



Characterization of hydrophobic and hydrophilic polythiophene–silver–copper thin film composites synthesized by DC glow discharges

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ABSTRACT

Polythiophene with Ag and Cu particles were synthesized using DC glow discharges in order to study the transport properties and wetting behaviour of these polymer–metal composites. X-ray diffraction, scanning electron, transmission electron and atomic force microscopies were used to characterize the composites. The results indicated that the composites had nanotextures and microtextures with a thermally activated conduction mechanism at a low critical metallic volume fraction. The wetting behaviour of the composites varied from hydrophilic to highly hydrophobic as a function of the roughness and metallic content. In particular, the composites with a superficial nanotexture demonstrated a highly hydrophobic tendency.

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1. Introduction

Polythiophene (PTh) has attracted considerable attention over the past years due to numerous solid state potential applications in many fields, such as microelectronic devices [1], catalysts [2], organic field effect transistors [3] and chemical sensors and biosensors [4,5]. For many years, the synthesis of PTh has been done mainly via electrolytic reactions due to the relatively high oxidative potential of thiophene that complicates its polymerization by other methods. However, in the last decade, the syntheses of PTh in gas phase by plasma have been acquiring importance due to the variety of possibilities that can be obtained. Maybe one of the most important is the formation of thin film composites with polymers, metals and different dopants with good adherence, branching, crosslinking and a high environmental and thermal stability [6,7]. One of the variables that can be partially manipulated in these syntheses is crosslinking, which can enhance the film strength as opposed to polymers formed by other methods.

Recent studies about the plasma polymerization have investigated the effect of power [8], dopants and humidity in the electrical conductivity of polypyrrole, polyaniline and polythiophene [6,9,10]. One disadvantage that has been observed in plasma polymerized PTh is that their electrical conductivity is lower than that of the semiconducting polymers synthesized by other methods. However,

it has also been stated that the conductivity can be enhanced by adding metals to the polymers during the synthesis. This can be done releasing metallic atoms from the electrodes used to apply the electrical field in the reactor [11,12].

These polymer–metal composites can vary from insulators to conductors, depending on the metallic fraction. Conducting polymers may be good matrices for dispersing metallic particles, allowing an easy flow of electronic charges through the composites with a low ohmic drop. The size and distribution of these particles play an important role in the properties of the entire composite.

Another important factor is wettability, which has been less considered in these materials and that can be fundamental in a great number of possible applications. It is well known that this property is governed by both, roughness and chemical properties of the surfaces. Roughness and texturing have been studied in polypyrrole, polythiophene [6,10] and some of their metal–polymer composites [11] synthesized by plasma in order to manage the superficial energy in water repellent materials [13,14].

Now in this work, polythiophene with particles of Ag and Cu (PTh–Ag) were synthesized by DC glow discharges with the objective to study the effect of texture on the wettability of the composites. The syntheses started with thiophene in competitive cathode sputtering and polymerization. The characteristics of the electric field applied to the reactor promoted both processes simultaneously, which is difficult to obtain by other methods. In terms of wettability, the metal particles may increase the interaction of the surfaces with some liquids, which is studied in this work through their contact angles. The metallic percolation in the composites and the transport of charges are related

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in order to synthesize polymer–metal composites with controllable electrical conductivity and wettability for specific applications.

2. Synthesis

The glow discharges were carried out in a glass cylindrical reactor with stainless steel flanges and flat electrodes at each side, see Fig. 1. Both the flange and electrode of each side, were maintained at the same electrical potential. The anode was 65 mm diameter made of stainless steel and the cathode was 35 mm diameter made of a 90–10% Ag–Cu alloy. The distance between electrodes was 3 mm. A mechanical vacuum pump for corrosive gases Alcatel Pascal 2015C1 was used to reduce the pressure in the system. The electrodes were cleaned with water, soap and acetone before each synthesis.

Thiophene (Fluka, 98%) was introduced to the reactor in vapour phase. The monomer feed rate was regulated by a flow control valve. The electrical potential between the electrodes was applied with a power supply (MDX Advanced Energy magnetron drive) operated under constant voltage mode with the output power regulated at 800 W. In these conditions, part of the monomer feed was consumed in the polymerization and the other fraction was retained in a cold trap, cooled with liquid nitrogen, located between the reactor and the vacuum pump. The time of syntheses was in the 180–300 min interval. The total pressure inside the reactor was regulated between 0.3 and 0.5 mbar using air as a carrier gas. A flow control valve was used to let air enter into the reactor when low monomer feed rates were needed.

The polymers covered most of the internal walls of the reactor, but they concentrated in the area surrounding the electrodes. The front faces of the electrodes remained almost uncovered because of the continuous erosion during the syntheses. Lower film growth rates were obtained compared with those in other similar plasma polymer syntheses [6].

The composites were formed on glass substrates placed on the reactor walls at 3 cm from the electrodes, in the space between the electrodes and the negative flange. Most of the films were analyzed directly on glass substrates because their swelling was difficult to obtain with common solvents. However, the samples for transmission electron microscopy (TEM) analysis were carefully separated from the glass substrates. The swelling was a function of the metallic content in the polymers in which the samples with lower content swelled more easily than the others.

