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Original article

Adsorption of cationic copolymer nanoparticles onto bamboo fiber surfaces measured by conductometric titration

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ABSTRACT

Monosized nanoparticles of 57.3 nm were prepared by cationic emulsion polymerization using a polymerizable emulsifier DMHB. The adsorption of nanoparticles onto bamboo fibers was measured by conductometric titration. The results indicated that the adsorption capacity increased with increasing contact time until 120 min. The equilibrium data for nanoparticles adsorption onto bamboo fibers were well fitted to the Langmuir equation. Moreover, the monolayer adsorption capacity of nanoparticles in the concentration range (from 0.03 g/L to 0.6 g/L) studied, as calculated from Langmuir isotherm model at 25 °C, was found to be 38.61 mg/g of fibers. The SEM images showed that the nanoparticles form a uniform monolayer on bamboo fiber surfaces.

1. Introduction

Cationic latexes have emerged as the subject of vigorous research for applications in paints, coating industries, papermaking, textile and fiber treatments, functional materials, and so on [1–7], because cationic copolymer nanoparticles with positive charge have many attractive characteristics such as preferentially adding/adsorbing the negative charge on surfaces, eliminating electrostatic repulsion, and improving properties of materials and subsequent process [8,9].

As a new regenerated cellulose fiber, bamboo fiber is hygroscopic and permeable with natural antibacterial and bacteriostatic properties. Further, it is soft and smooth, as well as opaque to ultraviolet light. Thus bamboo fibers have wide applications in different areas. In most cases bamboo fiber surfaces have negative charges, and cationic polymers nanoparticles are readily adsorbed onto bamboo fiber surfaces by electrostatic attraction. Therefore, the adsorption of positively charged colloidal nanoparticles on bamboo fibers is becoming a promising way to manufacture functional textiles and to enhance paper strength [10–13]. Recently, much more attention has been given to the adsorption of cationic nanoparticles onto cotton fibers [14–16], however, the adsorption of cationic nanoparticles onto bamboo fibers has rarely been reported.

Spherical polymer nanoparticles with positive surface charges are often prepared by emulsion polymerization [17,18]. Cationic nanoparticles obtained by common emulsifiers are sensitive to water used in processing [19]. Thus, more stable cationic nanoparticles were synthesized by using polymerizable emulsifiers [20].

The aim of the present work is to investigate the adsorption mechanism of cationic nanoparticles onto bamboo fibers by conductometric titration. We investigate the adsorption rate and adsorption mechanism of the nanoparticles onto bamboo fibers. In addition, the morphology of bamboo fiber surfaces deposited by the nanoparticles is also observed by a field emission scanning electron microscopy (FE-SEM).

2. Experimental

2.1. Method

Conductometric titration [21–23] was carried out by adding $AgNO_3$ solution to the nanoparticle dispersion. To obtain high-resolution data with a constant concentration ($AgNO_3 = 5.875 \times 10^{-3}$ mol/L), separate titrations were carried out using a wide range of nanoparticle (from 0.03 g/L to 0.6 g/L) concentrations. In addition, all the measurements of the conductometric titration were carried out at room temperature and atmospheric pressure, and all the conductivity data were automatically compensated to 25 °C by the conductivity meter. The electrode was immersed in the dispersion for 1–2 min, and then the conductivity value was

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Table 1
Recipes used in the emulsion polymerizations.

Reagent	Consumption (g)
Emulsifier (DMHB)	0.4
Monomer (St)	19.2
Monomer (BA)	0.8
Initiator (AIBA)	0.105
Deionizer water (H_2O)	80

recorded. The same measurement was repeated several times to check the reliability of the data and the averaged values were given for the measurement.

2.2. Materials

The materials used in this investigation and their sources are as follows: Styrene (St) was purchased from Tianjin Guangcheng Chemical Co., Ltd., China, butyl acrylate (BA) was purchased from Shanghai Aibi Chemical Co., Ltd., China, and they were purified by washing with a 10% (w/w) sodium hydroxide aqueous solution and stored at -18 °C. The cationic polymerizable emulsifier, methacryloxyethyl hexadecyl dimethylammoniumbromide (DMHB, purity >98.5%), was prepared according to the reference. The cationic initiator used was 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AIBA, purity 98%, Qiongdao Kexin Materials Technology Co., Ltd.). Silver nitrate ($AgNO_3$) was purchased from Shanghai Chemical Reagent Factory. Deionized water was purified by standard procedures and used in all the experiments. Bamboo fibers, deionized and scoured were supplied by Huafang Co., Ltd., China. Other materials and solvents were used as received.

