Colloids and Surfaces A: Physicochem. Eng. Aspects xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Electrokinetic properties of biodegradable conducting polyaniline-*graft*-chitosan copolymer in aqueous and non-aqueous media

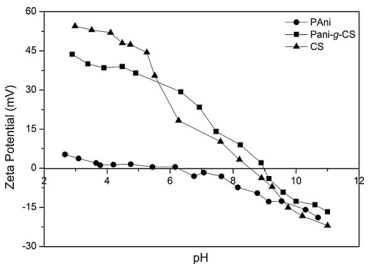
Mehmet Cabuk[a,b,*], Mustafa Yavuz[b], H. Ibrahim Unal[c]

[a] Department of Chemistry, Faculty of Arts and Sciences, Muş Alparslan University, Muş, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, Süleyman Demirel University, Isparta, Turkey
[c] Department of Chemistry, Faculty of Science, Smart Materials Research Laboratory, Gazi University, Ankara, Turkey

HIGHLIGHTS

- PAni-*g*-CS was synthesized by radicalic polymerization.
- PAni-*g*-CS was characterized by ^{1}H NMR, UV–vis, TGA and SEM techniques.
- ζ-Potential of PAni shifted to more positive regions after grating with CS.
- ζ-Potentials were found to be in colloidally stable range in both aqueous and non-aqueous SO media.
- PAni-*g*-CS showed an improved antibacterial activity against *Escherichia coli*.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form 18 February 2014
Accepted 23 February 2014
Available online xxx

Keywords:
Chitosan
Polyaniline
Colloidal stability
Zeta potential
Non-aqueous media
Antibacterial activity

ABSTRACT

In this study, biodegradable and conducting polyaniline-*graft*-chitosan (PAni-*g*-CS) copolymer was synthesized by radicalic polymerization using ammonium persulfate $(NH_4)_2S_2O_8$ as initiator. The synthesized copolymer was characterized by using particle size, density, band gap, ^{1}H NMR, TGA, and SEM measurements. The characterization results revealed the successful synthesis of the graft copolymer of PAni and CS. Electrokinetic properties and colloidal stabilities of PAni-*g*-CS dispersions were examined as a function of time, pH, electrolytes, various surfactants, and temperature by means of ζ-potential measurements in polar (water) and non-polar (silicone oil) media. The ζ-potential of PAni shifted to more positive region after grating with chitosan. In acidic medium, ζ-potential of the copolymer was observed to increase up to +44 mV. The presence of monovalent (Nacl) electrolyte had no impact on ζ-potential of the copolymer dispersions whereas; divalent ($BaCl_2$) and trivalent ($AlCl_3$) electrolytes caused the ζ-potentials of the dispersions to shift to more positive regions. The most effective surfactant on the ζ-potential of the PAni-*g*-CS was determined to be sodium dodecyl sulfate, which reduced the value of ζ-potential to −39 mV. Elevated temperatures caused almost no change on the ζ-potential of the copolymer dispersions. In non-aqueous media, ζ-potential of PAni-*g*-CS was found to be in colloidally stable region. Further, PAni-*g*-CS was tested against *Escherichia coli* and showed an improved antibacterial activity when compared to that of pristine PAni and CS.

1. Introduction

Chitosan (CS) is an amino polysaccharide, which contains free amino groups (−NH_2) at neutral and alkaline pH values, but they

* Corresponding author at: Department of Chemistry, Faculty of Arts and Sciences, Muş Alparslan University, Muş, Turkey. Tel.: +90 5354433221; fax: +90 4362130054.
E-mail addresses: m.cabuk@alparslan.edu.tr, mhmtcbk@gmail.com (M. Cabuk).

http://dx.doi.org/10.1016/j.colsurfa.2014.02.053
0927-7757/

are protonated ($-NH_3^+$) under acidic conditions, thus making possible ionic interactions upon the reaction with anions. In contrast to other natural polymers, CS is a hydrophilic polymer with positive charges that come from weak basic groups, which outfits it with special characteristics from the technological point of view [1]. Also, CS is a natural biodegradable polymer which most simply means a material that has the ability to break down, or decompose back into the natural environment without causing harm [2,3]. Chemical modification of CS is an important topic for production of multi-functional materials [4–6].

Conducting polymers are used for several applications such as actuators, sensors, electronic devices, diodes and electrorheology. Among the conducting polymers, polyaniline (PAni) has attracted intense attention due to its environmental stability, ease of synthesis, exciting chemical, electrical and optical properties [7]. Among the four basic forms, emeraldine form of PAni in the highly conducting state has good antibacterial activity [8]. On the other hand, there is a need for using various supportive polymeric materials, i.e., grafting with other polymers, to enhance their surface properties, conductivity, colloidal stability, thermal and mechanical properties without altering their bulk properties [9,10].(ζ)-potential measurements are very useful technique which provides information about the material surface–solution interface and colloidal stability of dispersed particles in a suspension. ζ-Potential cannot be measured directly, but can be determined using electrokinetic techniques such as streaming current or potential, electric conductivity, and electrophoretic mobility [11]. When the ζ-potential is low, attraction of suspended particles with each other overcomes the repulsive forces and the particles tend to aggregate. It is generally accepted that dispersions' particles having ζ-potential values between 30 mV$\leq \zeta \geq -30$ mV will tend to be stable. Some parameters such as time, pH, ion and surfactant concentrations and types, and temperature may affect the values of ζ-potentials of a dispersion [12].

