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ARTICLE TYPE

Smart Moisture Management and Thermoregulation Properties of Stimuli-Responsive Cotton Modified With Polymer Brushes

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Thermoresponsive PNIPAM polymer brushes are grafted onto the surface of cotton fabrics to construct a smart hierarchical system. The smart system exhibits thermoregulation by responsively absorbing perspiration at different atmospheric temperatures.

Introduction

Clothing primarily aim to protect the human body and provide comfort.[1] The ideal clothing should provide thermal insulation in cold climates, whereas protection from sunburn damage and wicking perspiration are commonly important in hot climates. An individual should change clothing under different thermal and moisture conditions; clothing is indispensable to body temperature regulation and thereby to personal survival. Developing novel fabric materials with moisture management and smart thermoregulation properties is important not only in daily clothing and sportswear,[2] but also in clinical applications, wound healing, tissue engineering, dermatology, and so on.

Comfortable clothing should transmit moisture and heat in the form of sensible and insensible perspiration from the body to the environment to regulate thermal insulation caused by moisture build-up. [3]Fabrics primarily aim to maintain body warmth and prevent perspiration evaporation when the temperature of the environment is lower than that of the body. Thus, cotton fabrics are primarily and popularly used as underwear materials with high moisture regain to maintain body warmth. Sensible perspiration drips off the skin rather than evaporate to exert a cooling effect when the temperature of the environment is higher than that of the body; fabric surface properties affect sticky perception during insensible perspiration. Fabrics in contact with the skin should be dry to the touch. As a result, perspiration can be rapidly expelled from the fabric during the contact and more sweat must be evaporated from the body surface to prevent increased core temperature and injuries to the body. Hence, synthetic fibers exhibit an advantageous dry fit function particularly in sportswear.[4]

Such responsive fabric materials have not been reported; these materials present smart interfacial properties with perspiration and thermoregulation during environmental temperature changes to adjust comfort of textiles. Thermoresponsive polymers are smart materials that undergo physical changes in response to external temperature stimulus. A dynamical balance of hydrophilic and hydrophobic phase behavior exists in the polymer chain; this property is typical for polymers that form hydrogen bonds with water. Thermoresponsive polymers originate under a low critical solution temperature (LCST),at which the polymer lines are converted between hydrophobic to hydrophilic; LCST can be modified by adding hydrophobic branches.[5,6]

In this study, we present a facile and efficient strategy for grafting a thermoresponsive polymer on cotton surface to form smart surfaces/interfaces.[7] Poly(N-isopropylacrylamide) (PNIPAM) was selected because its LCST (32°C) is similar to the skin temperature of humans; PNIPAM has also been extensively studied in controlled drug delivery systems, bio-conjugation, tissue engineering, biosensors, water collection and nano-lithography.[5, 7-13] In the present report, we successfully grafted thermoresponsive polymer brushes on cotton surfaces by using surface-initiated atomic transfer radical polymerization (ATRP). Thermal responsiveness of the modified fabrics was investigated by determining moisture regains, hygroscopicity, surface contact angle, and responsive thermoregulation at lower/higher temperature than LCST.

PNIPAM brushes were prepared by immersing the cotton substrates grafted with an initiator into the ATRP solution. The procedure of grafting and the chemical structures of the initiator and PNIPAM are illustrated in Figure 1a. Compared with other reports[12] we use only one step to the initiator onto the surface of cotton fabrics. The initiator we used in this work is trichlorosilane who can directly react with hydroxyl of cotton to form silicon-oxygen covalent bond. The initiator grafted samples was washed by acetone, ethanol and toluene for three times to remove any physisorbed initiator on the surface. Water contact angle measurements show that on the fabric before and after initiator grafting, the contact angle increase from 0° to 18°, which is main evidence for the successful grafting.

Scanning electron microscopy (SEM) images show typical trench morphology on the surfaces of raw cotton fibers (Figure 1 c) and cotton fibers modified by the initiators (Figure 1d), where as a smoother morphology is observed on PNIPAM-grafted fibers (Figure 1e). The attenuated total reflectance infrared (FTIR) analysis provides a compelling evidence regarding the growth of the polymer brushes (Figure 1b); the result shows the following characteristic peaks of PNIPAM as also reported in the literature[14]: amide I band (1,640 cm^{-1}) attributed to the primary amide –C=O stretching, amide band II (1,540 cm^{-1}) attributed to the secondary amide –N–H stretching.

