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Synthesis and characterization of composites based on polyaniline and styrene–divinylbenzene copolymer using benzoyl peroxide as oxidant agent

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ABSTRACT

This work presents a method to prepare composites based on polyaniline (Pani) and styrene–divinylbenzene copolymers (SD) by *in situ* polymerization of aniline using benzoyl peroxide as oxidant agent. The composites were obtained from copolymers with two degrees of porosities which have higher and lower surface areas. Emeraldine Pani was prepared using hydrochloric acid as dopant. One cycle or four cycles of aniline polymerization were performed. The copolymers and their respective composites characterizations were performed by infrared spectroscopy, thermogravimetric analysis, physical nitrogen adsorption–desorption measurements, morphology analysis, elemental analysis and determination of Brönsted acid sites. The Pani was distributed overall porous SD copolymer producing composites with high surface area. Then, they were evaluated as catalysts for esterification reaction of a fat acid. It was found that that composites prepared with four cycles of *in situ* polymerization presented best catalytic activity than one cycle composites.

1. Introduction

Electrically conducting polymers are a class of organic compounds that combine the chemical and mechanics characteristics of polymers with the electronic properties of metals and semiconductors [1]. Polyaniline (Pani) is a electrically conducting polymer that have attracted great interest because of its possibilities of applications in many areas, such as electrostatic discharge materials, gas sensor (NH_3 and volatile organic compounds), acid–base indicator, ion-exchange material, energy storage devices and solar cell [2–7]. The easy synthesis from an inexpensive monomer, good conductivity and remarkable environmental stability are some reasons why Pani has been one of the most studied conductor polymers [8,9].

Pani can be obtained through electrochemical and chemical oxidation synthesis. Currently, chemical oxidation has the advantage to result better yields being preferred for larger scale processes [10,11]. Furthermore, the chemical oxidation route allows modifications of Pani chain structure [12]. Many oxidizing agents can be used to produce polyaniline by the chemical oxidation route, for example, potassium iodate [13,14], ferric chloride [15], hydrogen peroxide [16], potassium dichromate [17], and the most commonly used ammonium persulfate [18–23].

One of the biggest problems concerning electrical conducting materials as Pani has been the difficulty associated with the processing, especially for that synthesized by chemical oxidation of the monomers [24]. The oxidative polymerization of aniline or pyrrol in the presence of supports is one way to produce conducting polymeric materials with definite shape. Composites materials of conducting polymers and conventional polymers have been prepared in order to produce membranes and Pani coated latex. Tan et al. prepared composites of Pani and a sulfonated styrene–divinylbenze (SD) copolymer membrane through oxidative polymerization of aniline with different oxidants [25]. They concluded that the Pani layer was found solely at the surface, within, or both at the surface and within the membrane by the control of aniline polymerization conditions. The polymerization of Pani in the presence of polystyrene (PS) latex can be carried out to produce nearly monodispersed Pani-PS composites with core–shell morphology, where the conducting polymer forms the shell [26]. Wang and Jing synthesized Pani by chemical oxidative polymerization of aniline with ammonium persulfate in the presence of sulfonated cross-linked polystyrene particles in neutral water obtaining a core–shell morphology. Since they used a low DVB:styrene molar ratio (1:15) and no diluents to form pores the structure of the copolymer should be gel type, i.e., nonporous [27]. Although the polystyrene chains were sulfonated, the aniline polymerized preferentially on the particle surface forming a continuous shell. More recently, Ince et al. produced composites of Pani and SD copolymer also with a

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core–shell structure but with very rough surface. They grafted polystyrene on the SD copolymer particles via surface initiated atom transfer radical polymerization. Then the polystyrene chain brushes on the particle surface were sulfonated and neutralized with aniline which was polymerized with potassium persulfate as oxidant [28]. For the core–shell morphology presented by some Pani composites with gel type SD copolymers is expected specific surface areas relatively low. For the composites of Pani over particles containing grafted polystyrene chains was suggested an increase of specific surface area due the very rough surface of the particles, although the authors did not presented no surface area measurement.

Yagudaeva et al. prepared Pani coatings of a sulfonated SD copolymer (Dowex-gel type) and composite materials based on silica gel surface modified by a sulfonated SD copolymer [29]. Aniline was polymerized with ammonium persulfate as oxidant forming a thin polymeric coating on the macroporous support surface based on silica gel and sulfonated SD copolymer. It is expected these macroporous Pani composites present higher specific surface area than Pani/Gel type SD copolymer composites. The morphology of the macroporous Pani composites and the original support were characterized by mercury porosimetry but no SEM image was showed.

