



## Synthesis of poly(N-isopropylacrylamide) polymer for fabrication of thermo-responsive cotton fabric

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Thermo-responsive poly (N-isopropylacrylamide) (PNIPAM) polymer has been synthesized by free radical addition polymerization method. The chemical structure of the synthesized polymer has been clarified by FTIR spectroscopy and <sup>1</sup>H NMR analyses. Turbidity test shows that the synthesized polymer exhibits thermo-responsive properties, depending on change in temperature. Its lower critical solution temperature (LCST) value is measured as 31°C by DSC analysis. The PNIPAM polymer is then applied onto the cotton fabric in two different concentrations using double-bath impregnation method. Change in hydrophilic character of the fabric, which is temperature dependent, has been revealed by drop and absorption capacity tests, contact angle measurement and surface energy calculation. The test results show that the fabrics exhibit thermo-responsive behavior. Their hydrophilic character is turned to the hydrophobic character above LCST of the polymer. The water vapor permeability of the polymer treated fabrics at temperatures above LCST increases as compared to the untreated fabric due to the increase in fabric porosity. Below LCST, water vapor permeability is increased because of the increasing hydrophilicity. Consequently, it is concluded that the water vapor permeability of the fabrics can be controlled by changing the temperature-dependent hydrophilic/hydrophobic characteristic and porosity, resulting from swelling or shrinkage of the polymer molecules.

**Keywords:** Cotton fabric, Poly (N-isopropylacrylamide), Smart textile, Stimuli-responsive, Thermo-responsive polymer

### 1 Introduction

Today, the standard of living rises and consumers' expectations from textiles also change in parallel with the developing technology. The need to have an active role of garment to adapt changes in the physiological needs of the wearer in accordance with the user's activity and changes in the environment has become more and more important. In recent years, this innovative feature known as "active comfort regulation" can be achieved by using smart polymer coating technology. With the application of the smart polymers, textile materials have been produced that can detect and interpret changes in the environment (temperature, humidity, pH, etc.) and respond appropriately<sup>1</sup>.

Smart polymers have received great attention from researchers all over the world in recent years. The most commonly used polymers among this group are thermo-responsive polymers<sup>2</sup>. Thermo-responsive polymers have been used in production of cosmetic and skin care products<sup>3</sup>, obtaining self-cleaning surfaces in

water<sup>4, 5</sup> and improving clothing comfort in the textile field<sup>6-9</sup>. They exhibit volumetric phase change suddenly and reversibly if they are stimulated by temperature. These polymers have an activation temperature known as the lower critical solution temperature (LCST). They exhibit swelling and shrinkage behavior below and above LCST respectively and change their hydrophilic-hydrophobic properties reversibly<sup>10, 11</sup>. Thanks to these features, they find many usages, such as drug release<sup>12-14</sup>, material separation<sup>5, 15, 16</sup>, tissue engineering<sup>17</sup> and smart textile fabrication<sup>4, 6, 18-21</sup>. According to the literature survey, the thermo-responsive polymers could be applied to textile products in different forms as micro gel, hydro gel or polymer<sup>7, 20, 22-24</sup>.

In this study, it was aimed to develop smart textile materials responding to the change in temperature. For this aim, PNIPAM [poly(N-isopropylacrylamide)] polymer was synthesized to be used as thermo-responsive polymer and applied onto the cotton fabric using double-bath impregnation method. The chemical characterization of the synthesized polymer was performed by Fourier-Transform Infrared (FTIR) spectroscopy and <sup>1</sup>H-Nuclear magnetic resonance (<sup>1</sup>H NMR) analyses. Its thermo-responsive property

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was investigated by turbidity test. Thermal analysis of the PNIPAM was carried out by differential scanning calorimeter (DSC).

The morphology and cross-section of the fabrics treated with PNIPAM was examined by scanning electron microscopy (SEM) analysis. Thermo-responsive properties of the fabrics were determined by examining change in wetting behavior, water absorption property and water vapor permeability, measured at temperatures below and above the LCST. Contact angle, surface energy and its components were measured. Moreover, washing resistance of the thermo-responsive property and effect of polymer application on the bending rigidity and tear strength of the fabrics were also investigated.

## 2 Materials and Methods

### 2.1 Materials

N-isopropylacrylamide (Sigma-Aldrich) (NIPAM) as monomer was used without purification. Polymer synthesis was carried out in distilled water using 2,2'-azobis (2-methylpropionamide) dihydrochloride (AMPA) as an initiator. The initiator AMPA was used as supplied.

A scoured and bleached, plain weave, 100 % cotton fabric supplied from Söktaş (Turkey) was used for thermo-responsive polymer application. The fabric with weight of 151 g/m<sup>2</sup> has 61 yarns per cm in warp direction and 38 yarns per cm in weft direction. To bind the synthesized thermo-responsive polymer to the fabric, 1,2,3,4-Butanetetracarboxylic acid (BTCA) (Sigma-Aldrich, 99%) was used as cross-linker and catalyzed by sodium hypophosphite (Sigma-Aldrich). Seta mordant T (supplied from Setaş (Turkey)) was used as cationizing agent. Triton X 100 (Sigma Aldrich) was used as surface active material and sodium hydroxide was used to increase the solubility of the cationizing agent.

### 2.2 Synthesis of Thermo-responsive Polymer

Thermo-responsive PNIPAM polymer was synthesized using free radical addition polymerization

method. NIPAM (1 g) monomer was dissolved in 15 mL of distilled water. AMPA (0.4 g) initiator dissolved in distilled water was added drop wise to the monomer solution. The reaction solution was poured into the glass tubes and purged with nitrogen for 1 min to remove the oxygen. Polymer synthesis was carried out in water bath at 80 °C for 5 h. After polymerization was completed, water was removed to obtain powder PNIPAM polymer. The schematic representation of the PNIPAM synthesis is given in Fig. 1.

### 2.3 Cationization of Cotton Fabric

The cotton fabric was cationized before the PNIPAM polymer application. For this aim, a solution containing Triton X100 (3 g/L), seta mordant T (150 g/L) and NaOH (25 g/L) was prepared. The fabric was exhausted with this solution at 80 °C for 40 min. In the cationization process, flote ratio was used as 1:50. After treatment, the fabric was washed with acetic acid solution of 2 g/L and nonionic ECE detergent of 3 g/L respectively. Finally, the fabric was rinsed with cold water and leaved to dry at room temperature (25 °C).