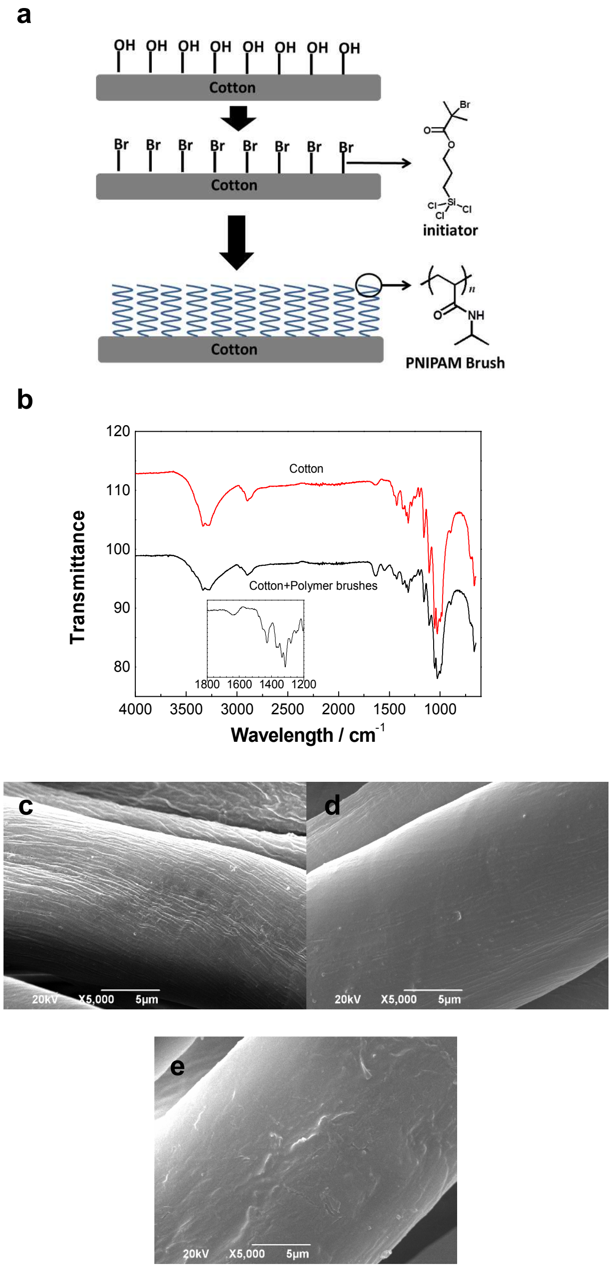
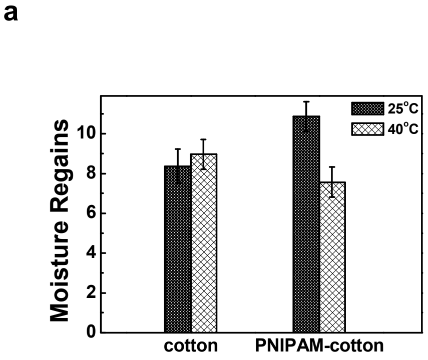


Figure1. (a)Schematic of the grafting of PNIPAM brushes on cotton.(b) FTIR analysis of cotton grafted with PNIPAM brushes and control. SEM analysis of the original cotton fiber surfaces (c),cotton fiber modified by initiators (d),and cotton fiber covered with polymer brushes (e).

Clothing should transmit perspiration from the skin to the outer surface to achieve a comfortable state. Human body perspires in two forms: insensible (in vapor form) and sensible perspiration (in liquid form). In insensible perspiration, water vapor is transmitted from the skin to the outer surface through the fabric by diffusion and absorption–desorption method. This process maintains a constant vapor concentration in the surrounding air by absorbing the perspiration from the skin; hence, water vapor is transmitted from the skin to the outer surface. Capillary action starts when the moisture content in the fibers becomes saturated. Sensible perspiration is formed at saturation or high moisture level; capillary wicking and diffusion are the major mechanisms of moisture transport in the liquid form. Thus, clothing should possess liquid transmission property to feel comfortable under high activity condition with high liquid perspiration production. Moisture regain and hygroscopicity of the fabrics were determined to investigate the transmission properties of the two forms of perspiration (water vapor and liquid water).

