European Polymer Journal 44 (2008) 2087–2098

Contents lists available at ScienceDirect

European Polymer Journal

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

Chemical and electrochemical polymerisation of pyrrole on polyester textiles in presence of phosphotungstic acid

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ARTICLE INFO

Article history:
Received 25 January 2008
Received in revised form 25 March 2008
Accepted 7 April 2008
Available online 12 April 2008

Keywords:
Polypyrrole
Phosphotungstate
Polymer coating
Conducting textiles
Electropolymerisation

ABSTRACT

Polypyrrole (PPy) was chemically synthesised on polyester (PES) textiles to produce conducting textiles. Two different types of counter ion were employed: anthraquinone sulfonic acid (AQSA) and phosphotungstate ($PW_{12}O_{40}^{3-}$). Textiles covered with PPy were characterised by means of FTIR-ATR, SEM, EDX, cyclic voltammetry (CV), surface resistivity measurements and electrochemical impedance spectroscopy (EIS). Additionally, friction and washing assays were done to test the resistance of the layer of conducting polymer ($PPy/PW_{12}O_{40}^{3-}$). Electropolymerisation of $PPy/PW_{12}O_{40}^{3-}$ in acetonitrile medium onto chemically synthesised $PES–PPy/PW_{12}O_{40}^{3-}$ showed the improvement of the coating properties.

1. Introduction

The electrical properties of polypyrrole were first reported by Weiss et al. in a complete study [1–3]. In this study polypyrrole was obtained through pyrolysis of tetraiodopyrrole. The first electrochemical polymerisation of pyrrole was reported by Diaz et al. [4–6].

On the other hand, development of textiles with new properties and applications has received great attention during the last years. One of these properties is the electrical conductivity in textiles. Applications of conducting textiles are varied and numerous; like antistatic applications [7], gas sensors [8], biomechanical sensors [9], electrotherapy [10,11], heating devices [12–14], microwave attenuation [15], dye removal [16]. Different methods have been used to produce conducting textiles; like employing metallic fibres mixed with non-metallic fibres, chemical metallisation of fibres [17], extrusion of fibres with conductive particles like carbon or the synthesis of conducting polymer films on textiles. The last is the method employed in this paper to produce polypyrrole conducting textiles.

In [18] it can be seen the patent literature evolution on the polymerisation of pyrrole on different textile substrates. Different textile materials have been used to produce polypyrrole conducting textiles obtained by chemical reaction, like polyester [7,8,15,19], nylon [9,10,20,21], cotton [12,22], silk [22], cellulose derivatives [23–25], polyester-nylon [13] and polyaramide [26]. The methods employed in chemical polymerisation are: in situ polymerisation [8,20], two steps polymerisation [9,10,12,13,19,21–26] and emulsion polymerisation [7]. When in situ polymerisation is employed, all the reagents are added at the same time and reaction occurs. Two steps polymerisation has one step of adsorption of certain reagents and the stage of reaction when the rest of reagents are added. Emulsion polymerisation is less employed. Vapour phase polymerisation [22,23] has been employed as a method available to be automated. The method employed was the two steps process with a previous adsorption of oxidant and counter ion and the subsequent exposure to pyrrole vapours; occurring the polymerisation.

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doi:10.1016/j.eurpolymj.2008.04.007

In the polymerisation of pyrrole to form polypyrrole, positive charges are created in the polypyrrole structure. These positive charges need to be neutralised to maintain the electroneutrality; these negative charges are provided by a counter ion. Low size anions like Cl^- have been employed as counter ions, but their stability is low [15]. Typical counter ions employed in textiles covered with polypyrrole are organic molecules with high size; like anthraquinone sulfonic acid (AQSA) [8,13,15,19,21,27], dodecylbenzene sulfonic acid (DBSA) [7,21], *p*-toluene sulfonic acid (PTSA) [8,15,20,21], naphthalenedisulfonic acid (NDSA) [9,15,21], benzenesulfonic acid (BSA) [10,26], naphthalenesulfonic acid (NSA) [15,20], anthraquinone disulfonic acid [23,25]. The higher size of the counter ion, the more difficult the expulsion of the counter ion from the structure is.

Polyoxometalates, POMs, are small oxide clusters whose size and solubility have caused them to be traditionally considered within the framework of molecular chemistry. They are indeed complex molecules with several metallic ions coordinated by shared oxide ions, forming a highly symmetrical metal oxide cluster [28]. They present the possibility to produce a hybrid material when combined with conducting polymers such as polypyrrole. These polyoxometalates are trapped into the polymeric matrix due to the electroneutrality principle when the synthesis occurs. Therefore, a hybrid material with combined properties (organic–inorganic) is synthesised. The new material has higher density and conductivity than polypyrrole alone [29]. The presence of active ionic species immobilised in the polymeric matrix force the cations instead of the anions present in the medium to diffuse through the polymer structure when an oxidation or a reduction reaction occurs. In addition, polyoxometalates are anions of high volume and charge, so their diffusion coefficient is low, and the exchange with anions present in the solution is prevented. Polyoxometalates have been combined with polypyrrole to produce hybrid materials on Pt [30–32] and carbon steel electrodes [33].

Polyoxometalates have not been employed as counter ions to produce conducting textiles to our knowledge. The aim of this paper is to produce polyester textiles covered with the hybrid material $PPy/PW_{12}O_{40}^{3-}$. Additionally, polyester textiles covered with PPy/AQSA have been produced to compare the results with that obtained with the hybrid material. When the size of the counter ion is high its diffusion is prevented and it remains in the polypyrrole structure [34]. This is the basis for employing $PW_{12}O_{40}^{3-}$ with high molecular size that would difficult the expulsion of the counter ion. The presence of W in the hybrid material with a high atomic weight allows the knowledge of the superficial distribution of the counter ion employing SEM combined with backscattered electrons. Furthermore, $PW_{12}O_{40}^{3-}$ has a high negative charge and catalytic properties that make this hybrid material interesting for catalytic reactions. Electrochemical characterisation with CV and EIS has been employed to characterise the films of conducting polymers on textiles. EIS has not been employed to characterise textiles covered with conducting polymers to our knowledge. Only a few assays of CV have been performed on conducting textiles; in the reference [20] we can see a study of cyclic voltammetry on nylon membranes coated with PPy.

Electropolymerisation of pyrrole has been employed as a method to produce conducting textiles [11,35]. Bhadani et al. [35] covered a Pt anode with cotton fibre. Electrolysis at 40 mA with pyrrole and PTSA was realised. The result was the indirect formation of polypyrrole on cotton fibres. Kim et al. [11] covered nylon/spandex chemically and later electrochemically similarly to [35]. Chemically polypyrrole covered textile was put between stainless steel plates and electropolymerisation occurred. In our study the PES textile covered chemically with polypyrrole is employed as anode material to polymerise electrochemically the hybrid material $PPy/PW_{12}O_{40}^{3-}$.

2. Experimental

2.1. Reagents

Analytical grade pyrrole, sodium sulphate, ferric chloride, anthraquinone sulfonic acid sodium salt (AQSA), sulphuric acid, sodium dihydrogenophosphate, disodium hydrogenophosphate and Lichrosolv. acetonitrile were purchased from Merck. Analytical grade phosphotungstic acid hydrate was supplied by Fluka. Normapur acetone was from Prolabo. Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q RG system with a resistivity near to 18.2 MΩ cm.