The composites of Pani and SD copolymers described before were produced with the sulfonated copolymer in general with a gel-type porosity. In this paper we used macroporous SD copolymers with different surface areas and no previous chemical modification to produce composites with Pani. SD copolymers have been widely used to prepared ion exchange resins. They were chosen because the surface area, porosity and particle size can be easily controlled to produce different polymeric supports [30,31]. The effects of porogenic agent or diluent type, dilution degree and divinylbenzene (DVB) content on the porosity and swelling properties of SD copolymer are well known [30–32]. The use of diluents which solvate the copolymer chains produce small pores and higher surface areas than nonsolvating diluents. The SD copolymer prepared with solvating diluents swell more in good solvents than that prepared with nonsolvating ones. Generally, a large amount of DVB also leads to increasing in the specific surface area. For the SD copolymers prepared with nonsolvating diluents the increasing in DVB content has little effect on swelling of the entangled chains [32]. In this work we prepared two macroporous SD copolymers with different DVB contents in order to produce SD copolymers/Pani composites with high and low specific surface areas. We used high proportions of nonsoltanting diluents to produced structures with similar swelling properties.

In a previous work, the *in situ* polymerization of aniline in a macroporous SD copolymer with ammonium persulfate as oxidizing agent and HCl as dopant did not produce a homogeneous distribution inside the support [18]. The high hydrophobicity of the copolymer and the beginning of polymerization as soon as the oxidant was added favored the Pani formation on the support external surface. In order to overcome this difficulty, we chose an alternative Pani synthetic route using benzoyl peroxide as oxidizing agent. Benzoyl peroxide (BP) has been described as an oxidizing agent for Pani synthesis, presenting advantages as good stability in the synthesis conditions, the reaction can be carry out at room temperature and BP can be easily solubilized in organic solvents [33–37].

Pani has been described as a promising polymer to be used as catalyst in the esterification reaction of carboxyl acids and transesterification of triglycerides. Palaniappan et al. [36] has presented good results for direct esterification of lauric, caproic, stearic and cinnamic acids obtaining above 90% yield of product conversion under 70 °C, 24 h and 20 wt% of polyaniline as catalyst. Zieba et al. [38] has synthesized polyaniline over carbon support and applying it to the esterification of ricinoleic acid obtaining ester yields about 95%.

The aim of this work was to produce SD copolymer/Pani composites with high porosity and surface area with Pani dispersed overall support surface. The *in situ* polymerization was carried out with one and four cycles to vary the amounts of Pani in the supports. The composites were evaluated as acid catalyst in the esterification of stearic acid with methanol.

2. Experimental

2.1. Materials

1,4-Dioxane UV/HPLC grade stabilized with 1.5 mg/L of 2,6-di-tert-butyl-4-methyl-phenol, toluene 99.5%, heptane 98%, acetone 99.5%, methyl alcohol 99.8%, ethanol 99.5%, hydroxyethylcellulose, gelatin powder, benzoyl peroxide 65% (BP), Aniline PA, sodium chloride 99%, sodium dodecyl sulfate 99%, sodium hydroxide 97%, phenolphthalein 1% solution, stearic acid 95%, sulphuric acid 95–98%, nitric acid 65%, hydrochloric acid 37% were used as received. Styrene and divinylbenzene were purified washing with NaOH solution followed by reduced pressure distillation.

2.2. Synthesis

2.2.1. Synthesis of styrene–divinylbenzene (SD) copolymers

Copolymers synthesis was carried out through aqueous suspension polymerization in a 1 L three-neck round-bottom flask, equipped with a mechanic stirrer, reflux condenser and a thermometer. The aqueous phase (AP) was composed by hydroxyethylcellulose at 0.26% (w/v), sodium chloride at 0.59% (w/v) and gelatin at 0.12% (w/v). The organic phase (OP) was prepared dissolving 1% of initiator BP in a mixture containing styrene and divinylbenzene monomers at room temperature. Heptane and toluene were used as porogenic agents with a volume ratio of 85/15 and 150% dilution degree in relation to monomers volume. Two kinds of copolymers were produced and denominated SD29 and SD84 for which nominal molar percentages of DVB were 29% and 84%, respectively. The real percentages of DVB were approximately 16% and 46%, since technical grade DVB used had concentration of 55%. The proportion between AP and OP was maintained 4/1 (v/v). The organic phase was added to aqueous phase leaving the system under stirring about 15 min before initial heating. The temperature was kept at 70 °C with stirring at 250 rpm for 24 h. Finally, the copolymer beads were filtrated and washed with water and then with ethanol at 50 °C about 1 h several times until the filtrated to be miscible with water. The copolymers were dried at 70 °C for 24 h. The copolymer beads were sieved and the particles in the range of 400–600 μm were used to prepare the composites.

