International Journal of Pharmaceutics xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Pharmaceutics

journal homepage: www.elsevier.com/locate/ijpharm

Electrochromic properties of polyaniline-coated fiber webs for tissue engineering applications

Mihaela Beregoi[a,b], Cristina Busuioc[a,b], Alexandru Evanghelidis[a], Elena Matei[a], Florin Iordache[c], Mihaela Radu[d], Anca Dinischiotu[d], Ionut Enculescu[a,*]

[a] National Institute of Materials Physics, RO-077125 Magurele, Romania
[b] University POLITEHNICA of Bucharest, RO-011061 Bucharest, Romania
[c] Institute of Cellular Biology and Pathology "Nicolae Simionescu", RO-050568 Bucharest, Romania
[d] University of Bucharest, Department of Biochemistry and Molecular Biology, RO-050095 Bucharest, Romania

ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form 18 November 2015
Accepted 29 November 2015
Available online xxx

Keywords:
Polyaniline
Fibers
Electrospinning
Artificial muscles
Tissue engineering
Biomimetics

ABSTRACT

By combining the electrospinning method advantages (high surface-to-volume ratio, controlled morphology, varied composition and flexibility for the resulting structures) with the electrical activity of polyaniline, a new core–shell-type material with potential applications in the field of artificial muscles was synthesized. Thus, a poly(methylmethacrylate) solution was electrospun in optimized conditions to obtain randomly oriented polymer fiber webs. Further, a gold layer was sputtered on their surface in order to make them conductive and improve the mechanical properties. The metalized fiber webs were then covered with a PANI layer by *in situ* electrochemical polymerization starting from aniline and using sulphuric acid as oxidizing agent. By applying a small voltage on PANI-coated fiber webs in the presence of an electrolyte, the oxidation state of PANI changes, which is followed by the device color modification. The morphological, electrical and biological properties of the resulting multilayered material were also investigated.

1. Introduction

The development of new materials with applications in the field of biomimetics is a continuous challenge for the researchers who aspire to improve the quality of life. In this context, tissue engineering is an important part of the regenerative medicine, which combines the synthesis strategies of different structures with the complex investigations of their biological activity for designing artificial systems with properties and functions similar with those of the natural ones (Li et al., 2010; Quaglia, 2008). In particular, artificial muscles are devices with good mechanical properties, which can reversibly modify their shape under the influence of external stimuli (temperature, pH, electric potential) (Shahinpoor, 2003; Maeda et al., 2010). There are several types of materials that can be used for the fabrication of artificial muscles, such as electroactive polymers (Detsi et al., 2013; Mirfakhrai et al., 2007), shape memory alloys (Tang and Felicelli, 2015; Taniguchi, 2013) or electroactive ceramics (Rozniecka et al., 2005), the first class being the most intensively studied.

Conducting polymers, like polyaniline, polypyrrole, polythyophene and their derivatives, are a special class of electroactive polymers and also good candidates for manufacturing devices that mimic natural muscles due to their chemical structure which allows the reversible permeation/release of cations from an electrolyte by applying an electric potential. These processes make possible the expansion/contraction of the entire structure, which is associated with the conformational changes of the polymer chains. Besides the electroactivity, these materials have the property to change their color simultaneously with the dimensional modification (Otero and Martinez, 2014; Torop et al., 2014).

Polyaniline (PANI) (Otero, 2013; Otero et al., 2012) has a unique electronic conduction mechanism, achieved by protonation, as well by p-type doping. The extended use of this polymer can be explained by its interesting properties, such as variable monomer oxidation state, electrical and optical activity, low cost *etc*. PANI is more or less conductive depending on the oxidation state and protonation degree; the highly conducting state is called emeraldine (base or salt form, as a function of amine and imine groups ratio), the fully reduced is leucoemeraldine and the most doped is pernigraniline. Starting from aniline, the polymer can be chemically or electrochemically synthesized onto conducting

* Corresponding author. Fax: +40 21 3690177.
E-mail addresses: encu@infim.ro, i.enculescu@gmail.com (I. Enculescu).

