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The Application of Temperature-Sensitive Hydrogels to Textiles: A Review of Chinese and Japanese Investigations

Abstract
Scientists have made many attempts to develop smart textiles by grafting the copolymerisation of environment-responsive polymers (ERP) onto the surface of fabrics. Among the ERPs used for this purpose, poly(N-isopropyl acrylamide) (PNIPAAm) has attracted considerable attention due to its well-defined lower critical solution temperature (LCST) in an aqueous medium of temperature about 32-34°C, which is close to body temperature. This article summarises recent advances in the application of PNIPAAm and its copolymer hydrogels to temperature-sensitive hygroscopic fabrics, environment-sensitive deodorant fibres and stimuli-sensitive nutrient delivery fabrics. Another temperature sensitive poly(2-ethoxyethyl vinyl ether)/poly(hydroxyethyl vinyl ether) copolymer (EOVE200-HOVE40) is also briefly introduced, with regard to its application in thermally-controlled Vitamin E release.

Key words: *poly(N-isopropyl acrylamide), temperature sensitive, hydrogel, deodorant, controlled release, fabrics.*

Introduction

Poly(N-isopropyl acrylamide) (PNIPAAm) is an intensively investigated temperature-sensitive polymer which has a simultaneously hydrophilic and hydrophobic structure (see Figure 1), and demonstrates a low critical solution temperature (LCST) at about 32 °C [1, 2]. In an aqueous solution, the macromolecular chains of PNIPAAm experience reversible solubility and exhibit a significant hydration-dehydration change in response to temperature stimulus [3, 4]. Due to its sharp temperature-induced transition and well-defined LCST, which is close to body temperature, the PNIPAAm (and in particular the PNIPAAm hydrogel) has been widely applied to temperature-sensitive drug delivery systems [5-9], separation membranes [10, 11], and tissue engineering scaffolds [12, 13]. Recently, scientists have made many attempts to develop stimuli-sensitive textiles, or so-called smart textiles, by grafting the copolymerisation of environment-responsive polymers (ERP) onto the surface of fabrics [14, 15]. Among the ERPs used for this purpose, PNIPAAm has attracted considerable attention, and research into it may lead to novel temperature-sensitive smart fabrics.

In view of the great potential applications of smart fabrics in many areas, we will review the recent achievements in smart fabrics, mainly covering Chinese and Japanese work on the application of PNIPAAm and its copolymer hydrogels in the textile field. The temperature-sensitive delivery behaviour of vitamin E from the poly(2-ethoxyethyl vinyl ether)/poly(hydroxyethyl vinyl ether) copolymer (EOVE200-HOVE40) is briefly introduced, and its potential application in cosmetic and pharmaceutical fields is also considered.

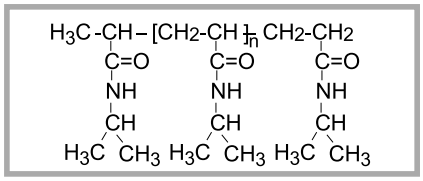

Figure 1. *The structure of poly(N-isopropyl acrylamide).*

Applications of environment-sensitive hydrogels to textiles

Temperature-sensitive hygroscopic textiles

Environment-sensitive polymer hydrogels can be grafted or adsorbed onto the surface of polymer fibres. When the hydrogel is exposed to external stimuli, it will display swelling/shrinkage or hydration/dehydration properties, and cause changes in the water vapour transmission rates (WVTR), permeance and permeability of the fabrics.