2.2.2. Synthesis of SD copolymer/Pani composites

SD copolymer/Pani composites prepared using SD29 and SD84 with one reaction cycle were called SD29/Pani-Cl and SD84/Pani-Cl, respectively. In a 100 mL Erlenmeyer, 4 g of each resin were put in contact with 40 mL of ethanol/aniline solution with a volume ratio of 80/20. Each system was mechanically stirred in a shaker for 3 h in order the copolymer become swollen by aniline. In another 100 mL Erlenmeyer, a reactive solution were prepared mixing 2.3×10^{-3} mol of benzoyl peroxide (BP) in 20 mL of dioxane, 1.4×10^{-3} mol of sodium lauryl sulfate in 6 mL of water and 0.06 mol of hydrochloric acid. The swollen copolymer in the first Erlenmeyer was filtrated and added to the reactive solution. The aniline polymerization was carried out under mechanical stirring in a thermo regulated bath at 25 °C for 24 h. After, the composites were vacuum filtrated and washed with methanol and ketone until the filtered solution became colorless. The composites were dried at 70 °C for 24 h. All procedure was repeat 4 times to prepare the four cycle composites which were called SD29/Pani-Cl* and SD84/Pani-Cl*.

2.3. Physico-chemical characterization

2.3.1. Fourier transform infrared spectroscopy

Fourier-transform infrared spectra were recorded using a Perkin Elmer Spectrum ASCII 1.60 in the range of 4000–400 cm^{-1} for SD29 and SD84 copolymers and the synthesized composites. Samples were prepared as KBr tablets.

2.3.2. Thermogravimetric analysis

Thermogravimetric curves of all samples were recorded on a DTG 60 Shimadzu thermogravimetric analyzer from 25 to 800 °C at a heating rate of 10 $°\text{C min}^{-1}$ under air atmosphere at 50 mL min^{-1} flux.

2.3.3. Nitrogen adsorption measurements

The specific surface area and pore size distribution measurements were performed using a Micrometrics ASAP 2010 nitrogen sorption porosimeter. Analysis was via nitrogen sorption carried out at 77 K. Specific surface area was determined by BET method and the pore size distribution by the BJH method based on nitrogen desorption isotherm.

2.3.4. Morphology analysis

Morphology of SD copolymers and synthesized composites were examined by scanning electron microscopy (SEM) using a JSM-6610 instrument. Samples were coated in gold prior to SEM imaging.

2.3.5. Elemental analysis

CHNS elemental analysis was performed using a Thermo Scientific Flash 2000 Organic Elementar Analyzer. Nitrogen content indicates the polyaniline amount adhered on resin surface. Eq. (1) was used to estimate the amount of polyaniline in the composites from the nitrogen percent weight:

$$\%\text{Pani-Cl} = [n\text{N}/4] * [M_{\text{RU}} + +2M_{\text{HCl}}] \tag{1}$$

where %Pani-Cl = percent weight of emeraldine polyaniline; n_{N} = nitrogen mol number in 100 g of composite (% m_{N}/14); M_{RU} = molar mass of repetitive unit of emeraldine polyaniline; M_{HCl} = molar mass of HCl. The molar mass of HCl was multiplied by two because it was considered that the two imine groups are preferentially protonated [39].

2.3.6. Acid capacity

The total amount of Brönsted acid sites was determined by acid–base titration. The composites were put in contact with 50 mL of NaOH (0.01 mol L^{-1}) during 24 h at room temperature. Then, the composites were filtered and the liquid was subsequently titrated with hydrochloric acid solution (0.005 mol L^{-1}).

2.3.7. Catalytic tests

Esterification was performed using commercial stearic acid (0.01 mol), with methanol (0.3 mol). This reaction was carried out in a 100 mL round-bottom flask coupled with a reflux condenser, on an oil bath magnetically stirred heated to 70 °C for 8 h. All synthesized composites were used as catalyst at 15% weight related to carboxylic acid mass. At the end of each reaction the product was recovered and analyzed by GC/MS Agilent 7890 GC equipment using a HP-5 column.