The dampness of the fabrics in the skin under insensible perspiration is predicted using moisture regain, in which permeability determines the breathability of clothing materials. Moisture regain is the percentage of moisture that clothing materials absorbed from the ambient environment. Fabric materials, such as cotton, wool, and silk, with high moisture regain are comfortable, warm, and resistant to static build-up.[15]

The moisture regains of PNIPAM grafted on cotton and control at 25 °C and 40 °C is shown in Figure 2. At 25 °C (lower than LCST), the moisture regain substantially increases by approximately 30% after grafting with PNIPAM brushes. As the temperature increases to 40 °C (higher than LCST), the moisture regain of modified cotton rapidly decreases compared with that at 25°C; the decreased temperature is lower than that of the unmodified cotton. Hence, the moisture regains of the control cotton fabrics increases because the increasing temperature accelerates the diffusion of water molecules within the cotton fibers.



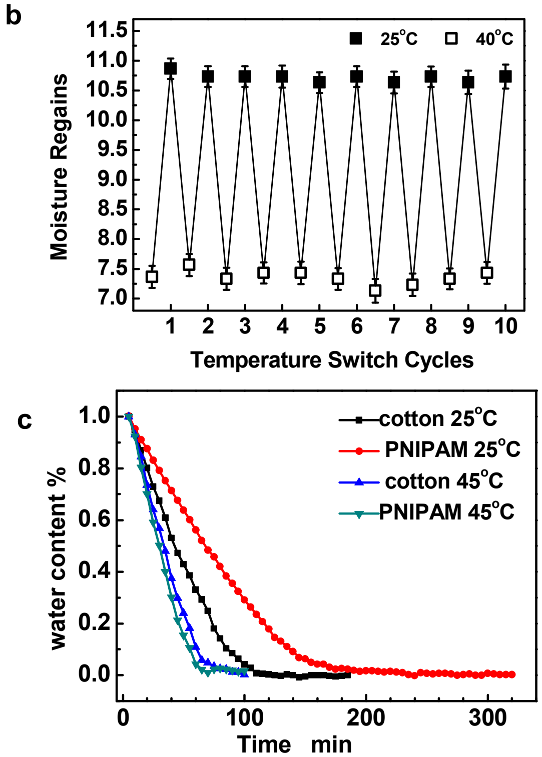


Figure 2. (a) Moisture regains of cotton fabrics grafted with PNIPAM polymer brushes and control at 25 and 40 °C;(b)Moisture regain of the modified cotton fabrics during 10 temperature switch cycles; and (c) Hygroscopicity of cotton fabrics grafted with PNIPAM polymer brushes and control at 40 and 25 °C.

The moisture regain of PNIPAM-modified cotton is higher than that of the unmodified fabric at an atmospheric temperature of 25 °C. The results of moisture regain are significantly reversed when the atmosphere temperature is increased to 40°C; the moisture regain of the modified cotton is lower than that of the raw cotton. Figure 2 shows that the moisture regain of the unmodified cotton minimally increases with the increasing temperature; hence, high temperature causes higher rates of diffusion of water molecules in the less crystalline areas of cellulose. This phenomenonis attributed to the hydrophilic property of the PNIPAM line at LCST; the exposed acidamide groups can also interact with water molecules by forming hydrogen bonds. More repeat functional hydrophilic units exist on the fabric with polymer brushes compared with the unmodified cotton. Water vapors permeate into the internal structure of the cotton fibers by promoting the hydrophilic PNIPAM brushes as the interfacial bridge. At ambient temperatures higher than the LCST of PNIPAM brushes, the acidamide groups are interiorly reversed to the inner part of the polymer brushes and the interfacial property becomes hydrophobic. The hydroxyl groups on the surface of the cotton fibers are also replaced; hence, water molecules cannot be incorporated with the chemical groups on the cotton surface, restricting permeation into the fiber. The translation from hydrophobic to hydrophilic plays a role as functional “sudoriferous pore”, which can control water absorption from the atmosphere to the cotton fibers as the temperature changes. Supporting experiments were further conducted to confirm this deduction. PNIPAM brushes were grafted on the polypropylene (PP) fabric surface, whose moisture regain is 160 times lower than that of the cotton. The grafted PNIPAM brushes exhibit limited effect on the water absorption of PP fabrics, and water could hardly permeate into the PP fabrics. Consequently, PNIPAM brushes play a role as sudoriferous pore to control the absorption of water. At temperature higher than LCST, the moisture fills up the inter-fiber and inter-yarn cellulose of the cotton. Conversely, the water molecules are hardly absorbed by the cotton fabrics when the temperature is lower than LCST. The observed phenomena are attributed to the responsiveness of the grafted polymer brushes, which function as a sensor of temperature and as a valve to regulate water vapor permeability into the modified cotton.