### 2.4 Application of PNIPAM Polymer to Cotton Fabric

To produce thermo-responsive cotton fabric, PNIPAM polymer was applied onto the cotton fabrics by double-bath impregnation method. In the method, polymer application was carried out at two-stages. The fabric was impregnated with the first bath containing cross-linker and catalyst, followed by the second bath containing polymer solution. In the first bath solution, 3.75 g of BTCA cross-linker was used for 1 g of polymer and the ratio of cross-linker to catalyst was selected 4/1. The fabric samples were passed from first bath solution on foulard under the conditions of 2 bar pressure and 2 m/min speed, dried at 80 °C for 5 min and cured at 160 °C for 5 min. The second bath was prepared by dissolving the powder PNIPAM polymer in distilled water. The concentr-

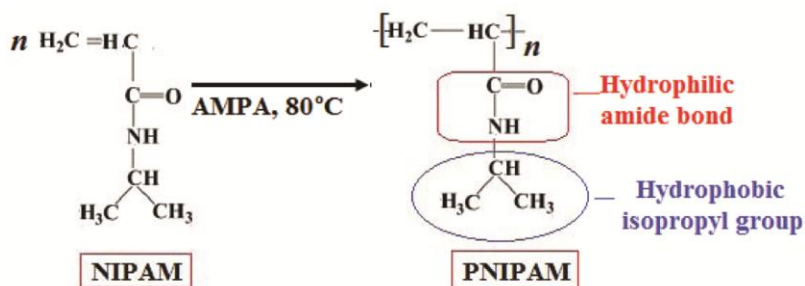


Fig. 1 — Schematic representation of PNIPAM synthesis by free radical polymerization reaction

ations of the polymer solution were adjusted at 30 g/L and 50 g/L. The fabric treated with the first bath was left in the second bath containing the polymer solution for 1 h and then subjected to drying at 80 °C and curing at 160 °C for 5 min. Fabrics treated with 30 g/L and 50 g/L of concentrations of the polymer solution were named as CF-PNIPAM-3 and CF-PNIPAM-5 respectively. To investigate the effect of BTCA application on the fabric properties, the fabrics treated with different amounts of BTCA were also tested. These fabrics were named BTCA-3 and BTCA-5.

### 2.5 Characterization of Thermo-responsive Polymer

The chemical structure of the synthesized PNIPAM polymer was analyzed by <sup>1</sup>H NMR analysis and FTIR spectroscopy (Perkin Elmer Spectrum BX). <sup>1</sup>H NMR analysis was performed using a Bruker 400 MHz instrument. In the analyses, deuterated dimethyl sulfoxide (DMSO) for monomer and D<sub>2</sub>O (Deuterium oxide) for polymer were used as solvents. FTIR analyses were performed on KBr disks, between wave numbers of 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. The cryoscopy method was used to determine the molecular weight of the synthesized polymer. In this method, the molecular weight is determined by the reduction in the freezing point of a solution in which the organic material is dissolved. In the analysis water was used as solvent. Molecular weight of PNIPAM was calculated by using following equation:

$$\Delta T_d = \frac{1000 \times K_d \times W_2}{M \times W_1} \quad \dots (1)$$

where  $\Delta T_d$  is the freezing point lowering;  $M$ , the molecular weight of solute;  $W_1$ , the weight of solvent (g);  $W_2$ , the weight of solute (g); and  $K_d$ , the freezing temperature drop constant.

A turbidity test was carried out to determine the thermo-responsive property of the PNIPAM polymer. PNIPAM polymer (1% w/v) solution in distilled water was prepared. The solution was heated at a range of 20- 45 °C with an increase of 5 °C. The turbidity of the solution was observed on the photographs taken at each temperature. LCST value of the PNIPAM aqueous solution was determined by DSC analysis. DSC measurement was performed using Netsch Polyma instrument. The sample was heated between -10 °C and 60 °C at a rate of 5 °C/min. The analysis was carried out under an inert nitrogen gas atmosphere at a flow rate of 60 mL/min. The onset point of the endothermal peak was evaluated as LCST. Besides, LCST was

investigated by determination of the temperature at which the aqueous polymer solution began to change color. In this test, the solution was gradually heated from 30 °C to 40 °C at 1 °C increment and photographed at each temperature. The temperature at which polymer solution began to become cloudy was determined as the LCST value.

### 2.6 Characterization of Thermo-responsive Fabric

In this study, the PNIPAM polymer was cross linked to cotton fabric using a BTCA cross-linker. During the curing process of the fabric, the esterification reaction of the cotton cellulose with BTCA occurs. Cellulose esterification with a BTCA proceeds first to form a cyclic anhydride, and then to form an ester with the hydroxyl group (-OH group) of the cellulose macromolecule. On the other hand, carboxylic groups of BTCA can react with amide groups of PNIPAM polymer. As a result of the chemical reactions of BTCA with amide side groups of the PNIPAM and hydroxyl groups of cotton, PNIPAM polymer is cross-linked to the cotton cellulose<sup>22</sup>. To determine graft yield (GY) of PNIPAM polymer on the fabric, the fabric samples were weighed before and after the grafting process. The GY was calculated using the following equation:

$$GY \% = \frac{W_2 - W_1}{W_1} \times 100 \quad \dots (2)$$

where  $W_1$  is the weight of the fabric sample before grafting; and  $W_2$ , the weight of grafted fabric sample.

The morphology of the modified cotton fabric was examined by scanning electron microscopy (SEM, Phillips XL-30S FEG model). The samples were coated with thin gold layer before analysis. To investigate the polymer distribution in the fabric cross-section, the fabric samples were broken with liquid nitrogen and cross-section images were recorded with a current of 10 μA and a high magnification power of up to ×1000. FTIR spectroscopy (Perkin Elmer Spectrum BX) was used to analyze the chemical structures of the PNIPAM polymer applied cotton fabrics. The analyses were performed on KBr disks, between wave numbers of 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. The presence of the PNIPAM polymer on the cotton fabric was also examined by TG analysis. TG analysis was carried out using Perkin Elmer Diamond instrument under nitrogen atmosphere with heating rate of 10 °C/d in the range of 0-500 °C.

In order to investigate the thermo-responsive property of the PNIPAM treated fabrics, a simple test

method proposed by Hengrui<sup>25</sup> was used. In this test, transition in the hydrophilic/hydrophobic character of the fabric depending on the temperature was examined. In the test, untreated cotton fabric and PNIPAM treated fabric samples were put into the water at 20 °C and 40 °C separately, and their behavior in water was observed. To investigate thermo-responsive properties of the polymer-treated fabrics, the wetting times of the fabrics with 20 °C or 40 °C of surface temperatures were measured according to the AATCC 79 test standard.

The surface contact angles of the fabric samples were measured on sessile drops by a goniometer (Data physics OCA 15 plus model instrument) and a CCD camera. Measurements were performed on the fabric surfaces in the air environment having a relative humidity of 10–25 %. During measurements, the surface temperature of the fabric was increased between 25 °C and 50 °C by 5 °C increment. The temperature of the fabric surface was controlled by a thermal camera (Fluke Ti100 Thermal Imager) during the measurements. A 15 µL drop volume of water was dropped on the fabric surface by a micro-syringe (Hamilton). Measurements were made on five different regions of the fabric and the average contact angle was calculated. The surface energy and its components for the PNIPAM treated fabric samples were calculated using contact angles measured on the fabric at 20 °C and 40 °C, using various liquids. Contact angle measurements were performed on fifteen different regions of the fabric samples for each test liquid. Water, glycerin, and ethylene glycol, having a surface tension of 72.8 mN/m, 63.40 mN/m, and 48mN/m respectively, were used as test liquids. The surface energy and its components were calculated according to the method of Owens & Wendt.

