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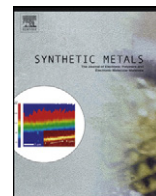
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Improving polyaniline processability by grafting acrylic copolymer

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ABSTRACT

In this study styrenesulfonate of polyaniline/acrylic copolymers were synthesized via free radical polymerization through polymerization in dispersed medium. The resulting materials were applied onto glass-ITO slides using the air-brushing technique to obtain PANi based thin films. Analyses by scanning electron microscopy in TEM mode (STEM) indicated that depending on the acrylic monomer combination (methyl methacrylate, methacrylic acid or butyl acrylate) the adhesion on the substrate was better than styrenesulfonate of polyaniline (PANi-SSA) homopolymer. The effect of the combination of the acrylic monomers on the electrical properties was determined by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Results indicated that the electrical properties of the acrylic copolymer could be enhanced by varying the glass transition temperature. From these findings it was concluded that the inclusion of butyl acrylate in the copolymer was the critical condition to improve adhesion and electrical properties.

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1. Introduction

In the last decades intrinsic electrically conductive polymers (ICPs) have been studied because of their unique applications. Current commercial applications of ICPs include, thin film transistors, batteries, supercapacitors, gas, bio and chemical sensors, activators, electromagnetic shielding, artificial muscles, light emitting diodes, fuel and solar cells, fillers, corrosion protective coating [1–8]. Polyaniline (PANi) is one of the most extensively investigated ICPs due to its environmental and chemical stability, unique electronic properties and ease of synthesis. However, as well as in the case of other ICPs, PANi is insoluble and infusible, which restricts its application due to difficulties in processing and manipulation [9].

In the past few years, much progress has been made to improve these aspects. One way to modify the solubility and processability of PANi is the polymerization in various acids [10]. The variety of polyaniline doped materials has been well-investigated [11–14]. It has been reported that the doping of polyaniline with functionalized protonic acids showed improved solubility in organic solvents due to the interaction between counterion and solvent [15]. The doping of PANi not only affects the solubility but also enhances the conductivity. According to reports, upon acid doping, conductivity attains values in the range of 10^{-2} to 100 S cm^{-1} , depending on the doping agent due to the increased electronic delocalization [16]. In parallel to the research on the solubility/processability of

polyaniline, composites/blends of polyaniline are often seen too [17–19]. On the other hand, copolymers of PANi are also of potential research interest, which retain the properties of polyaniline with additional newer properties [20–22]. These properties of copolymers can also be tuned. Copolymerization of aniline with other aniline derivatives can be performed either by chemical or electrochemical methods [23–25]. Copolymerizations of aniline with different types of monomers have also been reported. Copolymers of polyaniline with polystyrenesulfonate were synthesized and their composite films were optimized as the electrode for rechargeable lithium batteries [26]. Recently, Ge et al. copolymerized acrylic acid and polyaniline for covalent immobilization of glucose by in situ emulsion polymerization [27]. Other research groups have reported various copolymerization types of polyaniline, i.e., block copolymers [28,29], graft copolymers and ring opening graft copolymerization [30]. Recently, the synthesis of poly(ethylene glycol)-*g*-polyaniline via an *N*-alkylation reaction between Na^+ salt of polyaniline and chlorinated poly(ethylene glycol) (PEGCl) was reported as a useful material in electrochromic devices [31]. Jung et al. and Bae et al. worked on water soluble and conductive poly(styrenesulfonic acid)-*g*-PANi-SSA copolymers [32]. They gave the idea that the copolymerization method, gives conductive copolymers with increased chemical interaction between the polymers, and hence gives better conductivity and mechanical properties [33]. Graft copolymerization of acrylamide, sodium salt of styrenesulfonic acid and acrylic acid on polyaniline has been studied [34]. Also polyaniline block copolymers have been synthesized on the emeraldine form of polyaniline films and powders with surface-grafted acrylic acid (AAc) [35].

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Among the various techniques used to improve polyaniline processability, the copolymerization with acrylic monomers onto PANi seems to be an attractive option. Thus, in this work we report on grafting acrylic copolymers on styrenesulfonate of polyaniline (PANi-SSA), as a strategy to improve PANi processability without altering importantly its electrical properties. The polymerization of polyaniline has been performed by chemical oxidative polymerization of aniline doped by styrenesulfonic acid. Combinations of acrylic monomers (methyl methacrylate, butyl acrylate and methacrylic acid) were used to produce copolymers with different film properties. The key point in this study was to use the vinyl group of styrenesulfonate counteranion (doping agent) as the link to graft the acrylic copolymers onto the PANi-SSA particles. Therefore, once the acrylic copolymer is grafted the film properties of the polyaniline would be improved. Thin films of PANi/acrylic copolymer were deposited onto glass-ITO slides by the air-brush technique. From these films the electrical properties were determined by cyclic voltammetry and impedance spectroscopy. It must be mentioned that the formation of PANi films onto glass/ITO substrates have been studied since 1989 by using various techniques [36]. Stejskal et al. produced thin films of PANi onto glass substrates during in situ polymerization of polyaniline [37]. The average thickness of the films was 125 ± 9 nm. Electrochemically depositions of PANi onto ITO substrates have also been well studied [38,39].

2. Experimental

2.1. Reagents

Aniline, sodium styrene sulfonate, hydrochloric acid and ammonium persulfate (Aldrich Co.) were used as received. Butyl acrylate (BuA), methylmethacrylate (MMA) and methacrylic acid (MAA) monomers (Aldrich Co.), were distilled under vacuum prior to polymerization. The initiator 2,2'-azobisisobutyronitrile (Akzo Nobel) was recrystallized from a saturated aqueous solution before using.