2.2. Chemical synthesis of $PPy/PW_{12}O_{40}^{3-}$

Chemical synthesis of polypyrrole on polyester textiles was done as reported by Lin et al. [19]. Size samples were 6 cm × 6 cm approximately. Polyester was degreased with acetone in ultrasound bath previously to reaction. Pyrrole concentrations employed in chemical polymerisations were 0.5, 1 and 2 g/l. The molar relations employed in the chemical synthesis bath were pyrrole:$FeCl_3$:AQSA (1:2.5:0.6); when $PW_{12}O_{40}^{3-}$ was employed as counter ion the relation was 1:2.5:0.2. The molar relation of counter ion is three times lower when $PW_{12}O_{40}^{3-}$ is employed than when AQSA is used, due to the fact that $PW_{12}O_{40}^{3-}$ has three negative charges; on the other hand AQSA only posses one negative charge. Next stage was the adsorption of pyrrole and counter ion ($V = 200$ ml) (AQSA or $PW_{12}O_{40}^{3-}$) on the textile during 30 min at 0 °C without stirring. Passed this time, $FeCl_3$ solution (50 ml) was added and reaction elapsed during 150 min at 0 °C without mechanical agitation. Adsorption and reaction elapsed in a precipitates beaker. Polymerised textile was washed with water to remove polypyrrole not joined to fibres. The conducting textile was dried in a desiccator during at least 24 h before measurements. The weight increase for the textile covered with $PPy/PW_{12}O_{40}^{3-}$ was measured obtaining a value between 7–10% for polymerisations where 2 g/l pyrrole was employed.

2.3. Electrosynthesis and cyclic voltammetry

Electrosynthesis and cyclic voltammetry (CV) experiments were performed using an Autolab PGSTAT302 potentiostat/galvanostat. All electrochemical experiments were realised at room temperature and without stirring. Stainless steel counter electrodes (CE) were employed; the pre-treatment consisted on polishing, degreasing with acetone in ultrasonic bath and washing with water in the ultrasonic bath. In electrochemical synthesis two CE were used to equalise the electrical field around the working electrode (WE) of conducting polymer. Potential measures were referred to Ag/AgCl reference electrode. Oxygen was removed from solution by bubbling nitrogen gas. The pH study was made employing solutions in the range 1–13.

In electrosynthesis and CV experiences the WE were made by cutting a tyre of the material and controlling the area with Teflon®. The conducting textile has an ohmic fall that we need to consider in cyclic voltammetry and electrosynthesis, in a different way the measured potentials will not be real. In these experiments the ohmic fall was measured and entered in the potentiostat/galvanostat. CV measures were done after 1 h of contact of the conducting textile electrode with the measuring solution in N_2 atmosphere to achieve the equilibrium stage; it has been corroborated that contact time had influence in the voltammetric response.

Electrosynthesis was performed in acetonitrile medium with 0.01 M $H_3PW_{12}O_{40}$ and 0.2 M pyrrole in N_2 atmosphere. The conducting textile electrode was soaked with the solution during 10 min to allow the diffusion of species to the electrode. The synthesis potential was determined by CV. In this medium the potential was cycled between 2.5 V and −0.8 V. When the slope of the voltammogram rises is a sign that polymerisation is occurring. In our electrochemical system, the determined synthesis potential was 1.5 V. For the potentiostatic synthesis the conducting textile electrode was immersed at open circuit potential and then the potential was risen up to the synthesis potential of 1.5 V, going on the electrosynthesis the necessary time to achieve the desired electrical charge. After synthesis, the electrode was washed with acetonitrile. After that, the electrode was immersed in the measuring solution during 1 h and characterised by means of CV.

2.4. FTIR-ATR spectroscopy

Fourier transform infrared spectroscopy with horizontal multirebound attenuated total reflection (FTIR-ATR) was performed with a Nicolet Magna 550 Spectrometer equipped with DTGS detector. An accessory with pressure control was employed to equalise pressure in the different solid samples. A prism of ZnSe was employed. Spectra were collected with a resolution of 4 cm^{-1}, and 100 scans were averaged for each sample.

2.5. SEM and EDX

A Jeol JSM-6300 scanning electron microscope was employed to obtain the morphology of the samples and perform EDX analyses. SEM analyses were performed using an acceleration voltage of 20 kV. EDX measures were realised between 0 and 20 kV. Secondary electrons were employed to obtain micrographs and additionally the samples that contained W were also analysed with backscattered electrons.

2.6. Abrasion and washing assays

Abrasion resistance tests of polypyrrole covered textiles were performed as explained in the norm ISO 105-X12:2001. Each sample was abraded against cotton abrasive fabric for 10 cycles. This analysis was performed only for chemically synthesised samples due to the big sample size needed (20 × 18 cm). Washing fastness was determined as related in the norm ISO 105-C01.

Surface resistivity measures were performed employing a surface resistivity meter Model SRM-232-2000, 0–2000 Ω/square (Guardian Manufacturing) that employed the 4-point probe technique. Electrochemical Impedance Spectroscopy (EIS) (Autolab PGSTAT302 potentiostat/galvanostat) was employed to measure surface resistivities higher than 2000 Ω/square and characterise the material with this technique. EIS measures were carried out using two rectangular copper electrodes (0.5 cm × 1.5 cm) separated by 1.5 cm and pressed to the textile sample. The measured area of the textile was a square of 1.5 cm × 1.5 cm, so the measured resistance (Ω) was equal to the surface resistivity (Ω/square).

3. Results and discussion

3.1. FTIR-ATR spectroscopy

Fig. 1 shows the spectra of PES, PES chemically covered with the hybrid material PPy/$PW_{12}O_{40}^{3-}$ and covered with PPy/AQSA. If we compare the FTIR spectra of PES and PES covered with the hybrid material, it can be distinguished the band centred at 1550 cm^{-1} associated to the pyrrole ring stretching vibration (C=C) [23,25]. The characteristic bands of the bending vibration of pyrrole can be observed at 775, 1030 and 1160 cm^{-1} [23,25]. Other bands overlapped with PES bands partially can be observed; like C–C stretching (1450 cm^{-1}) [23,25] and C–N stretching (1300 cm^{-1}) [23,25]. The band overlapped with PES band partially at 1075 cm^{-1} (P–O stretching) [36,37] indicates the presence of the polyoxometalate. This band can be observed more defined in the Fig. 2 for a concentration of pyrrole of 1 g/l or 0.5 g/l. The other bands of $PW_{12}O_{40}^{3-}$ are overlapped with those of PES. EDX analyses were realised to make sure the presence of $PW_{12}O_{40}^{3-}$. FTIR spectrum is not changed substantially when AQSA is employed as counter ion. Additionally to the mentioned bands of polypyrrole, two bands centred at 1670 cm^{-1} and 710 cm^{-1} were observed, attributed to the AQSA structure [38].

The effect of pyrrole concentration in the FTIR spectrum can be observed in Fig. 2. It can be seen a general increase of all the bands mentioned previously when the concentration of pyrrole is increased from 0.5 g/l to 1 g/l. When pyrrole concentration is increased from 1 g/l to 2 g/l the tendency is to maintain the band intensity.