The change in the water uptake values of the polymer-treated fabrics depending on the change in temperature was measured by the gravimetric method<sup>22</sup>. The test was carried out between 25 °C and 40 °C, increasing temperature by 2 °C. All test samples were kept in a water bath for 30 min before starting the test to achieve equilibrium. During the test, the samples were kept in the water for 5 min. Then, the surface water of the fabrics extracted from the test water was removed using a wet filter paper and the weights of the fabrics were measured by precision scales. The tests were repeated five times for each sample and the average was calculated. The

water uptake values of the fabrics were calculated using the following equation:

$$WU = \frac{(W_w - W_i)}{W_i} \times 100 \quad \dots (3)$$

where  $WU$  is the amount of water uptake;  $W_i$ , the dry weight of the sample before the test; and  $W_w$ , the weight of the tested fabric sample.

The temperature dependent water vapor permeability of the PNIPAM treated-fabrics was determined according to a modified BS 3424 control dish method. Tests were performed at 20 °C and 40 °C in a drying oven to study thermo-responsive behaviors of the fabric at temperatures above and below LCST. Before testing, all fabric samples were conditioned under standard atmospheric conditions (20 ± 2 C, 65 ± 2% relative humidity) for 24 h. The water vapor permeability value of the fabrics was calculated using the following equation:

$$WVP = \frac{24 \times M}{A \times t} \quad \dots (4)$$

where  $WVP$  is the water vapor permeability;  $M$  (g), the loss in mass over the time period;  $A$  (m<sup>2</sup>), the area of the exposed test specimen; and  $t$  (h), the time between consecutive weighing.

The SPSS 20.0 statistics software was used for statistical analysis of the test results. Analysis of variance (ANOVA) was carried out and a Duncan Multiple Dispersion Test was used to determine significant differences ( $p < 0.05$ ). To determine the effect of polymer application on tear strength, the fabrics were tested according to the TS EN ISO 13934-2: 2014 standard using a Lloyd LR5K Plus electronic tensile tester. Moreover, the bending rigidity of fabrics was measured according to the TS 1409 standard. The variance analyses of the tear strength and bending rigidity tests were performed statistically on the SPSS 20.0 statistical software, and Tukey HSD (Honestly Significant Difference) Multiple Comparison Test ( $\alpha = 0.05$ ) was used to determine significant differences ( $p < 0.05$ ). In order to investigate the durability of the thermo-responsive properties on the PNIPAM treated fabrics after repeated washings, the fabrics were washed at 30 °C for 30 min according to the test standard TS EN 20105-C06: 2001. The samples were subjected to multiple washings. The weight loss ratio after washings was calculated using the following equation<sup>6</sup>:

$$\text{Weight loss rate} = \frac{m - m_1}{m - m_0} \times 100\% \quad \dots (5)$$

where  $m$  is the weight of PNIPAM treated-fabric;  $m_0$ , the weight of untreated cotton fabric; and  $m_1$ , the dry weight of PNIPAM treated-fabric after washing.

In the study, the water uptake test was performed on the fabrics subjected to multiple items of washing to investigate the durability of the thermo-responsive effect of the fabrics after repeated washings.

### 3 Results and Discussion

#### 3.1 Characterization of PNIPAM Polymer

##### 3.1.1 FTIR Analysis Results

To confirm the syntheses of PNIPAM polymer, NIPAM monomer and synthesized PNIPAM are characterized by FTIR spectroscopy. As seen from Fig. 2 (a), the spectrum of NIPAM shows a major peak at  $1620\text{ cm}^{-1}$  due to C=C stretching<sup>26</sup>. This peak disappears in the FTIR spectrum of the synthesized PNIPAM because of the polymerization reaction carried out between the monomer radicals formed by the opening of the double bonds during the free radical addition polymerization reaction. In the FTIR spectrum of PNIPAM, the stretching vibration of C=O (amide I) at  $1636\text{ cm}^{-1}$  and bending vibrations of NH (amide II) at  $1560\text{ cm}^{-1}$  and  $1542\text{ cm}^{-1}$  are found available. Besides, C-N group in PNIPAM polymer backbone and the asymmetric and symmetric bending of  $-\text{CH}_3$  in isopropyl groups occur at  $1176\text{ cm}^{-1}$ ,  $1388\text{ cm}^{-1}$  and  $1366\text{ cm}^{-1}$  respectively<sup>26-28</sup>. These findings prove PNIPAM polymer synthesized successfully by a free radical addition polymerization reaction<sup>29,30</sup>.

##### 3.1.2 <sup>1</sup>H NMR Analysis Results

<sup>1</sup>H-NMR analysis of NIPAM and PNIPAM has been performed to demonstrate the synthesis of PNIPAM polymer. NMR spectra including molecular formulas of the monomer and polymer are shown in Fig. 2 (b). According to the <sup>1</sup>H NMR spectrum of the monomer, methyl protons in the isopropyl group are observed at 1.05 and 1.07 ppm. The protons illustrated with "b" and "c" in the molecule formula occur at 5.52-5.55 ppm and 6.02-6.21 ppm respectively. The single proton in the isopropyl group of the monomer illustrated with "d" is found at 3.9 ppm in the spectrum, while the peak of the NH proton is appeared at 7.95 ppm. The peaks at 2.5 ppm and 3.8 ppm in the spectrum of the monomer belong to DMSO, which is used as a solvent. As seen in Fig. 2 (b), the peaks in the monomer spectrum shows some changes in the polymers. The peaks of the vinyl groups completely disappear. In addition, a peak assigned to D<sub>2</sub>O solvent used in the <sup>1</sup>H NMR analysis

of the polymer occur at 4.8 ppm<sup>31</sup>. These findings prove that PNIPAM polymer is successfully synthesized from NIPAM monomer.

##### 3.1.3 Molecular Weight

The number average molecular weight of the PNIPAM polymer is calculated as 4300 g/mole by the cryoscopy method. This value shows that the PNIPAM polymer has a low molecular weight.

##### 3.1.4 Turbidity Test Results

The turbidity test has been carried out to examine thermo-responsive behavior of the PNIPAM polymer. Photographs of the polymer solution taken in the temperature range 20–45 °C (heating by 5 °C increments) are given in Fig. 3 (a). The polymer solution is transparent up to 35 °C, as the hydrophilic polymer is dissolved in water. The solution becomes completely opaque between 35 °C and 45 °C, as the polymer becomes insoluble in water. At these temperatures, the interaction between hydrophobic groups in the structure of the PNIPAM polymer is found dominant and polymer exhibits hydrophobic character<sup>19</sup>. The turbidity test indicates that the PNIPAM polymer exhibits thermo-responsive behavior, which causes hydrophilic character to changes depending on change in temperature.