2.3. Semicontinuous polymerization of cationic copolymer nanoparticles

P(St-co-DMHB-co-BA)$^{n+}$·Br_n^- was obtained by semicontinuous emulsion copolymerization of Styrene and DMHB with BA in different molar ratios. The steps are as follows: The polymerizations were carried out in a 250 mL round bottomed flask equipped with a stainless steel stirrer, nitrogen inlet tube, and reflux condenser. The nitrogen was injected into the flask after the device was prepared, and then part of DMHB and deionized water (80 g) were added. After 15 min, parts of St and BA were added at room temperature for 30 min to make the emulsifier evenly dispersed. After a part of initiator AIBA was added, the reaction system was heated to 80 °C. Then residual mixed monomer (St and BA) were dropped into the reaction system within 1.5 h. After that, residual DMHB and AIBA were added into the emulsion, and the reaction system was kept at 80 °C for 3 h and cooled to room temperature. A dispersion of cationic nanoparticles, P(St-co-DMHB-co-BA)$^{n+}$·Br_n^-, was obtained at the end of the reaction. The recipes used in the emulsion polymerization were given in Table 1.

2.4. Adsorption of the nanoparticles

Square pieces of bamboo fabric (2 g) of about 1 cm^2 were washed with deionized water several times. The washed samples were put into the aqueous suspension of cationic latexes (200 mL) and kept at 60 °C for 1 h. The adsorption of cationic nanoparticles onto bamboo fibers was conducted at 25 °C and a moderate shaking speed in an SHA-V shaker (Changzhou Guohua Electric Appliance Co., Ltd., China). After that, these samples were washed thoroughly with deionized water. The conductivity of the dispersion was measured several times to check the reliability of the data. Subsequently, the bamboo samples were dried under vacuum at 50 °C for 30 min for other tests.

2.5. Characterization

2.5.1. Size and distributions of the cationic nanoparticles

The size and distributions of the nanoparticles were measured by using a Nano-ZS90 instrument (Malvern, UK) at 25 °C. All samples were diluted with deionized water before test.

2.5.2. Scanning electron microscopy (SEM)

SEM images were obtained using a Hitachi SU-8010 field emission scanning electron microscope. Prior to the observations, the samples were coated with Au.

3. Results and discussion

3.1. Properties of the cationic nanoparticles

P(St-co-DMHB-co-BA)$^{n+}$·Br_n^- was prepared by a semicontinuous emulsion polymerization, and sizes and distributions of seeded nanoparticles were measured using the Nano ZS90 at 25 °C. Scanning electron micrograph (SEM) of the nanoparticles was shown in Fig. 1. And it is also clear that most of the nanoparticles have a diameter less than 100 nm (see Fig. 2). The average diameter of the prepared nanoparticles in water is 57.3 nm, and the PDI is 0.122. The colloid titration analysis indicates that the charge density and density of the nanoparticles are 0.821×10^{-4} C/cm^2 and 1.003 g/cm^3, respectively. The positive charges on the nanoparticles surfaces came from the cationic groups of the cationic initiator and the cationic emulsifier.

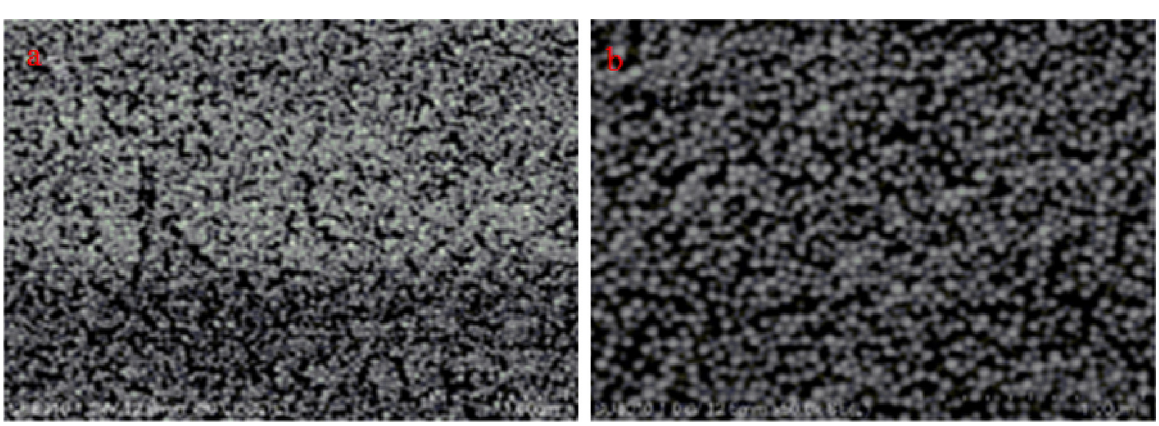

Fig. 1. SEM photograph of P(St-co-DMHB-co-BA)$^{n+}$·Br_n^- nanoparticles prepared by semicontinuous emulsion polymerization.