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Determination of the swelling behavior of superabsorbent polymers by a tracer-assisted on-line spectroscopic measurement

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ABSTRACT

This work reports on a method for the accurate determination of kinetic swelling behavior and properties of superabsorbent polymers by a tracer-assisted on-line spectroscopic measurement. Based on monitoring the spectral absorption of a tracer compound (blue dextran 2000) at 610 nm in a superabsorbent polymer containing solution, the swelling (water absorption) of the polymer during the process can be followed, from which the parameters in a kinetic equation can be obtained. The results showed that the data obtained by the present method has a good measurement precision and accuracy, in which the relative differences were less than 4.0% when comparing the data measured by a reference method (i.e., the tea bag method). Since the present method can perform an on-line measurement, it is much superior to the current tea bag method and therefore is very suitable to be used in the process related study for the swelling behavior of superabsorbent polymers in many applications.

1. Introduction

Superabsorbent polymer (SAP), with tightly cross-linked networks of hydrophilic polymer chain, is a sort of material that can absorb water as high as thousand times of its own weight in aqueous media [1]. The kinetic swelling (i.e., water absorption) behavior of such a material is particularly important in many applications, e.g., sanitary napkins and disposable diapers for use in the personal care [2]. The factors, such as the structure of polymer network, crosslink density and hydrophilicity, resin particle size, salt concentration in solutions, and temperature, can significantly affect the swelling rate [3–8]. Therefore, an effective method that can determine the kinetic swelling behavior of SAPs is important in the product design, manufacture process control, and routine quality check for the commercial products.

Several traditional methods, such as filtration, tea bag weighting, capillary and microscopic analysis, have been used to determine water holding capacity of the absorbent materials [9–12]. However, these methods are not suitable to be used for studying their swelling kinetics, since the process for the water absorption could be very quick. Heretofore, the calorimetrical analysis [11] and conductance method [13] are the typical methods to be used for tracing the swelling kinetics for the relative materials. The major problem in the calorimetrical analysis is that the energy change in the system is almost zero after a short-time exothermic process, thus it is insensitive to be used for tracing the whole swelling process [11]. Conductance method is based on measuring the conductivity change of sodium chloride in the tested solution during the process, because superabsorbent material would not absorb sodium chloride until its swelling ratio reaches a certain value [13]. The major problem of the conductance method is that the sodium chloride species can also be absorbed by the superabsorbent material although it is slower than that of water. Therefore, the derivation of the equation for calculating the water absorption in the material is very complicated, in which some assumptions and calibrations are required [13]. Moreover, the application of such conductance method is only limited to the electrolyte contained in the aqueous solution.

SAPs are the porous materials with the particle size distributions of 100–1000 μm, in which the pore sizes on the surface of the particles are much smaller [14,15]. The diffusion of molecules throughout the porous matrix of SAPs is mainly by capillary forces in their macro-porous structure [1]. Therefore, the higher the molecular weight, the slower the penetration rate into the pores, along with water molecules. If such as a high molecular weight

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compound [16] is used as a tracer, the concentration of the compound in the solution is expected to increase (due to the water loss) during the water absorption experiment. Thus, the kinetic swelling behavior of SAPs can be followed by monitoring the concentration change of the compound in the tested solution.

In this work, we proposed a simple method for determining the swelling behavior of superabsorbent polymers based on a tracer-assisted kinetic spectroscopic measurement. Blue dextran 2000 (BD), a water soluble solid powder compound with an average molecular weight of 2,000,000 g mol^{-1} (2000 kDa) was used as the tracer in this study. The main focus of this novel research were based on: i) the selection of the detecting wavelength for the tracer, ii) the establishment of the methodology, iii) the determination of adsorption proportionality coefficient, iv) the conditions for the sample swelling. According to the regression analysis and theoretical derivation, the relationship between tracer concentration change and the swelling ratio was obtained.

2. Experimental

2.1. Chemicals and materials

Reagent-grade blue dextran 2000 (the relative molecular weight = 2,000,000 g mol^{-1}) and NaCl (purity > 99.9%) were purchased from Sigma Aldrich. The SAPs were acrylic polymers (with particle size ranging from 75 to 150 μm) purchased from commercial source.

2.2. Apparatus

A UV/Vis spectrophotometer (Agilent 8453 UV–Visible System, USA) equipped with a flow-cell was used for the on-line spectroscopic monitoring. A peristaltic pump (Model LR 44845 M312, made in France), a vessel (250 mL of beaker) with magnetic stirring, tubing, and a custom-made metal net-filter (400 mesh) were used in the configuration of the real-time process monitoring system for the superabsorbent polymer water absorption study.