3.2. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX)

In this section the PES and PES covered with polypyrrole morphology is analysed by means of SEM obtained by

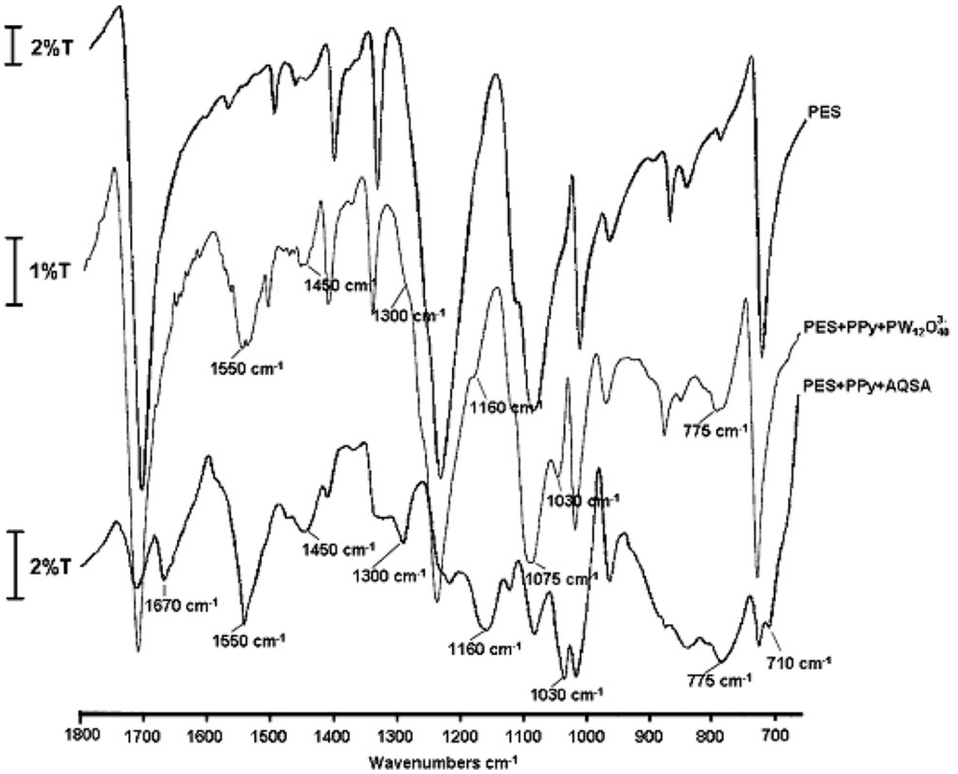

Fig. 1. FTIR-ATR spectrum of PES, PES covered with PPy/$PW_{12}O_{40}^{3-}$ (2 g/l pyrrole) and PES covered with PPy/AQSA (2 g/l pyrrole). Resolution 4 cm^{-1}, 100 scans.

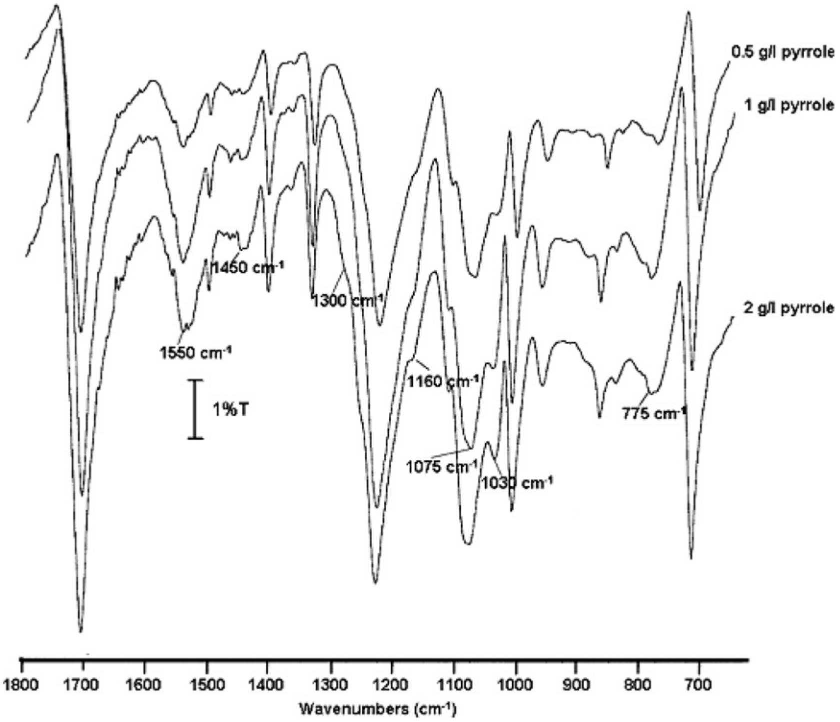

Fig. 2. FTIR-ATR spectrum of PES covered with the hybrid material PPy/$PW_{12}O_{40}^{3-}$ with pyrrole concentrations of 0.5, 1 and 2 g/l in the synthesis solutions. Resolution 4 cm^{-1}, 100 scans.

secondary electrons and back-scattered ones. Zonal analysis with EDX was employed to analyse zones of interest by focussing the electron beam in the selected area. The substrate morphology (PES) can be observed in Fig. 3a. Fig. 3b–d corresponds to the coating of PPy/$PW_{12}O_{40}^{3-}$. Fig. 3e and f shows the PES covered with PPy/AQSA.

PES fibres are covered completely with the hybrid material and the surface has a smooth appearance. The presence of polypyrrole aggregates that were not removed in the washing stage can be seen in Fig. 3b and d. Elements of high atomic weight (W has an atomic weight of 183.85) backscatter more electrons, so in the micrograph are observed as white colour zones. This fact can be observed in the micrograph 3-c. All the fibres appear white coloured, indicative that $PW_{12}O_{40}^{3-}$ is distributed homogeneously in the entire textile surface. Polypyrrole is well distributed consequently, due to the fact that $PW_{12}O_{40}^{3-}$ is the polypyrrole counter ion. Fig. 3e shows the morphology when AQSA