##### 3.1.5 Determination of LCST Point

To investigate the LCST value of the polymer definitely, the polymer solution is heated from 30 °C to 40 °C with increment of 1°C and photographed at each temperature. LCST value is a temperature at which the polymer solution starts showing turbidity [Fig. 3 (b)]. Thermo-responsive polymers are soluble in water at temperatures below the LCST due to their dominant hydrophilic groups. In contrast, the hydrophobic groups in the structure of the polymer become dominant when the temperature rises above the LCST value. At these temperatures, thermo-responsive polymers are insoluble in water. Phase separation occurs due to hydrophobic interactions between hydrophobic groups of the polymers, and their aqueous solutions become cloudy<sup>21,32</sup>. In the study, the LCST value of the PNIPAM polymer is determined using this information. As seen from Fig. 3 (b), while the temperature at which the PNIPAM polymer solution becomes turbid is 31 °C, the distinct turbidity is occurred at 32 °C. The LCST value is determined as 31 °C.

The LCST value is also confirmed by DSC analysis. The hydrogen bonds between the water and

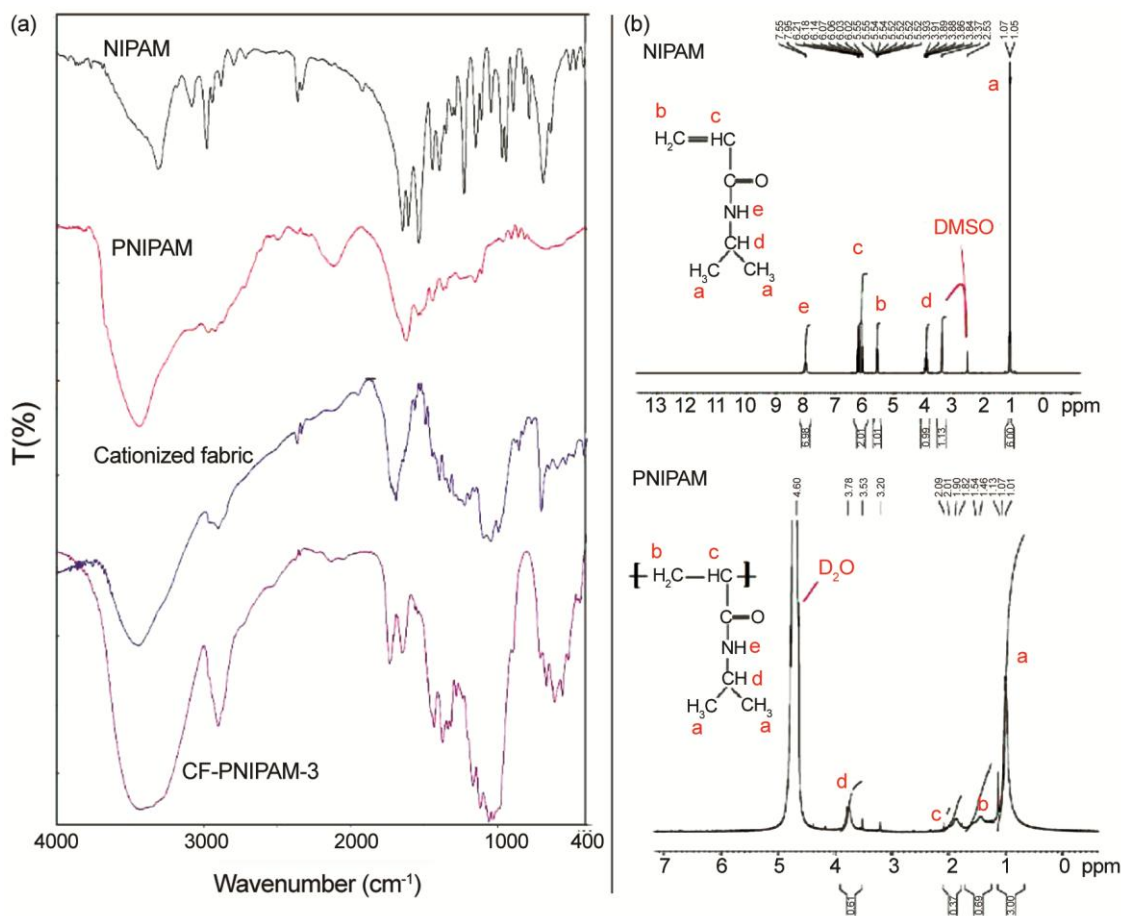


Fig. 2 — FTIR spectra (a), and <sup>1</sup>H-NMR spectra (b) of NIPAM and PNIPAM



Fig. 3 — Thermo-responsive behavior of PNIPAM polymer solution (a) at 20–45 °C (with 5 °C increment) and (b) at 30–40 °C (with 1 °C increment)

the polymer molecules are broken when the polymer transforms from swollen state to shrunk state with an increase in temperature. This is an endothermic

process and the onset point of the endothermal peak in the DSC thermograms represents the LCST value of the polymer<sup>33,34</sup>. According to the DSC thermogram, the LCST value of the PNIPAM is determined as 31 °C. It is found that this result is consistent with the turbidity test result.

### 3.2 Characterization of Thermo-responsive Fabric

#### 3.2.1 Determination of Grafting Yield

After the application of polymer onto cotton fabrics, graft efficiency is calculated to determine the amount of polymer in the fabric structure. Grafting yield is calculated as 9.72 % for CF-PNIPAM-3 fabric and 11.7 % for CF-PNIPAM-5 fabric. As expected, the polymer presence in the fabric structure is increased as the applied polymer concentration increases.

#### 3.2.2 SEM Analysis Results

The surface morphology of the treated fabrics has been investigated by SEM images. The SEM micrographs of untreated, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics are given Fig. 4. SEM images of

untreated cotton fabric specimen in Fig. 4 (a) clearly show the standard surface morphology. SEM images of the CF-PNIPAM-3 [Fig. 4 (c)] and CF-PNIPAM-5

[Fig. 4 (e)] fabrics show that PNIPAM polymer is completely coated onto the fibre surfaces and forms inter-fibre connections. The uniform and smoother