Chen et al. [16] have grafted a PNIPAAm hydrogel onto nonwoven fabrics by photo-induced graft polymerisation and studied the fabrics' temperature-responsive characteristics. In their work, a temperature-sensitive PNIPAAm hydrogel was grafted onto a plasma-activated polyethylene terephthalate (PET) film and a polypropylene (PP) nonwoven fabric surface. Factors affecting the formation of a PNIPAAm hydrogel by photo-induced graft polymerisation were investigated in terms of the type of additives. The additives used were ammonium persulphate (APS as initiator), N,N,N′,N′-tetra-methylethylene-diamine (TEMED as promoter), and N,N′-methylene-bisacrylamide (MBAAm as cross-

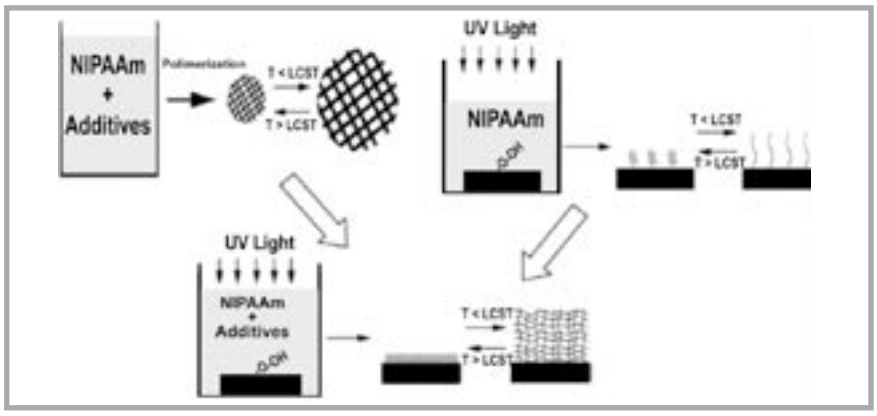

Figure 2. *Schematic description of photo-induced grafting polymerisation of NIPAAm gel onto PET film and the PP nonwoven fabrics surface [16].*

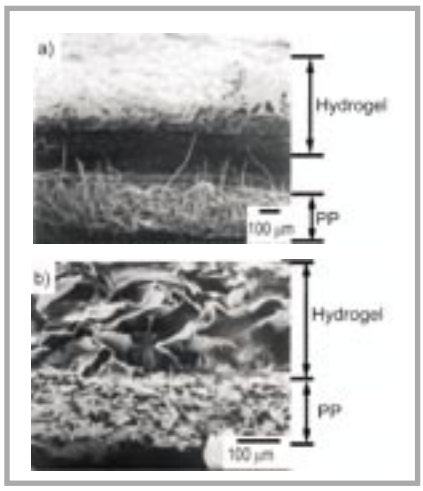

Figure 3. *SEM Images of PNIPAAm-g-PP nonwoven fabrics (after freeze drying); (a) without pretreatment (b) with Argon plasma pretreatment [16].*

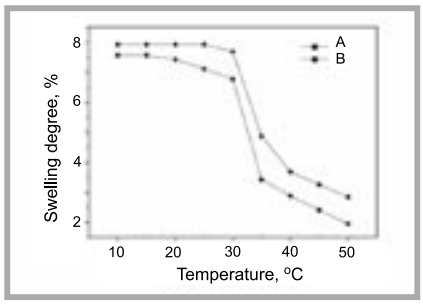

Figure 4. *Temperature effect on the swelling degree of PNIPAAm; (A) without grafting, (B) grafted on the PP Fabrics surface [16].*

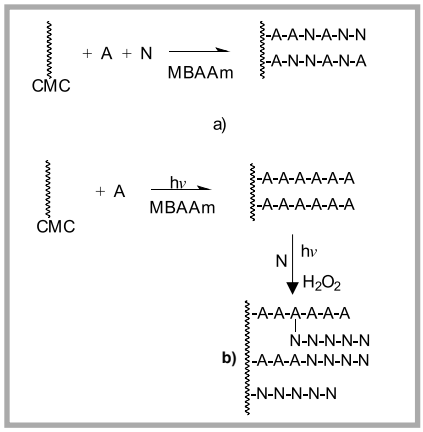

Figure 5. *Photografting mechanism of AA and PNIPAAm binary monomer; a) one-step and b) two-step (A: Acrylic acid, N: NIPAAm) [17].*

linking agent). The results indicated that the additives of APS, TEMED, and MBAAm were beneficial in promoting the grafting yield. These grafted hydrogels exhibited a lower critical solution temperature (LCST) of about 32 °C, indicating that the temperature-sensitive behaviour of the bulk PNIPAAm hydrogel was maintained. Plasma pre-treatment has also been studied. A pre-treatment with the use of argon plasma was carried out, and a subsequent photo-induced surface graft polymerisation was employed to graft NIPAAm. A schematic diagram of the photo-induced grafting polymerisation is presented in Figure 2.

