Colloids and Surfaces A: Physicochem. Eng. Aspects 452 (2014) 82–88

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Adsorption of cationic copolymer nanospheres onto cotton fibers investigated by a facile nephelometry

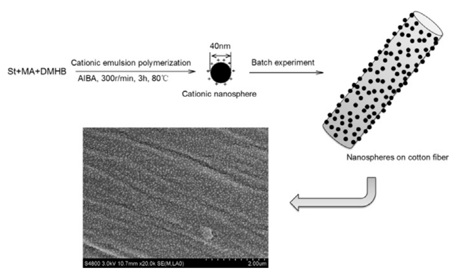
Daiming Liu, Longyun Hao, Kuanjun Fang*

Laboratory of Fiber Materials and Modern Textiles, The Growing Base for State Key Laboratory, College of Chemical and Environmental Engineering, Qingdao University, Qingdao 266071, Shandong, China

HIGHLIGHTS

- A facile nephelometry for measuring very low nanosphere concentrations.
- A uniform mono-layer of cationic copolymer nanospheres was coated on cotton fibers.
- The adsorption of cationic nanospheres on cotton fibers followed the Langmuir model.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form 21 March 2014
Accepted 22 March 2014
Available online 3 April 2014

Keywords:
Adsorption
Copolymer
Cationic nanospheres
Cotton fibers
Nephelometry

ABSTRACT

A facile nephelometry for measuring very low nanosphere concentrations was established by using a very common nephelometer in order to monitor the adsorption of polymer nanospheres from liquid phase onto cotton fiber surfaces. Monosized nanospheres of 40 nm were prepared by cationic emulsion polymerization of styrene and methyl acrylate with a polymerizable emulsifier, methacryloxyethyl hexadecyl dimethylammoniumbromide. The turbidity of aqueous suspension liquid decreased rapidly within the first contact time of 50 min for CMC-modified cotton fibers. The maximum amount of nanospheres deposited on CMC-modified cotton fibers was 15 mg per gram fibers, far higher than the amount of 4.8 mg per gram fibers on unmodified cotton fibers. The adsorption of cationic nanospheres on cotton fibers followed the Langmuir adsorption model. SEM observation reveals that a uniform mono-layer of nanospheres presented on CMC-modified cotton fiber surfaces.

1. Introduction

Particle adsorption onto solid surfaces is a very important process in a variety of fields such as filtration and flotation, paper making and textiles, functional materials, pharmaceutical and cosmetic industries [1–5]. For example, hydrophobic, conductive and antibacterial textiles could be fabricated by coating fibers with nanoparticles [6–9].

In most cases cellulose fiber surfaces have negative charges. Therefore, the adsorption of positively charged colloidal nanoparticles on cellulose fibers is becoming a technological promising way to manufacture functional textiles and to enhance paper strength [10–12]. Spherical polymer nanoparticles with positive surface charges are often prepared by emulsion polymerization [13–15]. Cationic nanospheres obtained by common emulsifiers are sensitive to water in application process [16]. Therefore, more stable cationic polymer nanospheres were synthesized by using polymerizable emulsifiers [17].

* Corresponding author at: Laboratory of Fiber Materials and Modern Textiles, The Growing Base for State Key Laboratory, 308 Ningxia Road, Qingdao 266071, Shandong, China. Tel.: +86 13808980221; fax: +86 053285956039.
E-mail address: kuanjunfang@gmail.com (K. Fang).

http://dx.doi.org/10.1016/j.colsurfa.2014.03.079
0927-7757/

In order to understand the adsorption of nanospheres on solid surfaces, methods for measuring particle concentrations have been established, which can be divided into two categories. One is by measuring the change of solid surface properties in the process of adsorption, such as streaming potentials [18,19]. The other one is by directly measuring the nanoparticle concentrations during adsorption. Methods for measuring nanoparticle concentrations include gravimetry, UV–visible spectrophotometry and ultrasonic attenuation spectroscopy. The accuracy of gravimetry is relatively not good especially when nanoparticle concentrations are very low. UV–visible spectrophotometry is quite suitable for measuring metal nanoparticle concentrations [20,21]. Turbidimetric analysis based on Mie scattering theory measures the intensity of an incident light by a spectrophotometer and is only valid when the nanoparticle size closes to the wavelength of incident light [22]. Ultrasonic attenuation method uses the attenuation spectrum of an ultrasonic impulse [23,24]. However, this method is quietly time-consuming and complicated [25].