2.2. Synthesis of styrene sulfonate of polyaniline (PANi-SSA)

PANi-SSA was synthesized via oxidative polymerization in the oxidation state of emeraldine base. Typical synthesis proceeded as follows: first, aniline (0.01 mol) was dispersed in 50 mL distilled water; in a second vessel, sodium styrene sulfonate (0.01 mol) was dissolved in 30 mL distilled water and in a third vessel, ammonium persulfate (0.02 mol) was dissolved in 20 mL of distilled water. The contents of the first (aniline) and second vessels (styrene sulfonate) were thoroughly mixed in a glass flask, followed by the addition of HCl (0.01 mol). This solution was left for 20 min to stabilize with gentle continuous stirring. The solution of ammonium persulfate (APS) was transferred to a glass pipe, and poured to the reactor dropwise for 1 h. The polymerization was allowed for 24 h. Finally, the solids, styrene sulfonate of polyaniline (PANi-SSA), were collected on a filter paper and washed with distilled water. Afterwards, the solids were re-dispersed in 100 mL of distilled water and sonicated for 5 min.

2.3. Copolymer synthesis

A three-neck-round-bottomed 250 mL glass flask with nitrogen bubbling, cooling, heating and mechanical stirring systems was used as the reactor. All experiments were planned to consist of 1 part in weight of PANi-SSA and 1.333 parts in weight of acrylic copolymer. A typical copolymerization was performed as follows: PANi-SSA was sonicated for 15 min to disperse particle agglomerations. Afterwards, the PANi-SSA dispersion was loaded to the reactor, which was preheated to 70 °C. Nitrogen was bubbled for

Table 1

Different formulations of PANi-SSA copolymers studied.

Copolymer	PANi-SSA (g)	MMA (g)	MAA (g)	BuA (g)	AIBN (g)
(MMA-co-MAA)/PANi-SSA	1	1.2	0.1336	–	0.013
(BuA-co-MAA)/PANi-SSA	1	–	0.1336	1.2	0.013
(BuA-MMA-co-MAA)/PANi-SSA	1	0.325	0.1336	0.875	0.013

30 min to evacuate dissolved oxygen in the water. The specified mixture of monomers and 2,2'-azobisisobutyronitrile (AIBN) were fed to the reactor. All copolymerizations were allowed for 4 h. Once the polymerizations finished, the copolymers were kept in bottles for posterior application on the glass-ITO slides. Evaluated formulations are summarized in Table 1.

2.4. Deposition of conducting dispersions

The three types of copolymers and PANi-SSA were deposited as thin film onto standard glass slides covered with ITO using the air-brush technique. Before deposition, the materials were dispersed in distilled water to obtain 0.5 wt% dispersions. The dispersions were applied using the spray coating method. For this method a SURTEK air brush set 108085 was used at a spraying pressure of ~35 psi. While painting, the glass-ITO slides were heated at ~110 °C, which was sufficient to dry the sample in a few seconds. Fast vaporizing avoided particles reagglomeration and improved films homogeneity. Through this methodology ~0.0001 g of samples of the PANi-SSA and the PANi-SSA copolymers were applied.

2.5. Characterization

2.5.1. Thermogravimetric analysis

Samples of PANi-SSA and (MMA-co-MAA)/PANi-SSA, (BuA-co-MAA)/PANi-SSA and (BuA-co-MMA-co-MAA)/PANi-SSA copolymers, were characterized by thermogravimetric analysis (TGA). This analysis was achieved using a TA Instruments 2960 Simultaneous DTA-TGA. Samples for analysis were prepared by weighing ~10 mg of dried sample into aluminum cups. The characterization was performed under air atmosphere with a flow rate of 50 cm³/min at a heating rate of 10 °C/min. All analyses were carried out between room temperature and 800 °C.

2.5.2. Infrared spectroscopy

Samples of PANi-SSA and PANi-SSA copolymers were run in a Perkin-Elmer Spectrum GX FT-IR spectrophotometer, with the detector Smiths Detection durasamp R II. Prior to the analysis all samples were precipitated by adding methanol. The solids were recovered by filtration and washed several times with water before drying at 80 °C for 24 h.

2.5.3. Scanning electron microscopy

Scanning electron microscopy in standard mode (SEM) and in transmission mode (STEM) were used to analyze the morphology and the thickness of the deposited films onto the glass-ITO slides and particle morphology, respectively. The microscope used was a JEOL JSM-7401 F Field Emission, with ultra high vacuum and 1 nm resolution. For particle analysis, the samples were prepared by dispersing 2 drops of the aqueous dispersion in 50 mL of distilled water. The diluted dispersion was sonicated for 5 min to break apart particle agglomerations; afterwards, a drop of the dispersion was placed on a holey-carbon-cooper-grid. In the case of the film morphology and the thickness analysis a fragment of glass-ITO slide, with deposited sample, was directly placed in the sample container. To obtain the fragment a complete slide was frozen in liquid

nitrogen and then crashed against a solid profile. The film thickness was determined by tilting the glass slides to the vertical position.

2.6. Electrochemical analysis

2.6.1. Electrochemical impedance spectroscopy

A Solatron Interfase Electrochimic model 1287 was used to determine electrochemical impedance spectroscopy. Analyses were run at 100 mV with frequencies between 0.1 and 100,000 Hz. The analyses took approximately 40 min. The software Z-Plot was used to process data, whereas software Z-Wiew 2 was used for building plots.

2.6.2. Cyclic voltammetry

A Solatron Impedance Analyze model 1260 was used to run cyclic voltammetry studies. After setting the potentials between -1.5 and 1.5 V, the CVs were run at a scan rate of 25 mV/s. The data was processed using the CorrWare software and the CorrView 2 was used to visualize the graphics.

2.6.3. Electrolyte preparation

EIS and CV were carried out to determine the electrochemical activity of the copolymers. For both analyses it was necessary to prepare an electrolyte, which consisted of 0.5 g of lithium perchlorate (LiClO_4) salt in 100 mL of propylene carbonate ($\text{C}_4\text{H}_6\text{O}_3$).