Their experimental results indicated that such a pre-treatment can improve the binding ability between the hydrogel and matrix (see Figure 3), increase graft density, and endow the grafting PP with good permeability. After freeze-drying, a hydrogel with pore structure can be obtained.

It can be seen from the swelling-deswelling curves that the PNIPAAm displayed similar temperature sensitiveness with/without grafting on the PP nonwoven fabrics surface (see Figure 4). Thus, grafting almost does not alter the LCST of PNIPAAm. The PNIPAAm-g-PP nonwoven fabrics may be used in smart fabrics with a function of temperature-sensitive water vapour permeability.

Kubota et al. [17] synthesised cellulosic adsorbents (CR-CMC) by photografting acrylic acid(AA) onto fibrous carboxymethyl cellulose in the presence of N,N-methylenebisacrylamide (MBAAm) as a crosslinked agent. The CMC sample was firstly pre-treated with hydrogen peroxide in the presence of sulphuric acid to prepare CMC peroxides, and next AA and NIPAAm monomers were photografted onto the CMC surface. The peracid on the pre-treated CMC was decomposed as a polymeric photoinitiator in the following grafting process. Two types of preparation methods, the one-step method and the two-step method, were used in this work (Figure 5). For the one-step method, NIPAAm and AA were photografted simultaneously onto the CMC in the presence of the MBAAm crosslinked agent. For the two-step method, AA was first coupled on the CMC in the presence of MBAAm, and then PNIPAAm was photografted.

The relationship between water absorbency and the temperature of these two samples is compared in Figure 6. It is obvious that the water absorbency of the latter method is much greater than that of the former. The latter samples also displayed a notable temperature-sensitive behaviour. The CR-CMC prepared by the two-step method may be used as smart fabrics with a function of temperature-sensitive water absorbence.

NIPAAm was also grafted onto the surface of cotton fibres by using the 60Co irradiation method [18]. The DSC results indicated that the PNIPAAm-g-cotton still maintains its temperature-sensitivity. The phase transition temperature of PNIPAAmp-g-cotton is around 35 °C, near to the body temperature (Figure 7). This research may be applied to developing environmentally responsive fabrics.

Apart from the grafting methods mentioned above, ammonium cerium (Ⅳ) nitrate (CAN) can also be used to initiate the grafting reaction onto the cellulose fabric surface [19]. The ordered crystalline and orientation structure of cotton cellulose was destroyed by pre-treatment by boiling in an NaOH solution and $ZnCl_2$ solution at room temperature respectively. The pre-treated cotton cellulose was introduced into 10 ml of 20mM CAN for 15 min, wiped with tissues for the removal of extra CAN, and then immersed in 5 ml of an NIPAAM/MBAAm solution for 30 min. The co-polymerisation was performed under N_2 protection for 48h,; the grafting yield can reach up to 400% by using this grafting technology. Figure 8 shows the SEM images of a cellulose-supported PNIPAAm hydrogel. The smooth thick

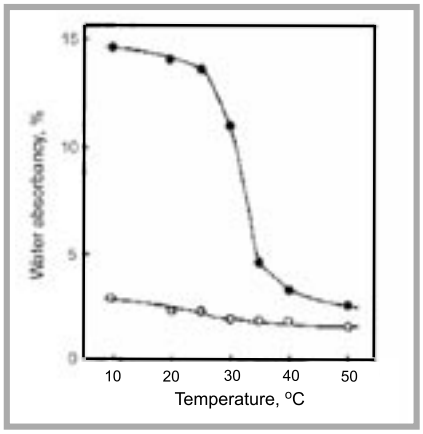

Figure 6. *Relationship between water absorbency and temperature in (○) one-step and (●) two-step prepared samples [17].*