3. Results and discussion

The suspension polymerization process produced Sty-DVB copolymers (SD) in the form of opaque and white beads with characteristics of macroporous resins. The polianiline/SD composites presented green color characteristic of Pani emeraldine salt form, which became darker with the increase of the polymerization cycle number. Beads of the different composites were cut off with a blade and showed a homogeneous distribution of Pani inside the particles. The following sections describe the characterization results of the SD copolymers (SD29, SD84), the composites prepared with one polymerization cycle (SD29/Pani-Cl, SD84/Pani-Cl) and the composites prepared with four polymerization cycle (SD29/Pani-Cl*, SD84/Pani-Cl*).

3.1. Infrared spectroscopy

Fig. 1 shows the FTIR spectra for copolymers and composites. It can be note that the spectra profiles of one cycle composites are very similar to copolymers spectra profiles, probably due to its lower Pani content indicated by lighter green color. The four cycle composites spectra were also similar but they show more clearly some characteristics bands of Pani. A spectrum of emeraldine salt Pani was included in order to facilitate the identification of Pani bands in the composites.

The Pani characteristic bands are observed at: 1589 cm^{-1} and 1491 cm^{-1}, attributed to the stretching of the quinone (Q) and benzenic (B) rings, respectively; 1310 cm^{-1}, attributed to the symmetrical stretching of CN groups of secondary aromatic amines; 1248 cm^{-1}, attributed to the symmetric stretching of the bipolar

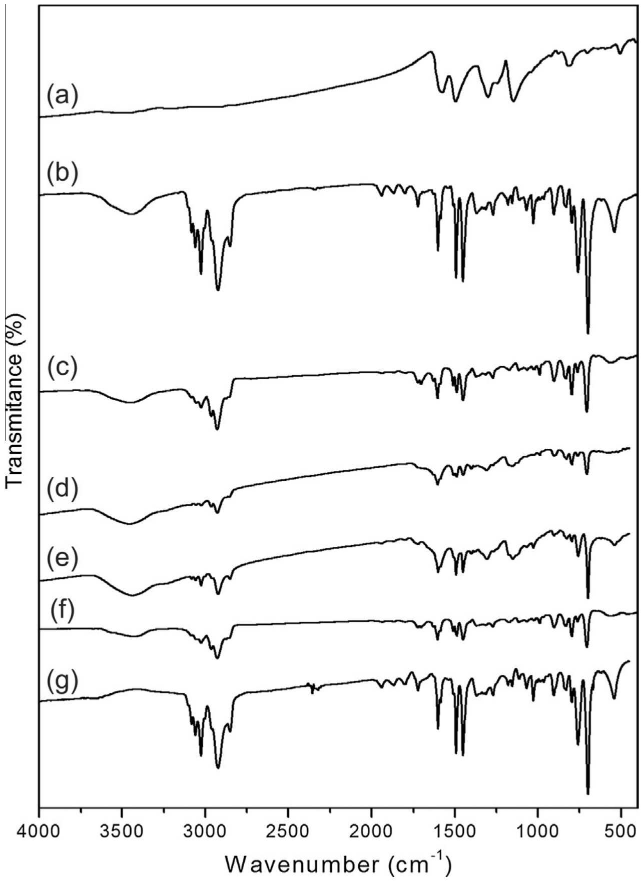

Fig. 1. Infrared spectra of copolymers and composites: (a) Pani-Cl; (b) SD29; (c) SD84; (d) SD84/Pani-Cl*; (e) SD29/Pani-Cl*; (f) SD84/Pani-Cl and (g) SD29/Pani-Cl.

$CN^{\cdot +}$ group of benzenic species; 1159 cm^{-1} attributed to the CH group, which is an electronic or vibrational band due to nitrogen linked to the quinone group [40].

3.2. Thermogravimetric analysis

TGA experiments were performed to evaluate the thermal stability of the produced composites at air atmosphere. Fig. 2 shows the copolymers and composites thermal degradation curves. It can be seen that the thermal degradation of composites occurred at higher temperatures than the corresponding Sty-DVB copolymer, specially, for the four cycle composites (SD29/Pani-Cl*, SD84/Pani-Cl*). Further, we observed that until the point where decomposition begins the composites kept their structural integrity, after that the mass losses occurred more suddenly than for the corresponding copolymers.

Table 1 presents degradation onset temperature for copolymers and composites determined by DTG curves (not showed). The Pani composites presented higher onset temperatures than the original SD copolymers. Kim et al. attributed higher onset temperature for Pani than for polystyrene chains [41]. Davodi et al. also found an increase of onset temperature of polystyrene particles covered by thin Pani layers [42]. The composites beads cut off showed green color characteristic of emeraldine Pani inside the particles, i.e., they did not presented a core–shell morphology. Then, the increasing of the onset temperature can be explained by the protection induced by Pani covering all surface of the macroporous SD copolymers.