Nephelometry follows the principle of the Rayleigh scattering. This technique is usually used to measure the content of suspended solids in water. In the present work, a nephelometry for measuring very low concentrations of polymer nanospheres was established by using a very common nephelometer. The structure and properties of copolymers can be easily designed due to wide sources of monomers. Using copolymer nanospheres as a template to study the adsorption of nanoparticles on fibers could guide us to prepare functional materials with high performances. Mono-sized copolymer nanospheres of 40 nm were synthesized by cationic emulsion polymerization using polymerizable methacryloxyethyl hexadecyl dimethylammoniumbromide as an emulsifier to avoid the influence caused by emulsifier desorption and to enhance the stability of nanosperes. The adsorption of cationic nanospheres on cotton fibers was investigated through measuring nanosphere concentrations by using the facile nephelometric method established.

2. Method

2.1. The nephelometric principle

When a light beam passes through an aqueous suspension, it is subjected to scatter due to the presence of particles in the suspension. The amount of light scattered as an indication of turbidity can be measured by electronic photo detectors. It has been extensively proved that the shape, size and composition of particles and the light wavelength affect the amount of light scattered and the scattering pattern [26]. Although the color and temperature of suspension liquid may also bias turbidity measurement, but these effects are negligible [27]. Rayleigh scattering is fitted well to particles smaller than 50 nm. The simplified Rayleigh scattering formula is as follows [28]:

$$I = kCMI_0 \tag{1}$$

where I is the intensity of light scattered, I_0 the intensity of incident light, C the concentration of scattering particles, k is a ratio and M is the molecular weight of scattering particles. Therefore, when the intensity of incident light and the molecular weight of scattering particles are certain, the intensity of scattered light is directly proportional to the concentration of scattering particles. A nephelometry is based on the intensity measurement of light scattered by particles at right angles to the incident light beam. Here, we use a common nephelometer to measure the nephelometry (τ), which is defined as the ratio of incident light intensity and scattered light intensity [29].

$$\tau = \frac{I}{I_0} = kM \cdot C \tag{2}$$

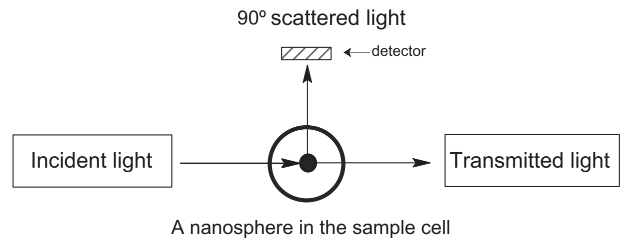


Fig. 1. Schematic principle of the nephelometer used.

Nephelometric measurement is preferred at low particle concentrations because of irrelevant scattering and less interaction between nanospheres. The schematic of nephelometry is shown in Fig. 1.

2.2. Relationship between particle concentrations and nephelometric turbidities

According to Eq. (2), the particle concentration is linearly correlated with the nephelometric turbidity measured. Therefore, a series of suspension liquids with different particle concentrations were prepared and the nephelometric turbidities were measured, the result is shown in Fig. 2. It is obvious that a well linear relationship presented between the particle concentration and the nephelometric turbidity. The correlation coefficient R^2 value reached 0.996. Using the fitted linear equation $\tau = 55.86C + 5.54$, the particle concentrations could be easily calculated by the turbidities measured.

3. Experimental

3.1. Materials

Styrene (St) and methyl acrylate (MA) were purchased from Shanghai Aibi Chemical Co., Ltd., China, and purified by washing with a 10% (w/w) sodium hydroxide aqueous solution and stored at −18 °C. The following reagents were used as received, the cationic initiator 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AIBA, purity 98%, Qingdao Kexin Materials Technology Co., Ltd.), the cationic polymerizable emulsifier methacryloxyethyl hexadecyl dimethylammoniumbromide (DMHB, purity 96.5%), carboxymethyl cellulose (CMC, purity 99.8%, Tianjin Fuchen Chemical

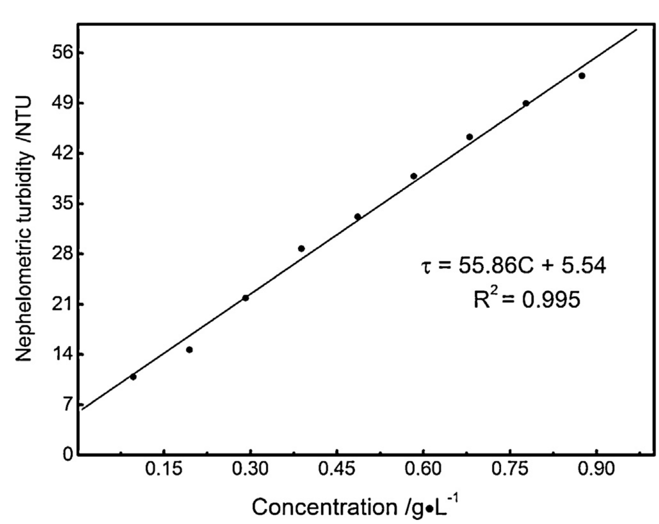


Fig. 2. The linear relationship between the nephelometric turbidity and the concentration of cationic copolymer nanosphere suspensions.