3. Characterization

The structure of the metal in PTh–Ag was studied by X-ray diffraction (XRD) with a Siemens D500 diffractometer. The scanned range was 2–120° 2θ , with a step of 0.02° and 1.2 s. The metallic volume fraction, x , and the metal distribution in the polymer matrix were studied by energy dispersive spectroscopy (EDS). A Leica–Cambridge (Stereoscan 440) scanning electron microscope (SEM) coupled with an EDS (Pentafet) microprobe and a JEM 1200EX

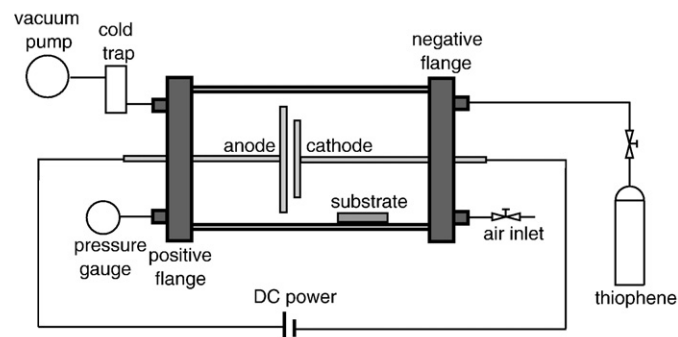


Fig. 1. Schematic representation of the reactor.

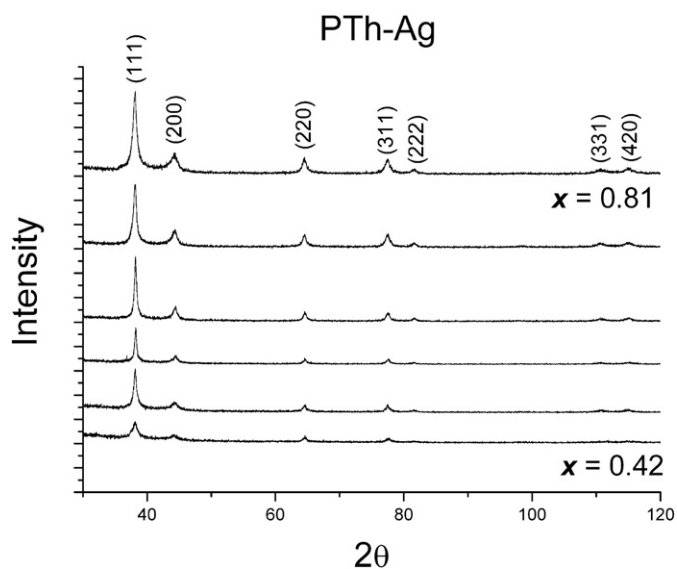


Fig. 2. XRD patterns of PTh–Ag composites with metal concentration from $x=0.42$ to $x=0.81$. Higher intensities are observed as x increases. The peaks correspond to cubic silver with preferred orientation of the (111) planes.

transmission electron microscope were used. The topography of PTh–Ag was studied by Atomic Force Microscopy (AFM) (JEOL JSPM-421) under atmospheric pressure conditions.

Contact angles between bidistilled water and the composites were measured at 37 °C by the Sessile drop method using a Rame–Hart Goniometer. The contact angles reported in this work, θ , are the average values obtained with drops of 8, 12 and 16 μL . At least 18 experiments were carried out for each case. The DC electrical conductivity of the composites was measured from 25 °C to 120 °C by the two-probe method.

4. Results and discussion

Thin films with thickness from 0.3 to 1.3 μm were obtained. The metallic volume fractions of Ag and Cu, x , were estimated using the density and the atomic fractions of the materials. Polymers with x from 0 to 0.81 were prepared. The XRD patterns of PTh–Ag with high metal concentration, from 0.42 to 0.81, are shown in Fig. 2. Higher intensities are observed as x increases. The peaks correspond to cubic silver, $a=4.09$ Å, with the same structure as the cathode. Intense peaks in 38.1° and 44.2° 2θ are due to the (111) and (200) reflections. The intensity ratio between them can be associated to a preferred orientation of the (111) planes, as it has been observed in other polymer–metal composites synthesized by plasma [11].

As the XRD analyses are sensitive to the mass fraction of the components, which in this work is 90% Ag and 10% Cu, the more intense reflections of Cu in 43.4° and 50.5° are hidden by the Ag reflections. Consequently, the peaks of Cu are not perceptible, even in the upper pattern of Fig. 2. The elemental analysis of the metal particles also shows the same Ag/Cu ratio as the cathode. Unlike Ag/PTh composites prepared by other syntheses [15], no indication of chemical interaction between the metal and the PTh matrix was found in plasma PTh–Ag.

The SEM and TEM images in Fig. 3 show polymer matrices with metal particles of different sizes corresponding to composites with different x values. The structure of the composites is the result of many chemical and physical effects like reactivity, substrate temperature, etc. Two important factors in the synthesis are the competitive polymerization and metallic nucleation on the surfaces. The nucleation and growth of Ag particles highly depend on the average interatomic distance of the Ag atoms arriving to the substrate. Near the electrodes, high x values and large metal particles were observed.

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