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Preparation and characterization of CS-*g*-PNIPAAm microgels and application in a water vapour-permeable fabric

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ABSTRACT

Chitosan-graft-poly(*N*-isopropylacrylamide) (CS-*g*-PNIPAAm) was synthesised using sonication with and without the crosslinker, *N*,*N*′-methylenebisacrylamide (MBA). FTIR, variable-temperature ^{1}H NMR spectroscopy, atomic force microscopy, UV–vis spectrophotometry, differential scanning calorimetry, and dynamic light scattering were used to characterize the microgels' chemical constituents, structures, morphologies, lower critical solution temperatures (LCSTs), and thermo- and pH-responsiveness. The chemical structures of the two CS-*g*-PNIPAAm materials were found to be similar and both exhibited dual responsiveness towards temperature and pH. The microgel containing MBA had a higher LCST, smaller diameter, and more compact structure, but exhibited opposite pH- and similar thermo-responsiveness. Although the structure of the microgel particles prepared without crosslinking was unstable, the stability of the crosslinked microgel particles enabled them to be finished onto fabric. Because the microgel prepared with MBA retains thermosensitivity, it can be used to impart controllable water vapour permeability properties. The incorporation of the MBA-crosslinked CS-*g*-PNIPAAm microgel particles in cotton fabric was accomplished by a simple pad-dry-cure procedure from an aqueous microparticle dispersion. The water vapour permeation of the finished fabric was measured at 25 and 40 °C and 50 and 90% relative humidities. The finished fabric displayed an obviously high water vapour permeability at 40 °C.

1. Introduction

Because clothing is worn very close to the body, it may be considered as an extension of our physiological characteristics, and garments that enhance the qualities of human skin (protection, breathability, sensing) would be salutary. Constructed from "smart" fabrics, the clothing should sense and respond to changes in local environmental conditions, whether human or ambient. However, this surface finishing should not screen or impair the textile's regular performance.

The application of microgels based on thermosensitive polymers is an effective way to achieve "smart" water vapour permeability for fabrics. Thermosensitive microgels are monodisperse colloidal dispersions based on cross-linked polymers, which exhibit either a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) in water (Sierra-Martin, Retama, Laurenti, Fernández Barbero, & López Cabarcos, 2014). Microgels based on poly(*N*-isopropylacrylamide) (PNIPAAm) have sharp LCSTs at 32 °C and undergo volume phase transitions in which they shrink or swell in response to changes in temperature. A microgel with this performance feature can be incorporated by appropriate methods into "smart" fabrics with controllable water vapour permeation properties. The mechanism underlying this "smart" water vapour permeability control is based on changes of the microgel particle size in response to temperature, such that a microgel-modified fabric would be highly permeable at higher temperature and less so at lower temperature (Lavrič, Warmoeskerken, & Jocic, 2012). The most commonly used microgel to control the water vapour permeability in textiles is poly-NIPAAm/chitosan (CS).

The stimuli-responsive poly-NIPAAm/CS microgel can be obtained by the aqueous copolymerization of *N*-isopropylacrylamide (NiPAAm) with CS. Poly-NiPAAm is a well-known

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Abbreviations: APS, ammonium persulfate; BTCA, 1,2,3,4-butanetetracarboxylic acid; CS, chitosan; DLS, dynamic light scattering; kcps, scattered light intensities; KPS, potassium persulfate; LCST, lower critical solution temperature; MBA, *N*,*N*′-methylenebisacrylamide; MWCO, molecular weight cut-off; NiPAAm, *N*-isopropylacrylamide; PNIPAAm, poly(*N*-isopropylacrylamide); SHP, sodium hypophosphite; SLS, static light scattering; UCST, upper critical solution temperature.

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thermo-responsive polymer with an LCST value that falls between human body temperature and ambient temperature, and is particularly suitable for the development of smart materials for clothing applications. CS is a biopolymer that responds to changes in the pH of the surrounding medium. The result of the copolymerization of poly-NiPAAm with CS is a microgel that is responsive to both temperature and pH. When this stimuli-responsive poly-NIPAAm/CS microgel is incorporated into a fabric, controllable water vapour permeability results from shrinkage of the poly-NIPAAm microgel at temperatures above the LCST, which causes the surface pores to enlarge. Additionally, the incorporation of CS into the network supplies a large number of hydrophilic groups that also increase water vapour permeability. Finally, combining the natural product CS with a synthetic polymer such as poly-NiPAAm imparts certain advantages to the surface modification system, such as biocompatibility and an increased number of active sites for subsequent crosslinking with cotton (Lavrič et al., 2012).

Currently, there are several copolymerization methods for the synthesis of poly-NiPAAm/CS microgels. Lee, Wen, and Chiu (2003) prepared poly(CS-*N*-isopropylacrylamide) complex particles by the soapless dispersion polymerization method. Glampedaki et al. (2012) prepared polyelectrolyte microgels through the combination of the components. Other groups have prepared stimuli-responsive poly-NiPAAm/CS microgels by the self-assembly method (Chen et al., 2013; Chuang, Don, & Chiu, 2010; Chuang, Don, & Chiu, 2011; Huang, Wang, Don, & Chiu, 2013). Wang et al. (2013) prepared a series of CS-g-PNIPAAm copolymers based on different molecular weights of CS by the self-assembly method.