2.6.4. Preparation of the three-electrode configuration

Each electrode configuration comprised: a working electrode, a counter electrode, a reference electrode and the electrolyte. The working electrode was the glass-ITO slide; the counter electrode used was a slide of platinum (Pt) and the reference electrode was a Sigma–Aldrich glass reference electrode, which contains Ag/AgCl solution.

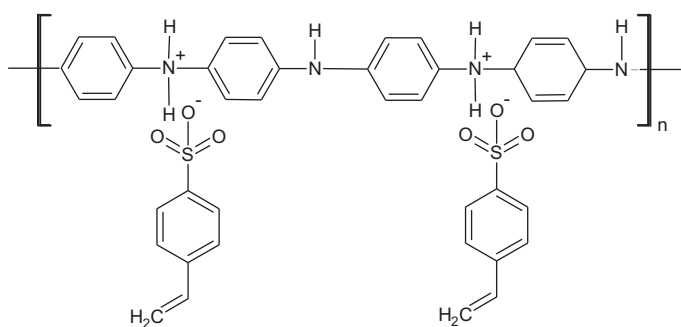
3. Results and discussion

3.1. Synthesis of PANi–SSA via oxidative pathway

Conducting polyaniline was synthesized via oxidative polymerization in the oxidation state of emeraldine base salt. The synthesis was based on the chemical oxidation of aniline by using ammonium persulfate (APS) as the oxidizing agent. Through this methodology aniline was firstly, protonated to anilinium chloride salt and later, to anilinium styrene sulfonate through the interchange of counterions. PANi was polymerized as styrenesulfonate of polyaniline (PANi–SSA) as illustrated in Scheme 1.

3.2. Free radical copolymerization in dispersed medium

Series of poly(MMA-co-MAA)/PANi–SSA, poly(BuA-co-MAA)/PANi–SSA and poly(BuA-co-MMA-co-MAA)/PANi–SSA



Scheme 1.

copolymers, were synthesized via polymerization in dispersed medium. The hypothesis was that by considering the presence of the carbon–carbon double bond on the counteranion, the mixture of acrylic monomers would graft onto the double bond of the styrenesulfonate via free radical polymerization. It was important to consider monomer solubility in water while planning experimentation; thus MAA, which is water soluble, was introduced in the reactor as part of a monomer–AIBN hydrophobe solution, in order to promote MAA copolymerization in the organic phase. This way, according to the characteristic of the monomers the mixture of MMA–MAA generates copolymers which are glassy at room temperature; however, mixtures of BuA–MAA and BuA–MMA–MAA generate copolymers which are soft at room temperature. It is important to comment that MAA was included in the copolymers to improve adhesion of the copolymers with the substrate; besides, AIBN was used as the initiator to direct copolymerization to the styrenesulfonate on the PANi–SSA particles and to restrict particle nucleation in the aqueous phase, which could form a separate phase of polymer (emulsion polymerization). In addition, AIBN does not modify oxidation state of PANi as organic or inorganic peroxide initiators.

3.3. Morphology

Morphology studies were performed by SEM in transmission mode (STEM). Fig. 1(a–d) illustrates the morphology of the PANi–SSA and PANi–SSA copolymers. As observed, PANi–SSA was in the form of large agglomerations, comprising semispherical particles of ~ 30 nm with the interparticle frontier quite clear. In the case of the (MMA-co-MAA)/PANi–SSA copolymer, the picture also showed agglomerations formed by semispherical particles, with similar particle size. It could be expected a difference in morphology considering the presence of the acrylic copolymer; however, there was no appreciable difference with respect to PANi–SSA. Concerning the (BuA-co-MAA)/PANi–SSA copolymer, a clear difference was observed with respect to the first copolymer and PANi–SSA. It was observed that the particles were immersed in a kind of continuous phase and that many particles presented elongated shape. These differences can be explained as the affect of the low glass transition temperature of the poly(butyl acrylate) fraction present in the copolymer, which causes the polymer flow at room temperature, which lead to film formation under these conditions. Finally, in the case of the (BuA-co-MMA-co-MAA)/PANi–SSA copolymer, the behavior was intermediate between (MMA-co-MAA)/PANi–SSA and (BuA-co-MAA)/PANi–SSA; that is, the particle frontiers were not so clear as in (MMA-co-MAA)/PANi–SSA (or PANi–SSA) but deformation was not as evident as in (BuA-co-MAA)/PANi–SSA. It is important to comment that in any of the samples pure polystyrene polymer particles were observed, which indicated that the strategy to restrict conventional emulsion polymerization worked well in these experiments.

FTIR spectra, ran directly from the films on glass slides by using FTIR reflectance technique, are represented in Fig. 2. As observed, all spectra showed a broad transmittance band at wavenumbers higher than 2000 cm^{-1} . According to Epstein et al. [40] and Ping [41], this is a FTIR typical profile of the conducting PANi. The spectra exhibited two peaks in the range of 3100 – 3400 cm^{-1} , which were attributed to stretching vibration of N–H of aromatic amine bonds [42,43]. The weak peak at 1590 cm^{-1} was assigned to quinone (Q) groups and the strong peaks at 1500 – 1400 cm^{-1} to benzoide (B) ring deformation, whereas the strong peak observed at 1300 – 1200 cm^{-1} which can be attributed to the stretching vibration of C–N bonds, as reported by Yadav and Puri [44]. It is noteworthy that this set of bands is observed stronger in the spectrum of PANi than in the PANi–SSA copolymers due to the content of PANi in the sample. Another group of bands is observed