Table 1
Degradation onset temperature of SD copolymers and their composites.

Sample	Degradation onset temperature (°C)
SD29	238
SD29-Pani-Cl	300
SD29-Pani-Cl*	314
SD84	268
SD84-Pani-Cl	285
SD84-Pani-Cl*	303

3.3. Nitrogen adsorption measurements

Fig. 3 shows that even after incorporation of polyaniline over copolymer surface only small changes in their morphological characteristics were observed. The total volume adsorbed by composites and copolymers are very close. Copolymers and composites have the same kind of isotherm (type IV), typical for meso or macroporous absorbents. This kind of isotherm is a function of pore size effect upon adsorption phenomena. According to IUPAC,

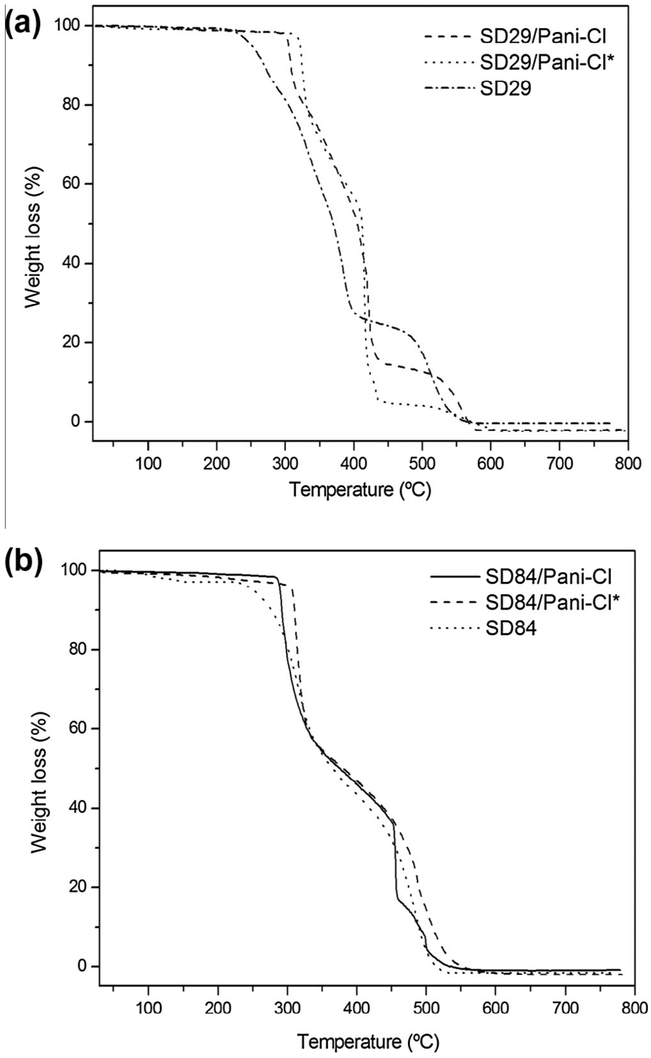

Fig. 2. Thermal degradation of (a) SD29 and (b) SD84 copolymers and their composites.