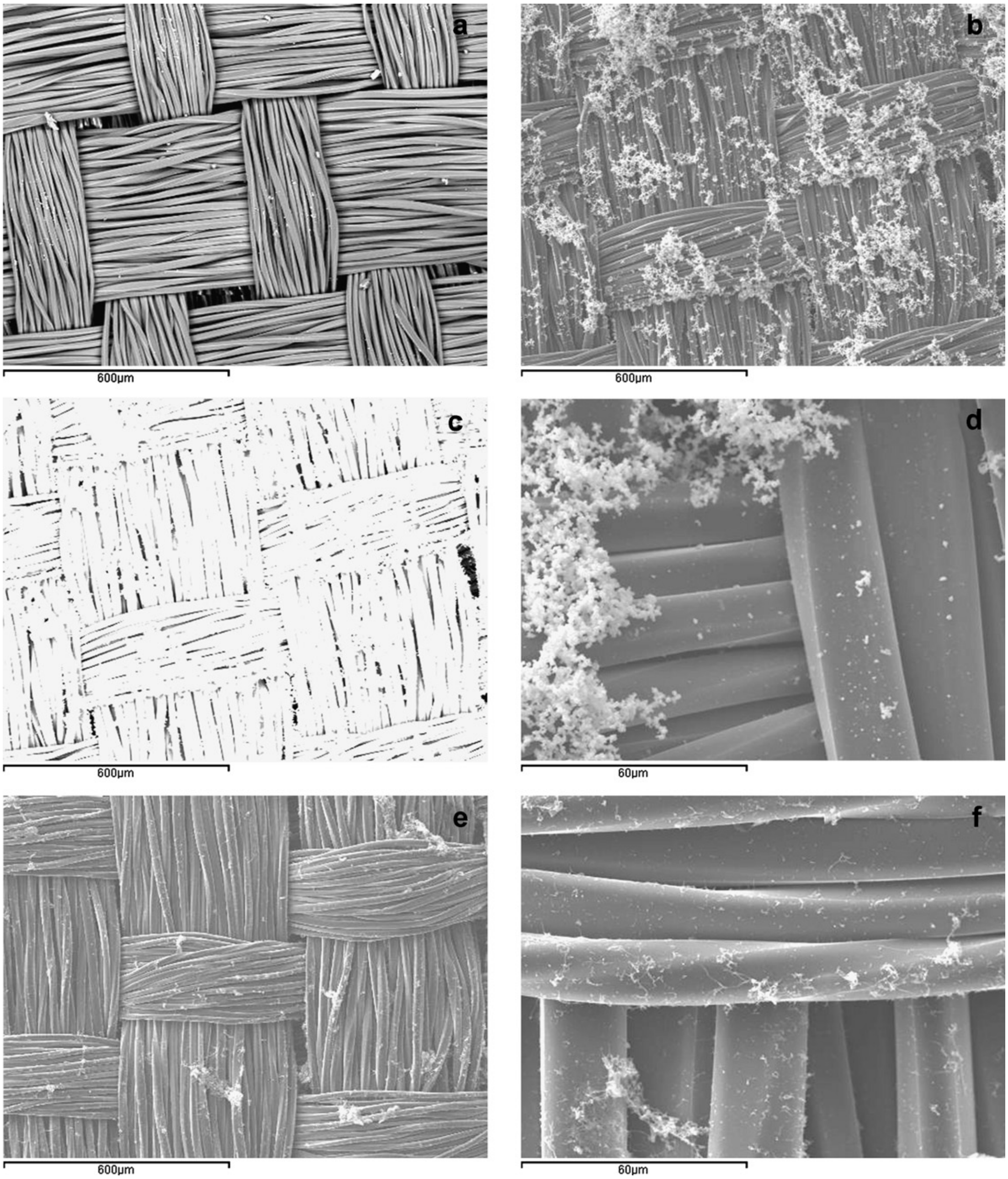

Fig. 3. SEM micrographs of the following samples chemically synthesised (2 g/l pyrrole): (a) PES (×100); (b) PES covered with PPy/$PW_{12}O_{40}^{3-}$ (×100); (c) PES covered with PPy/$PW_{12}O_{40}^{3-}$ (×100, backscattered electrons); (d) PES covered with PPy/$PW_{12}O_{40}^{3-}$ (×1000); (e) PES covered with PPy/AQSA (×100); (f) PES covered with PPy/AQSA (×1000).

is employed as counter ion. The presence of aggregates in textile's surface is less than in the case of $PW_{12}O_{40}^{3-}$ use. The coating degree of the fibres is complete too and the surface is smooth. Hakansson et al. [13] demonstrated for PPy/AQSA deposition on PES/Lycra that the reaction at low temperatures (4 °C) contributed to the development of a smooth surface morphology. Smooth surfaces stabilise the conducting polymer films, due to the inhibition of the oxygen penetration [15]. On the other hand more porous morphology facilities the oxygen diffusion through the film [15] and the subsequent degradation and loss of conductivity. Kuhn et al. [15] demonstrated that the type of counter ion had influence in the morphology, obtaining smoother surfaces with AQSA and more porous surfaces with Cl^-. So the morphologies obtained with the counter ion AQSA and $PW_{12}O_{40}^{3-}$ facilitate the stability of the conducting polymer films due to the smooth surfaces obtained that hinder the oxygen diffusion.

Fig. 4a–c corresponds to EDX analysis performed on textiles covered with PPy/$PW_{12}O_{40}^{3-}$; and in Fig. 4d and e AQSA was employed as counter ion. Fig. 4f shows a zonal EDX analysis of PES. In Fig. 4a and d EDX analysis were performed in the entire area of the micrograph. On the other hand in Fig. 4b, c, e and f EDX analyses were realised in concrete zones indicated in the adjacent micrograph. The spectrum of Fig. 4a reveals the presence of W so the molecule $PW_{12}O_{40}^{3-}$ has been incorporated in the polypyrrole structure as counter ion. Fe and Cl also appear in the spectrum and their presence is due to the $FeCl_3$ employed as oxidant. Chlorides could be incorporated as counter ions partially. In the Fig. 4b an EDX analysis was performed in a zone of the fibre where the presence of aggregates of polypyrrole was not observed. The result obtained was the same, the presence of W that confirmed the presence of $PW_{12}O_{40}^{3-}$. EDX spectrum of the Fig. 4c was done in a zone with aggregates presence and showed that the aggregate nature was similar to the hybrid material coating on the fibres. Fig. 4d shows the presence of S that is present in AQSA structure. An analysis performed in a zone without aggregates showed the same result (Fig. 4e). Moreover Ti is present as impurities; that were observed in EDX analysis of the original textile fibres (Fig. 4f).

3.3. *Electrochemical synthesis of PPy/*$PW_{12}O_{40}^{3-}$

Electrochemical synthesis was performed in acetonitrile medium with 0.2 M pyrrole and 0.01 M $H_3PW_{12}O_{40}$ in N_2 atmosphere. A potentiodynamic synthesis was employed in order to determine the synthesis potential with our experimental conditions. As can be seen in Fig. 5, around 1.2 V occurs a sudden change of the slop in the voltammetric curve; this fact is indicative that polymerisation begins