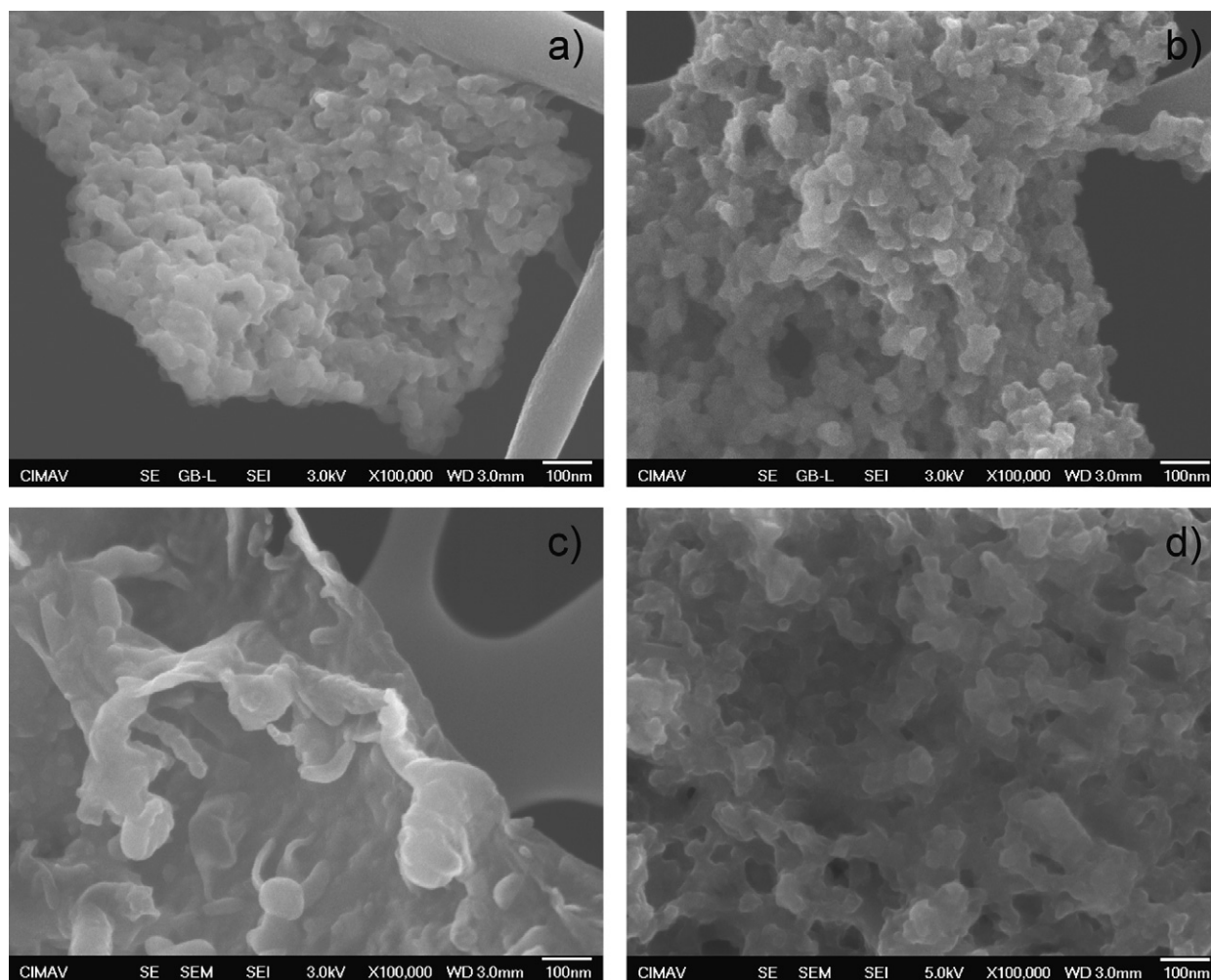


Fig. 1. STEM images of the morphology of (a) PANi-SSA and (b) poly(MMA-co-MAA)/PANi-SSA, (c) poly(BuA-co-MAA)/PANi-SSA and (d) poly(BuA-co-MMA-co-MAA)/PANi-SSA.

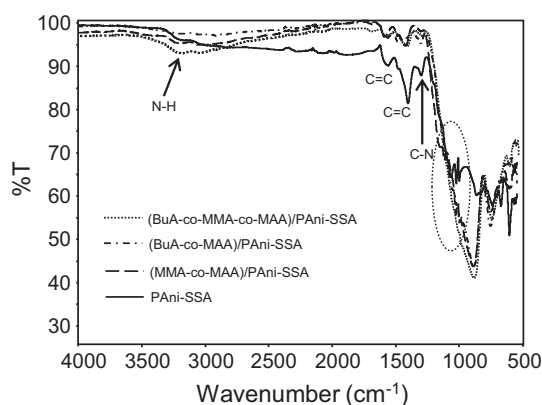


Fig. 2. FTIR spectra of PANi-SSA and PANi-SSA copolymers.

around 1000 and 1150 cm^{-1} , which were assigned to stretching vibrations of $-\text{SO}_3$ and $-\text{SO}_2$ of styrene sulfonate unit, as suggested by Lascelles and Armes [45]. The peaks arising from 650 to 950 cm^{-1} were assigned to C–H bending of the hydrocarbon structure of the PANi-SSA and the copolymers [44]. In the case of the PANi-SSA copolymers, the bands present in PANi-SSA spectrum are clearly observed. However, the signals of C–H bonds of CH_2 and CH_3 groups of the acrylic components, that should appear in the

region of 2800–3000 cm^{-1} and the characteristic peak of stretching vibration at $\sim 1700 \text{ cm}^{-1}$ of C=O bond in the acrylic polymers, was not observed in the spectra. As an assumption, it is possible to say, that these peaks were not shown as PANi is partially opaque to infrared spectroscopy and does not allow the emission-absorption mechanism as conventionally occurs in this analytical technique. Nevertheless, the large band at $\sim 900 \text{ cm}^{-1}$ was present only in the spectra of the PANi-SSA copolymers, which can be attributed to the C=O bonds and indicates the presence of the acrylic components.

