Reactive & Functional Polymers 73 (2013) 1255–1261

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

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

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

B.H.F. Moura, R.H.B. Assis, P.I.B.M. Franco, N.R. Antoniosi Filho, D. Rabelo *

Instituto de Química, Universidade Federal de Goiás, P.O. Box 131, 74001-970 Goiânia-GO, Brazil

ARTICLE INFO

Article history:
Received 7 February 2013
Received in revised form 30 May 2013
Accepted 21 June 2013
Available online 28 June 2013

Keywords:
Polyaniline
Styrene-divinylbenzene copolymer
Porosity
Composites

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 crosslinked 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

* Corresponding author. Tel.: +55 (62) 3521 1097; fax: +55 (62) 3521 1167.
E-mail address: denilson@quimica.ufg.br (D. Rabelo).

1381-5148/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2013.06.008

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-ditert-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