Chemical deposition and characterization of thin polypyrrole films on glass plates: role of organosilane treatment

Abstract Thin chloride-doped polypyrrole films (PPyCl) were deposited chemically onto untreated and silane-treated planar glass plates from aqueous solutions. The organosilanes used to treat the glass substrates were methyltriethoxysilane (Cl), propyltrimethoxysilane (C3), octyltrimethoxysilane (C8) and aminopropyltriethoxysilane (APS). The decreasing order of hydrophobic character of silane-treated glass slides, as measured by water contact angle measurements, was glass–APS ≅ glass–C8 > glass–C3 > glass–Cl > glass. X-ray photoelectron spectroscopy was used to determine the surface chemical composition of the glass plates before and following coating with the silane coupling agents and/or the PPy thin layer, respectively. The attenuation in intensity of the glass Na\textsubscript{1s} peak enabled the average thickness of the various organosilane overlayers to be estimated. Atomic force microscopy showed that the morphology of the organosilane overlayers was islandlike. The domains have a structure which depends upon the nature of the organosilane in question. Scanning electron microscope images showed that the morphology of the PPyCl thin films was homogeneous when coated onto glass–APS and glass–C8, but wrinkled at the surface of glass, glass–C1 and glass–C3 plates. Qualitative peel tests using 3M adhesive tape showed very good adhesion of PPyCl to the glass–APS substrate, whereas adhesion was fairly poor in the case of glass–PPy and PPy–alkylsilane–glass interfaces. The results of this multitechnique study suggest that hydrophobic interactions are important to obtain homogeneous and continuous thin PPy films, but Lewis acid–base interactions are the driving forces for strong and durable PPy–glass adhesion.

Key words Polypyrrole · Glass · Organosilanes · Wettability · Hydrophobic interactions

Introduction

Polypyrrole (PPy) is known to be insoluble, infusible and intractable after electrochemical (film) or chemical (powder) synthesis, which seriously limits its processability [1]. To overcome these poor mechanical properties, pyrrole polymerization must be carried out directly onto the substrate material of interest. Electrically conducting PPy films can be easily prepared electrochemically on conducting substrates, but only chemical synthesis can be employed with insulator substrates such as silica or glass. Many studies have reported the synthesis and characterization of PPy composites where an inorganic material has acted as a support for the in situ chemical synthesis of the conducting polymer or, alternatively, where the conducting polymer particles are dispersed in an insulating polymer matrix [2]. Maeda and Armes [3–4] reported the synthesis of PPy in the
presence of an ultrafine silica sol leading to unusual nanoscale hybrid PPy–silica particles with a raspberry morphology. Such particles possess a silica-rich surface as found by X-ray photoelectron spectroscopy (XPS) [5] and zeta-potential measurements [6]. These silica-rich nanocomposite particles could be surface-aminated using aminopropyltriethoxysilane (APS) [7]. Faverolle et al. [8] reported the preparation of conducting PPy-coated glass fibres where the glass fibre was pretreated with aminosilane and pyrrole-functionalized silane coupling agents before vapour-phase pyrrole polymerization. In the case of the pretreatment by pyrrole-functionalized silane, PPy adhesion to the glass fibre was found to be extremely strong. This is believed to be due to chemical bonding of PPy to glass via the pyrrole-functionalized silane coupling agent, which acts as a site for the polymerization initiation. Silica gel particles [9] and silica beads [10] have been modified by PPy to act as novel stationary reverse and anion-exchange phases in liquid chromatography. Improved selectivity of silica towards polyaromatic hydrocarbons was achieved after modification by PPy [10]. In the case of PPy coatings on octadeysilane-treated silica beads (silica–C18–PPyC1), the capacity factors of several molecular probes were similar to those obtained with silica–C18, thus indicating that PPy did not contribute to the retention properties.