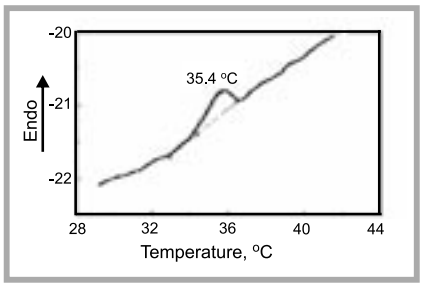

Figure 7. *DSC curves of PNIPAAm-g-cotton in wet condition [18].*

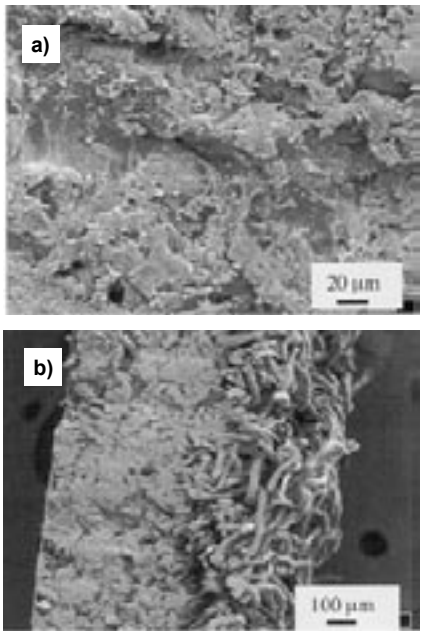

Figure 8. *SEM images of cellulose-supported PNIPAAm hydrogels [19]; a)Surface Layer b) Cross Section.*

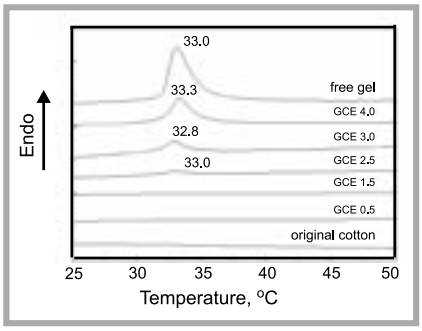

Figure 9. *DSC heating thermograms of the hydrated samples (GCE0.5, GCE1.5, GCE2.5, GCE3.0, and GCE4.0 indicated monomer concentrations 0.5%wt, 1.5%wt, 2.5%wt, 3.0 %wt and 4.0%wt).*

hydrogel layers were coated on the surface of the cellulose, making the fibres nearly invisible. The onset temperature of the phase-transition is between 28 °C and 40 °C, and the swelling degree of the hydrogel deceased with the increase in temperature. Shrinkage of the cellulose-supported hydrogel is observed near the phase transition temperature. The cellulose-supported thermo-sensitive hydro-gel is potentially useful in wound-dressing materials and nutrient-controlled release cosmetics.

In order to create a dual temperature/pH-sensitive hydrogel grafted fabrics, our groups synthesised a vinyl-capped polyurethane anionomer (VPUA), which was then grafted onto the nonwoven cotton cellulose together with NIPAAm by random copolymerisation initiated by ammonium persulphate (APS). The DSC result of the PNIPAAM-co-VPUA free hydrogel displayed a typical endothermic peak at about 33 °C, close to the low critical solution temperature (LCST) of pure PNIPAAm, suggesting that the incorporation of PU did not affect the thermal transition of PNIPAAm (Figure 9). The cotton cellulose grafted by PNIPAAm/VPUA hydrogel also showed a similar phase transition temperature. At the same time, the water absorbency of the grafted cellulose can be tuned by adjusting the environmental temperature (Figure 10). Apart from the temperature sensitivity, the grafted cotton cellulose has pH sensitivity as well. It can be seen from Table 1 that the water absorbency considerably decreases in acid and increases in alkali media respectively, compared to that in a neutral medium.