3.4. Thermal analysis

The thermogravimetric analysis (TGA) traces of PANi-SSA and PANi-SSA copolymers are shown in Fig. 3. As shown in PANi-SSA thermogram, three-step thermal degradation is observed. The weight loss in the range of 0–100 $^{\circ}\text{C}$ was associated with the loss of moisture. The second step, that commences at $\sim 145 \text{ }^{\circ}\text{C}$ and continues until $\sim 420 \text{ }^{\circ}\text{C}$, indicated a weight loss in the range 23–40 wt%, this transition was associated to the degradation of $\text{NH}^+ \dots \text{SO}_3^-$ interaction between the polymer chain and the doping agent and some oligomers of aniline [46]. The transition stage at $\sim 400 \text{ }^{\circ}\text{C}$ was attributed to the removal of the doping agent, which has been related to styrene sulfonate degradation [47]. And the last stage, with weight loss of 30–40 wt%, can be ascribed as the degradation of the PANi backbone. Similar behavior has been proposed previously

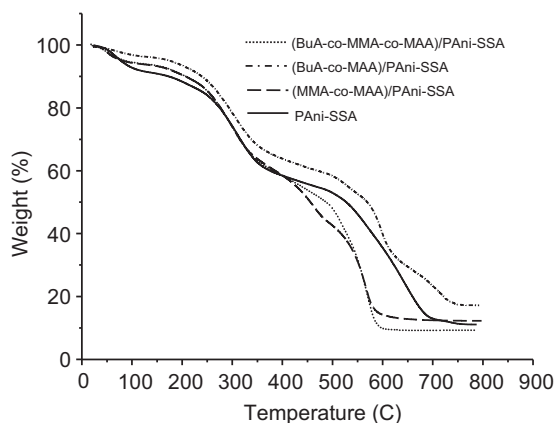


Fig. 3. TGA traces of PAni-SSA and PAni-SSA copolymers.

[48]. Many authors have reported that **PAni** doped with organic acids shows increased thermal stability [49,50]. Pure polyaniline typically shows thermal degradation in the range from 300 to 600°C [51]; however, as observed in the thermogram, polyaniline degradation occurred between 500 and 700°C, which indicated that doping by SSA improves PAni thermal stability such like other organic acids.

The thermal stability of the three different copolymers is also illustrated in Fig. 3. The first inflection, which is in the range of room temperature to 100°C was due to release of absorbed water due to the hydrophilic character imparted by MAA to the copolymers, as suggested by Wang et al. [52]. The second transition was the characteristic of PAni-SSA, as discussed above. Literature indicates that the transition in the range of 350–600°C is ascribed to a complex process including decomposition of the carboxylic groups [53]. So, this transition was attributed to PAni and copolymer degradation. The copolymers are thermally stable until 600°C. Thus, it can be remarked that thermal stability increased by doping PAni with styrenesulfonate and by crosslinking the acrylics with respect to typical PAni. It is also worth saying that the TGA technique, according to thermal degradation patterns, gave an indirect evidence of the graft of the acrylic copolymers onto the PAni-SSA, since the degradation profile of PAni-SSA homopolymer was substantially modified.

3.5. Film morphology and adhesion

The films were deposited using the spray coating method; every material was sprayed from a distance of ~30 cm away from the slide. After painting the slide, the samples were kept at 90°C until complete water evaporation was achieved. Afterwards, all of the described procedure was repeated once again. The quantity of the applied material on the slides was ~0.0001 g.