2.3. Measurement procedures

One hundred (100) mL of water solution containing 400 mg/L blue dextran 2000 (BD) was placed in a vessel and the solution was circulated peristaltic pump at a flow rate of 0.30 mL/min through the flow-cell of a UV/vis spectrophotometer. The schematic diagram of this system is shown in Fig. 1.

A 0.1000 g of SAPs was added into the vessel containing a given volume of the solution and the spectrophotometer recorded the spectra during the water absorption process. Distilled water was used as the blank for the UV/vis measurement.

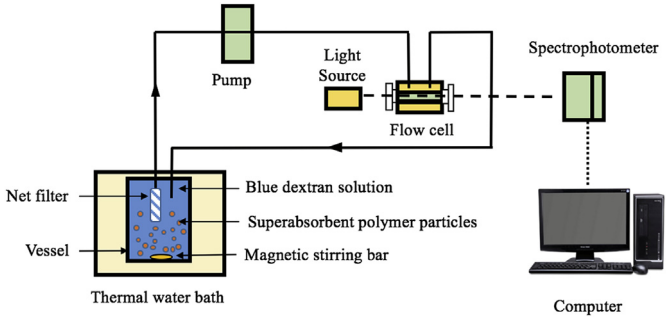

Fig. 1. Schematic diagram of the UV/vis system used in the present study. Shown in the sampling mode.

2.4. A reference method –tea-bag method

A tea-bag with a volume of 100 mL and pore size of 400 meshes was used. After adding 0.1000 g of SAPs in the bag, it was dipped into a test solution for 1 h (to reach the saturation). Then, the bag was hanged until no liquid was dropped off. By weighing the bag before swelling and after swelling/hanging, the amounts of water absorbed by the SAPs in the tested solution can be calculated.

3. Results and discussion

3.1. UV/vis spectrum of blue dextran 2000 aqueous solution

Fig. 2 shows UV/vis spectra of BD standard solutions with different concentrations. It was shown that BD covers the whole UV/vis spectra measured by our equipment. An important band at ca. 500–700 nm is observed with the maximum absorption at 610 nm. Therefore, the band of 610 nm was used as a reference for the further swelling measurement. As mentioned above, the blue dextran 2000 is much slower rate than that of water to be absorbed by the superabsorbent polymer material. Therefore, the concentration of BD in the aqueous solution will increase due to the water loss during the water absorption experiment. As a result, the absorbance of BD (e.g., at 610 nm) increases in the spectral measurement.

3.2. The profile of blue dextran absorption during water absorption process

Fig. 3 shows the spectral absorption of BD at 610 nm in two solutions (different concentrations) during the polymers swelling process. Because the water loss by polymers absorption is much faster than that of BD, the concentration of BD in the solution increases and thus leads to the increase of spectral absorbance at 610 nm. From Fig. 3, it is noticed that although the concentration of BD in these solutions are different, their time-dependent profiles for the spectral absorbance are basically the same.

In order to check if there was also an adsorption of BD on the SAPs, we conducted a test by adding the BD to the solution at the SAP reached its saturated state. As shown in Fig. 4, the spectral absorbance for BD keeps constant during the whole process, indicating that the BD adsorption is neglected on the SAPs if they are already saturated by water. Therefore, any loss of BD in the solution

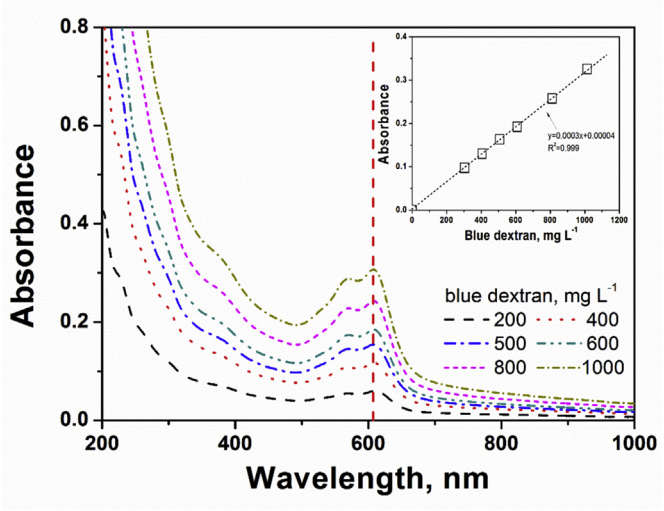

Fig. 2. UV/vis spectra of blue dextran 2000.