Silane coupling agents are a broad class of surface-modifying chemicals widely used as adhesion promoters in composite materials [11]. They are very effective in preparing graftable silica for selective interactions with analytes in liquid chromatography [12]. Surface modification of quartz by aminosilane led to the immobilization of dendrimers and polystyrene microspheres, both bearing surface aldehyde groups [13]. Organosilanes were also suggested as an alternative to the classical, but toxic, chromic acid for corrosion control coatings on steel [14]. Of relevance to our ongoing research studies, Si/SiO₂ and glass surfaces were modified by C18 to act as templates for the selective deposition of conducting PPy and polyaniline [15]. Using patterned self-assembled monolayers of C18 as templates, it was possible to obtain patterned microstructures of conducting polymer coatings. Recently, we reported the effect of APS treatment of silica gel particles in the preparation of novel PPy–silica composite materials [16–17]. These composites were found to be conductive owing to a PPy-rich surface as a result of the in situ polymerization of pyrrole in the presence of APS-treated silica particles. The conductivity threshold was obtained for an initial APS concentration of 1% (v/v) although the weight percent of PPy did not exceed 12%. Moreover, the resulting conducting composite PPy–silica particles were found to be high-surface-area materials (160–180 m²/g) compared to bulk PPy powder (15–25 m²/g) [18].

In this work, we used glass-plate substrates as model planar surfaces for the chemical deposition of PPy in aqueous media. We wished to explore the effect of organosilane treatment of glass on the amount, morphology and adhesion of PPy coatings. Wettability by water, as determined by contact angle measurements, allowed us to quantify the hydrophobic character of untreated and silane-treated glass plates prior to pyrrole polymerization. XPS was used to monitor the change in the surface compositions of untreated and silane-treated glass plates before and after PPy deposition. The surface morphology of the untreated and silane-treated glass plates was observed by atomic force microscopy (AFM). In order to characterize the morphology of the PPy deposited onto untreated and silane-glass plates, PPy overlayers were imaged by scanning electron microscopy (SEM). Finally, adhesion of PPy to untreated and silane-treated glass plates was measured qualitatively by a simple peel test using 3M adhesive tape.

### Experimental

#### Sample preparation

**Chemicals**

Pyrrole (Acros) was purified by passing it through a column of activated basic alumina prior to polymerization. Iron chloride (i.e. FeCl₃·6H₂O, Aldrich) was used as an oxidant/dopant species and was employed without further purification. Methyltriethoxysilane (C₁₁, Aldrich, 99%), propyltrimethoxysilane (C₃, Aldrich, 98%), octyltrimethoxysilane (C₈, Aldrich, 96%) and APS (Aldrich, 98%) were used as received. Deionized water and ethanol (Prolabo, 95%) were used as solvents. Glass plates (Sintec, 2 × 1 × 0.1 cm) were first washed for 30 min in KOH solution (5 mol l⁻¹) then rinsed with copious amounts of deionized water before silane treatment and PPy deposition.

**Organosilane treatment of glass plates**

Organosilane coupling agents (42.5 mmol l⁻¹) were first hydrolysed for 2 h in a stirred water/ethanol solution (10/90 v/v). Glass-plate substrates were then immersed for 6 h in the solution, allowing the condensation of the different coupling agents at the glass-plate surface. The organosilane-treated glass plates were then rinsed with copious amounts of deionized water in order to remove the excess of physically adsorbed coupling agents and were dried overnight in a desiccator prior to analysis.

**Chemical deposition of PPy onto glass plates**

Untreated and silane-treated glass plates were immersed vertically in a stirred aqueous solution (40 ml) containing iron chloride (36.0 mmol l⁻¹). Pyrrole (0.1 ml) was then injected via a syringe into the solution. The solution was stirred for 12 h to achieve complete chemical pyrrole polymerization. The PPy-coated glass plates were then carefully rinsed with deionized water to remove all excess oxidant/dopant species and were left to dry overnight in a desiccator prior to analysis.

**X-ray photoelectron spectroscopy**

The organosilane-treated and PPy-coated glass plates were mounted onto stubs using double-sided adhesive tape. XPS spectra were recorded using a VG Scientific ESCALAB MKI system operated in