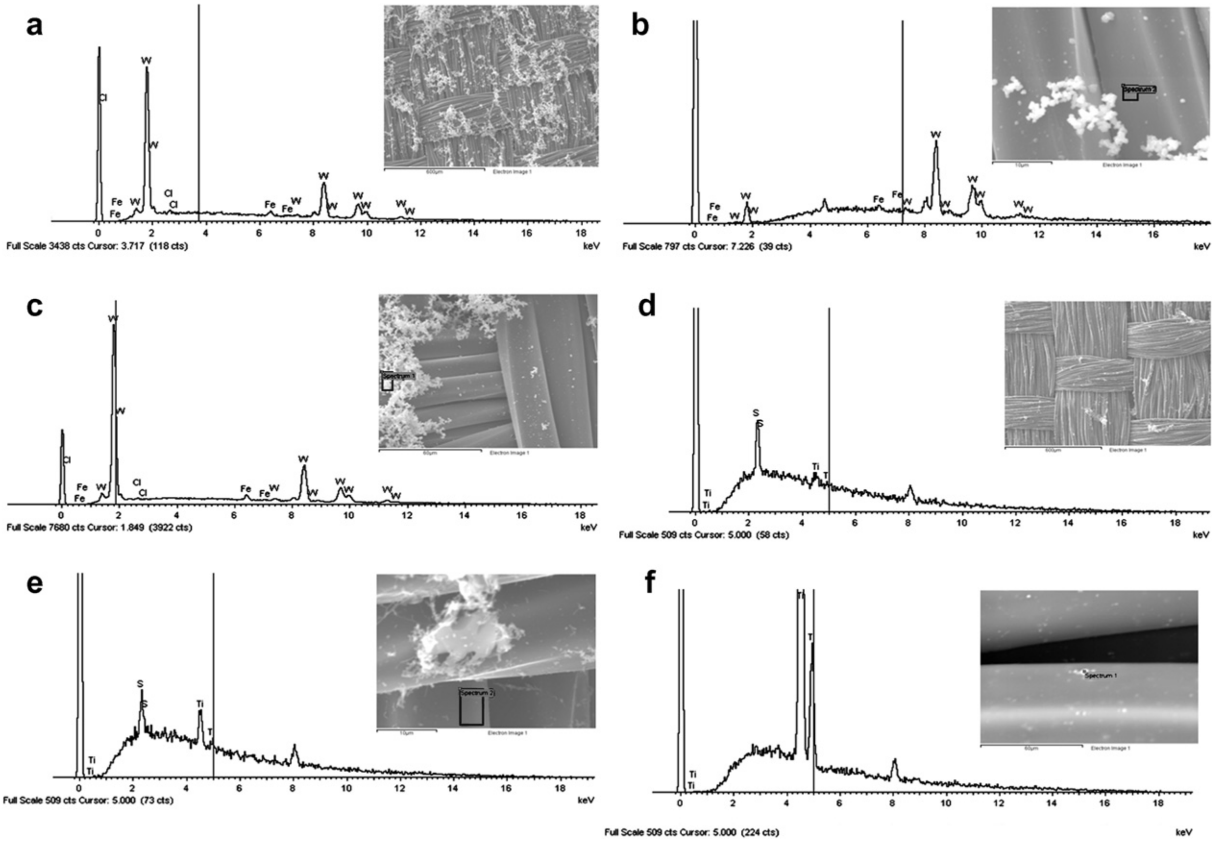

Fig. 4. SEM micrographs and EDX analysis of PES covered with chemically synthesised polypyrrole (2 g/l pyrrole): (a) PPy/$PW_{12}O_{40}^{3-}$ (×100); (b) PPy/$PW_{12}O_{40}^{3-}$ (×3500); (c) PPy/$PW_{12}O_{40}^{3-}$ (×1000); (d) PPy/AQSA (×100); (e) PPy/AQSA (×3500); (f) original PES (×3500).

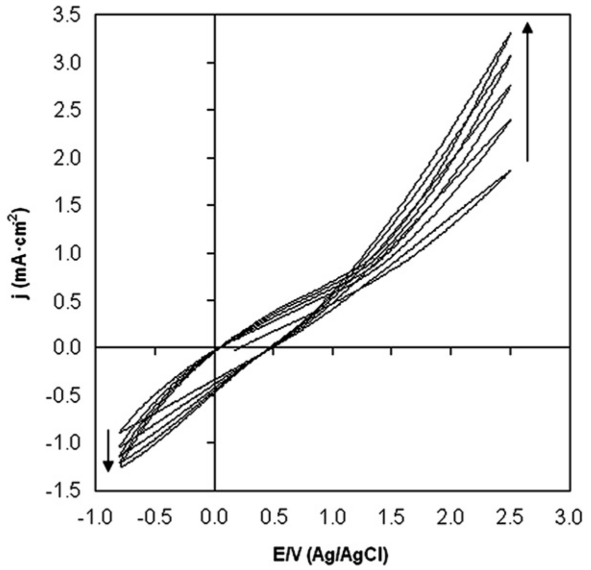

Fig. 5. Potentiodynamic synthesis of PPy/$PW_{12}O_{40}^{3-}$ on a substrate chemically polymerised previously (2 g/l pyrrole) with PPy/$PW_{12}O_{40}^{3-}$. 0.01 M $H_3PW_{12}O_{40}$ + 0.2 M pyrrole solution in acetonitrile medium. Scan rate 50 mV/s, cycle from −0.8 V to 2.5 V, five scans.

at this potential. The current density rises with the scan number, indicative that polymerisation is occurring. We selected 1.5 V for the potentiostatic synthesis because it was an adequate potential to assure electropolymerisation and avoid overoxidation. The films were electrosynthesised by potentiostatic techniques on PES substrate chemically covered with PPy/$PW_{12}O_{40}^{3-}$ previously. The electrode was introduced in the synthesis solution at the open circuit potential and then the potential was fixed at 1.5 V during the necessary time to achieve the desired polymerisation charge. Fig. 6 shows the current transient curve for potentiostatic synthesis of the hybrid material. The current obtained was around 2.5 mA cm^{-2}. The micrograph 7-a (×100) shows the electrochemically PPy/$PW_{12}O_{40}^{3-}$ covered textile for a polymerisation charge of 20.78 C/cm^2. As can be seen in this figure, the textile fibres are not observed and the electrogenerated polymer covers the textile entirely. If we compare the chemically polymerised polymer (Fig. 3b) with the electrochemically generated polymer (Fig. 7a) we can appreciate the great morphology difference. The chemically synthesised polymer produces a smooth surface and the electrochemically synthesised polymer has got a globular structure (Fig. 7b). The polymer grows on the fibres covered with the chemically synthesised PPy/$PW_{12}O_{40}^{3-}$ when the potential of 1.5 V is applied to the conducting textile. Polypyrrole chemically obtained grown predominantly in the plane of the textile (2-D). In the electrochemical polymerisation the growth is in 3-D. The electrochemically generated polymer presents a globular morphology (Fig. 7b) typical of polypyrrole obtained by electrochemical polymerisation and doped with high size dopants [39]. This morphology has been also observed in electrochemically covered conducting textiles [40].

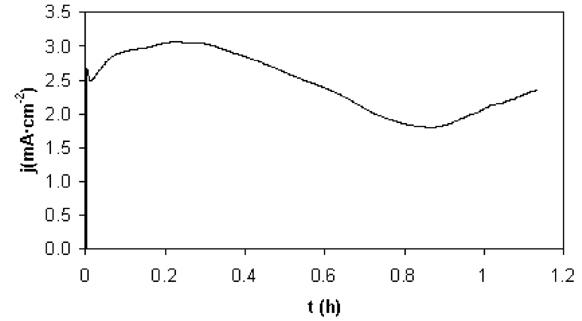

Fig. 6. Current transient curve for potentiostatic synthesis of PPy/$PW_{12}O_{40}^{3-}$ on a substrate chemically polymerised previously (2 g/l pyrrole) with PPy/$PW_{12}O_{40}^{3-}$. 0.01 M $H_3PW_{12}O_{40}$ + 0.2 M pyrrole solution in acetonitrile medium. Start potential: 0.2 V, synthesis potential: 1.5 V.