In hot climates or when exercise levels are high, sensible perspiration (in liquid form) is the main mechanism of metabolic heat loss to maintain body safety. Liquid sweat can transfer from next-to-skin to the outer surface to maintain dry skin, which is the main factor in comfort. The hygroscopicities of PNIPAM-modified and unmodified cotton fabrics were investigated at 25 and 40 °C. The experiment was performed in a normative laboratory by using equipment with controllable temperature and humidity.

Hygroscopicity significantly differs between the samples unmodified and modified with PNIPAM brushes. The hygroscopic performance of cotton modified with PNIPAM brushes is higher than that of the pure cotton fabrics at 25 °C, which is lower than LCST. However, at an ambient temperature of 40 °C, the hygroscopic performance of PNIPAM brushes grafted on cotton fabrics is lower than that of the cotton fabrics and an evident conversion is also observed. These results indicate minimal changes in PNIPAM/water interactions, particularly the release of water molecules from a polymer hydration layer into bulk water.

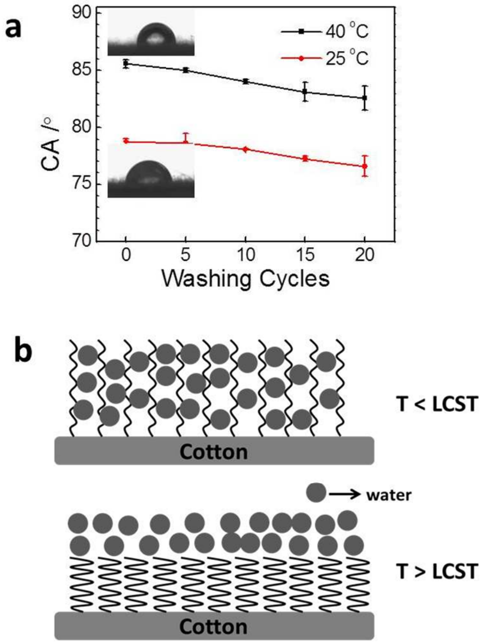
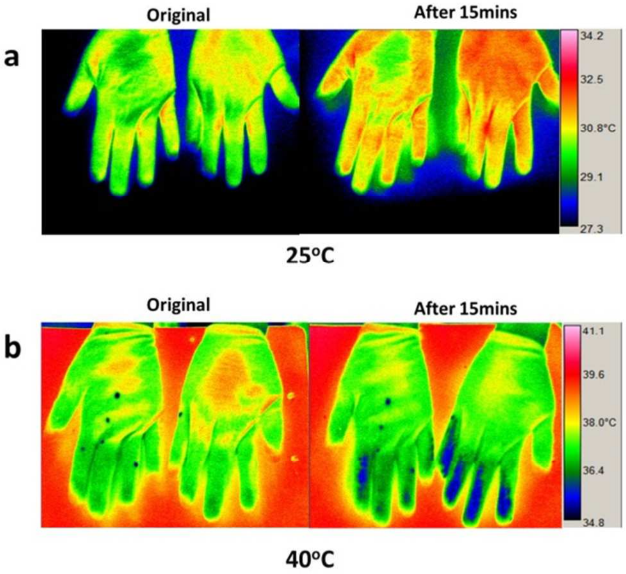


Figure 3. Surface contact angle of cotton fabrics grafted withPNIPAM polymer brushes and control during washing cycles

at 40and 25 °C, respectively(a) and the mechanism of the responsive interfacial phenomenon with water(b).