Recently, electrokinetic properties of polymers have gained much interest since they give valuable information on surface properties of particles, interactions between different particles and colloidal stabilities of dispersions. Du et al. have investigated the ζ-potential and antibacterial activity of CS nanoparticles and CS nanoparticles loaded copper ions; and reported that ζ-potentials of the samples increased up to 88 mV because of the loading of copper ions, whereas, ζ-potential of the CS nanoparticles was about 51 mV [13].

Electrokinetic properties of PAni-*g*-CS copolymer have not hitherto been reported in the literature. Aim of the present study was to reveal electrokinetic properties of biodegradable conducting PAni-*g*-CS copolymer dispersions. For this purpose, ζ-potentials of the conducting PAni-*g*-CS copolymer particles in aqueous colloidal dispersions were closely investigated as a function of time, pH, electrolytes, surfactants and temperature. To understand the colloidal behavior in non-polar medium, ζ-potential values of the PAni-*g*-CS was also determined in nonpolar SO. Finally, the relation between ζ-potential and antibacterial activity of PAni-*g*-CS were examined against bacterial strain *Escherichia coli* by means of inhibition zone method. The results obtained were compared with pristine PAni and CS.

2. Experimental

2.1. Materials

Chitosan, $\bar{M}w = 3.0 \times 10^5$ g mol^{-1} with 75–85% degree of deacetylation (DD), was obtained from Aldrich with analytical grade. $(NH_4)_2S_2O_8$ was used as oxidizing agent (Merck). Aniline (Merck) was used after vacuum distillation. Cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and Triton X-100 were Merck products with analytical grade. Silicone oil ($\eta = 4.57 \times 10^{-3}$ Pa s) and all the other reagents were obtained from Aldrich with analytical grade and used as received.

2.2. Synthesis of PAni-g-CS copolymer

Conducting and biodegradable PAni-*g*-CS copolymer was synthesized by radicalic polymerization and the synthesis procedure was schematically shown in Fig. 1. For this purpose, 1 g CS was dissolved in a flask in 1 wt.% acetic acid. In an another flask, 9.7×10^{-2} mol aniline was dissolved in 1 wt.% acetic acid and added into the above mentioned solution. After 1 h of mixing, pre-cooled $(NH_4)_2S_2O_8$ ($n_{oxidant}$:$n_{monomer}$ = 1.5:1) was added dropwise and kept stirring under nitrogen atmosphere at 0–5 °C for 16 h. The solution formed in dark green color was neutralized with 0.5 M $NaOH_{(aq)}$ solution to precipitate CS groups in the PAni-*g*-CS copolymer. To remove any impurities present, recovered crude graft copolymer product was washed with N-methylpyrrolidone (NMP), hot distilled water and distilled water, respectively, then filtered and dried in a vacuum oven at 70 °C for 48 h. Grafting yield of PAni onto CS was calculated as 275% according to the following equation:

$$GY(\%) = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where W_g and W_0 are the weights of grafted and pristine CS, respectively.

2.3. Characterizations

The materials synthesized were dried in a vacuum oven and ground milled to obtain homogeneous fine particles using a Retsch MM400 model milling machine (Germany) and subjected to the following characterizations. ^{1}H NMR spectra of the materials were recorded on a 500 MHz Bruker AV 500 spectrometer (Germany) by using DMSO-d_6/CF_3COOH (90/10, V/V) as a solvent at room temperature. Electronic structures and band gap values of the materials were determined from UV–vis absorption measurements as 0.01 g of sample in 2 mL of NMP solvent using a spectrophotometer (Perkin Elmer Model Lambda 20, USA). Thermal analyses of the samples were performed with a Perkin Elmer Diamond TGA/DSC thermal analysis instrument (USA). The specimens were heated at a heating rate of 10 °C min^{-1} under N_2 atmosphere from room temperature to 600 °C. The morphologies of the materials were examined using a scanning electron microscope (JEOL JSM 5500LV, Japan). Hydrodynamic particle sizes of the samples were determined using a Malvern Nano-ZS particle sizer (UK) in distilled water at ambient temperature. The self-optimization routine (laser attenuation and data collection time) in the Zeta-Sizer software was used for all the measurements. Solid pellets of the dried samples were prepared as discs of 13 mm diameter under the pressure of 700 MPa and used for apparent density and electrical conductivity measurements. Apparent densities of the samples were calculated using masses and volumes of the solid pellets. Electrical conductivity measurements of the sample pellets were determined by four-probe technique using a FPP-460A model electrical conductivity-measuring instrument (Entek Electronic Co., Turkey) at room temperature.

2.4. Electrokinetic studies

The ζ-potential measurements were performed with a Malvern Zeta-sizer Nano ZS (UK) which works with Laser Doppler Electrophoresis technique using folded capillary cell equipped with

Please cite this article in press as: M. Cabuk, et al., Electrokinetic properties of biodegradable conducting polyaniline-*graft*-chitosan copolymer in aqueous and non-aqueous media, Colloids Surf. A: Physicochem. Eng. Aspects (2014), http://dx.doi.org/10.1016/j.colsurfa.2014.02.053