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Dual responsive hydrogel-functionalized textile system for transdermal therapy

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***Abstract*— In this study, smart hydrogel-functionalized textile system with temperature and pH-sensitive property was prepared by coating a chitosan/poly(N-isopropylacrylamide) hydrogel onto cotton fabric. The stimuli-sensitive of hydrogel has been evaluated and confirmed in terms of the swelling/ deswelling as function of thermal and pH. The presence of hydrogel on the surface of finished fabrics has been confirmed by FTIR analyses. The capacity of material to respond to different stimuli (pH and temperature) was also studied. Results showed that pH and temperature-dependency behavior of the hydrogel was successfully transformed into fabric. Moisture management proprieties have also been investigated using moisture management tester (MMT) and discussed in details. The findings indicated that functionalized fabric present high moisture management performance. Therefore it may be suitable for skin care as a smart material with absorption for exudates and drug control releasing properties.**

***Keywords*—Responsive- Hydrogel, Chitosan, pNIPAAM, Fabric, Moisture Management.**

I. INTRODUCTION

Nowadays, the actual trend in producing textile materials is to ensure “smart” capability of interacting with environmental conditions [1]. Thus, it is necessary to consider further development of materials for performance textile with stimuli-responsive ability. The specific attribute of such a material could be activated “on demand” by sensing the stimuli in immediate surrounding environment and reacting to the environmental conditions.

Currently available approaches to implement controllable moisture and liquid management properties to cotton fabrics are based on the use of stimuli-responsive hydrogels as surface modification system of textile material [2].

Stimuli-sensitive hydrogels are hydrogels that undergo large changes in the swelling ratio by only a small variation in environmental conditions, such as temperature pH light electric field , and ionic strength [3, 4, 5].

Hydrogels responsive to temperature and pH have been the most widely studied systems since these two factors have a physiological significance. Versatile dual responsive hydrogels have been reported mainly for biomedical applications and a number of reviews coming up in this area in recent times address the latest developments [6, 7].

Owing to the need for biocompatibility and biodegradability, biopolymer based hydrogels are currently of great interest. Such hydrogels can be prepared by combining a natural based polymeric component with thermoresponsive synthetic polymer resulting in dual (pH and temperature) responsive hydrogel systems [8].

Among the wide choice of natural polymers, Chitosan, a naturally occurring polysaccharide, has attracted considerable attention due to its nontoxicity biodegradable, biocompatible and bioadhesive properties [9]. It is also a good example of pH-sensitive biopolymer which responds to changes in the pH of the surrounding medium by protonation/deprotonation that imparts charges on its amino groups [10].

Among synthetic polymers, poly(N-isopropylacrylamide) is the most intensively investigated because it exhibits a volume phase transition (i.e. hydration–dehydration due to side chain reconfiguration) in response to even slight temperature changes [11]. The abrupt conformational transition of it upon changes at temperatures around 32-34°C, which is close to body temperature, has stirred up explorations for technological applications [12, 13].

The aim of this research is to improve the cotton fabric quality and to provide it new and interesting features by functional finishing with thermal and pH responsive hydrogels.

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II. MATERIALS AND METHODES

A. Chemicals

Our study was based on 100% cotton fabric (of 245 g /m² weight per unit area, scoured and bleached). Chitosan (CS) ($C_6H_{11}NO_4$) and N-isopropylacrylamide (NiPAAm) monomer were purchased from Sigma Aldrich. Cross-linker [N,N-methylenebisacrylamide (BIS)], initiator [ammonium persulphate (APS)], caustic soda (NaOH, Chemi-pharma) and other chemicals were of analytical grade and they were used as received.

B. Methods

For the synthesis of hydrogels, chitosan solution was initially prepared by dissolving a mass of 1.0g chitosan with blending in 100mL of acetic acid solution (pH3-4) at room temperature.