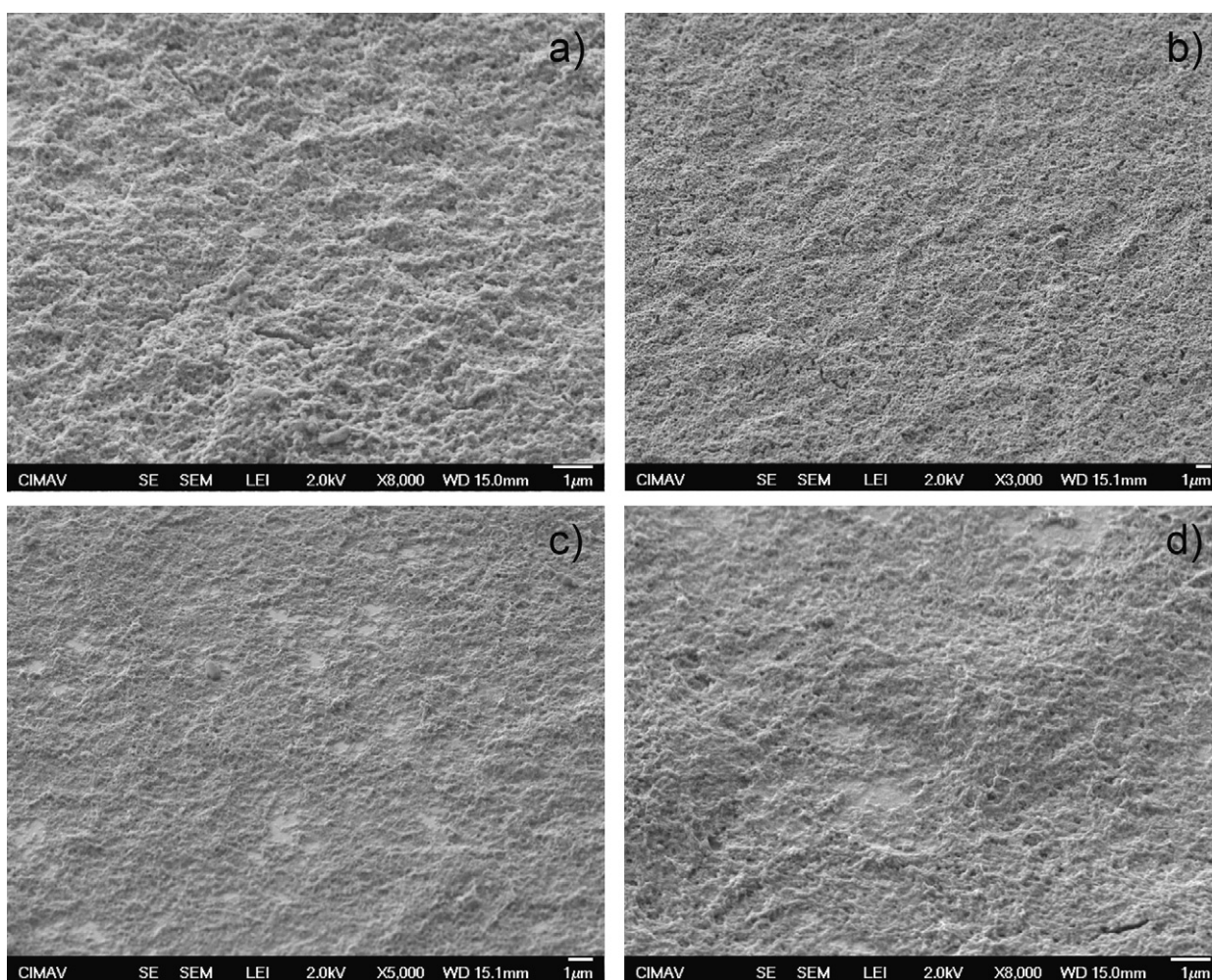


Fig. 4. SEM images of deposition of (a) PAni-SSA and (b) poly(MMA-co-MAA)/PAni-SSA, (c) poly(BuA-co-MAA)/PAni-SSA and (d) poly(BuA-co-MMA-co-MAA)/PAni-SSA, onto glass-ITO slides.

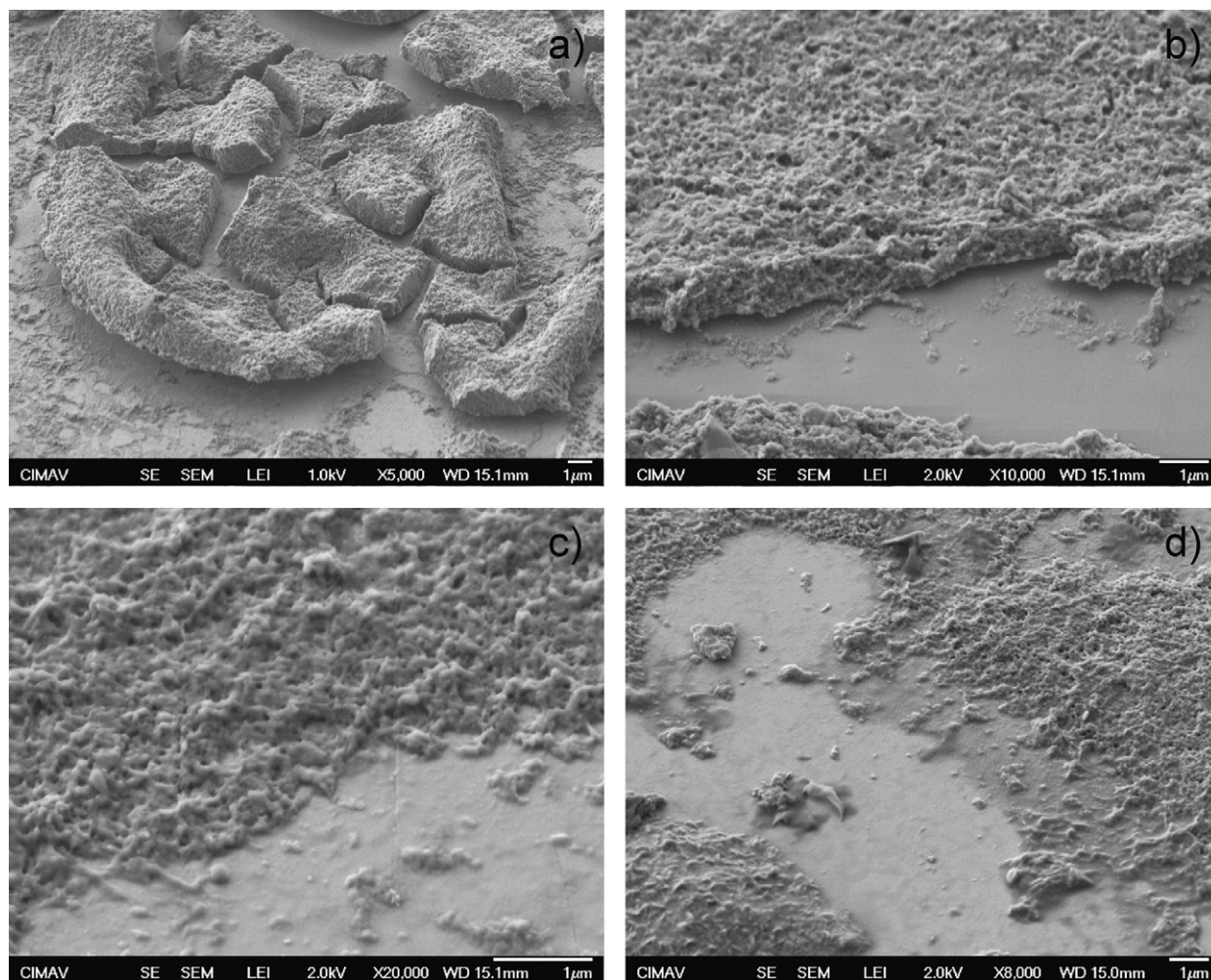


Fig. 5. SEM images of the adhesion of (a) PANi-SSA and (b) poly(MMA-co-MAA)/PANi-SSA, (c) poly(BuA-co-MAA)/PANi-SSA and (d) poly(BuA-co-MMA-co-MAA)/PANi-SSA, onto glass-ITO slides.