The contact angle of a textile indicated its wettability air, which is critical to provide comfortable undergarment. The water contact angles of the modified cotton fibers are measured at 25and 40 °C. Figure 3a demonstrates a significant difference (7°–8°) among the two different temperatures. The changes on the contact angle depending on different temperatures are attributed to the surface of PNIPAM polymer brushes. This surface exhibits a reversible switching between hydrophobic and hydrophilic as a consequence of the complex polarity of the molecules. A balance exists between the hydration at the amide groups and the hydrophobic aggregation of the isopropyl groups. At temperatures lower than LCST, the amide group on the polymer brushes binds to the water molecules via hydrogen bonding to form an interfacial expanded structure (Figure 3b). By contrast, the formed hydrogen bonds break, the polymer brushes expel water, and the polymer chains dehydrate to form a shrunken structure at temperatures higher than LCST.

The water contact angles of the modified cotton fibers versus the washing cycles are also presented and investigated in the figure. The contact angle is continuously maintained at a specific level throughout the wash cycles and shows minimal hydrophilic recovery ($\Delta CA<3^{o}$). This finding indicates that the polymer brushes with high adhesion force with the cotton substrates. Moreover, cotton fabrics grafted with the PNIPAM brush layer via ATRP is durable for normal dress.



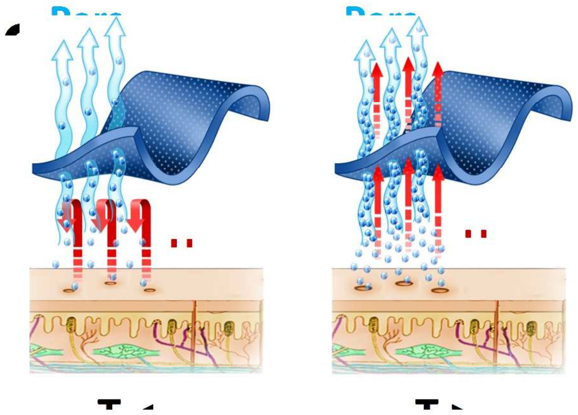


Figure 4.IR camera images of PNIPAM-grafted glove (left hand) and unmodified glove (right hand) in their original stage and after wearing for 15min. Ambient temperatures in the chamber are controlled at 25°C (a) and 40°C (b). (c) Schematic of thermoregulation and moisture management processes.

An IR camera was used to investigate the body surface temperature and reveal the variation in the temperature, thus determining the thermoregulation capabilities of PNIPAM-modified fabrics worn on a human body. A wearable glove grafted with PNIPAM brushes was worn on a volunteer's hand, and an unmodified glove was worn on the other hand. Experiments were carried out in a climate chamber at accurately controlled temperatures of 25 and 40 °C.

At the chamber temperature of 25°C, the surface temperature of PNIPAM-modified gloves increases by approximately 2°C compared with that of the unmodified glove after wearing for 15 min (Figure 4a). The glove modified with PNIPAM exhibits lower temperature because perspiration is derived from the skin when the temperature increased to 40 °C (Figure 4b). This result regarding the cooling property of PNIPAM brushes is similar to the results obtained by Stark*et.*[16]on cool buildings; in this study, temperature reduction is beneficial.

As shown in the IR pictures, the modified glove shows a heat retaining property at low temperature and a cooling property at high temperature. At an ambient temperature of 25°C, high moisture regain results in high thermal preservation. However, at 40 °C, sensible perspiration drips off the skin to exert a cooling effect on the body. The modified fabrics with superior hygroscopicity and dry fit function can cool the body temperature to prevent increased core temperature and injuries to the body.

Conclusions

Smart fabric materials with moisture management and thermoregulation properties can be fabricated by grafting thermoresponsive polymers on cotton surfaces via surface-initiated polymerization. A PNIPAM brush is selected because of its LCST, which is similar to the body temperature. The grafted polymer brushes can responsively and reversibly control the wettability and hygroscopicity of the cotton, whereas the smart surface can switch from high water absorptive state at temperature lower than LCST to low absorptive state at temperature higher than LCST. A system that comprises cotton modified with responsive polymer brushes and exhibits smart moisture management, smart thermoregulation, and latent heat dissemination is presented in this study. This system has potential applications in smart underwear, medical fabrics with controllable drug release, sportswear, and medical fabrics in dermatology and wound healing.

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Notes and references

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