In order to obtain chitosan/ poly(N-isopropylacrylamide) (CS/pNIPAAM) hydrogel, NiPAAm (0,8 g) and BIS (0,05 g) were added under stirring to 100 mL of chitosan solution, the temperature was raised to 50°C and then APS (0,15 g) was added to initiate the polymerization. The reaction medium turned turbid after 5 min and the reaction was allowed to proceed for 7 hours at 70 ° C. The resulting hydrogels were dialyzed against distilled water until the residual solution was neutralized.

The modification of the textile substrate with CS/pNIPAAM hydrogels was done according to the method proposed by Jocic [14].

This method consists at wetting scoured and bleached cotton fabric with the chitosan solution, followed by a gelation reaction. Samples are then padded at 70% and dried in air at room temperature.

C. Characterization of Chitosan/pNIPAAM hydrogel

The pH-responsiveness (swelling/deswelling) of CS/PEG and CS/Na_2SO_4 hydrogels was evaluated by means of the gravimetric measurements. The samples were immersed into solutions with varying pH values (3, 4, 6, 7 and 9). The water uptake (%) was measured at room temperature by varying time and then calculated from the following equation:

$$\text{Swelling }(\%) = \frac{WU_t - WU_0}{WU_0} \qquad (2)$$

Where WU_0 and WU_t were the sample weight before and after immersion, respectively.

D. Characterizations of functionalized fabrics

Fourier transform infrared spectroscopy (FTIR) was used to examine the surface chemistry of the modified cotton fabrics. The FTIR spectrum was recorded over the range of 400 - 4000 cm^{-1}.

The water uptake of samples functionalized by hydrogels was determined using a gravimetric method. Each sample of 0.5 g was immersed in buffered solutions of different pH values (4, 6, 7, and 9) at 25 and 37 °C for 1 h. Swelling ratio was calculated after removing excess liquid using the Eq. 1 and represents an average of at least three readings.

The unidirectional water transport was evaluated by a moisture management test (MMT) according to AATCC 195–2011. Moisture Management Test is used to analyze the behavior of dynamic liquid transfer in textile materials by measuring of electrical resistance which is directly related to the water content in the fabric [15].

III. RESULTS AND DISCUSSIONS

A. Characterization of chitosan/pNIPAAM hydrogel

In order to study the responsiveness of chitosan/pNIPAAM hydrogel, gravimetric method was used. Fig. 1 showed the swelling degree of chitosan/pNIPAAM hydrogel in the solutions with pH of 3, 4, 5, 7 and 9 at 25°C.

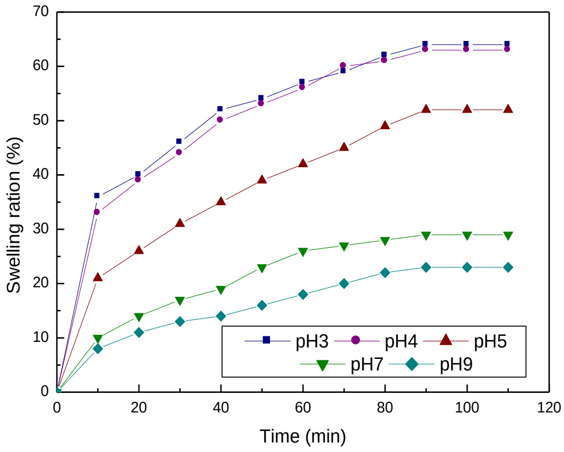

Fig. 1: Swelling ratio (%) in function of time of the Chitosan/pNIPAAM hydrogel at 25°C at pH 3, 4, 5, 7 and 9.

Fig. 1 suggested that an equilibrium of swelling can be reached after 90 minutes for all tested pH values. Chitosan/pNIPAAM hydrogel showed a higher swelling ratio in acidic mediums (pH 3, 4 and 5). The higher value was reached at pH 3 and 4 (about 64%). At higher pH values (pH 7 and 9), swelling percentages decreased remarkably.