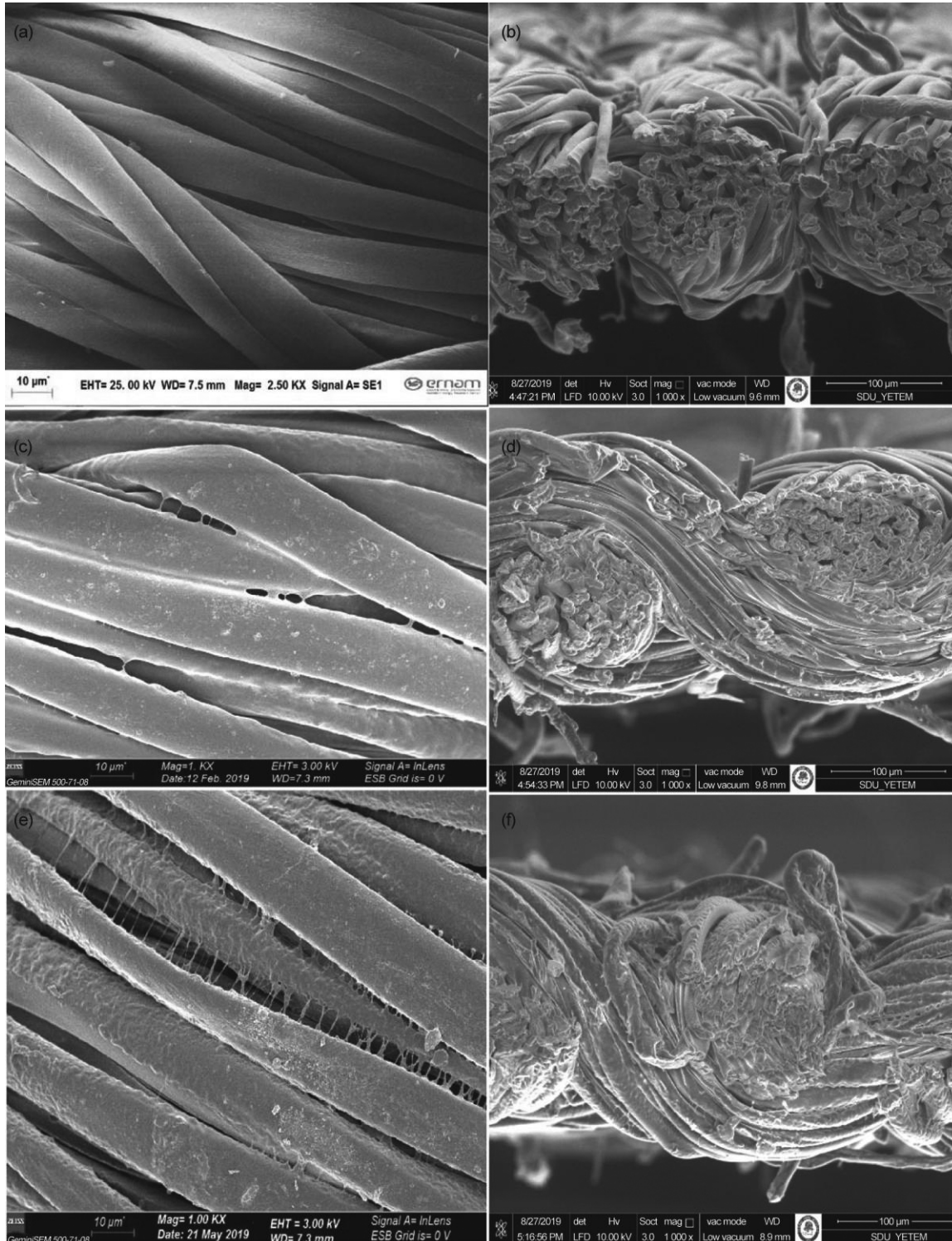


Fig. 4 — SEM images of untreated cotton surface (a), untreated cotton cross-section (b), CF-PNIPAM-3 fabric surface (c), CF-PNIPAM-3 fabric cross-section (d), CF-PNIPAM-5 fabric surface (e), and CF-PNIPAM-5 fabric cross-section (f)

coatings are formed throughout the fabrics, and 5 % polymer concentration (CF-PNIPAM-5) fabric shows more filling and inter-fibre connections among fibre.

In this study, fabric cross-sectional SEM images show the presence and placement of the polymer in the fabric cross-section. The SEM images of the CF-PNIPAM-3 [Fig. 4 (d)] and CF-PNIPAM-5 [Fig. 4 (f)] show that the cross-section of the polymer-treated fabrics increases as compared to raw cotton fabric [Fig. 4 (b)]. The increase in the cross-section of fabric is due to the coating of the fibre surfaces in the yarn cross-section with the polymer layer and the situation of swollen polymer molecules at room temperature (25°C).

### 3.2.3 FTIR Analysis Results

FTIR spectroscopy analysis has been used to obtain information about the chemical structure of the cotton fabric after polymer grafting. The characteristic cellulose peaks show band at around 1000–1200  $\text{cm}^{-1}$  in FTIR spectra of the fabrics. Other characteristic peaks of the cotton cellulose, which are hydrogen-bonded OH stretching peak at 3550–3100  $\text{cm}^{-1}$ , CH stretching peak at 2900  $\text{cm}^{-1}$ , and CH wagging peak at 1316  $\text{cm}^{-1}$ <sup>35</sup>, have also been observed in the spectra of fabrics. However, the H-bonded hydroxyl (O-H) stretching peak gets narrow in the FTIR spectrum of cationized cotton fabric because of the reaction of O-H groups with cationizing agent.

In the FTIR spectrum of PNIPAM polymer, the peaks of amide I and amide II stretching vibrations are revealed at 1638  $\text{cm}^{-1}$ , 1560  $\text{cm}^{-1}$  and 1540  $\text{cm}^{-1}$  respectively. The FTIR spectrum of the grafted cotton fabric shows essential differences as compared to the cationized cotton fabric. The spectrum of CF-PNIPAM-3 shows two bands at 1644  $\text{cm}^{-1}$ , 1560  $\text{cm}^{-1}$  and 1544  $\text{cm}^{-1}$ , which correspond to the typical amide I and II stretch vibrations of PNIPAM polymer. This finding indicates that the PNIPAM polymer is grafted onto the fabric surface by impregnation method<sup>36,37</sup>.

### 3.2.4 TG Analysis Results

In order to investigate the effect of polymer application on the thermal stability of the fabric and to prove the presence of the polymer on the fabric

structure, TG analysis has been performed for the untreated, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics. The data obtained from the TG analysis are given in Table 1. The initial weight loss of the untreated, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics is resulted from the evaporation of absorbed water by the fabric at 100 °C, 106 °C and 116 °C respectively. The important weight loss (75.51%) of the untreated fabric occurs in the temperature range 307-384 °C. Degradation of the saccharide rings in the structure of cellulose molecules and the breakage of the molecular chains cause this weight loss<sup>38</sup>. The major weight loss of the PNIPAM polymer incorporated fabrics is started at 295 °C for CF-PNIPAM-3 and at 291 °C for CF-PNIPAM-5. The weight loss value is determined as 58.62% for CF-PNIPAM-3 fabric and 60.07% for CF-PNIPAM-5 fabric in this degradation interval. According to the literature findings, the degradation of the PNIPAM polymer takes place in two stages, with the first mass loss at 241 °C and the second mass loss at 429 °C<sup>39</sup>. It is concluded that the thermal decomposition of the polymer-treated fabrics starts at lower temperatures with lower weight losses as compared to the untreated fabric. This early degradation in the fabric structure is due to the presence of PNIPAM polymer added to the fabric structure. On the other hand, esterification of the cellulose molecules with BTCA before polymer application causes the reduction of thermal degradation in cellulose molecules, resulting in lower weight loss in this degradation step. As known, esterification of cellulose molecules with BTCA increases the thermal stability of the structure<sup>40</sup> and provides flame retardant property<sup>41</sup>.