3.4. *Cyclic voltammetry (CV)*

Fig. 8a–c compares the voltammetric response obtained for the textile covered with PPy/$PW_{12}O_{40}^{3-}$ chemically and electrochemically synthesised (polymerisation charge of 2.23 C/cm^2) at different pH solutions (pH 1, pH 7 and pH 13, respectively). In Fig. 8d the voltammogram of the chemically synthesised textile at pH 13 is extended to observe the different peaks that appear in the voltammogram. The current density obtained for the chemically synthesised textile at different pH varies in this order: pH 7 > pH 1 > pH 13. With a buffer solution of pH 7 the current density doubles that obtained at pH 1. With a basic solution (pH 13) the current density is decreased dramatically due to the deprotonation of oxidised polypyrrole. This process happens near pH 10 (p*K*a 10) and results in polymer conjugation breaking, so the conductivity is decreased [41]. This loss of conductivity is observed in the Section 3.6; when the conducting textile is soaked with a basic solution (pH 13) during one hour, the resistivity rises two order of magnitude. The voltammetric response is also affected, so the current density decreases significantly. The voltammetric characterisation of the electropolymerised polymer shows the increase of the current density compared to the chemically polymerised polymer. This tendency is observed at all pH solution, but at pH 13 the increase is more obvious. The electropolymerisation produces a more conductive film so the voltammetric response is higher than that obtained for the chemical polymer. Only with the chemically synthesised polymer at pH 13 the characteristic voltammetric peaks of polypyrrole are observed clearly. Three main peaks are observed in the Fig. 8d. The cathodic peak at −0.55 V is attributed to the reduction of polypyrrole and $PW_{12}O_{40}^{3-}$ [42]. The anodic peaks at −0.42 V and −0.16 V are due to the oxidation of the hybrid material [42].

3.5. *Abrasion and washing tests*

Visual inspection of samples after abrasion tests showed loss of part of the conducting polymer; where it can be distinguished the band that had been submitted to friction. In the Table 1 are showed the values of colour degradation for the textile and the values of colour dis-

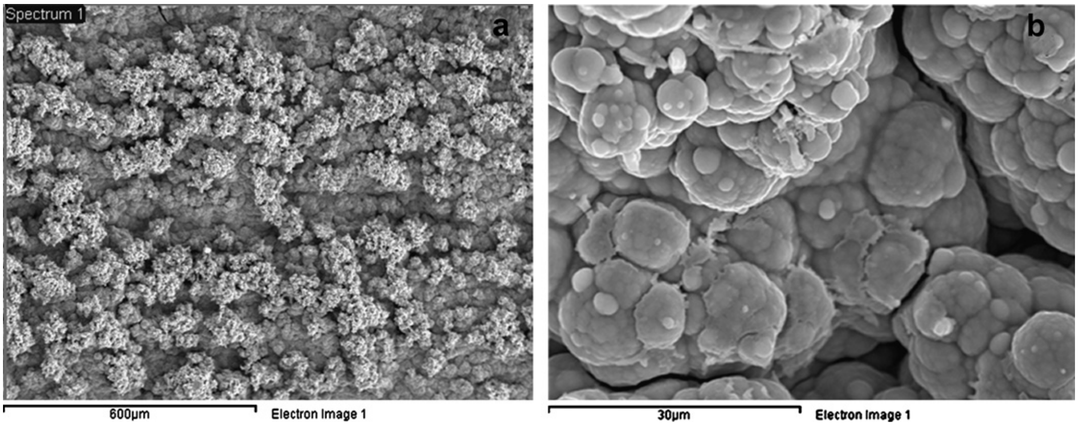

Fig. 7. SEM micrographs of PPy/$PW_{12}O_{40}^{3-}$ electropolymerised on a substrate chemically polymerised previously (2 g/l pyrrole) with PPy/$PW_{12}O_{40}^{3-}$. 0.01 M $H_3PW_{12}O_{40}$ + 0.2 M pyrrole solution in acetonitrile medium. Start potential: 0.2 V, synthesis potential: 1.5 V, polymerisation charge: 20.78 C/cm^2. (a) ×100, (b) ×2000.

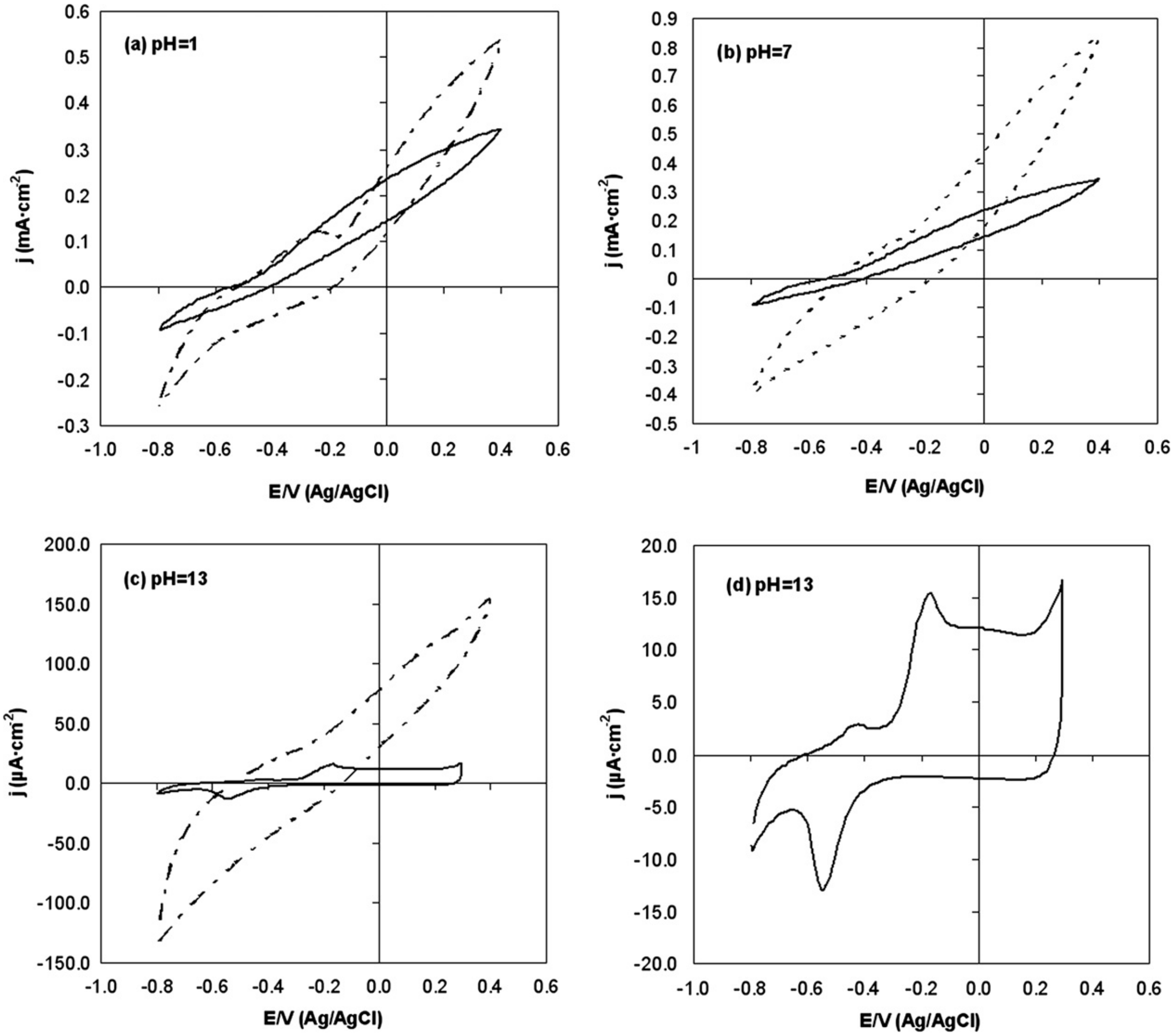

Fig. 8. Cyclic voltammetry of PES covered with chemically synthesised PPy/$PW_{12}O_{40}^{3-}$ (2 g/l pyrrole) (——) and electrochemically (2.23 C/cm^2) (— - —) at different pH: (a) pH 1 (0.1 M H_2SO_4), (b) pH 7 (phosphates buffer + 0.1 M Na_2SO_4), (c) pH 13 (0.1 M NaOH + 0.1 M Na_2SO_4), d) pH 13 (magnified). Scan rate 50 mV/s, cycle from −0.8 to 0.4 V, fifth scan for all samples.