As pH is bellow pKa of chitosan, which is around 6,3, some amino groups (NH_2) of chitosan were protonated and the electrostatic repulsion between the amine groups (NH^{+3}-NH^{+3}) resulted in an enhancement of the swelling capacity [16]. Moreover, at 25°C, which is a temperature lower than the LCST of pNIPAAM (LCST around 34°C), pNIPAAM chains had an extended conformation and the hydrophilic group (CONH-) becomes dominant through the formation of H- bonds between water and -OH, -NHCO and -NH_2 groups in the hydrogel [17]. These two factors were thus responsible for a higher degree of swelling in the acidic medium at 25°C.

When the pH reached 4, all the amino groups (NH_2) of chitosan were converted to the protonated (NH^{3+}) form and the maximum swelling was obtained which accounted for similar swelling behaviors at pH of 4 and 3. At a neutral and basic condition (pH7 and pH9), NH^{3+} groups on chitosan were converted to the deprotonated form (NH_2) which resulted in the decreased swelling ratio of the hydrogel

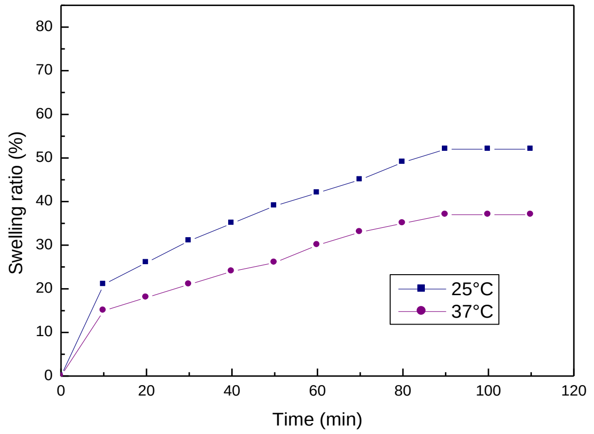

Fig. 2: Swelling ratio (%) in function of time of the Chitosan/pNIPAAM hydrogel at pH5 at 25°C and 37°C.

Fig. 2 showed swelling profiles of hydrogel at 25 °C and 37°C as a function of time at pH 5. Equilibrium of swelling was reached after 80 minutes. The degree of swelling of pNIPAAM/chitosan hydrogel underwent appreciable change with external temperature. Swelling ratio at 37°C was minimal (only 37%).

Since the hydrogel contains pNIPAAM in its network which tended to contract bellow LCST value due to collapse of the polymer coil leading to compact conformation, Then, hydrogen interactions between pNIPAAM and water were broken leading to polymer dehydration at 37°C.

B. *Characterization of functionalized fabrics*

1) *FTIR Mesurement*

FTIR spectra of original cotton fabric and modified fabric with Chitosan/pNIPAAM hydrogel was shown in Fig. 3.

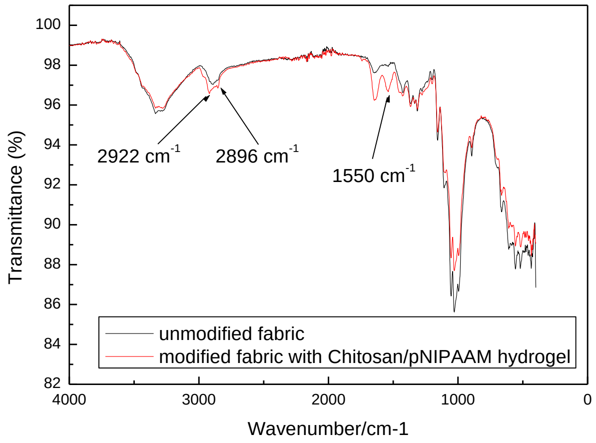

Fig. 3: FTIR spectra of unmodified fabric and modified fabric with Chitosan/pNIPAAM hydrogel.