Both the morphology and the thickness of the films were studied by SEM. As seen in Fig. 4(a–d) films' thickness was not homogeneous along the sample; that is, some regions were thicker than others. It must be commented that by the applied methodology, it was not possible to get homogeneous films; however, it is worth saying that this technique is cheap and very fast of application and for practical purposes it is good enough. It was also notable that especially the films made of PANi-SSA and (MMA-co-MAA)/PANi-SSA copolymer presented fractures, which was related to the stiffness of the material; that is, film forming properties of both materials are poor. However, in the case of the (BuA-co-MMA-co-MAA)/PANi-SSA and the (BuA-co-MAA)/PANi-SSA copolymers, adhesion on the substrate was much better, as fractures were not observed. This feature was related to the properties of poly(butyl acrylate) component in the copolymers, since this element is typically added to provide stickiness and film forming properties to coatings and adhesives.

A more detailed analysis of the adhesion of the different materials is depicted in Fig. 5(a–d). In these samples thinner depositions were performed. It was clear that the adhesion of PANi-SSA on the substrate was poor. In a similar way, (MMA-co-MAA)/PANi-SSA copolymer presented some regions of detachment, although not as abundantly as in PANi-SSA deposition; that is, the compatibility with the substrate was much better than PANi-SSA. And in the cases of the (BuA-co-MMA-co-MAA)/PANi-SSA and the (BuA-co-MAA)/PANi-SSA copolymers, the adhesion with the substrate was

very good, since no evidence of detachment from the surface was observed. These analyses allowed us to conclude that copolymerization of PANi with both low glass transition acrylic copolymers and film forming properties such as BuA-co-MMA-co-MAA or BuA-co-MAA can considerably improve adhesion and film properties. It is worth noting that while differential scanning calorimetry (DSC) analyses were performed, clear evidence of the glass transition temperature was not obtained.

Estimations of the film thicknesses were determined by SEM. For this analysis a film deposited on glass was frozen in liquid nitrogen and then crashed against a solid object. A fragment of the slide was observed transversally to determine thickness. A digital photo of a film of (BuA-co-MAA)/PANi-SSA copolymer deposited on glass and a SEM micrograph showing the film thickness are illustrated in Fig. 6(a,b). In average, the films' thicknesses of the different depositions were in the range of 280–600 nm. These average values were used in the determination of electrical properties.

3.6. Electrical properties

3.6.1. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were used to determine the electrical conductivity of PANi-SSA and the PANi-SSA copolymers. Electrical conductivity measurements require precise dimensions of the films, such as diameters and thickness apart from the resistance. Experimentally, the

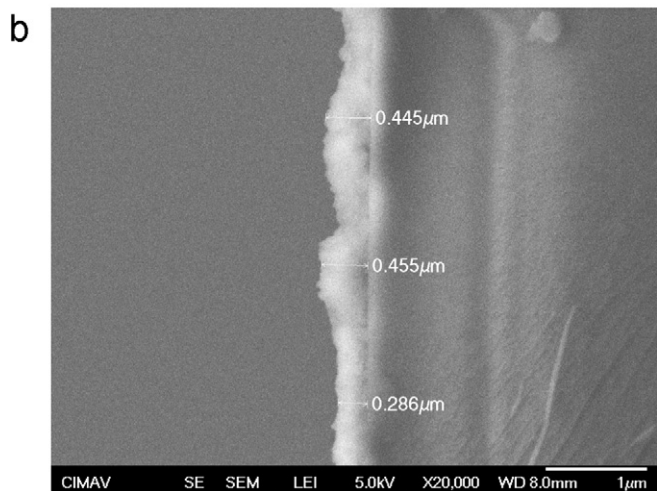
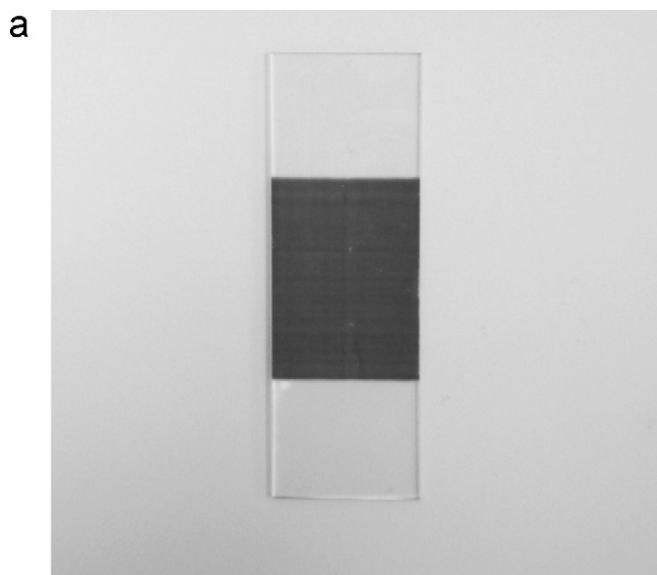


Fig. 6. (BuA-co-MAA)/PAni-SSA copolymer onto glass (a) digital image of deposition and (b) thickness calculation image by SEM.

dependence upon properties of the electrolyte solution and the resistance of the substrate on the glass-ITO slide can be expressed by Eq. (1):

$$R = \rho \frac{t}{A} \tag{1}$$

where R stands for resistance (Ω), ρ is resistivity ($M\Omega\text{ cm}$), t is thickness of the substrate on the ITO slide (nm) and A is the total surface (cm^2) of the material on the slide. By grouping the resistivity with the thickness, the resistance can be written as sheet resistance equation (R_S) [54], as illustrated in Eq. (2):

$$R_S = \frac{R}{A} \tag{2}$$

Table 2 Resistivities and conductivities of the depositions of PAni-SSA and PAni-SSA copolymers onto glass-ITO slide.

