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Electrical impedance spectroscopy investigation of surfactant–magnetite–polypyrrole particles

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Abstract

We report an electrical impedance spectroscopy (EIS) characterization of composite systems formed by emulsion polymerization of polypyrrole (PPY) in concentrated aqueous solutions of sodium dodecyl sulfate (SDS) containing dispersed magnetite particles. SDS–(Fe_3O_4)–(conducting polymer) microaggregates with different iron contents were prepared by varying in a reciprocal manner the relative amounts of the metal oxide and PPY. We have measured the zeta-potential and the average size of the corresponding dispersed particles and examined their relative composition through energy dispersive X-ray (EDX) microanalysis and Fourier transform infrared (FTIR) spectroscopy. Important aspects of the charge transport in these composite particles can be identified by mapping the real and imaginary parts of their complex impedance as a function of the frequency of the applied external electric field. For instance, for binary composites SDS–(Fe_3O_4) polarization effects are dominant at the low-frequency regime, with a well-defined dielectric relaxation easily identifiable. On the other hand, when the relative amount of PPY is progressively increased in the ternary SDS–(Fe_3O_4)–PPY composites, a transition between different charge transport mechanisms is observed at higher frequencies. The EIS results suggest that in these ternary aggregates the PPY chains envelop the metal oxide clusters and effectively shield them from the external field, and that only in binary samples that do not contain PPY is that the surfactant molecules can directly enclose the magnetite particles. These results are consistent with the fact that the average size of the aggregates in the ternary composites is in general larger than those of either SDS–PPY or SDS–magnetite binary particles.

Keywords: Emulsion polymerization; Polypyrrole; Magnetic iron particles; Organic–inorganic hybrid composites; Electrical impedance spectroscopy

1. Introduction

Considerable advances in the research of new materials where colloidal particles incorporate conducting polymers [1] have been verified in recent years [2,3]. It is expected that the peculiar chemical and physical properties of this kind of composite system could represent new opportunities for applications in the fields of biomedicine [4], microelectronics, and in different areas of the information industry [5]. Another promising possibility is the use of these systems as corrosion protection layers of metallic surfaces [6–8].

At the same time, a recent trend in the use of colloidal systems corresponds to the introduction of metallic particles in the core of micelles [9,10], where conducting polymers are also present. Metal–organic composite materials that simultaneously exhibit a conductive character and ferromagnetic properties are already used in batteries and electrochemical displays and in electromagnetic interference (EMI) shielding materials, such as those used in antiradar systems [11]. Since conducting polymers not only reflect but also absorb radiation, when they are included as part of composite materials significant improvements can be attained in the effectiveness of active components used in EMI devices [12].

Magnetic composite materials have also found different biomedical applications, where the size of the iron oxide particles

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is an important parameter to be controlled. While particles below 100 nm can more easily evade physiological detection, and therefore have longer blood circulation times [13], recent advances in medical imaging technology have opened up the possibility of detecting single micrometer-sized iron oxide particles not only in vitro but also in cultured cells and in experimental in vivo systems [14]. Magnetic microparticles have also been used in ultrasensitive bio-barcode assays for the early detection of Alzheimer-related proteins [15].

Polymers have been traditionally used as coagulants of magnetic iron oxide particles prepared by chemical methods [16,17]. Similar techniques can be applied to prepare hybrid (conducting polymer)/(iron oxide) particles that, among other desired properties, possess promising EMI characteristics [11,18] and can be used for electrochemical storage [19] or DNA hybridization [20]. Because of its environmental stability, PPY has been one the conducting polymers most used for obtaining such binary composites through different preparation methods such as the sol–gel [20,21] and emulsion polymerization [19] techniques, and chemical polymerization on colloidal silica-coated magnetite particles [22]. Also, PPY-coated Fe_3O_4 fillers have been added to epoxy blends as a means of conferring the right amount of electrical conductivity to the composite material [23].

