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Effects of high frequency ultrasound irradiation on incorporation of SiO_2 particles within polypyrrole films

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ABSTRACT

This paper deals with the effect of ultrasound on polypyrrole/SiO_2 composite film elaboration through various steps (particle dispersion, electrosynthesis). Experiments were carried out on stainless steel in phosphoric acid solution. An efficient method for dispersion of SiO_2 particles prior to electropolymerization, based on low frequency irradiation (20 kHz), was proposed. It was shown that mechanical effects of high frequency ultrasound (*i.e.* mass transfer improvement) led to enhancement of electropolymerization kinetics. Scanning electron microscopy imaging and glow discharge optical emission spectroscopy revealed localization of SiO_2 particles in the outer region of the films as well as better incorporation of particles under high frequency ultrasound irradiation. Finally, anticorrosion behavior of formed films was investigated in sodium chloride solution by Open Circuit Potential and anodic polarization methods. The results showed that polypyrrole/SiO_2 films elaborated under ultrasound irradiation exhibit the best protective performances.

1. Introduction

Ever since the discovery of conducting polymers in the late 70s, polypyrrole (PPy) has received most attention due to its interesting properties, *i.e.* easiness of preparation from organic or aqueous solvent, good electrical conductivity, a large number of possibilities of functionalization. It can be potentially used in biosensing devices [1–3], solar cells [4,5], interference shielding and radar system [6], and ion-exchange processes [7]. PPy has also been successfully deposited on active metals such as copper [8–10], zinc [11–16] or steel [17,18], mainly for anticorrosion purposes which showed interesting results. To this end, electrochemical polymerization is the most common method. However, the choice of supporting electrolyte is very important since it will permit the formation of a pseudo-passive layer preventing surface dissolution, while allowing polymer growth above.

With the development of nanoscience and nanotechnology over the last decade, considerable attention has been paid to the synthesis and application of polymer/inorganic oxide composites. Particles such as zinc oxide (ZnO), titanium oxide (TiO_2), and silicon oxide (SiO_2) have been incorporated in polymeric matrices [19–22]. SiO_2 has received particular attention due to its broad applications [23] and low cost. Two main steps are to be considered: the preparation of stable particle dispersion and the incorporation of these particles into the polymer matrix. Ultrasound can make a very powerful contribution during both steps. Indeed, propagation of a power ultrasound wave through a liquid medium leads to major mechanical, physical and chemical perturbations such as acoustic cavitation. This cavitation effect is due to the growth and collapse of bubbles inside the liquid, caused by the sudden change in internal pressure generated by the ultrasound wave. During the collapse (which can occur either in a symmetric manner inside the bulk or in an asymmetric manner at an electrode surface) a large stress pulse is generated, followed by a high velocity fluid jet. The difficulty of obtaining homogeneous dispersions of particles in solution is a known fact. Mechanical stirring, often applied to improve the homogeneity of the dispersion, can hardly prevent particles from aggregation or agglomeration. To overcome this problem, ultrasound and particularly low frequency has been proved to be very efficient for elimination of agglomerates [24,25] in a preliminary step, before using the suspension to elaborate the relevant composite. Not only can ultrasound irradiation be applied to disperse particles but it can also provide beneficial effects in the following steps of the process, *i.e.* during the electrochemical synthesis of composite polymers. It has recently been shown that structural properties of conducting polymer films can be greatly affected by ultrasound [26–37]. Indeed, previous

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works showed that low frequency ultrasound can lead to more resistant polymer films, with a thinner and more homogeneous surface structure [26,30]. However, at these frequencies, cavitation phenomena can be so violent that they can lead to partial destruction of the electrodeposited polymer [38]. At higher frequencies, the behavior of cavitation bubbles is completely different, and the destructive effect of ultrasound towards the polymer surface is greatly reduced, while maintaining many other beneficial effects on electropolymerization. Therefore, conducting polymer films electrosynthesized under high frequency ultrasound irradiation on many different substrates (FTO, Pt, Cu, Zn coated steel) still exhibit a more compact and more homogeneous structure [33–37]. This increase in compactness has been proved to have an effect on the mobility of small ions [36]. Moreover it has been shown that high frequency ultrasound irradiation increases doping level of conducting polymers (*e.g.* from 25% for silent polypyrrole to 33% for irradiated polypyrrole) [33,34,36]. The reasons for this increase in doping level were claimed to come from oxidation of polymer films by radical species (typically OH°) produced during ultrasound activity [39].