The temperature-controlled release behaviour of the PNIPAAm/VPUA hydrogel-grafted fabric was also studied in our research. Vitamin C was used as a model nutrient in this investigation. The preliminary results displayed that the release of vitamin C can be controlled by varying the surrounding temperature. The cumulative release amount of vitamin C was higher at 37 °C than at 20 °C, since at the elevated temperature the PNIPAAm network collapsed, squeezing more of vitamin C out of the gel (Figure 11).

Environmental sensitive hydrogels in deodorant fibres

β-cyclodextrin (β-CD) is a cone-shaped molecule. The β-CD is hydrophilic at the outer surface of the cavity thanks to the existence of many hydroxyl groups, while it is hydrophobic in the cavity. So β-CD is soluble in water, and a variety of hydrophobic guest molecules can be encapsulated in its non-polar cavity. This characteristic has been widely applied in the fields of drug-controlled release [20], separation [21] and adsorption [22]. Figure 12 exhibits the molecular structure of β-cyclodextrin.

Table 1. *Water absorbency determined in different media of pH.*

pH	Original cellulose	GCE0.5	GCE1.5	GCE2.5	GCE3.0	GCE4.0
1.0	1.98	2.46	2.46	1.98	2.71	10.68
7.0	2.17	2.62	2.60	2.60	3.25	15.89
13.0	2.40	2.78	2.77	3.23	3.34	22.49

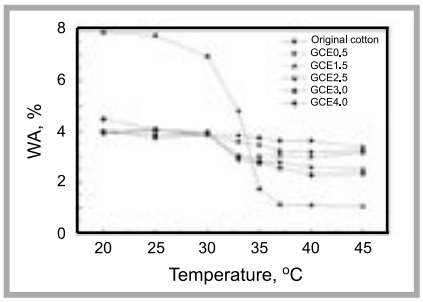

Figure 10. *The variation of water absorbency as a function of temperature.*

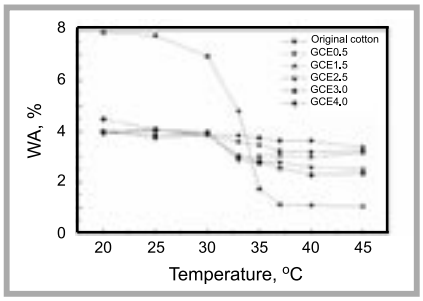

Figure 11. *The cumulative release amount of vitamin C as a function of time determined at different temperatures; (GCE51: NIPAAm/PU feeding ratio was 5/1, monomer concentration 5.0% wt).*

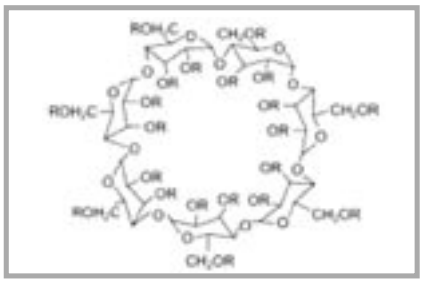

Figure 12. *Molecular structure of β-cyclodextrin.*

Lee et al. [23] used formic acid as a catalyst to copolymerise N-methylol-acrylamide (NMA) and β-cyclodextrin(β-CD) (CD-NMA). The CD-NMA was grafted onto cotton fibres by using CAN as an initiator. Figure 13 shows the effect of the reaction temperature on the graft yield. It demonstrates that a temperature of 40 °C is the optimum temperature; above this temperature value, the graft yield decreases. The optimum graft yield can be acquired from adjusting the grafting time, reaction temperature, and CAN concentration.