In the above studies, the crosslinker *N*,*N*′-methylenebisacrylamide (MBA) was often incorporated in the reaction system when preparing the copolymer microgel, but MBA was not used during self-assembly processes. In this paper, we prepared dual-responsive poly-NiPAAm/CS microgels with and without MBA, and evaluated their structures, morphologies, and responses to stimuli. We employed sonication instead of the conventional stirring technique during microgel preparation in order to reduce the reaction time and simplify the procedure. The microgel obtained by sonication with MBA had a smaller particle size, greater structural stability, and exhibited the same response properties as the microgel without MBA. The advantages imparted by this change were the reduction in preparation time, the easier fabric finishing due to the smaller particle size, and the increased stability of the fabric properties. The responsiveness of the microgel could impart “smart” properties to the fabric.

Finally, the microgels were incorporated into cotton by a pad-dry-cure process (Bashari, Hemmatinejad, & Pourjavadi, 2013; Lavrič et al., 2012) using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinker, and the water vapour permeation properties were studied under different temperature and humidity conditions.

2. Experimental

2.1. Materials

The *N*-isopropylacrylamide (NIPAAm) monomer was generously provided by Kohjin, Tokyo, Japan. It was recrystallized from hexane prior to grafting. Chitosan (CS, degree of deacetylation, 95%; average molecular weight, 300,000 g/mol), the MBA and BTCA crosslinkers, the initiator (potassium persulfate, KPS), and sodium hypophosphite (SHP, catalyst) were purchased from Sigma Co. De-ionized water was used in all experiments. The warp and weft densities of the cotton fabric were 390 × 246 roots/10 cm, respectively. All other chemicals were analytical grade or above and used as received.

2.2. Sonication preparation of CS-g-PNIPAAm

The poly-NiPAAm/CS microgels were prepared by the surfactant-free dispersion copolymerization method according to the procedure reported by Kratz, Hellweg, and Eimer (2000). In this procedure, a normal ultrasound bath was employed instead of the conventional stirring technique. A CS solution was prepared by dissolving CS (0.25 g) in 25 mL water containing 0.2 mL glacial acetic acid and stirring for 24 h at room temperature. The NiPAAm/CS copolymerization was carried out in a two-necked round-bottomed flask equipped with a condenser and nitrogen inlet to maintain the reaction under nitrogen atmosphere. The CS solution was poured into the flask, placed in the ultrasound bath, and degassed with nitrogen for 30 min at room temperature while sonicating. Subsequently, the NiPAAm monomer (1 g) (with or without the crosslinking agent MBA (0.01 g)) was dissolved in 30 mL water and the solution was added into the reactor. The temperature was raised to 70 °C. KPS (0.02 g, 2% monomer) was dissolved in water (5 mL), preheated to 70 °C, and poured into the solution to initiate the polymerization. The reaction medium became turbid after 5 min and the reaction was allowed to proceed for 100 min at 50 °C. A stable milky-white suspension was obtained. The PNIPAAm microgel was synthesised by a surfactant-free emulsion polymerization method similar to the above procedure but in the absence of CS solution; thus, the NiPAAm (1 g) monomer and MBA (0.01 g) were dissolved in 55 mL water. To remove the unreacted *N*-isopropylacrylamide monomer and oligomeric impurities, the reaction solution was dialyzed over one week against water. A membrane with a molecular weight cut-off (MWCO) of 12,000–14,000 Da was chosen in order to keep the CS, poly-NiPAAm, and the microparticles (CS-g-PNIPAAm-1 (without MBA) and CS-g-PNIPAAm-2 (with MBA)) in the suspension.

2.3. Characterization of the copolymer microgel

Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Fisher) using an attenuated total reflectance (ATR) accessory and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR, Avance 400, Bruker) were used to characterize the chemical structures of the copolymer microgels. The samples were first dried by lyophilisation and then scanned by ATR-FTIR. Meantime, the NMR samples were prepared by the redispersion of freeze-dried particles (20 mg) in D_2O (1 mL) before recording the NMR spectra at 25 and 40 °C.

The microgel morphologies were examined by atomic force microscopy (AFM, NanoScopeIV, Veeco). A drop of the microparticles solution was placed on a silicon substrate and air-dried at 20 °C. The silicon substrate was washed with absolute ethanol and dried before the drop was placed.

The LCSTs of the microgels were determined by differential scanning calorimetry (DSC, 204F1, Netzsch) and UV–vis spectrophotometry (Lambda 35, Perkin Elmer). Weighed microgel aliquots were placed in an aluminium pan. The pan was sealed and placed in the sample holder next to an empty aluminium pan used as a reference. The temperature was raised from 25 to 60 °C at a rate of 5 °C/min. During the DSC measurements, heating and cooling were performed under a N_2 gas flow of 30 mL/min. The solution of microgel was diluted with water to an appropriate concentration before it was poured into a quartz cuvette for the measurement of LCST by a UV-visible spectrophotometer. The transmittance at 500 nm was continuously recorded from 20 to 45 °C at a rate of 0.5 °C/min. The LCST was determined as the first derivative peak temperature of the transmittance curve.

The particle sizes in the dispersions and the effects of temperature (20 and 40 °C) and pH (pH 4 and 6) on the hydrodynamic diameters of the microparticles were determined using a static light