Consequently, the aim of this paper is to study the effects of ultrasound irradiation to acquire an overview of the valuable effects of ultrasound of SiO_2 particle incorporation within the polymer matrix, by acting on the preparation step (particle dispersion at low frequency) as well as on the synthesis itself (electropolymerization at high frequency). Cavitation obviously occurs more markedly at low frequencies, leading to observable erosion in the reactor (either at the horn surface or on an aluminum foil exposed to wave propagation). In the meantime, presence of a geyser at the air/water interface in high frequency sonoreactors indicates marked absorption of the ultrasonic wave by liquid, the energy of which is converted into convective motion. Thus, ultrasound irradiation parameters were determined at 20 kHz to obtain stable particle dispersion with uniform size distribution. Then, electrosynthesis was performed in presence of 500 kHz ultrasound, and the films' physico-chemical properties were characterized in terms of thickness, composition and morphology. Finally, improvement of the protective aptitude of the composite films was evaluated. The substrate chosen was thus stainless steel in order to further investigations into corrosion studies.

2. Experimental

2.1. Chemicals

Pyrrole (Py) (Acros, P99%, 109-97-7) was distilled before use. All other chemicals were of the highest quality commercially available and were used as received without further purification: phosphoric acid H_3PO_4 (Fluka), sodium chloride NaCl (Fluka) and silica powder SiO_2 (AEROSIL 200, evonik industries).

2.2. Working electrodes

The samples used in this study were AISI 304 stainless steel (SS) (in wt.%) C ($\leqslant$0.07), Cr (17.00–19.00) and Ni (8.5–10.5) embedded in epoxy resin. The exposed electrode area was 0.28 cm^2. Before each experiment, the working electrode was mechanically polished with abrasive papers (400–1200 mesh) on a Buehler polished table and washed with ethanol and distilled water.

2.3. Sonoelectrochemical cell

All high frequency experiments were performed at 500 kHz in a cell filled with 750 ml electrolyte. Ultrasound is produced parallel to the liquid surface, face to face with the working electrode surface. The circular transducers consist of a piezoelectric ceramic fixed on a circular plate (56 mm) made of glass. An electronic circuit consisting of a variable inductance and capacitor allows the adjustment between the generator impedance and the strong capacitive transducer impedance. The sonoreactor used was described and characterized in previous works [34,35,40] by calorimetry, mass transfer measurements and sonochimiluminescence. Ultrasound activity seems to be more concentrated at the solution/air interface. The working electrode surface is always placed at this interface to ensure maximum benefit is derived from ultrasound activity.

The low frequency cell (20 kHz) used for dispersion of SiO_2 particles has been characterized in previous works [41], and the entire reactor volume is concerned by the irradiation.

2.4. Electrochemical procedures

Electrochemical measurements were taken in the sonoreactor using a Taccusel potentiostat–galvanostat, type PGZ 301, piloted by the electrochemical software voltamaster 4, and a classical three-electrode setup consisting of a saturated calomel reference electrode (SCE), a platinum counter-electrode and a SS working electrode. Polymer films were grown by cyclic voltammetry with a scan rate of 10 mV/s and by chronocoulometry applying a potential of 1000 mV/SCE. Experiments were carried at ambient temperature in two solutions: S_1 (1 M H_3PO_4 + 0.1 M Py) and S_2 (S_1 + 3 g/L SiO_2). Anticorrosion behavior of polypyrrole (PPy) and polypyrrole/SiO_2 (PPy/SiO_2) films elaborated on SS was evaluated in a classical electrochemical cell with three electrodes closing 100 ml of 3% NaCl solution at ambient temperature, without stirring and normally aerated. Techniques employed were registration of the Open Circuit Potential (OCP) for 20 h and plotting of polarization curves (scan rate: 2 mV/s) after immersion for 1 h in sodium chloride solution.

2.5. Characterization studies

Glow discharge optical emission spectroscopy (GD-OES) was used to observe element repartition profiles within different coatings using a Horiba Jobin Yvon GD Profiler. The substrate was placed as a cathode, and then sputtered in an argon atmosphere by applying a power of 10 W and a pressure of 400 Pa. Polymer surface was characterized by Scanning Electron Microscopy (SEM, JEOL 5600) and optical surface profiler (Alicona Infinite Focus Intralux dc-1100) to appraise surface morphology and roughness. Particle sizes were measured using Malvern Zetasizer 3000 HS.

3. Results and discussion

3.1. Effects of ultrasound during different steps of composite film elaboration processes

3.1.1. Use of low frequency ultrasound for preparation of SiO_2 particle dispersion

The first step in the process is the preparation of dispersion solution from dry SiO_2 powder. This is usually a difficult process due to strong interactions between particles. Usually good dispersion can be achieved by surface modification of particles under appropriate processing conditions [42]. In this paper, a variety of approaches (Table 1) have been tested to disperse particles in distilled water such as: mechanical stirring for 24 h (M_1 method), classic ultrasonic bath over different periods of time (M_2 method), high frequency ultrasound irradiation for 5 min for powers of 10 W and 25 W (M_3 and M_4 methods), and low frequency ultrasound irradiation for 5 min for powers of 60 W and 180 W (M_5 and M_6