CD-NMA-grafted cellulose fibres can be used in the aroma finishing of cotton. The fragrance of CD-NMA-grafted cellulose fibres treated with vanillin was retained

Table 2. *Results of Sensory Test of Vanillin Fragrance (from Ref.[23]); a - stored at 80 °C after storing at room temperature for 7 days, o - fragrance detected, x - nofragrance.*

	Time, day													
	1	2	3	4	5	6	7	1a	2a	3a	4a	5a	6a	7a
Sample	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Control	o	o	x	x	x	x	x	x	x	x	x	x	x	x

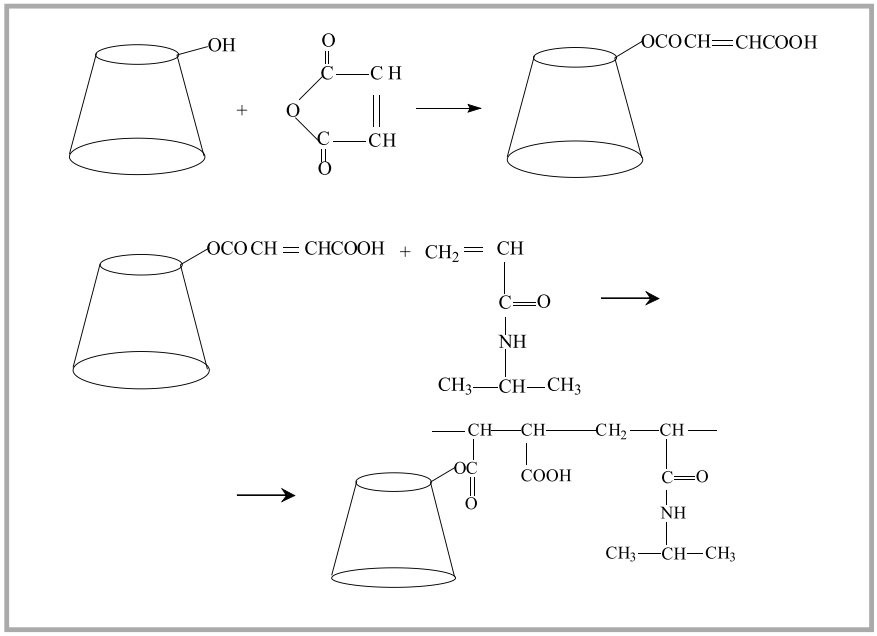

Figure 14. *Synthesis route of PNIPAAm/β-CD copolymer [24].*

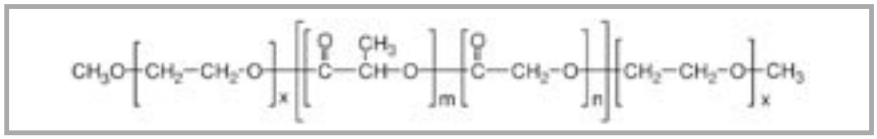

Figure 16. *Poly(ethylene oxide-co-propylene oxide-co-polyethylene oxide) (PEO-PPO-PEO).*

even after prolonged storage, initially at room temperature for 7 days, following holding at 80 °C for 7 days. In contrast, the untreated cotton fibres only retain the fragrance for less than two days (see Table 2).

It is noted that the CD-NMA-attached cotton fibres only release the vanillin in a passive mode. Recently, Liu et al. [24] have synthesised a novel hydrogel, poly(isopropyl acrylamide-co-maleic anhydride-β-cyclodextrin), with pH and temperature sensitivity plus a molecular inclusion function. This novel hydrogel was obtained using free radical polymerisation in an aqueous solution. Firstly, a reactive β-CD based monomer carrying vinyl carboxylic acid functional groups was synthesised via the reaction of β-CD with maleic anhydride(MAH) in N,N-dimethylformamide (DMF) at a temperature of 80 ºC. The poly(NIPAAm-co-MAH-β-CD) was obtained by copolymerisation of the monomer with N-isopropyl acrylamide(NIPAAm). Figure 14 shows the synthesis route.