### 3.2.5 Determination of Hydrophilic-hydrophobic Properties

Thermo-responsive properties of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics are examined by observing the sinking behavior of the fabrics in the water at different temperatures. The photos of the fabric samples in the water with 20 °C and 40 °C are shown in Fig. 5. As seen in Fig. 5, all the fabric samples (untreated, CF-PNIPAM-3 and CF-PNIPAM-5) sink in water at 20 °C because of their hydrophilic character. When the water is heated to 40 °C, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics move to towards the surface of the water and remain there. At

Table 1 — TG data and weight loss of the PNIPAM polymer-treated and untreated cotton fabrics

Sample	Degradation temperature Interval, °C	Weight loss, %	Residual weight at 320 °C (T <sub>320</sub> ), %	Weight loss after washing,%		
				1 washing	5 washings	10 washings
Untreated cotton fabric	307-384 (1st Step)	75.51	87.76	0.00	0.00	0.00
CF-PNIPAM-3	295-358(1st Step)	59.12	77.26	12.50	14.29	14.29
CF-PNIPAM-5	291-354 (1st Step)	59.34	76.18	18.18	25.00	25.00



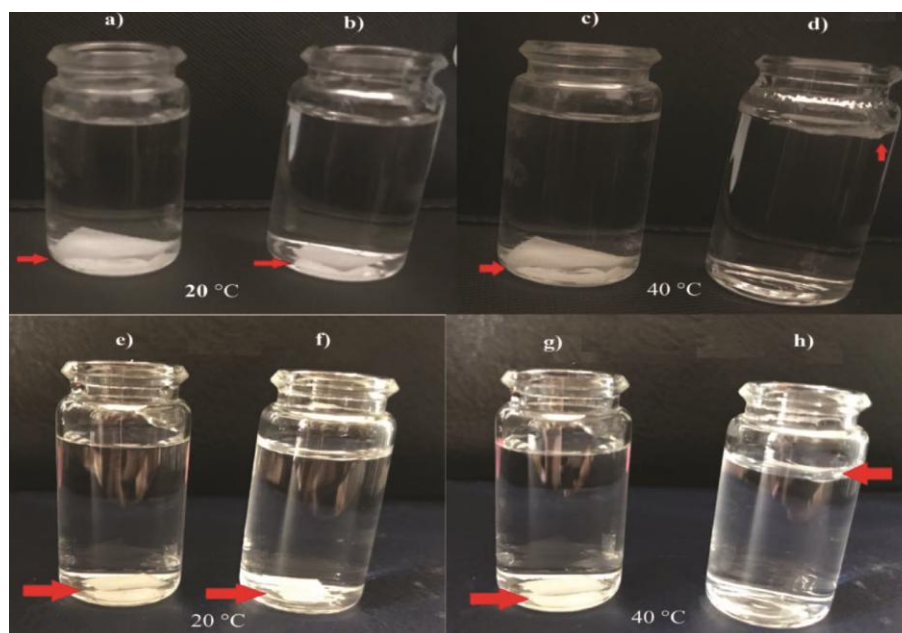


Fig. 5 — Images of fabrics in distilled water at 20 °C and 40 °C [(a) untreated fabric at 20 °C, (b) CF-PNIPAM-3 at 20 °C, (c) untreated fabric at 40 °C, (d) CF-PNIPAM-3 at 40 °C, (e) untreated fabric at 20 °C, (f) CF-PNIPAM-5 at 20 °C, (g) untreated fabric at 40 °C, and (h) CF-PNIPAM-5 at 40 °C]

temperature above the LCST of the polymer, polymer molecules on the fibre surface changes their characteristics from hydrophilic to hydrophobic and the surface tension between polymer molecules and water molecules is increased<sup>25, 42</sup>. In contrast, untreated cotton fabric stays at bottom of the water because of its hydrophilic character. These findings indicate that CF-PNIPAM-3 and CF-PNIPAM-5 fabrics exhibit hydrophilic/hydrophobic transition, depending on change in temperature.

### 3.2.6 Wetting Time Test Results

Thermo-responsive hydrophilic/hydrophobic properties of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics are investigated by wetting time test carried out at different temperatures (20 °C and 40 °C). The wetting time at 20 °C is measured to be 0 s (water drop absorbed instantly by the surface) for untreated fabric. CF-PNIPAM-3 and CF-PNIPAM-5 fabrics absorbed the water drop at 3.25 s and 4.3 s respectively. Test results indicate that the fabrics exhibit hydrophilic character. When the temperature of the fabric surfaces is increased from 20 °C to 40 °C, the wetting time increases from 3.25 s to 42.6 s for CF-PNIPAM-3 fabric and from 4.3 s to 80.93 s for CF-PNIPAM-5 fabric. In contrast, wetting time of the untreated cotton fabric does not change, depending on increasing temperature. Consequently, PNIPAM polymer-treated cotton fabrics exhibit changing

wetting behavior, depending on the change in temperature. Besides, increase of polymer presence in the fabric structure causes the thermo-responsive transition to become more pronounced.

### 3.2.7 Water Uptake Test Results

The water uptake test is carried out at temperatures between 25 °C and 40 °C, increasing the temperature at 2 °C intervals. The test is performed to investigate thermo-responsive water uptake properties of the fabrics. As seen in Fig. 6 (a), no significant change is observed in the water uptake behavior of the cationized, BTCA-3 and BTCA-5 fabrics depending on increasing temperature. However, BTCA-3 and BTCA-5 fabrics show less water absorption capacity as compared to the cationized fabrics. The water absorption of the cotton fabric depends on H bonds formed between OH groups of the cellulose molecules and water molecules. The cellulose molecules in the amorphous region and situated in the outer surface of the crystal region allows formation of H-bonds with water molecules. As a result of the cross-linking of the cellulose with BTCA, OH groups of the cellulose molecules are blocked by the carboxylic acid groups of BTCA due to esterification reactions. This is the reason of decreasing water uptake of the fabric<sup>41</sup>. The water uptake values of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics start reducing significantly at around the LCST of PNIPAM polymer. The temperature at which the water uptake value of the