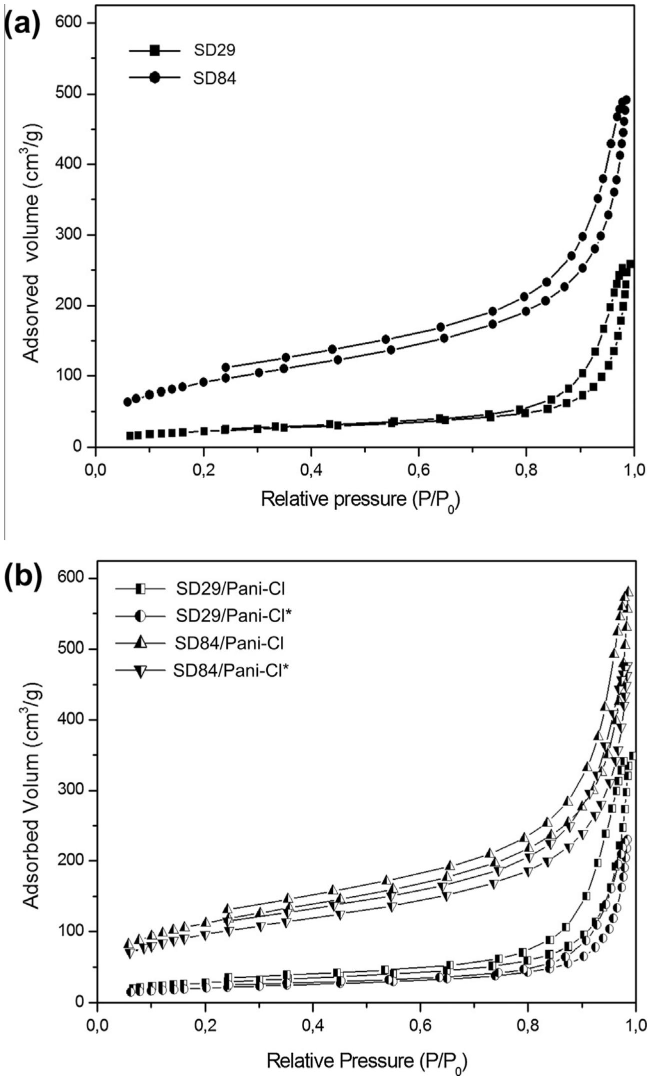

Fig. 3. Adsorption Isotherms for (a) SD copolymers and (b) their composites.

hysteresis of all samples in Fig. 3 fit H1 of adsorbent with cylindrical pores [43]. It was observed for SD84 and their composites, as expected, higher adsorbed volumes in comparison to SD29 and their composites. The high cross-linking degree in SD84 promotes a stronger phase separation during the copolymer synthesis [30–32].

According to IUPAC, micropores do not exceed 2 nm of diameter, mesopores occurs between a range of 2–50 nm and macropores are larger than 50 nm. Fig. 4 shows that pore size distribution was also very similar for copolymers and composites, where most pores are in the range of 10–60 nm. So both copolymers and their composites presented meso and macropores. We can also observe that the composites from SD84 had a considerable amount of pores between 3 and 10 nm which contribute to its higher adsorbed volume and surface area in comparison to composites from SD29.

Table 2 shows the specific surface areas, total pore volumes and average pore diameters of SD copolymers and their composites with Pani. The surface areas of the Pani composites varied between 77 and 412 $m^2 g^{-1}$ indicating good characteristics for use as catalysts. Both composites prepared with one cycle of aniline polymerization presented an increasing of their specific surface areas and pore volumes in relation to the starting copolymers. This probably happened due the copolymer be in a swollen state during aniline polymerization. So the porosity increased even with the filling of pores by the Pani and after drying process. For composites synthesized with one cycle, the considerable increase in specific surface area suggests the formation of a thin layer of Pani overall SD copolymer surface. Yagudaeva et al. observed a small reduction on porosity of macroporous support based on silica gel and sulfonated SD copolymer after aniline polymerization [29]. The structure of silica gel is rigid so its pores cannot expand as the pores of SD copolymers solvated by aniline.

Table 2
Textural proprieties of SD copolymers and their composites.

Sample	S_{BET} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)	D_m (nm)
SD29	85	0.40	20
SD29/Pani-Cl	106	0.54	22
SD29/Pani-Cl*	77	0.35	22
SD84	341	0.71	11
SD84/Pani-Cl	412	0.83	12
SD84/Pani-Cl*	354	0.67	11

S_{BET} ($m^2 g^{-1}$): specific surface area; V_P ($cm^3 g^{-1}$): total pore volume; D_m (nm): average pore diameter.

