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ALEXANDRU IOAN CUZA UNIVERSITY OF IASI
FACULTY OF PHYSICS
Iasi Plasma Advanced Research Center (IPARC)

CHARACTERIZATION OF POLYTHIOPHENE FILMS OBTAINED IN ATMOSPHERIC PRESSURE PLASMA REACTORS

- Thesis abstract -

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Scientific coordinator,
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Iasi, 2015

In attention off

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ALEXANDRU IOAN CUZA UNIVERSITY OF IASI
FACULTY OF PHYSICS

We do know that on **29 September 2015** at **10:00**, in the Ferdinand Conference room, **Teodora Lăcrămioara TESLARU** will hold in a public session the doctoral thesis

''Characterization of polythiophene films obtained in atmospheric pressure plasma reactors'',

in order to obtain scientific title of **doctor** in the fundamental field EXACT SCIENCES, the doctorate field PHYSICS

The examination commission of thesis:

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We invite you in this way, to attend at public hearing of the PhD thesis.

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Motivation

In the last year's polymeric materials obtained by plasma polymerization processes had a major impact in science and industry due to potential applications in the field of electronic devices, sensors, as well in the biomedical field. Polymeric materials are used in medicine because they can be founded and processed in various compositions and complex forms (solids, fibers, gels, films).

Polytiophene films are used in a wide range of biomedical applications such as: tissue engineering (migration and cell adhesion) neurology, biosensors, immobilization of biomolecules etc. According to the application, these polymer films must comply with certain requirements relating to the biocompatibility, hydrophobicity, conductivity, biostability, transparency etc. In this case the polymer film should by biostable, biocompatible at interaction with biological media, meaning materials should not release toxic products and modify their properties in time at interface with biological medium, shall not be biodegradable.

The topic of this thesis ***''Characterization of polythiophene films obtained in atmospheric pressure plasma reactors''*** is employed into a multidisciplinary field, involving knowledge of physics, chemistry, biology and medicine and requiring a fundamental and interdisciplinary approach.

This thesis has an applicative and also, a fundamental research component. Thus, the manuscript proposes a new polymerization technique based on the use of Dielectric Barrier Discharge (DBD) which operates at atmospheric pressure, in order to obtain polymer films with imposed properties. The paper aimed not only physico-chemical characterization of the films, but also analysis of plasma by electrical and optical diagnosis during polymerization reactions.

The main objective of this thesis is to obtain and characterize polythiophene films in atmospheric pressure plasma reactors, for various applications in medicine. Furthermore, it is very important to approach physico-chemical processes at interface biological media-polymer materials.

Processes that occur at the interface polymer material-biological medium are influenced by physico-chemical properties of polymer surface and the nature of biological medium. Therefore, the functional performances of the polymer used in biomedical application, are depending both on the interface polymer- substrate and also on the interface polymer-biological medium.

Thesis structure

This thesis is structured into six chapters, containing results from literature, the methods of synthesis, characterization and applications of polythiophene films and, also the personal contributions regarding at this topic.

In ***Chapter 1,*** entitled ***''Methods of obtaining polymers films with conductive properties'',*** are presented the polymerization mechanism in conventional chemistry and polymerization reactions in the plasma reactors. Also, this chaper includes an overview about conducting polimers and methods used for synthesis of polythiophene (PTh). It also highlighted the physico-chemical properties and biomedical application of PTh.

In ***Chapter 2,*** entitled ***''Characterization techniques of the polymer films''***, are presented techniques and methods used for the characterization of pPTh films, such as: X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (RMN), UV-Vis Spectroscopy, Impedance Spectroscopy (IS), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Contact Angle Method.

In order to characterize the interface between biological medium and polymer material, it is necessary to know the nature and the origin of the biological medium. Thus, it was made a classification of biological media, in particular it has been a presentation concerning the importance of identification of iodine ions in the biological environments.

In ***Chapter 3,*** entitled ***''Plasma at atmospheric pressure used to obtain polythiophene films (pPTh)'',*** are presented the experimental configurations of dielectric barrier discharge at atmospheric pressure used to obtain pPTh films. Also, they are described the principle and operating parameters for each configuration, as well as plasma diagnosis from electrical point of view (based on the discharge current analysis) and optical (by optical emission spectroscopy, OES). Thus, it was found that the intensity of discharge current depends on the position of the intel of the working gas, the nature of gas (helium/argon) and nature of substrate (quartz, glass, NaCl). Excited speacies in the plasma volume, also the relative intensities of emision lines/bands of the excited species of the helium atom (*He*), the nitrogen atom (*N*), molecular nitrogen (N_2), molecular nitrogen ion (N_2^+), oxygen atom (*O*) and hydroxyl group (*OH*) are significantly changed at introduction of thiphene vapors in the discharge volume, due to the fragmentation and dissociation of the monomer molecules and the initiation of polymerization process.

Chapter 4, entitled ***''The preparation and characterization of pPTh films''*** , is dedicated to a comparative study of properties of pPTh films obtained in the plasma at atmospheric pressure reactors in different configurations and mixture of tiophene vapors and argon, respectively thiophene vapors and helium. Thus, are presented and discussed the chemical composition, wettability and surface morphology, also the electrical properties of pPTh films. Spectroscopic analyses (XPS and FTIR) reflect the retention of the thiophene ring in the structure of pPTh film. Nonetheless, the high reactivity of the plasma phase and efficient generation of oxygen based radicals lead to in increased content of carbonyl (C=O), alkyne (acetylene C≡C-H) and aliphatic (CH_2) groups in the plasma polymer film. Also the ^{1}H-NMR spectrums confirm the presence of intact thiophene molecules in pPTh matrix a fact that could be due to rapid polymerization process and the pulsed mode of dielectric barrier discharge operation. The pPTh films have a higher hydrophobic character, a granular structure without defects, as well a semiconductor behavior. The results show that the nature of the working gas (helium, argon), also, duration of polymerization processes influences the physico-chemical properties of the polymer film.

Chapter 5, entitled***''Stability of pPTh films in biological media'',*** is devoted to the characterization of the interface pPTh – water/PBS test liquid and interface pPTh – iodine vapors. In this chapter we have demonstrated that the polythiophene films obtained in plasma reactors at atmospheric pressure are unstable in biological medium. After immersion of pPTh film in biological medium, a process of swelling was observed, followed by a process of detachment of film from the substrate.

In order to improve the adhesion of pPTh films to the substrate, we performed a chemical pre-treatment of the substrate by using a coupling agent based on silane molecules, respectively 2- (3 -trimethoxysilylpropylthio)thiophene. The results show that the silanization of substrate surface substantially improves adhesion of the pPTh film to the substrate.

The *in situ* UV-Vis measurements and XPS analysis proved that the pPTh film absorbs iodine vapors.

Chapter 6 is dedicated to general conclusions, we also highlighted the personal contributions related to the configurations of experimental device, selection of operational parameters of the plasma used to obtains pPTh films with imposed properties. It was characterized the films and proposed a surface pretreatment, improving the adhesion of pPTh film to the substrate.