In the work described in this paper, we have initially used emulsion polymerization methods [24,25] to prepare mixed systems where particles of magnetite and polypyrrole chains are simultaneously enclosed within surfactant aggregates, and then applied electrical impedance spectroscopy (EIS) to investigate how the dominant charge transport mechanisms are affected by changes in the relative concentration of the conducting polymer present in the composites.

2. Experimental

2.1. Materials

High-purity sodium dodecyl sulfate (SDS) and pyrrole were obtained from Aldrich (USA). $FeCl_3{\cdot}6H_2O$ (Synth, Brazil), $FeSO_4{\cdot}7H_2O$ (Reagen, Brazil), and NH_4OH (Quimex, Brazil) were the reagents used for the preparation of the magnetic particles.

2.2. Preparation of the composite colloidal systems

For obtaining the metallic particles, we have followed the initial procedure indicated in Refs. [26,27] and prepared a 0.1 M $FeCl_3{\cdot}6H_2O$ and 0.5 M $FeSO_4{\cdot}7H_2O$ solution using ultrapure water obtained from a Nanopure system (Barnstead, USA). A volume equal to 200 ml of this solution was then transferred to a three-necked round-bottom flask and maintained under intense stirring on a nitrogen atmosphere for 30 min until its pH was reduced to 1.7. Small quantities of a 1.5 M aqueous solution of NH_4OH were progressively added to the bottom flask until the liquid turned blackish and the pH increased to 8. The system was then stirred for an additional period of 12 h, after which the resulting magnetite particles could be magnetically separated.

Table 1
Relative composition of the SDS–Fe_3O_4–PPY solutions investigated in this work

Sample	Pyrrole (μl)	Fe_3O_4 (ml)	Pyrrole (%)	Fe_3O_4 (%)
S1	173.0	0.00	100	0
S2	147.0	0.10	85	10
S3	121.0	0.25	70	25
S4	95.0	0.40	55	40
S5	69.0	0.55	40	55
S6	43.3	0.70	25	70
S7	17.3	0.85	10	85
S8	0.0	1.00	0	100

Note. The total volumes of each individual solution used (see text) are indicated; the percentage columns refer to the relative amount of pyrrole [Fe_3O_4] present in a given solution compared to the corresponding maximum amount used (in samples S1 [S8]).

For the preparation of the colloidal suspensions where the conducting polymer chains are trapped inside the surfactant aggregates, we have started from a small volume (10 ml) of a diluted (0.012 M) solution of SDS and 0.25 M in pyrrole [28]. If this solution is energetically stirred (600 rpm), the molecules of pyrrole become progressively incorporated in the interior of the aggregates. When 400 μl of a 1 M $FeCl_3{\cdot}6H_2O$ aqueous solution is added to the recipient, the oxidative polymerization begins to take place both in the interior of the aggregates as externally to them. In fact, the presence of the surfactant increased the rate of polymerization, since several additional active sites become available in the interior of the micelles [24,25,29]. (In Fig. 1 we present a schematic view of the preparation process.) A final filtration is sufficient to eliminate the largest agglomerates from the solution. (In all cases, the pH of the medium was acidic (<4.4).) It is known that the presence of SDS in the preparation of PPY samples not only improves the smoothness of the resulting films [26,28] but also contributes to their better adherence to the substrate; for these reasons, surfactant-conducting polymer composites have already been used as anticorrosion paints [6–8].

We have prepared different SDS–Fe_3O_4–PPY samples (Table 1) in which the amounts of polypyrrole and magnetite are varied in a reciprocal manner; in this manner, by analyzing a relatively small number of samples, we can estimate how the global charge transport mechanisms in the composites are affected by changes in the relative PPY–Fe_3O_4 concentration.

3. Results

3.1. Scanning electronic microscopy (SEM) and X-ray energy dispersive (EDX) microanalysis

We have used a JSM 5900 electron microscope (JEOL Instruments, Japan) to perform an initial SEM investigation of the nature and size distribution of the colloidal particles present in our samples. For this, a small quantity of the colloidal solution of interest was placed atop a SEM stub and, after waiting for the solvent (water, in our case) evaporation, a thin gold layer