

Using an Inverse Surfmer in the Synthesis of Polystyrene / Polyaniline Core-Shell Composites. II. Morphology, and Electrical and Thermal Properties.

Claudia Hernández¹, Alejandro Vega¹, Flor Rentería¹, Sergio Flores¹, Armando Zaragoza^{1*}.

1: Centro de Investigación en Materiales Avanzados, S.C. Chihuahua, Chih., México.

*armando.zaragoza@cimav.edu.mx

Abstract

Anilinium dodecylsulfate (DS-AN) was used as the surfmer in the synthesis of polystyrene / polyaniline core-shell composites, first performing as the surfactant to stabilize the emulsion polymerization of styrene, and later as the monomer to synthesize polyaniline via oxidative polymerization. Here, the surfmer function was directed towards the external phase instead of to the internal phase, as with conventional surfmers with carbon-carbon double bonds. Consequently, the term inverse surfmer is proposed. Analysis of composite microstructure showed no separate phase of PANi, indicating that most of the conducting polymer was deposited on the polystyrene particles. Thermogravimetric analysis allowed determining DS-AN conversion. Except composites with 6 and 10 wt% PANi, the rest reached conversions close to 90%. Concerning electrical conductivity, it increased linearly between 6–30 wt% PANi, with values in the range of 10^5 to 10^2 S cm⁻¹.

Keywords: Core-shell composite, Morphology, Polyaniline, Thermal properties, Surfmer.

Sesión: Nanocompuestos y materiales poliméricos compuestos.

1 INTRODUCTION

Polymerizable surfactants (surfmers) are a special family of surfactants. These compounds are especially attractive because, aside from acting as conventional emulsifiers, they can link covalently to a latex particle surface (Guyot, 1996; Guyot, et al., 2003). This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and to shearing of the latex (Guyot, 2004). Numerous reports have described state-of-the art over the years (Jiang and Du, 2005; Uzulina et al., 2002).

Recently, we reported for the first time results of anilinium dodecylsulfate (DS-AN) as a new concept of surfmer: concept. inverse surfmer (Zaragoza-Contreras et al., 2012). The functionality of this salt lies on the anilinium group and not on a polymerizable carbon-carbon double bond. Its reactivity does not develop towards the organic phase of some emulsion system as with traditional surfmers (Lacroix-Desmazes and Guyot, 1996; Ábele et al., 1997). These features greatly distinguish DS-AN from the traditional surfmer. However, the intention is similar that DS-AN performs as a surfactant because it exhibits a critical micellar concentration and stabilizes emulsion polymerizations, and it performs as a monomer because polyaniline is obtained from it by oxidative polymerization. In the first approach, we applied DS-AN in the synthesis of polystyrene / polyaniline core-shell composites. The core-shell structure was evidenced by electron microscopy, solubility in THF, and thermogravimetric analysis. Consequently, the feasibility and versatility of this new concept of reactive surfactant was demonstrated. Herein,

we report result of electrical and thermal properties of the core-shell composites to supplement the characterization, and to exhibit the advantages of the employed methodology. It is noteworthy that several methodologies to produce core-shell colloidal polymer composites of vinyl or acrylic polymers with polyaniline have been reported (Xie et al., 1998; Haba et al., 2000).

2 EXPERIMENTAL SECTION

2.1 Materials

Aniline, sodium dodecylsulfate (SDS), ammonium persulfate (APS) and hydrochloric acid (Aldrich Co.) were used as received. Styrene monomer (Aldrich Co.) was distilled under vacuum. 2,2'-azobis(2-methylpropionamide) dihydrochloride (WAKO pure Chemical Industries, Ltd.) was recrystallized from a saturated aqueous solution at 60°C.

2.2 Methods

2.2.1 Core-shell composites

The synthesis of the polystyrene / polyaniline core-shell composites has been reported previously (Zaragoza-Contreras et al., 2012). On the one hand, the polystyrene core was synthesized by conventional emulsion polymerization using DS-AN (20 mmol L⁻³) as the stabilizer, and 2,2'-azobis(2-methylpropionamide) dihydrochloride (0.00184 mol L⁻³) to launch polymerization. On the other hand, the polyaniline shell was obtained via oxidative

polymerization. In this stage, extra amount of DS-AN was added as the monomer of polyaniline. Ammonium persulfate (APS) was used as the oxidizing agent at a molar ratio of 1.2 : 1 (DS-AN : APS).