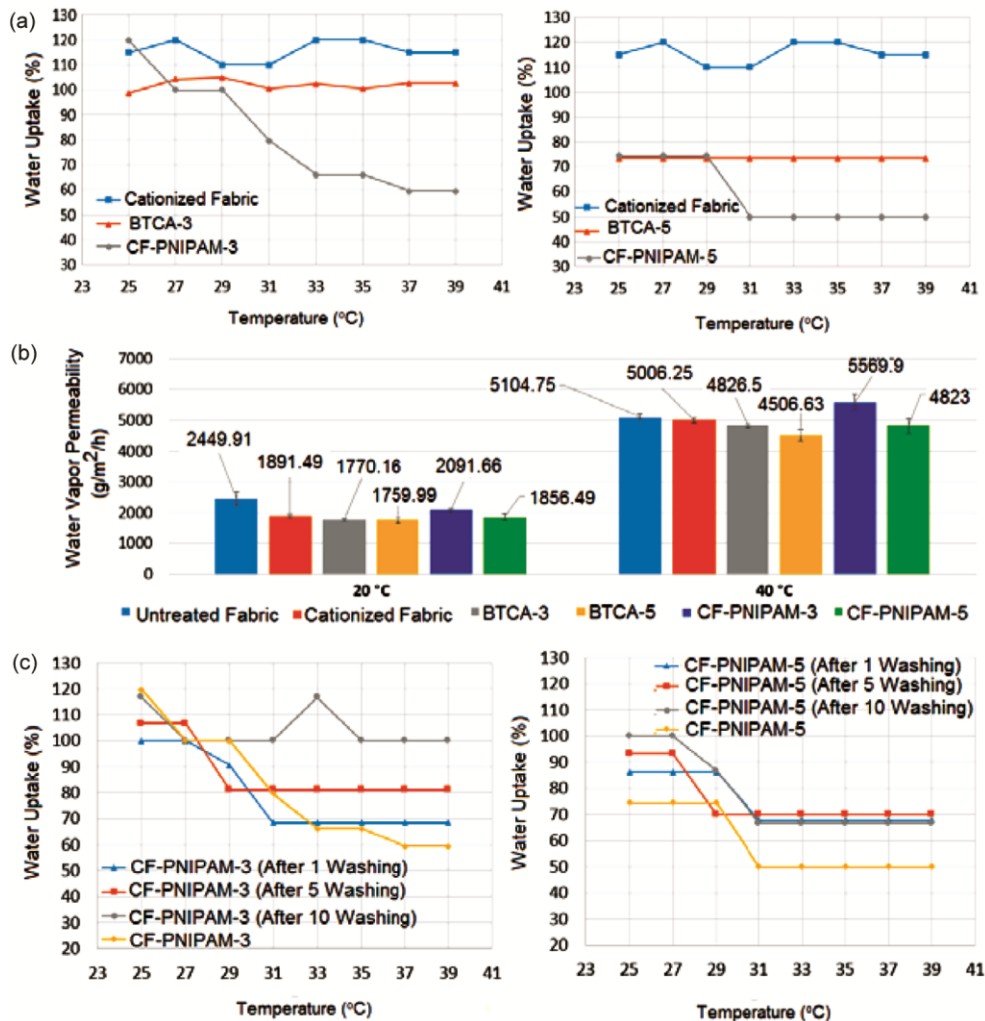


Fig. 6— Test results of CF-PNIPAM-3 and CF-PNIPAM-5 fabrics [Water uptake (a), water vapor permeability (b), and water uptake after washing (c)]

fabrics starts decreasing is determined as 29 ° C. The water uptake ability is decreased from 100 % to 59 % for the CF-PNIPAM-3 fabric and from 73 % to 50 % for CF-PNIPAM-5 fabric. The change in the water uptake values of the fabrics done to the increase in temperature is more prominent for CF-PNIPAM-3 fabric. It is determined that this result is due to the high hydrophilic character of the CF-PNIPAM-3 fabric as a result of the application of BTCA at low concentration. Thus, the transition from the hydrophilic character to the hydrophobic character becomes more evident. In conclusion, decrease in water uptake values of the polymer-treated fabrics at around the LCST value of the PNIPAM polymer indicates that the fabrics alter their hydrophilic character to hydrophobic character depending on increase in temperature. This finding proves that the fabrics exhibit thermo-responsive water uptake property.

### 3.2.8 Contact Angle Measurement Results

Contact angle of the fabrics has been measured on fabric surfaces heated from 25 ° C to 50 ° C. The contact angle of the untreated cotton fabric could not be measured both of temperatures because of absorption of the drop of water and it is accepted to be 0°. Unlike untreated fabric, a certain contact angle at 25 ° C is measured for the polymer-treated fabrics. It shows hydrophilic character of the fabrics, which is decreased insignificantly because of the BTCA cross-linking of cellulose molecules before polymer application. On the contrary, the contact angles of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics start increasing at around the LCST value (31 ° C) of the PNIPAM polymer. The maximum contact angle is measured as 62.77° for CF-PNIPAM-3 and 62.76° for CF-PNIPAM-5. Increase in contact angles of CF-PNIPAM-3 and CF-PNIPAM-5 results from the

thermo-responsive property of the PNIPAM polymer in the fabric structure. At temperatures above the LCST value of the PNIPAM polymer, its hydrophobic groups become dominant, which causes the fabric hydrophobic property. However, the contact angle values of the polymer-treated fabrics are found below  $90^\circ$  and does not reach high enough to demonstrate their hydrophobic. This is due to the reduced surface roughness as a result of inter-fibre gaps filled by polymer molecules.

### 3.2.9 Surface Energy Results

In order to analyze of the thermo-responsive property and investigate surface energy change in the fabrics due to the change in temperature, their surface energy values are calculated using static contact angles for different liquids (water, ethylene glycol, ethanol). The surface energy of the untreated cotton fabric goes up from 166.26 mN/m to 174.11 mN/m with the increase in temperature. This result reveals the hydrophilic character of the untreated fabric, improving slightly with increasing temperature. The surface energy of the CF-PNIPAM-3 fabric (143.90 mN/m at  $20^\circ\text{C}$ ) is decreased to 48.53 mN/m at  $40^\circ\text{C}$ . Similarly, its polar components are decreased from 127.39 to 47.84 when the temperature is increased from  $20^\circ\text{C}$  to  $40^\circ\text{C}$ . The decrease in fabric surface energy and polar groups due to the increase in temperature shows the increase in the hydrophobic character of the fabric<sup>43-45</sup>. Consequently, the hydrophilic character of the CF-PNIPAM-3 fabric is changed to hydrophobic above the LCST of the polymer.

