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Development of Temperature and pH Responsive Smart Cotton Fabrics by P(NIPAM–co-MAM) Copolymer Finishing

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ABSTRACT

In this study, fabrication of smart polymer and cotton fabrics with temperature- and pH-responsive as well as antibacterial activity was aimed. For this aim, random poly(N-isopropylacrylamide-co-methacrylamide) P(NIPAM-co-MAM) copolymers containing different ratio of NIPAM/MAM monomers were synthesized through free radical addition polymerization method via 2,2'-azobis (2 methylpropionamide) dihydrochloride as an initiator. Analysis results showed that the copolymers were synthesized successfully and their LCST values were in the range of 33°C to 41°C. A selected sample of the synthesized copolymers was applied to the cotton fabric via double-bath impregnation method and thermo-responsive wetting property of the fabric was examined via wetting time and water uptake tests, contact angle measurement. The test results indicated that hydrophilic character of the fabric changed to the hydrophobic character reversibly depending on change in temperature. Besides, the fabric exhibited pH-responsive water absorption ability. The fabric could manage water vapor permeability via changing its pore size as well as hydrophilic character depending on temperature. Besides, it was concluded that the fabric had strong antibacterial activity against *S.aureus* bacteria.

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KEYWORDS
Smart textile, thermo-responsive polymer, stimuli responsive, pH-responsive, cotton fabric

1. INTRODUCTION

Clothing textiles are objects with a large surface area used notably for the protection of the body from environmental conditions. Therefore, they can be used with great benefit for the wearer as a smart interface. For example, the fabrics used to fabricate clothing could develop better thermal exchange with the environment as active surface to manage temperature and moisture of the body. The conventional clothing fabrics save passive thermophysiological comfort to the clothing, which is inadequate to adapt to the changes in environmental conditions and activity levels of the wearer. However, the feature, known as active comfort regulation which means to manage the heat transfer between the body and environment in a dynamic environment and keep the body temperature constant in sudden environment (temperature and humidity) change, can be achieved with the smart fabrics. The active comfort regulation function of the clothing can be provided by application of the various smart materials such as stimuli-responsive polymers, shape memory polymers and phase change materials to the clothing fabrics. [1,2] Nowadays, the textile industry shows an increasing interest in environmentally responsive or stimuli-responsive textiles containing stimuli-responsive polymer which is one of the kind of the smart polymers.[3]

Temperature-responsive polymer which is one of the type of the stimuli responsive polymers has a critical solution temperature (CST), which can be defined as a critical temperature. The solution of the polymer exhibits a phase separation at the CST, which moves from the isotropic state

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to the anisotropic state. The lower critical solution temperature (LCST) defined as a critical temperature at which the polymeric solution shows a phase separation. A polymer with lower critical solution temperature (LCST) shows the solution phase below LCST and becomes insoluble over LCST. [4] Thermo-responsive polymers with LCST change their hydrophilic-hydrophobic properties reversibly depending on change in temperature. At temperatures below LCST, polymer macromolecules are swollen state because of the formation of hydrogen bonds between hydrophilic groups in the polymer chain and the water molecules taken into the structure, and exhibit hydrophilic character. At temperatures above LCST, polymer macromolecules shrink due to increased interaction between hydrophobic groups in molecular structure, and display hydrophobic character. [5-8] The change in porosity caused by the swelling or shrinkage of the polymer molecules enables use of these polymers for smart filters [9,10] and smart textile materials. [11-14] Recently, these polymers have been used in drug release [15, 16] and tissue engineering. [17] Poly(N-isopropylacrylamide) (PNIPAM) consisting of amide and propyl moieties is the most known of thermo-responsive polymer and exhibits temperature-dependent hydrophilic/ hydrophobic switching at the critical solution temperature of 32 °C. [18] Below LCST, water molecules solve the hydrophilic amide groups of the PNIPAM and causes it to be water soluble and in a flexible, coiled form. Above LCST, PNIPAM becomes insoluble in water, the interactions between its hydrophobic propyl groups become stronger and the hydrogen bonds weaken, resulting existing of globular form of the molecules. The polymer chains collapse and water loss from the structure occurs. LCST of the PNIPAM polymer can be changed by copolymerization of the NIPAM monomer with various polymers such as poly (ethylene glycol), poly (acrylic acid) and cellulose, etc. [19-21] The copolymerization with hydrophobic polymers results a decrease in LCST of the PNIPAM. On the other hand, copolymerization with hydrophilic polymers leads to an increase in LCST due to the overall increase in hydrophilicity of the molecule and hence an increase in the hydrogen-bonding interactions between the polymer and water molecules. [22] Additionally, copolymerization of the PNIPAM with ionic molecules offers pH sensitivity to the polymer as well as thermo-sensitivity. The pH responsive polymers are smart polymers that can react to pH change as a variable condition. There are acidic or basic ionizable groups in their structures which take or give a proton depending on change in pH. The proton exchange results change in the polymer chain conformation, resulting in swelling or shrinkage of the polymer. [23, 24] The pH responsive polymers with acidic side groups ionize when the pH of the medium is higher than their value of pKa (the acid dissociation constant), which causes an increase in the hydrophilicity of the polymer network. In contrast, the hydrophilicity of the pH responsive polymers with basic side groups rise at the pH value lower than pKb (the basic dissociation constant). [25-27] A pH and thermo-responsive copolymer attract or repel the water according to ambient pH and temperature. Hence, textiles functionalized with pH/thermo-responsive polymer are expected to exhibit controlled moisture/water management properties, depending on changes of their surrounding environment. Such functionalized textiles offer new opportunities for applicable to biomedical and protective clothing. [28]

