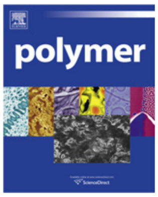
Polymer 52 (2011) 409–414

Contents lists available at ScienceDirect

Polymer

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



Controlling the morphology of micrometre-size polystyrene/polyaniline composite particles by Swelling–Diffusion–Interfacial-Polymerization Method

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ARTICLE INFO

Article history:
Received 5 September 2010
Received in revised form
19 October 2010
Accepted 13 November 2010
Available online 23 November 2010

Keywords:
Conducting polymer
Core-shell composite particle
Diffusion control

ABSTRACT

By means of the "Swelling–Diffusion–Interfacial-Polymerization Method" (SDIPM), we successfully coated polyaniline (PANi) onto micrometre-size, uncharged polystyrene (PS) particles, which were synthesized by dispersion polymerization. After initially forming aniline-swollen PS particles, diffusion of the aniline toward the aqueous phase was controlled through a slow addition of hydrochloric acid, eventually leading to its polymerization on the substrate particle surface. The resultant PS/PANi composite particles have been extensively characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared (FTIR) and Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and C, H, and N elemental microanalysis. At very low aniline/PS weight ratio, the thin, uniform, but intact PANi overlayer was obtained owing to its unique "inside-out" formation mechanism and considerably high efficiency of aniline to transform into the resultant composites. As increasing the initial amount of addition of aniline, the uniform size and well-defined morphology of the PS/PANi core-shell composite particles could still be maintained with a relatively high PANi mass loading yield.

1. Introduction

Synthesis of conducing composites has been focused on intense researches over the last 15 years for alleviating the poor processability of intrinsically conducting polymers [1–9]. Such hybrid materials have the advantages of unique properties owing to the core constituted by inorganic particle or vinyl-polymer endows the system with mechanical properties while a conducting polymer as the shell provides its conductivity [10–12]. Hence, as potential materials they are promising for application in versatile fields such as optoelectronic devices, chemical sensors, fuel cell, lightweight batteries and space science [13–17].

Amongst conducting polymers, polyaniline (PANi) is the most attractive one because of its electronic and optical properties, coupled with excellent environmental stability [18–24]. Up to now, the deposition of PANi onto various colloidal particle substrates has been extensively investigated, especially when polystyrene (PS) is used for the core, giving its spherical shape as well as monodispersity. Hence, PANi-coated PS latex is one of the most promising candidates for conducting polymer composites. Despite a massive amount of work on the synthesis and characterization of PS/PANi composite particles, total control over the structure and morphology, which has a significant effect on the ultimate properties of the composite particles, is not yet achieved and remains a scientific challenge.

In general, all the synthetic methods for preparing conducting composite particles can be divided into deposition method and in situ polymerization method based on the locus of polymerization of aniline monomer. Deposition method means the monomer is first dissolved in medium in the presence of the seed particles, and then polymerization is initiated by the addition of an aqueous solution of the oxidant. The suspended seed particles were coated with conducting polymer by in situ and induced deposition from the aqueous medium. Armes's group initiated the polymerization of aniline monomer in a strongly acidic solution in the presence of the PS seed latex stabilized by poly(N-vinylpyrrolidone) (PVP) and explored various surface modification strategies to improve the coating of PANi [25]. Reynaud and co-workers reported a relatively high coverage of PANi based on crosslinked PS particles stabilized by a surfactant bearing an amide group, which allows the formation of hydrogen bond with the PANi backbone [26]. In contrast to the simple deposition or induced deposition of the formed PANi by deposition method, in situ polymerization method means that one or more of the reactants is enriched or immobilized on the substrate surface inducing

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doi:10.1016/j.polymer.2010.11.025

polymerization of aniline monomer in a given area. Zhou and co-workers assembled polyelectrolyte (PE) multilayers onto melamine formaldehyde particles via the layer-by-layer (LbL) self-assembly technique [27]. Subsequently, aniline monomer was absorbed into PE multilayers and oxidized in situ. The amount of PANi mass loading and thickness of PANi shells were adjusted with the change of the initial PE layer numbers. Liu et al. immobilized oxidant on the surface of PS particles by electrostatic interaction, and then initiated polymerization of aniline monomer on the surface of PS particles [28]. Besides, in order to increase the thickness of the PANi shell, the seeded growth method was applied repeatedly. Obviously, time-consuming surface pretreatment of the work mentioned above complicates the synthetic procedure, even though it could generally optimize the deposition architecture of the PANi overlayer.

Recently, we reported a distinctly novel strategy, so-called "Swelling–Diffusion–Interfacial-Polymerization Method" (SDIPM), which could be classified into interfacial polymerization method [29]. It can fabricate sub-micrometre core-shell PS/PANi composite particles with well-defined shape regardless of the surface electrical property of the PS seed particles. In comparison with the widely used conventional methods containing in situ polymerization or induced deposition, SDIPM presents a unique "inside-out" mechanism to afford much more effective controlling over the structure and morphology of the resultant PS/PANi composite particles by simply changing the aniline/PS weight ratio or the rate of addition of the doping acid.