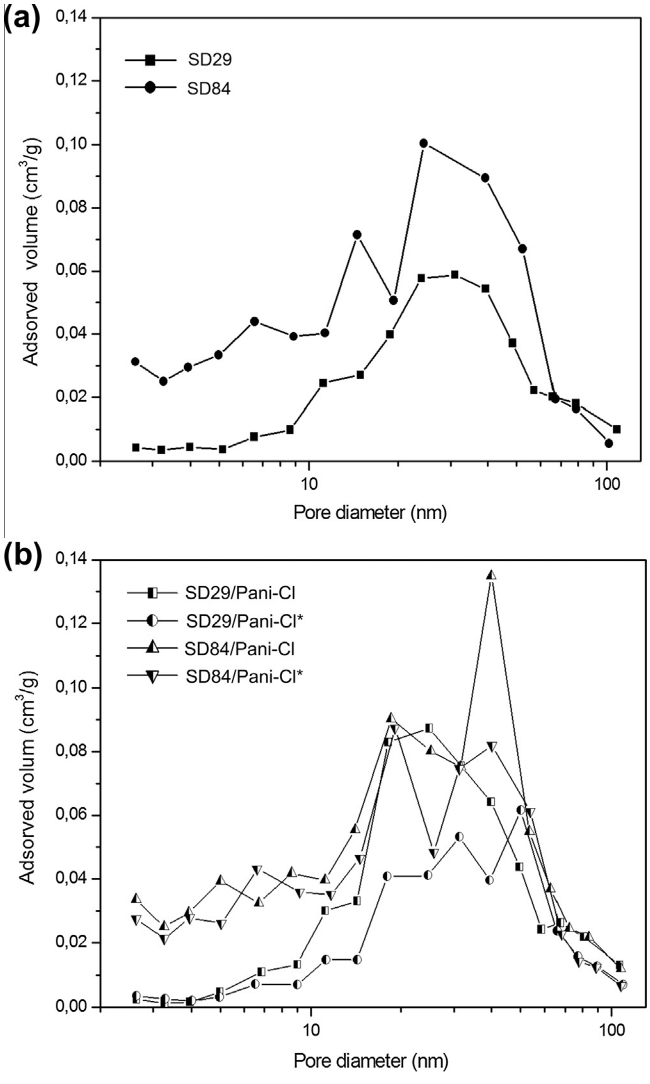

Fig. 4. Pore size distribution for (a) SD copolymers and (b) their composites.

For composites synthesized with four cycles of polymerization, it was observed that the specific surface area remains almost the same when compared to the starting copolymer, while the pore volumes had a small reduction. We believe that the larger amount of polyaniline filling the pores counterbalanced the swelling effect so that the starting copolymer characteristics were lightly changed. The average pore diameter of SD84 copolymer and their composites were smaller than of SD29 copolymer and their composites. The average pore diameters practically did not change between the SD copolymers and their respective composites.

3.4. Morphology analysis

Fig. 5 shows micrographs of external surface and inner of copolymers and their composites obtained by SEM. The SD29 copolymer presented a rough external surface (Fig. 5a) and an inner surface formed by microspheres agglomerates separated by meso and macropores (Fig. 5b). This morphology is characteristic of macroporous styrene–divinilbenzene copolymers [44]. Fig. 5c shows only the external surface of SD29/Pani-Cl, while Fig. 5d shows both internal and external portions of SD29/Pani-Cl* composite. It can be noticed that both composites are very similar to SD29 copolymer concerning external and inner portions.

Fig. 5e and f shows the inner of SD84 copolymer and SD84/Pani-Cl composite, respectively. It is clear the similarity between their internal morphology formed by microspheres agglomerates. It is important to remember that the four cycles composites presented a dark green color of emeraldine Pani inside the beads cut off. SEM results and the nitrogen adsorption measurements allow us to conclude that the composites were formed by polyaniline deposits overall copolymer surface copying its morphological structure. This distribution of Pani on the porous matrix is an interesting feature of these composites, since they have potentially the chemical properties of Pani with the copolymer textural properties.

3.5. Elemental analysis, acid capacity and catalytic tests

Table 3 presents the Pani content, acid capacity (A.C.) and the ester yield for the reaction of stearic acid with methanol. Esterification reaction was carried out using the produced composites as catalysts under the same conditions: 70 °C, 8 h, 15 wt% related to carboxylic acid mass. It can be observed that the four cycles composites presented, as expected, higher amounts of Pani and higher acid capacity than one cycle composites. The esterification using