According to the literature survey, copolymers of the PNIPAM with various co-monomers have been synthesized to tailor LCST for particular applications. Some researchers synthesized the PNIPAM copolymers be able to apply to the fabrics for usage in developing smart textiles. For example, Wang et al. (2016) were synthsized poly(N-isopropylacrylamide)/chitosan (PNIPAAm/Cs) hydrogels using redox initiator and applied to cotton fabric using glutaric dialdehyde (GA) as a crosslinker in order to increase the thermo-sensitive behavior and antibacterial activity. The LCST of the synthsized hydrogel was determined as 33 °C. Their results confirmed that the fabric exhibited hydrophobicity around the LCST and high antibacterial activity. [29] Štular et al. (2017) investigated the fabrication of stimuli responsive cotton fabric by applying temperature and pH responsive microgel and nanogel. They applied temperature responsive poly (N-isopropylacrylamide) and pH responsive chitosan hydrogels to the cotton fabric by pad-dry method. The results indicated that fabric having thermo-responsive air and moisture management ability was achieved regardless of hydrogel particle size. Besides, it was determined that their application at 4 times lower concentration, due to the decreasing size of the nanogels, gave lower stiffness as well as comparable responsiveness to the fabric. [30] Wang et al. (2017) synthesized a random poly(n-isopropylacrylamide-co-ethylene glycol methacrylate) P(NIPAM-co-EGMA) copolymer by atom transfer radical polymerization (ATRP) method and crosslinked it to cotton fabric via cross-linker citric acid. They concluded that increase in the molar ratio of ethylene glycol methacrylate (EGMA) increased the transition temperature of the copolymer due to the hydrophilic character of the EGMA. However, Tg of the copolymer significantly droped with increase in EGMA molar ratio because of its hydrophobicity and low Tg. The cotton fabrics cross-linked with P(NIPAM-co-EGMA) exhibited a dual function. Above transition temperature, air and moisture permeability of the cotton fabrics crosslinked by copolymer dramatically increased due to porous structure formed on the fabrics. The cross-linked fabrics were able to nearly recover the values of the untreated fabric although they were polymer coated. Additionally, the fabrics had significantly higher inhibition of bacterial adhesion at room temperature compared to that of original cotton, reaching values of PEGMA coatings. [31] Huang et al. (2019) was synthesized a random poly (N-isopropylacrylamide-co-furfuryl methacrylate) copolymer through free radical polymerization method using 2,2'-azobis (2-methylpropionitrile) (AIBN) as an initiator. The researchers determined that LCST value of the copolymer decreased compared to the PNIPAm polymer because of introduction of the hydrophobic comonomer. The nylon fabric treated with the synthesized copolymer could able to control its pore size by the shrinkage and swelling of the copolymer depending on change in temperature.[32] Chaudhuri and Wu synthesized a random poly[(N-isopropylacrylamide)-co-(2-hydroxyethylmethacrylate)-co-(N-methylolacrylamide)] copolymer using free radical polymerization method and coated it onto polyethylene terephthalate fabric. They revealed that thermo-responsive copolymer which LCST was tailored by changing the molar ratio of the comonomer was successfully synthesized. The fabrics treated with copolymers exhibited switchable wettability and moisture absorption/release properties as a function of the temperature. The moisture management feature of the fabric depending on temperature provided active thermophysiological clothing comfort by balancing the humidity of the microclimate with the surrounding air conditions. [33]