2.2.2 Electron microscopy

Scanning electron microscopy in transmission mode (STEM) was performed in a field emission electron microscope (JSM-7401F; JEOL) at 30 KV. To prepare the samples, two drops of latex were dispersed using sonication for 5 min in 30 mL of tridistilled water. Subsequently, a drop of latex was placed and left to dry on a holey-carbon-cooper grid. By this procedure, the polystyrene latexes, the composites, and the samples of pure PANi were analyzed.

2.2.3 Electrical conductivity

Electrical conductivity was determined by the 4-point technique using a homemade device. Pellets (2 mm width * 1 cm diameter) of each composite and pure PANi were prepared by compression. A conductivity meter (34410A 6 1/2 Digit, Agilent) was used to determine resistivity.

2.3.4 Thermal properties

The glass transition temperature (T_g) of the composites was evaluated using a differential scanning calorimeter (Q200 DSC, TA Instruments). The thermograms were obtained, first, heating the sample from ambient to 250 °C, to eliminate thermal effects fixed during the polymerization, then cooled to 30 °C, and heated again to 200 °C. The T_g was taken from the second heating process. The samples were run under air atmosphere and a heating rate of 10 °C min⁻¹. Sample of pure polystyrene and PANi were analyzed as references. Additionally, the composition of the composites was characterized using a thermogravimetric analyzer (SDT Q600, TA Instruments). The evaluations were performed under air atmosphere and a heating rate of 10 °C min⁻¹.

3 RESULTS AND DISCUSSION

3.1 Core-shell composites morphology

In this work, emulsion polymerizations stabilized with DS-AN were used to produce the polystyrene core of the composites. Free radical initiator V-50 was selected to launch the polymerizations (0.00184 mol L⁻³) because persulfate initiators induce aniline polymerization via an oxidative mechanism. The second stage of the composite synthesis was performed via oxidative polymerization. In this stage, only the latex synthesized with 20 mmol dm⁻³ was considered. Consequently, more DS-AN was added as the monomer of PANi. Series of composites corresponding

to the theoretical proportions of 6, 10, 15, 20, 30, or 40 wt% of PANi with respect to the content of polystyrene in the core were synthesized. Fig. 1(a,b) portrays micrographs of the polymer particles of pure polystyrene and of the core-shell composites with 40 wt% of PANi. As observed, in the composite there was no formation of clots or separated phase of PANi, which indicated that most of the PANi polymerized on the polymer particles surface.

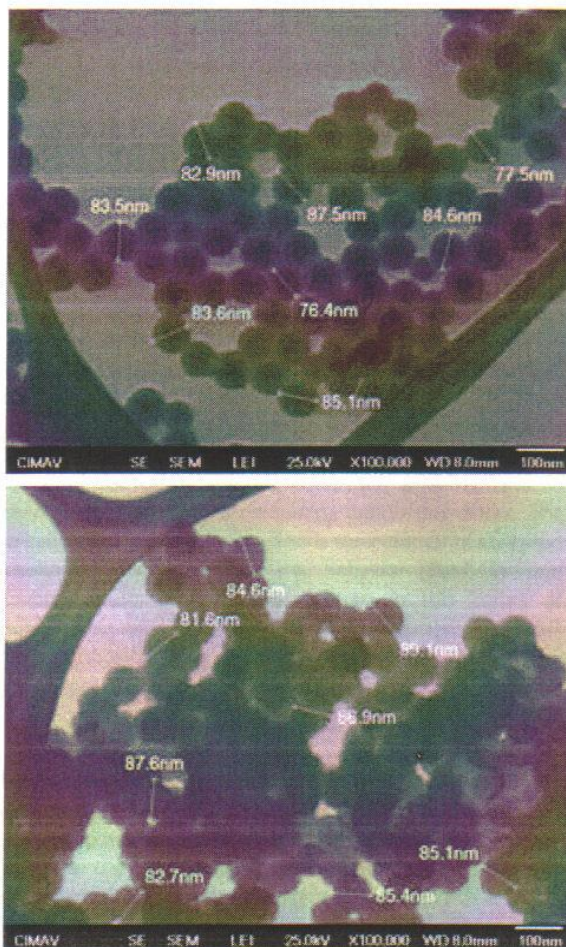


Fig. 1. Polymer particles of pure polystyrene (above), core-shell composite with 40 wt% of PANi (below).

3.2 Thermal properties

Thermogravimetric analysis was performed to determine composites composition. The traces of polystyrene obtained by emulsion polymerization using 20 mmol L⁻³ of DS-AN, pure polyaniline obtained with DS-AN via oxidative polymerization and the different core-shell composites are shown in Fig. 2. As shown, the core-shell composites present a clear combination of the profiles of the pristine polymers, with more similarity to the polystyrene at low concentrations, and to PANi at high