### 3.2.10 Water Vapor Permeability Test Results

As already known, water vapor permeability is a feature associated with fabric porosity and hydrophilic character. In this study, the effect of the thermo-responsive polymer application on the water vapor permeability of the fabrics is examined by the water vapor permeability measurements carried out at  $20^\circ\text{C}$  and  $40^\circ\text{C}$ . The water vapor permeability values of the untreated, the cationized, the BTCA and the polymer-treated fabrics are given in Fig. 6 (b). At  $20^\circ\text{C}$ , the water vapor permeability of the pretreated fabrics is decreased significantly as compared to untreated fabric. This result is attributed to the increasing hydrophobic character of the fabrics because of the crosslinking of the OH groups of the cellulose molecules with BTCA and cationizing agent. Similarly, water vapor permeability values of the

CF-PNIPAM-3 and CF-PNIPAM-5 fabrics decrease as compared to untreated fabric. However, their water vapor permeability is increased as compared to the pretreated fabrics (the cationized and cross-linked fabrics). The increase in water vapor permeability of the CF-PNIPAM-3 fabric is found significantly higher as compared to the pretreated fabrics ( $p < 0.05$ ). This significant increase is attributed to the increase in hydrophilicity of the fabric. According to the test results performed at  $40^\circ\text{C}$ , water vapor permeability of all the fabrics increases because of the evaporation of more water molecules at high temperature. However, the vapor permeability of the CF-PNIPAM-3 is found higher as compared to the untreated fabric. The CF-PNIPAM-3 has the highest vapor permeability statistically ( $p < 0.05$ ). Above the LCST, hydrophilic interactions decrease and hydrophobic interactions become dominant between the PNIPAM polymer molecules, resulting in shrinkage of the polymer structure. The fabric pores open because of the shrinkage of the polymer structure in the fabric structure. The opening pores in the fabric structure affect the water vapor permeability positively. However, water vapor permeability of the CF-PNIPAM-5 fabric is not as high as expected. The increase in the amount of polymer inside the fabric structure fills the gap between the fibre and causes limited pore opening due to polymer shrinkage. This finding is supported by fabric SEM images. As a result, the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics exhibit thermo-responsive water vapor permeability by changing their hydrophilic character and porosity with changing temperatures. The hydrophilic character and shrinkage of the polymer are determined as the effective parameters on the thermo-responsive water vapor permeability of fabrics. The hydrophilic character of the polymer below the LCST causes increase in water vapor permeability. On the contrary, the swollen polymer molecules in the fabric structure below the LCST reduces the water vapor permeability, because of the reduced porosity. On the other hand, increase in the porosity of the fabric above the LCST of the polymer effectively increases water vapor permeability.

### 3.2.11 Bending Rigidity Test Results

The fabric bending rigidity is a feature associated with the handle of the fabric, and the finishing treatments of the fabric cause regression of bending stiffness. In this study, the effect of PNIPAM polymer

application on the bending rigidity of the fabrics has been investigated. The bending rigidity of the untreated, BTCA-3, BTCA-5, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics are found to be 170.74 mg.cm, 193.36 mg.cm, 209.43 mg.cm, 213.24 mg.cm, 334.7 mg.cm respectively. The bending rigidity of the all treated fabrics increases significantly as compared to the untreated fabric. This increment in bending rigidity for BTCA-5 and fabrics containing polymer is found statistically significant ( $p < 0.05$ ). Besides, when polymer concentration is increased from 30 g/L to 50 g/L, the statistically significant increase is observed in bending rigidity compared to the all treated fabrics ( $p < 0.05$ ). The increase in bending rigidity stemmed from the fact that the polymer and BTCA covering the surface of the modified fabrics increases the resistance to bending by limiting the movement of fibre and yarns<sup>46</sup>.

### 3.2.12 Tear Strength Test Results

To investigate the effect of the PNIPAM polymer application on the fabric tenacity, tear strength test has been performed. Tear strength of the untreated, BTCA-3, BTCA-5 CF-PNIPAM-3, and CF-PNIPAM-5 fabrics are measured to be 4.95 N, 2.51 N, 1.99 N, 1.84 N, and 1.18 N, respectively. According to the test results, the fabric tear strength gradually decreases after each pretreatment and polymer application. Decrease in the tear strength values is found significant statistically ( $p < 0.05$ ). As previously explained, BTCA cross-linking and PNIPAM polymer application causes increase in bending rigidity of the fabrics. The bending rigidity of the fabric has a significant effect on tear strength of the fabric. When the force of the bending strength increases, tear strength decreases as a result of the breaking of yarns one by one<sup>47</sup>.

### 3.2.13 Durability of Thermo-responsive Property

In order to investigate the durability of thermo-responsive feature of the fabric, change in the water uptake value as well as weight of the fabrics after repeated washings has been investigated. Changes in the weight of untreated, CF-PNIPAM-3 and CF-PNIPAM-5 fabrics after 1 washing, 5 washings and 10 washings are given in Table 1. The weight of the untreated fabric does not change after the washing cycles and so the weight loss remains as 0%. The significant loss in the weight of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics occurs after the first wash. No change in the fabric weight after the fifth wash is observed. Besides, weight loss in the CF-PNIPAM-5

fabrics is higher. Based on this result, it is possible to say that the increased polymer concentration results in more weight loss after washing in fabric

In order to investigate whether PNIPAM applied fabrics exhibit thermo-responsive property after repeated washings, the change in absorption capacity of the washed fabrics depending on increase in temperature is also investigated and the results are given in Fig. 6 (c). As previously explained, absorption capacity of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics is decreased at temperatures above the LCST value of the PNIPAM polymer. This reduction results from the hydrophobic character and shrinkage of the polymer in the structure of the fabric. According to the results given in Fig. 6 (c), water absorption capacity of the CF-PNIPAM-3 and CF-PNIPAM-5 fabrics is gradually decreased after each washing. Consequently, after tenth washings, CF-PNIPAM-3 fabric lose its thermo-responsive water uptake property while CF-PNIPAM-5 fabric retains its thermo-responsive property.

## 4 Conclusion

In this study, PNIPAM polymer has been synthesized by free radical addition polymerization method and applied onto the cotton fabric by double-bath impregnation method in order to develop thermo-responsive intelligent textile material. According to the chemical and thermal analysis results, PNIPAM polymer that has LCST value of 31 °C and exhibits thermo-responsive property has been synthesized successfully. The number average molecular weight of the synthesized PNIPAM polymer is calculated as 4300 g/mole by cryoscopy method.

FTIR and SEM analysis results clearly show that the PNIPAM polymer has been successfully applied onto fabric. SEM images show that the PNIPAM polymer is completely coated onto the fibre surfaces and has formed inter-fibre connections. The uniform and smooth coatings are formed throughout the fabric surfaces. Polymer application causes increase in the thickness of the fabric at temperatures below LCST because of the coating of fibre surfaces by swollen polymer molecules. Wetting time and water uptake tests, contact angle and surface energy measurements performed at different temperatures show that the polymer-treated fabrics exhibit variable hydrophilic-hydrophobic properties depending on change in temperature. According to the water vapor permeability test, a polymer concentration of 3 % is found sufficient to manage water vapor permeability

of the fabric with the controllable swelling and shrinkage behavior and variable hydrophilic/hydrophobic character of the polymer molecules depending on change in temperature. However, the thermo-responsive feature of the fabric treated with the polymer at 3% concentration is lost after 10 washings. To produce more wash-resistant thermo-responsive fabric by applying PNIPAM polymer, the polymer with higher molecular weight can be synthesized or usage of different binders can be investigated.

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