Fig. 3 showed that the control cotton fabric depicted the absorption peaks at 3889, 2900, 1660, 1423 and 1035 cm -1 attributing to the OH stretching, CH stretching, OH of water absorbed from cellulose, CH_2 symmetric bending and C – O stretching, respectively. After depositing Chitosan/pNIPAAM hydrogel on the surface of cotton fabric, a new band appeared at 1550 cm^{-1} corresponding to the –NH bending (Amide II) of chitosan [18] confirming the presence of chitosan units in the modified fabric. In addition, the peaks correspond to CH_2 stretching vibrations of pNIPAAM can be observed at around 2896 cm^{-1} and 2922 cm^{-1} in this spectrum [19]. This indicated that hydrogels have been successfully incorporated onto the cotton surface.

2) *Stimuli-responsiveness measurements*

In order to determine pH and thermal responsiveness of modified cotton material, water uptake measurement was assessed by the same gravimetric method described elsewhere. The results are presented in Fig. 4.

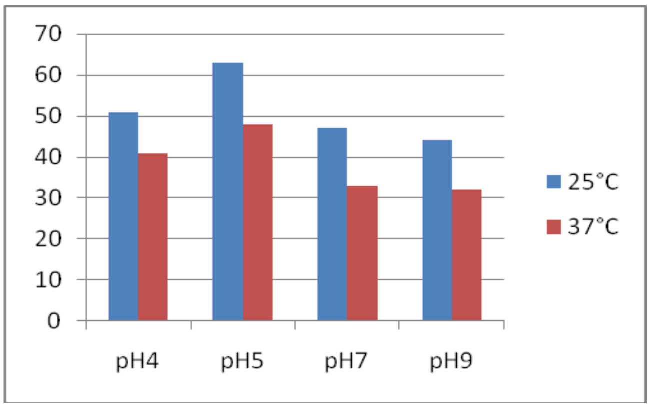

Fig. 4: Water uptake (%) in function of pH and temperature value of the modified cotton fabric with CS/pNIPAAM hydrogel

Fig. 4 showed that the obtained water uptake percentages of modified fabric with CS/pNIPAAM hydrogel increased in acidic medium (pH4-6). As well as, it showed an increase in hydrophilicity at 25°C. However, at 37°C the hydrophilicity of modified fabric decreased. This result was typical to previous results in the case CS/pNIPAAM hydrogel. This expected result was attributed to the pH responsiveness of chitosan as well as to the thermosensitive behavior of pNIPAAM. Thus, the pH and temperature dependency of the chitosan and pNIPAAM was successfully transformed into fabric.

Such hydrogel-functionalized cotton fabric can be used as a smart material with absorption for exudates and drug control releasing properties. In fact, due to its high absorbency at acidic condition and low temperature, this smart textile can absorb excess wound or burns exudate and warm to body temperature. This accelerates wound healing and promotes skin regeneration. Moreover, hydrogel coated-fabric be hydrophobic when the temperature is around the skin temperature thus allowing the release of drugs and keeps a moisture interface between the textile and the wound surface, which can assist the healing process.

3) Moisture management test (MMT)

MMT can be used to evaluate liquid moisture spreading and transporting properties on both surfaces of the fabric and transferring from one surface to the opposite. The measure time of the whole testing process was 120 s. The water location on the top and bottom surfaces was shown in Fig. 5.