http://dx.doi.org/10.1016/j.ijpharm.2015.11.055
0378-5173/

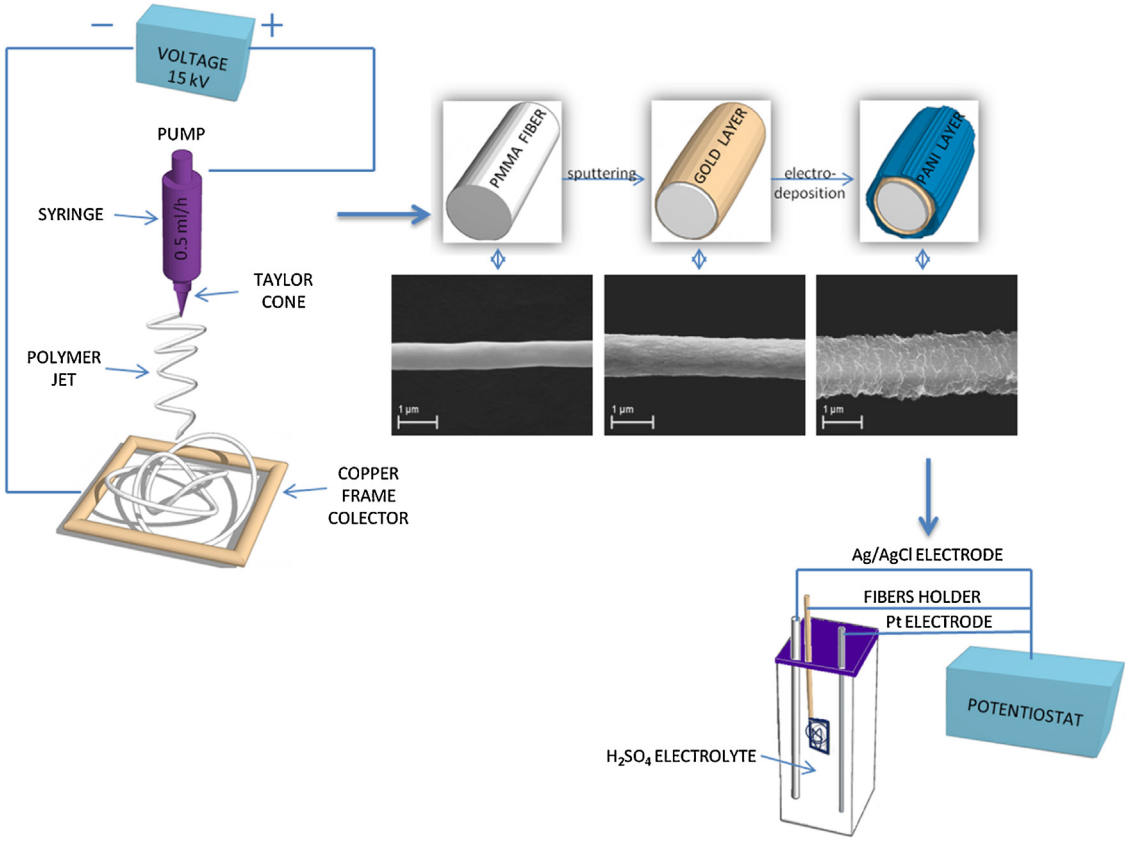

Fig. 1. Schematic representation of the electrochromic devices fabrication.

substrates from solutions which contain an oxidizing agent (strong inorganic or organic acids), where aniline exists as cation. The switching properties of PANI are assigned to the protonation/deprotonation of the polymer backbone, processes which occur in the presence of an ionic electrolyte that can be liquid (sulfuric acid or lithium perchlorate solutions), solid (solid polymer electrolytes) or polymeric gel (poly(methylmethacrylate)-based gels) (Alloin and Iojoiu, 2010). Once the redox reactions take place, the polymer color changes, which indicates the transition of PANI from one oxidation state to another. Frequently, materials with such properties are used for the fabrication of electrochromic devices due to the large number of switching cycles, high contrast during the switching process, electrochromic memory and long stability (Fu et al., 2014).

Moreover, in the past years, the electrospinnig technique has been attracting researchers' attention due to the capability of generating fibers with different diameters and characteristics by using accessible and inexpensive starting materials, which is reflected by the growing number of papers published on this topic (Ramakrishna et al., 2005; Greiner and Wendorff, 2007; Wang

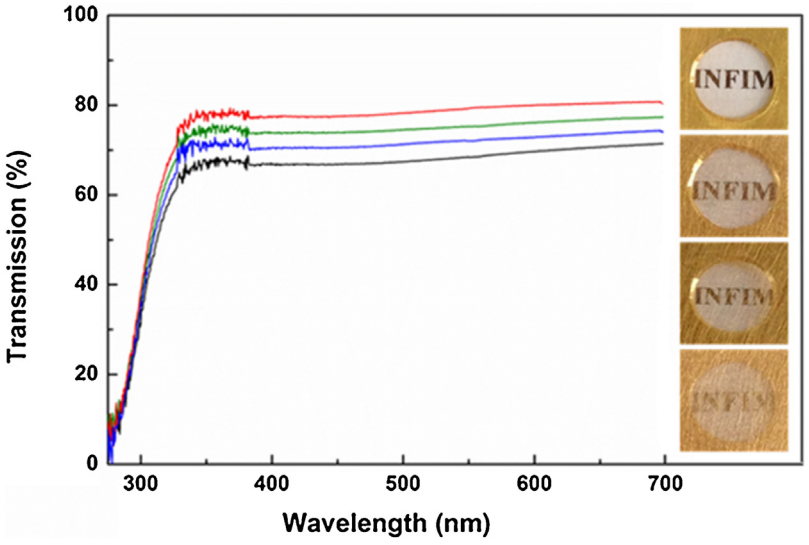

Fig. 2. Transmittance spectra and digital photographs of four metalized fiber webs with different fiber densities.

Please cite this article in press as: M. Beregoi, et al., Electrochromic properties of polyaniline-coated fiber webs for tissue engineering applications, Int J Pharmaceut (2015), http://dx.doi.org/10.1016/j.ijpharm.2015.11.055