The equilibrium swelling ratio (ESR) of hydrogel is affected by pH and temperature, as shown in Figure 15. Obviously, the equilibrium swelling ratio of hydrogel increased with the increase in pH. At a certain pH, the equilibrium swelling ratio decreased with the rising temperature. The equilibrium swelling ratio dropped drastically near the phase transition temperature.

The temperature/pH dual-sensitive hydro-gel has a great potential application in the field of smart fabrics. If a temperature/pH dual-sensitive hydrogel is grafted onto the fibre's fabric's surface, the fabric will achieve environmental sensitivity. It is anticipated that the fragrance molecules included in the β-CD are capable of releasing in a sustainable fashion by changing the temperature or pH. Novel deodorant fabrics could be developed by loading the fragrance molecules into the β-CD.

Environmentally sensitive hydrogels in nutrient/drug delivery fabrics

One special property of environment-sensitive hydrogel lies in its being an open thermodynamic system. When the external environment changes a little, the volume of the hydrogel will swell or shrink drastically. This characteristic

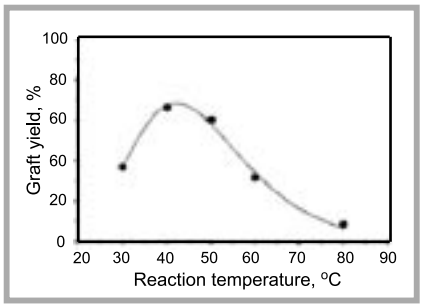

Figure 13. *Effect of the reaction temperature on the grafting yield; grafting conditions: cotton fibre, 0.5 g; CD-NMA, 10 g; CAN (0.012M in 1% HNO3), 50 mL; time, 60 min [23].*

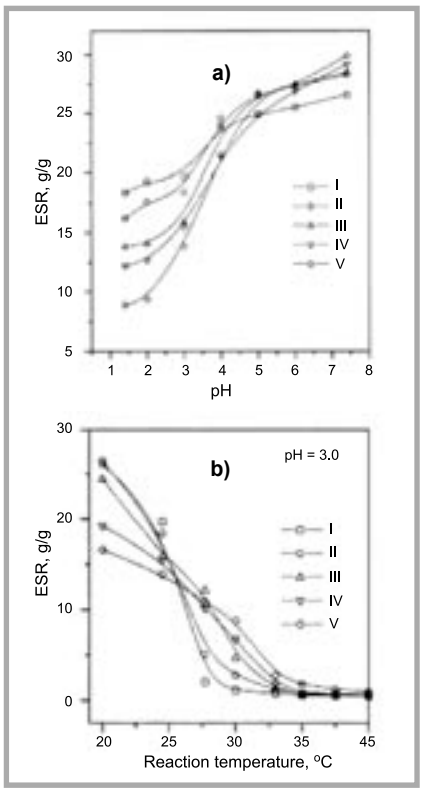

Figure 15. *Influence of pH (a) and temperature (b) on the equilibrium swelling ratio of PNIPAAm-CD hydrogel; hydrogel's chemical composition of NIPAAm/MAH-β-CD(%wt): (I)(99.3/0.7); (II) (98.6/1.4); (III) (98.2/1.8); (IV) (97.6/2.4); (V) (96.2/3.8) [24].*

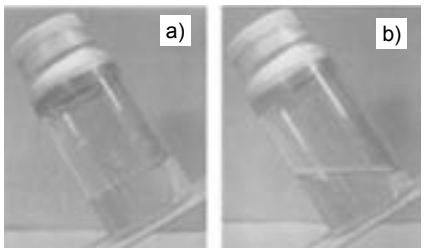

Figure 17. *Visual observation of sol and gel states of EOVE200-HOVE400 at 30 °C a) and 10 °C, b) [26].*