Material	$R (\Omega)$	$A (\text{cm}^2)$	$R_S (\Omega \text{ cm}^{-2})$	$t (\text{nm})$	$\rho (M\Omega \text{ cm})$	$\sigma (\times 10^7 \text{ S cm}^{-1})$
PAni-SSA	51.48	3.015	9.480	283	5.20	1.97
(MMA-co-MAA)/PAni-SSA	355.71	5.183	68.627	591	31.1	0.32
(BuA-co-MMA-co-MAA)/PAni-SSA	69.67	4.114	16.934	430	6.66	1.50
(BuA-co-MAA)/PAni-SSA	29.05	4.563	6.366	252	5.26	1.90

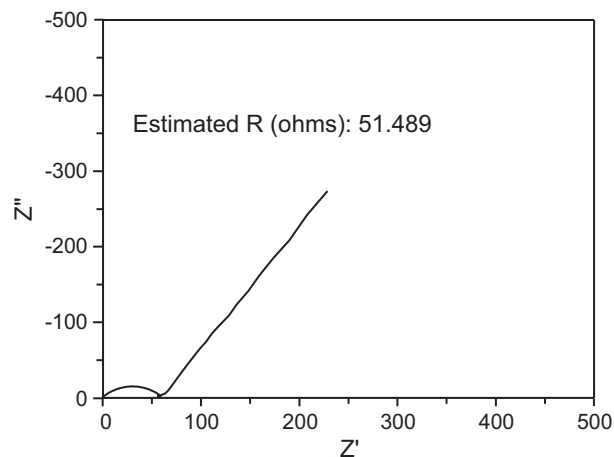


Fig. 7. Nyquist plot of PAni-SSA.

The common unit for sheet resistance is “Ohms per square centimeter”, $\Omega \text{ cm}^{-2}$, which is dimensionally equal to an ohm, but is exclusively used for sheet resistance. For PAni-SSA, as shown in Fig. 7, the intercepts of the semicircle with the X axis gives the resistance of the material in ohms. As known, the conductivity can be calculated through the reciprocal of the electrical resistivity [55].

The conductivities of PAni-SSA and the copolymers series are given in Table 2. The conductivity of the copolymers was close to the conductivity of the PAni-SSA. The conductivities of the films were in the following order: PAni-SSA > (BuA-co-MAA)/PAni-SSA > (BuA-co-MMA-co-MAA)/PAni-SSA > (MMA-co-MAA)/PAni-SSA. And the resistances of the films are order as: (BuA-co-MAA)/PAni-SSA > (BuA-co-MAA)/PAni-SSA > (BuA-co-MMA-co-MAA)/PAni-SSA > (MMA-co-MAA)/PAni-SSA. Results indicated that the inclusion of the brittle and nonconductive MMA component reduced the electrical properties of PAni-SSA, in accordance to Soo et al. [56]. It is probable that conducting PAni cannot distribute among the insulating regions of PMMA due to its implicated high rigidity.

As seen in all the voltammograms (Fig. 8), oxidation peaks were close to each other; this may be due to oxidation reactions of the PAni occurring at close potentials. Also the reduction peaks combined into a single peak because the reaction occurred at similar potentials. Although in PAni-SSA the reduction peaks were seen together, in the PAni copolymer depositions, the reduction peaks could be seen separately as these materials exhibited less electrical activity compared to PAni-SSA. This observation might be caused by the high velocity of the occurring reductions with respect to the slower scanning rate of the cyclic voltammetry. Thus, peaks are shown separately. Finally, it can be mentioned that the observed differences in the cyclic voltammograms of the PAni acrylic copolymers and the pure PAni-SSA were an indication of the presence of the acrylic components in the different materials (Table 3).

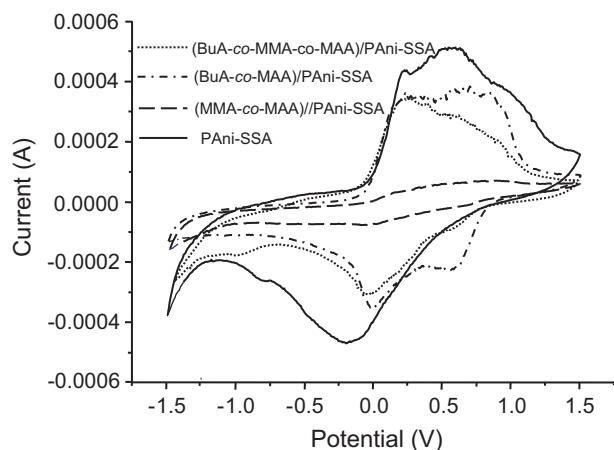


Fig. 8. Cyclic voltammetry profiles of PAni-SSA and PAni-SSA copolymers.

Table 3

The average peak potentials of oxidation and reduction reactions of PAni-SSA and PAni-SSA copolymers.

Material	E_1^0 versus Ag/AgCl	E_2^0 versus Ag/AgCl
PAni-SSA	0.035	0.500
(MMA-co-MAA)-g-PAni	0.147	0.705
(BuA-co-MMA-co-MAA)-g-PAni	0.134	0.570
(BuA-co-MAA)-g-PAni	0.105	0.6675

4. Conclusion

Through the applied methodology, electrochemically active PAni-acrylic based materials, with little reduction in the electrical conductivity with respect to the PAni-SSA homopolymer were obtained. The spray brush method allowed the application of conductive thin films, with thicknesses in the range of 280–600 nm. The film properties of the obtained materials were deeply related to the combination of the monomers (methyl methacrylate, butyl acrylate and methacrylic acid) forming the acrylic copolymer, as determined by scanning electron microscopy. It was found that the inclusion of BuA monomer in the copolymer produced the most prominent effect, as it reduced glass transition temperature, which improved the film properties and the adhesion of the films on the substrate. The film properties were reflected on the electrical properties, since the films with the best adhesion and homogeneity presented the highest electrical conductivities, as determined by electrical impedance spectroscopy. Finally, it can be mentioned that the grafting of the acrylic copolymers on the PAni-SSA, using the vinyl group of the styrenesulfonate counterion as the link between the polyaniline and the acrylic copolymer, allowed producing materials with electrical properties highly influenced by the film properties of the acrylic copolymer grafted. According to the results, the (BuA-co-MAA)/PAni-SSA copolymer presented the most interesting properties, which could be applied; for instance, in dissipative coatings, in conducting adhesives or in electrochromic devices.

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