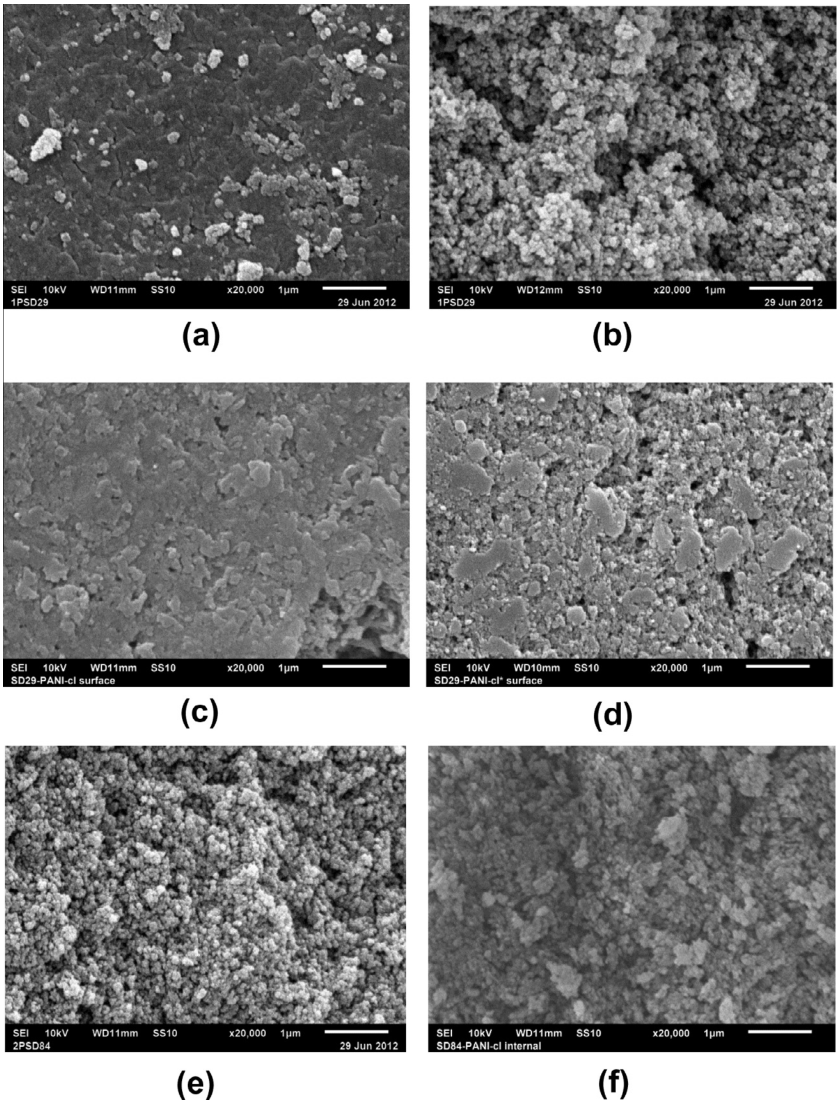

Fig. 5. Microscopy of (a) surface of SD 29 copolymer, (b) inner of SD29 copolymer, (c) surface of SD29/Pani-Cl, (d) surface and partial inner of SD29/Pani-Cl*, (e) inner of SD84 copolymer and (f) inner of SD84/Pani-Cl.

Table 3
Pani percentage, acid capacity and ester yield of SD copolymer/Pani composites.

Sample	% Pani-Cl	A.C. (H^+ mmol g^{-1})	Yield (%)
SD29/Pani-Cl	1.4	0.22	47
SD29/Pani-Cl*	9.0	0.63	96
SD84/Pani-Cl	2.6	0.25	29
SD84/Pani-Cl*	7.9	0.44	95

the one cycle composites as catalyst showed low yields due the low Pani content. The ester yield increased significantly with the improvement of Pani content and acid capacity of four cycles composites. Although SD84/Pani-Cl* composite had smaller acid capacity than SD29/Pani-Cl* the ester yield was very close. This can be explained by the high surface area of the SD84/Pani-Cl* composite and the homogeneous distribution of Pani overall porous structure indicated by SEM analysis and nitrogen adsorption measurements. Ram and Palaniappan prepared unsupported Pani using benzoyl peroxide as oxidant and H_2SO_4 as dopant [45]. They used the synthesized Pani salt as catalyst for the esterification of different carboxylic acids with methanol. The particle size of the Pani salt was found to be in the range of 0.3–300 μm and the specific surface area was 42 $m^2\,g^{-1}$. Most of the reactions were carried out with 1 g of carboxylic acid, 4 mL of methanol and 200 mg of Pani at 70 °C for 24 h. For stearic acid esterification the yield was 99%. In this paper we used a proportion of 4.3 mL of methanol and 150 mg of catalyst for 1 g stearic acid obtaining ester yield of 96% in only 8 h at the same temperature. Considering that Pani content in the four cycle composites was approximately 9%, the amount Pani used as catalyst was 13.5 mg. The high efficiency of the Pani in the composites compared to unsupported Pani can be attributed to their higher surface areas and the Pani distribution overall SD copolymer porous structures. Another advantage of the composites in relation to unsupported Pani is the particle size in the range of 400–600 μm so that the firsts are easily separated of esterification product by simple filtration. The particle size of unsupported Pani prepared with benzoyl peroxide in our laboratory was between 0.2 and 30 μm what require filtration with membranes or centrifugation to separate from esterification products.

4. Conclusion

The present work has demonstrated that SD copolymers/Pani composites can be prepared using benzoyl peroxide as oxidant.

The developed composites presented specific surface area and pore size distribution similar to the copolymers. Besides, SEM analysis indicated the distribution of Pani overall porous structure of copolymer. It was observed an increasing of thermal stability for the composites compared to the SD copolymers. The synthesized composites have demonstrated the potential application as catalysts in the esterification of carboxylic acids. The four cycles composites presented a higher ester yield than one cycle composites due the increasing of Pani content and acid capacity.

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