In this work, PS particles, synthesized by dispersion polymerization using azoisobutyronitrile (AIBN) as initiator, were chosen as the seed particles, and thus these particles bear no chemically bound ionic groups. By means of SDIPM, we explored the success of coating PANi onto the substrate particles almost without surface charge and furthermore, independent of any other assistance, to fabricate micrometre-sized PS/PANi core-shell conductive composites with uniform size and well-defined morphology. Additionally, the influences of PVP, presenting to the PS surface derived from the dispersion polymerization, on the morphology of PS/PANi composite particles were investigated.

2. Experimental section

2.1. Materials

Styrene and aniline (AR, Shanghai Chemical Reagent Co.) were purified by distillation under reduced pressure. Azoisobutyronitrile (AIBN) of chemical reagent grade (Shanghai Chemical Reagent Co.) was purified by recrystallization in 95% ethanol. Ammonium persulfate (APS) of analytical reagent grade (Shanghai Chemical Reagent Co.) was purified by recrystallization in water. All the other chemicals were analytical reagent grade and used as received. Poly(vinylpyrrolidone) (PVP) with an average molar mass of 58 kg/mol (PVP K-30) was purchased from Acros Organics. Absolute ethanol, 95% ethanol, isopropanol and hydrochloric acid were purchased from Nanjing Chemical Reagent Co. Distilled water was applied for all of the polymerizations and treatment processes.

2.2. Synthesis of polystyrene seed particles

Polystyrene (PS) particles were prepared by dispersion polymerization. The PVP stabilizer (2.8 g) were dissolved in isopropanol (160 mL) and heated up to 70 °C in a four-necked round-bottom flask. It was purged with nitrogen to eliminate the inhibiting effect of oxygen. A solution of AIBN initiator (0.2 g) predissolved in styrene monomer (20 g) was added to the reaction vessel, with vigorous mechanical stirring. The polymerization was allowed to proceed for 24 h before cooling to room temperature. Subsequently, the PS particles were purified by repeated centrifugation and redispersion cycle, washing three times with ethanol and then three times with water. Finally, the PS latex was diluted with water to solid content of 10 wt % before use.

2.3. Preparation of polystyrene/polyaniline composite particles

First, aniline was added to water at 0 °C and under ultrasonic treatment for 15 min followed by the addition of the PS seed particles. The mixture was stirred with ultrasonic assistance for 30 min at 0 °C to allow sufficient swell of aniline into PS seed particles, which was confirmed by the gradual disappearance of aniline droplets appearing initially after mixing the PS latex and aniline under optical microscope observation. The dispersion of aniline-swollen PS particles was transferred to a three-necked round-bottom flask in an ice bath. The aqueous solution of APS was added to the dispersion in one batch and the initial oxidant/monomer molar ration was fixed at 1:1. This was followed by the addition of hydrochloric acid (1 mol/L), also in an equimolar amount relative to aniline, dropwise via syringe. The temperature was maintained at 0 °C for the first 5 h of the polymerization, after which the polymerization was carried out for 18 h at room temperature. The solid content of the PS latexes was kept constant at 4 wt %, and the weight ration of aniline monomer to the seed latex was varied from 1:40 to 1:2. If the aniline/PS weight ratio was further increased, the system became colloidally unstable, and finally, macroscopic precipitation and its amorphous suspensions, derived from the dissolving of PS in aniline and thus the disintegration of the microspheres, were observed. The resulting green PS/PANi composite particles were washed repeatedly by centrifugation until the supernatant became colorless. Finally, the product was dried in a vacuum oven for 48 h at 40 °C.

2.4. Characterization

The morphology of the PS seed particles and the resultant PS/PANi composite particles were observed both by scanning electron microscope (SEM) using an S-4800 instrument (Hitachi Co., Japan) operated at an accelerating voltage of 10 kV and transmission electron microscope (TEM) using a JEM-100 CX (JEOL Co., Japan) microscope. The samples were not sputter-coated with a metal overlayer for SEM study. X-ray photoelectron spectroscopy analysis was carried out on a VG ESCALAB MKIIX-ray photoelectron spectrometer. Fourier transform infrared (FTIR) analysis was performed with a Bruker VECTORTM 22 FTIR spectrometer (Bruker Co., Germany). Raman spectrum was measured by use of the MultiRam spectrometer (Bruker Co., Germany). A continuous wave Nd:YAG laser working at 1064 nm was employed for Raman excitation. A total of 200 scans were averaged in each spectrum obtained with laser power 10 mW. C, H, N elemental microanalyses of both PANi bulk power prepared in the absence of latex particles and PS/PANi composite particles were carried out on a CHN-O-Rapid instrument (Heraeus Co., Germany).

3. Results and discussion

The schematic process for "Swelling–Diffusion–Interfacial-Polymerization Method" (SDIPM) is displayed in Scheme 1. In the initial stage, upon mixing the monomer (i.e., aniline) with the original seed latex, the former would be enriched inside the seed particles after a certain period according to their good affinity, eventually forming monomer-swollen seed particles [30]. That is, the monomer is distributed mainly in the solid seed particles while the other reactants participating in the chemical reaction exists in the continuous phase, and hence the polymerization is almost restrained at this stage. Following the change on factors of