Table 1
Colour degradation and colour discharge values for wet abrasion, dry abrasion and washing assays

Wet abrasion fastness	Dry abrasion fastness	Washing fastness
Colour degradation: 1–2	Colour degradation: 1–2	Colour degradation: 4–5
Colour discharge: 1–2	Colour discharge: 1–2	Colour discharge: 4–5

charge. Dry and wet assays did not show significant differences. Obtained values are small in the scale range (1–5); this implies a significant degradation of the polypyrrole layer.

Fig. 9a and c shows the textile micrographs after chemical synthesis, Fig. 9b, d and e illustrates the effect of dry friction on the layer of polypyrrole that covers polyester fibres and Fig. 9f shows the sample after the washing assay. The abrasion test degrades the polypyrrole coating of the fibres. The polypyrrole layer in the zone 1 of the textile (Fig. 9b) is completely degraded (Fig. 9d). The content of W in the surface fibres of this zone decreased substantially (0.01% atomic). The PPy layer in the zone 2 of the textile

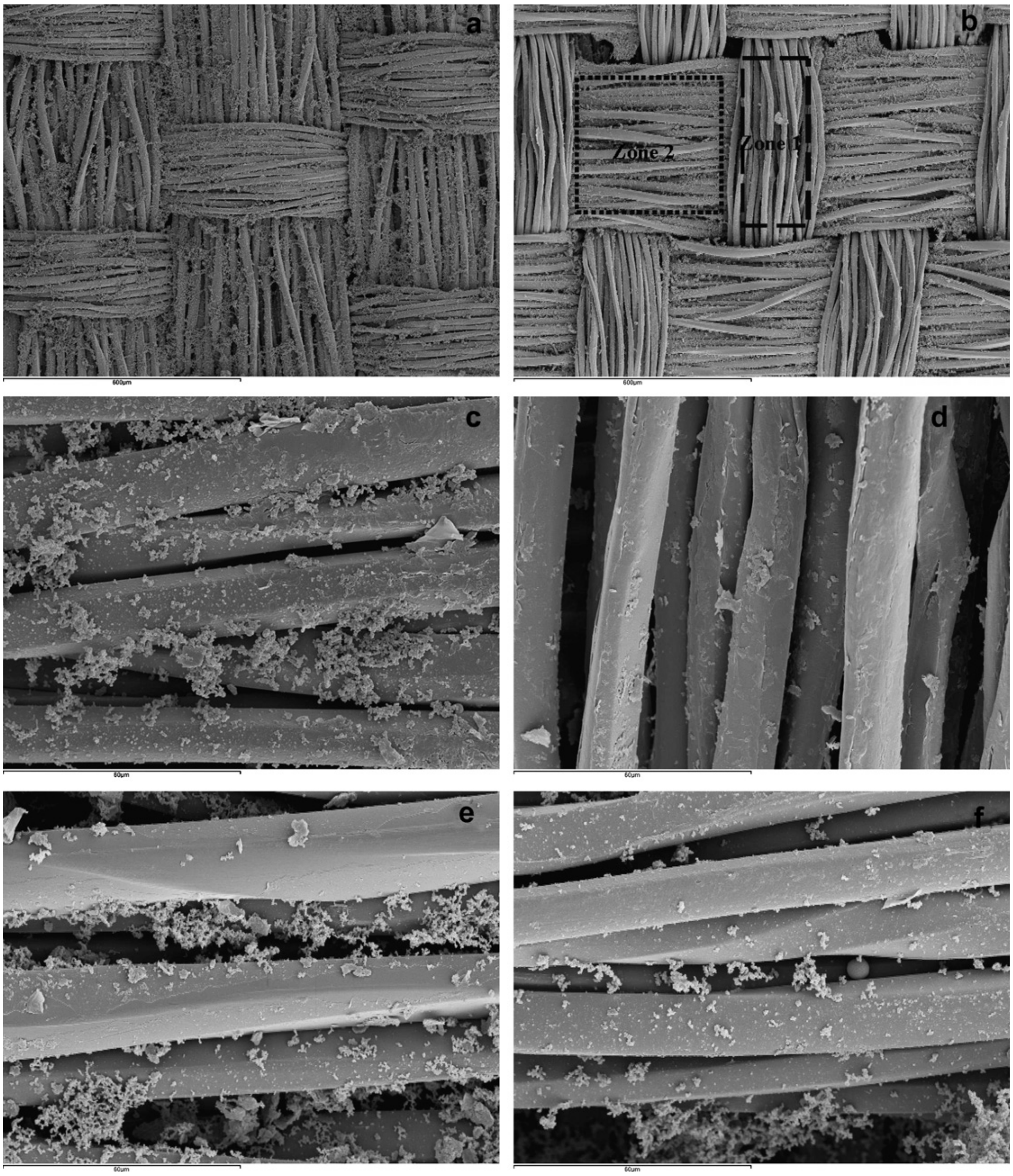

Fig. 9. SEM micrographs of different samples (2 g/l pyrrole): (a) PES+PPy/$PW_{12}O_{40}^{3-}$ (×100); (b) PES+PPy/$PW_{12}O_{40}^{3-}$ after abrasion (×100); (c) PES+PPy/$PW_{12}O_{40}^{3-}$ (×1000); (d) PES+PPy/$PW_{12}O_{40}^{3-}$ after abrasion in zone 1 (×1000); (e) PES+PPy/$PW_{12}O_{40}^{3-}$ after abrasion in zone 2 (×1000); (f) PES+PPy/$PW_{12}O_{40}^{3-}$ after washing assay (×1000).

(Fig. 9b) is only removed from the fibres partially (Fig. 9e). In this figure it can be seen that only the upper part of the fibres has lost polypyrrole aggregates and part of the polypyrrole layer that cover the fibres. The presence of W in the fibres of this zone is clear (0.55% atomic). Fibres in zone 1 are more raised than fibres in zone 2 and friction affects more the fibres of zone 1 due to this fact.

The washing assay of the textile covered with the hybrid material PPy/$PW_{12}O_{40}^{3-}$ showed no degradation of polypyrrole coating. The high values of colour degradation and colour discharge in the grey scale (Table 1) imply no significant degradation of the textile covered with PPy. Moreover the aggregates of polypyrrole could not be removed from the textile fibres surface completely (Fig. 9f). EDX analysis showed that W content in the surface fibre had normal values (0.64% atomic).