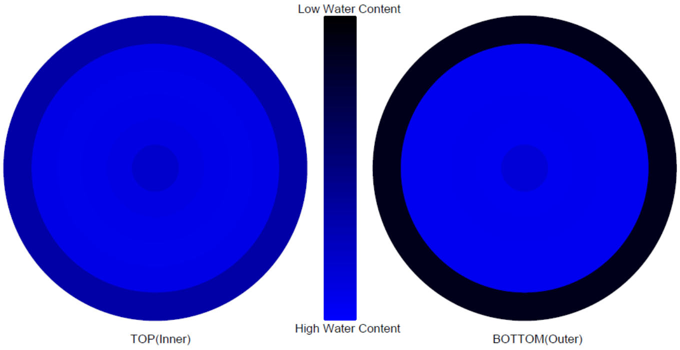

Fig.5: Diagram of water location of unmodified fabric

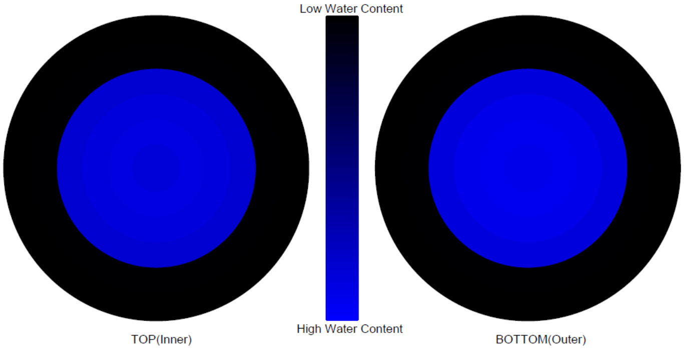

Fig.6: Diagram of water location of modified fabric

Fig. 5 demonstrated a very hydrophilic top surface and the water location of the bottom surface was much lower than that of the top surface. This indicated that most of the liquid was introduced onto the top surface of the fabric and not transferred to the bottom surface. Whereas, modified fabric showed a lower hydrophilic surface where the water location of the top surface was the same as that of the bottom surface (Fig. 6). In fact, the hydrogel coated fabric turns to be less hydrophilic when the temperature was around the skin temperature (37°C (skin temperature) >32°C (LCST of pNIPAAM)) allowing to keep a moisture interface between the textile and the wound surface, thus revealing the controllable transition between hydrophilicity and hydrophobicity of the hydrogel.

In the table 3, a set of indexes were provided for evaluating the moisture management propertiesof the hydrogel coated-fabric.

The accumulative one-way transport index (AOTI) is the cumulative liquid moisture difference between two sides of the fabric [20]. As it can be seen from table 1, textile material showed a sharp increase in AOTI value from 163% to 360% after modification with hydrogel. This implied that moisture transmission from the skin to the environment occurs quickly [20].

TABLE I
MOISTURE MANAGEMENT INDEXES

	Wetting Time (sec)		**Absorption Rate (%/sec)**		**Max Wetted Radius (mm)**		**Spreading Speed (mm/sec)**		**Accumulative one-way transport Index(%)**	**OMMC**
	Top	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**		
Unmodified fabric	3,276	3,369	40,1202	56,6925	25	25	4,0653	3,8719	163,39	0,6061
Modified fabric	6,084	6,084	23,2793	62,2145	15	15	1,779	1,6745	360,48	0,6573

The overall moisture management capability (OMMC) refers to the ability of fabric to transfer liquid moisture. The higher the value is, the better the performance of fabric is [20]. It was seen that modified fabric had higher OMMC (about 0,66) values similar to the findings in AOTI. As a result, the highly satisfactory liquid moisture spreading and transporting properties of the hydrogel-coated fabric were well demonstrated.

These results indicated that the topical skin area can be kept clean, breathable and comfortable during skin care and wound treatment using our hydrogel coated-fabric.

IV. CONCLUSIONS

This work reported the preparation of temperature and pH-sensitive fabric using stimuli-sensitive hydrogel. Hydrogel based on synthetic polymer (pNPAAM) and biopolymer (chitosan) were successfully synthesized and coated to cotton fabric. Chitosan/pNIPAAM hydrogel presented a big interesting pH and thermal stimuli-responsiveness at acidic medium at room temperature thanks to sensitivity of chitosan and NIPAMM, respectively, to pH and temperature. The obtained values of water uptake of modified fabric confirm the stimuli-responsiveness of functionalized cotton. Moreover, the moisture management test showed an improvement of moisture management properties. Thus, application of hydrogel techniques in textile industry can provide a better understanding of the development and design of new textiles-based transdermal therapies.

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