposites [4]. All the nanomaterials used in this work have been characterized by a number of techniques, which include vibrational spectroscopy, electron microcopies and thermal analysis.

Results and Discussion

The final morphological characteristics of the nanocomposite particles of Ag/P*t*BA depend on several parameters such as the Ag particle size and shape, capping agent and, as expected, on the polymerization conditions.

SEM and TEM analysis of the nanocomposites showed that the polymer is coating each single Ag NP. Thermal analysis showed that the glass transition temperature (T_g) of the nanocomposite decreased in comparison to the T_g of the pure polymer. These results will be discussed taking into account the possible effects of the Ag NPs on the polymer chain interactions.

The Ag/P*t*BA nanocomposites describe above were investigated in more detail as new SERS (Surface-Enhanced Raman Scattering) substrates. These nanocomposites are particularly promising for (bio)molecular detection due to the potential application as substrates in aqueous emulsions or as solid films.

Figure 2 shows the Raman spectrum of a drop of thiosalicylic acid solution (10^{-3} M) on the top of the solid nanocomposite substrate and pure polymer. These results showed an enhancement (see 1500-1600 cm^{-1} region) of the analyte Raman signal when Ag/P*t*BA was used as substrate. For sake of comparison, Fig.2 also shows the conventional Raman spectrum of thiosalicylic acid. Furthermore, we have investigated the dependence of the SERS signal of thiosalicylic acid when deposited onto the nanocomposites and at temperatures lower and higher than T_g.

Conclusions

New Ag/PtBA nanocomposites were prepared by *in situ* miniemulsion polymerization using the respective monomer and organically capped Ag nanoparticles. TEM analysis confirmed the encapsulation of the Ag nanoparticles in the polymer matrix and DSC showed a decrease of the polymer glass transition temperature (T_g) in the nanocomposite. The nanocomposites obtained revealed as new SERS sensitive substrates using thiosalicylic acid as molecular model. These results open new perspectives to develop a new class of Ag based substrates for (bio)molecular detection using Raman spectroscopy.

References

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Figures

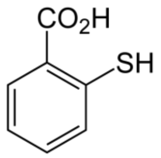

Figure 1

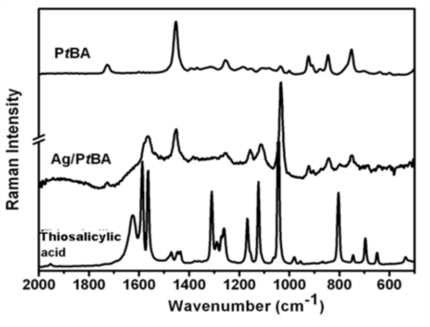

Figure 2

Figure caption

Figure 1: Structural formula for thiosalicylic acid
Figure 2: Conventional Raman spectrum for thiosalicylic acid. SERS spectrum of thiosalicilyc acid solution (10-3 M) dropped in Ag/PtBA solid film and the corresponding Raman spectrum when pure PtBA was used as substrate.