3.6. Measures of surface resistivity and EIS

The surface resistivity obtained for PES covered with the hybrid material measured with the four point probe test was 400–500 Ω/square and 60–70 Ω/square for PPy/AQSA. The counter ion has a significant influence in the polypyrrole conductivity films. The more planar the structure of the counter ion is, the more conductive film is obtained [43]. Anthraquinone sulfonic acid sodium salt has a planar conformation; on the other hand $PW_{12}O_{40}^{3-}$ is a three dimensional molecule that produces less conductive polymer than AQSA. When the electrochemical synthesis of PPy/$PW_{12}O_{40}^{3-}$ was performed on the conducting textile, the resistivity obtained was 17–20 Ω/square (20.78 C/cm^2 of polymerisation charge). The electrochemical synthesis produces a more ordered polymer with fewer defects, so the resistivity is lower than the case of chemical synthesis (one order of magnitude).

Surface resistivities of different chemically synthesised samples measured with EIS are showed in the Table 2. Samples were soaked with different solutions during 1 h, dried and measured with EIS. It can be seen that one hour of contact with neutral (phosphates buffer + Na_2SO_4 0.1 M) and acid solution (H_2SO_4 0.1 M) origins a decrease in textile surface resistivity. On the other hand, contact with basic solutions (NaOH 0.5 M + Na_2SO_4 0.1 M) causes a significant increase in the textile surface resistivity, this fact is related with the deprotonation of oxidised polypyrrole [41].

When the textile is submitted to a washing assay the textile resistivity is increased but not excessively. As SEM has proved, the layer morphology is not changed by the washing assay. The friction assay is more abrasive than the washing one and the conductivity loss is higher too. This phenomenon is due to the partial elimination of polypyrrole from the surface fibre that has been proved by SEM. The side that is abraded is affected only partially; only the upper fibres of the textile are degraded. Textiles have a lot of contact points between the fibres. When the layer of conducting polymer in a fibre is damaged with abrasion and has not got conductive areas other contact points between fibres allow the conduction in the textile. The electricity conduction is more difficult and the resistivity rises up consequently. In conclusion the damage of the polypyrrole layer in the textile submitted to abrasion is obvious but the effect in the electrical resistivity is lower than it could be expected.

Table 2
Surface resistivity values for different samples measured with EIS

Sample	Surface resistivity measured with EIS (KΩ/square)
PES + hybrid material	2.712
1 h contact at pH 1	0.444
1 h contact at pH 7	0.578
1 h contact at pH 13	292.7
After washing assay	4.79
After friction assay	38.8

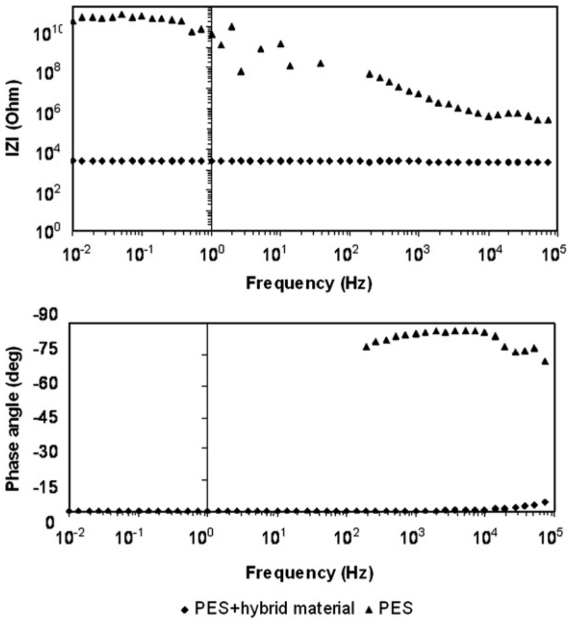

Fig. 10. Bode plots for PES and PES+PPy/$PW_{12}O_{40}^{3-}$ chemically synthesised (2 g/l pyrrole). Measurements between two copper electrodes above the textile samples. Distance between electrodes 1.5 cm. Textile measured area 1.5 cm × 1.5 cm. Frequency range from 10^{-2} to 10^5 Hz.

In the Fig. 10 it can be seen the Bode diagrams obtained by EIS for PES and PES + hybrid material. As can be seen, the impedance modulus for PES is much higher than the one for PES + hybrid material. Phase angle values around 90° were recorded for PES sample, showing a pure capacitative behaviour. Phase angle data for low frequencies are not showed because noise was observed, due to the very high impedance values obtained (impedance modulus about 10^{10} Ω) for PES sample. PES is an insulating material and acts as a capacitor. The PES + hybrid material showed a phase angle value near to 0°, showing a pure resistive behaviour. Conducting textile acts as a pure resistor.

4. Conclusions

The development of PES conducting textiles covered with polypyrrole and the incorporation of $PW_{12}O_{40}^{3-}$ as counter ion has been achieved. FTIR-ATR spectroscopy showed the presence of bands attributed to polypyrrole but do not showed the bands of $PW_{12}O_{40}^{3-}$ clearly, so EDX analyses were realised to corroborate the counter ion incorporation.

SEM showed complete coating degree of the fibres with $PPy/PW_{12}O_{40}^{3-}$ and the presence of aggregates of polypyrrole not removed in the washing stage. EDX analyses demonstrated $PW_{12}O_{40}^{3-}$ incorporation in the PPy structure and SEM combined with backscattered electrons demonstrated the homogeneous incorporation of $PW_{12}O_{40}^{3-}$ in the coating. Micrographs of samples submitted to friction showed partial polypyrrole layer degradation. Washing assay showed no degradation of the hybrid material layer.

Cyclic voltammetry (CV) showed that films of $PPy/PW_{12}O_{40}^{3-}$ were electroactive. The voltammograms were recorded at different pH to study the influence of the medium. The maximum current density values followed this order: pH 7 > pH 1 > pH 13. Only with pH 13 the typical polypyrrole voltammetric peaks were observed. The surface resistivity of $PES+PPy/PW_{12}O_{40}^{3-}$ conducting textile measured by the four point probe technique was 400–500 Ω/square. The Bode plots obtained by EIS measurements showed a phase angle value near to 0° for the conducting textile, typical value for a resistor, acting the sample as an electrical resistor. $PPy/PW_{12}O_{40}^{3-}$ electropolymerisation on the chemically synthesised polymer has been achieved and showed a current density increase in CV at all pH studied. The surface resistivity measured for this polymer was 17–20 Ω/square (20.78 C/cm^2 of polymerisation charge).

At present we are studying the electrical behaviour by EIS of the conducting textiles in solution to complete the study of these materials.

Acknowledgements

Authors thank to the Spanish Ministerio de Ciencia y Tecnología and European Union Funds (FEDER) (contracts CTM2004-05774-C02-02 and CTM2007-66570-C02-02) and the Universidad Politécnica de Valencia (Programa Incentivos a la Investigación 2005) for the financial support. J. Molina is grateful to the Conselleria d'Empresa Universitat i Ciència (Generalitat Valenciana) for the FPI fellowship. A.I. del Río is grateful to the Spanish Ministerio de Ciencia y Tecnología for the FPI fellowship.

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