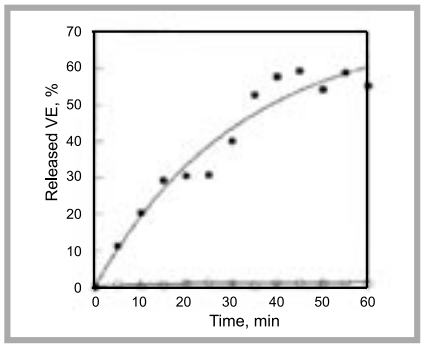

Figure 18. *Release behaviour of VE from EOVE200-HOVE400 at 10 °C (●) and 30 °C(○) [26].*

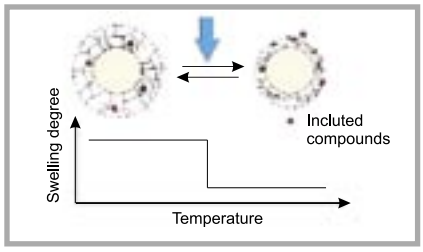

Figure 19. *Controlled release behaviour of reversible temperature-sensitive hydrogel layer on fibre surface.*

phenomenon enables a drug or nutrient loaded in the hydrogels to be released in a controlled manner. The following temperature-sensitive copolymer hydrogel was frequently used as a controlled release system (Figure 16) [25].

The release of vitamins, Chinese herbs, and therapeutic medicine has been widely used in the fields of therapy, health care and cosmetics. Ishida et al. [26] synthesised a temperature-sensitive copolymer (EOVE200-HOVE400) consisting of poly(2-ethoxyethyl vinyl ether) (EOVE200) and poly(hydroxyethyl vinyl ether) (HOVE400). Here poly(hydroxyethyl vinyl ether) (HOVE-400) was a hydrophilic segment. The temperature-sensitive segment EOVE200 caused a hydrophilic-hydrophobic transition at the lower critical solution temperature (LCST), while the hydrophilic segment HOVE400 was indifferent to temperature. The transition temperature of the 20% wt EOVE200-HOVE400 was 20.5 °C. The images of sol-gel transition of EOVE200-HOVE400 solution are shown in Figure 17.

EOVE200-HOVE400 was in sol-state and gel-state at 10 °C and 30 °C respectively. The sol-gel transition is also reversible. When vitamin E was dissolved in EOVE200-HOVE400 solution, a controllable release of vitamin E could be realised by a temperature-induced sol-gel transition (Figure 18).

It was apparent that there was no release of vitamin E from EOVE200-HOVE400 at 30 °C owing to the gelation of the solution. When the temperature was reduced to 10 °C, vitamin E was released from EOVE200-HOVE400, since the gel had converted to sol. If EOVE200-HOVE400 is grafted onto the surface of fabrics, a novel fabric with a function of temperature-tunable release of nutrient or drug will be created (see Figure 19).

If a temperature-sensitive hydrogel is grafted on the nonwoven fabrics, the nutrient or medicine can be encapsulated in the hydrogel. The release of a nutrient or herbs can be controlled by temperature changes. Another advantage of this technology is that the mechanical performance of the temperature-sensitive hydrogel can be improved. Such temperature-sensitive hydrogel-modified fabrics may be used in the cosmetic and pharmaceutical field.

Conclusion

The creation of smart fabrics not only represents an academic advance in the textile industry, but will also bring convenience to our lives. Smart polymers show capabilities of responding to external stimuli and have significant potential applications in a variety of fields. The environmentally responsive fabrics based on smart polymer modification can be tailored to respond to a variety of stimuli such as temperature, pH and so on. Meanwhile, a stimuli-sensitive fabric composite can be used in deodorant fabrics and nutrient/drug delivery fabrics. Owing to the above-mentioned attributes, smart textiles may keep us warm in a cold environment or cool in a hot environment, guard against bacterial attack, and provide us with considerable convenience, support, and even pleasure in our daily activities. Nonetheless, to make the dream of this kind of textile come true, close cooperation is needed between laboratory researchers and partners from industry.

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