Structural and Morphological Aspects Considerations of Bilayers Actuators Based on Polypyrrole/Polyethylene Glycol Composites

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Abstract—Polypyrrole-polyethylene glycol (PPy–PEG) composite films were synthesized on stainless steel electrode by electrochemical method. Presence of PEG as a plasticizing polymer in the solution of polymerization strongly affects the morphological and swelling characteristics of the composite films. Results indicated that the increase in PEG weight percent to 0.07 leads to bi-layer actuators that move faster 18\% than those made by neat polypyrrole. However, with further increase in PEG weight percent, the rate of movement decreases. On the other hand, at the same time, the efficiency of electrical energy conversion to the mechanical work decreases as wt\% of the PEG is increased. SEM pictures of electrochemically synthesized PPy and PPy–PEG layers prepared at the presence of various amounts of PEG showed that the thick layer of PPy is a cauliflower and granular structure. However PPy–PEG composites have a more integrate structure and smooth surface including small pores required to penetrate the counter ions.

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INTRODUCTION

Redox process in conducting polymers, are reversible reactions associated with solvated counter ions exchange and conformational movement of the polymer chains. This change in conformation stems from ingress or egress of ions and solvent molecules from polymer matrix to the surrounding environment. So the polymer swells or shrinks and an electrochemomechanical device is developed which is able to transform chemical energy into mechanical work as an artificial muscle [1–7]. A bilayer consisting of a non-conducting polymer tape and a volume changing conducting polymer is able to transform the molecular movement into a macroscopic angular movement [8–11]. A theoretical description of the bilayer movement was established by Otero et al [11]. A bilayer will be considered, consisting of an electroactive and homogeneous polypyrrole film adhering to a non-electroactive and flexible tape. Anodic or cathodic currents will pass through the polyanionic film to allow electrochemical oxidation or reduction processes. During oxidation, electrons are lost from the polymeric chains and solvated counter anions penetrate into the polymer to compensate the generated positive charges. The overall change in volume occurring during the oxidation of the polymer is expressed in terms of changes in the length of a given polymeric length (Δ\(l\)) can be separated into two components:

The first component is related to the relative change in the length of a polymeric segment (Δ\(l\)) will be proportional to the number of solvated counter ions penetrating into the polymer. The second one is related to charged polymer-charged polymer, charged polymer-anion, anion-anion and polymer-solvent interactions (Fig. 1).

![Fig. 1](image-url) Changes in (a) length and (b) concomitant bending in a bilayer muscle; \(d\) represents the thickness of the non-electroactive film, \(δ\) the distance of influence of the inactive tape, \(e\) the overall thickness of the polypyrrole layer and \(α\) the bending angle [11].

\(\Delta l = \Delta l_1 + \Delta l_2\)

\(\Delta l_1 = \frac{e - δ}{d + e + \delta}\)

\(\Delta l_2 = \frac{e + \delta}{d + e + \delta}\)

\(\alpha = \frac{l + \Delta l}{e + d}\)
The overall change in volume is proportional to the electrical charge consumed during the oxidation [11]. When the conductive polymer film is attached to a flexible and non-electro active tape, a stress gradient is arisen across the polymer interface and the swelling hindered by a mechanical opposite force [11]. Assuming a linear strain gradient from the interface to \( \delta \) (optimum thickness of conduction film to form a bilayer), change in the angle experienced by the free end of the bilayer as a function of the consumed charge can be obtained [11]:

\[
\alpha = h\varphi/(e + d) \quad (\text{if } e > \delta) \quad \text{or} \\
\alpha = h\varepsilon\varphi/\delta(e + d) \quad (\text{if } e < \delta),
\]

where \( \alpha \) is the bending angle, \( h \) is defined as the electrochemical swelling coefficient and depends on ion-solvent, charged polymer-charged polymer, charged polymer-anion, anion-anion and polymer-solvent interactions, \( l \) is the overall length of the bilayer, \( e \) and \( d \) are the thickness of conducting and inactive layers respectively and \( \varphi \) is the doping level (positive charges per volume unit), \( \varphi = Q/V_{\text{polymer}}, Q \) is the overall charge consumed during the oxidation process.

Hence, \( \alpha \) is a function of the conducting film thickness and the electric potential applied to the bilayer. On the other hand, the variation of bending angle (\( \alpha \)) with time (\( t \)) as a function of constant current flow will be given by the following equation [11]:

\[
\alpha = k_it \quad \text{or} \\
\alpha = \alpha/k_i,
\]

where \( k_i \) is a constant which includes all structural and geometrical parameters of the film:

\[
k = h/\sqrt{A \delta(e + d)},
\]

\( A \) is the area of the polymer-polymer interface.

As it is obvious, the bending time decreases when \( i \) increases and directly depends on various charge interactions (\( h \)). \( h \) which was named swelling coefficient can be strongly affected by the presence of additives such as polyethylene glycol (PEG) in the matrix of conductive polymer since of its ability to absorb the solvent and plasticize the polymer network. Many kinds of polymers, such as PVC [12], PTFE [13], PAI [14], PMMA [15] and PVA [16] have been used as supporting materials for chemical polymerization of pyrrrole. An attractive route is to introduce an insulating polymer, due to the excellent processability, without losing its conductivity [17, 18]. Among lots of insulating polymers, polyethylene glycol has attracted special interest due to its unique mechanical properties.

In order to improve mechanical stability, adherence, and chemical permeability of polypryrole deposited on steel [19], ITO [20] and titanium [21] electrodes PPy–PEG composite coating have been introduced. The effect of PEG concentration (as an insulating polymer) on increase in electrical conduc-

In this study, ClO\textsubscript{4}– doped polypyrrole was synthesized at the presence of various amounts of PEG, and then electrochemically studied in an attempt to investigate the conformational movement behavior of the prepared composites during the reduction and oxidation processes in relationship with the geometrical and structural parameter of the PPy/PEG. The major aspect of the composite films is the combination of electrical conductivity of PPy and mechanical properties of PEG such as flexibility, wettability and stability. Some other aspects of the PPy–PEG composites such as lifetime, energy conversion efficiency under loading, fatigue and training in devices based on bi-layer and tri-layer conducting polymer-polyethylene glycol (PEG) composite films were studied and reported elsewhere [24]. However, based on best of our knowledge, no work on artificial muscle and actuators constructed using PPy–PEG composite has been published in the literature by other researcher groups.

**EXPERIMENTAL**

All chemicals used were of reagent grad. Pyrrole (Py) was purchased from Merck and distilled at reduced pressure before use. NaClO\textsubscript{4} and PEG (FW 6000) were also prepared from Merck and used without further purification. PPy and PPy/PEG films were electrogenerated using potentiostatic mode (0.65 V vs. Ag/AgCl/Cl– reference electrode) from 0.2 M Py and 0.2 M NaClO\textsubscript{4} aqueous solution in the absence or presence of 0.02, 0.05, 0.07 and 0.10 wt % of PEG at 0.0^°C for 3 h. The working and counter electrodes were stainless steel 316 with the dimensions of 3.0 × 1.5 cm\textsuperscript{2}. Bilayer actuators were constructed exactly according to the method explained in the literature [6, 7]. Once the polypyrrole film has been electrogenerated, the coated steel was removed from the solution, the polymer being partially oxidized. The polypyrrole films (one from each side of the electrode) were stuck to a commercially available plastic tape. Once good adherence between the polypyrrole film and the plastic tape had been obtained, the bilayer was removed from the stainless steel. These devices were used as electrode in the background solution (1.0 M NaClO\textsubscript{4} aqueous solution). Electrical contact between the PPy layer and the current or voltage source was