Cotton is a natural, breathable fiber and has a soft attitude, high moisture and sweat absorption capacities. These properties make the cotton clothing the popular in daily life. However, the cotton fabric absorbs sweat and metabolic products, which may provide nutrient sources for the growth of microorganisms such as bacteria and fungi. These microorganisms under atmosphere conditions grow rapidly and lead to unpleasant odor, stains, discoloration, reducing the fabric mechanical strength and increasing cross-contamination probability. [34] To overcome these type problems and develop the thermal clothing comfort there is a high requirement for cotton fabrics having antibacterial activity and dynamic temperature regulation function in various end use areas such as sport wearing and medical textiles. Considering this requirement, this study aimed to fabricate cotton fabric having active thermal comfort regulation and antibacterial activity by cross-linking of a dual function polymer.

For this aim, LCST type temperature- sensitive polymer, which could provide dynamic thermal regulation by change from a warming fabric to a cooling fabric above the LCST, was preferred. Among these polymers, PNIPAM polymer, whose LCST value was close to human body temperature, was chosen. In the study, it was focused on synthesis of a random PNIPAM copolymer containing components responsible for temperature/pH sensitivity and antibacterial activity. The authors in their previous work, a thermo-responsive PNIPAA homopolymer was synthesized and grafted onto the cotton fabric using free radical polymerization in order to fabricate thermo-responsive cotton fabric capable of smart moisture/water management. In the study, polymer synthesis and grafting to the cotton fabric were carried out simultaneously by a single process.[7] In this study, unlike their previous studies, the authors focused on synthesizing a new PNIPAM copolymer providing antibacterial activity and pH sensitive functions as well as smart moisture management and wettability depending on temperature to the cotton fabric. For this aim, P(NIPAM-co-MAM) copolymers were synthesized by free radical addition polymerization method using different ratio of NIPAM/MAM monomers and then applied to the cotton fabric by a double bath impregnation process. In the study, the effect of the addition of methacrylamide to the poly(N-isopropylacrylamide) back bone on the LCST of the copolymer was also investigated. The chemical structures of the synthesized copolymers were examined using Fourier- Transform Infrared (FT-IR) spectroscopy and 1H-Nuclear magnetic resonance (1H NMR) analyses. Turbidity test was performed to investigate the thermo-responsive behavior of the copolymers. The cotton fabrics capable of pH and temperature responsive smart moisture/water management were fabricated by application of the synthesized P(NIPAM-co-MAM) copolymer. For this, the copolymer with the closest LCST value to body temperature was cross-linked to the cotton fabric accompanied by a carboxylic acid-based cross-linker (BTCA) via a double bath impregnation method. Scanning Electron Microscopy (SEM) analysis was carried out to study morphology of the copolymer-applied fabrics. To characterize thermo-responsive hydrophilic/hydrophobic behavior of the fabrics, the wetting time test, water uptake test, contact angle measurements and water vapor permeability test were performed at temperatures below and above the LCST. To study pH sensitivity of the fabrics, the alteration in their water absorption ability at acidic, neutral and basic pH values was determined at temperature of 20 °C. Antibacterial activity of copolymer containing fabric against *S. aureus* bacteria was tested by quantitative test method. The effect of polymer application on the mechanical properties of the fabrics was measured by tear strength and bending stiffness tests. Besides, durability of the thermo-responsive property of the copolymer-applied fabrics was investigated after repeated washings.

2. MATERIAL AND METHOD

2.1 Material

N-isopropylacrylamide (NIPAM) purchased from Sigma Aldrich company was used as monomer to synthesize temperature responsive polymer. Methacrylamide (Acros Organics) (MAM) and 2,2'-azobis (2 methylpropionamide) dihydrochloride (AMPA) (Acros Organics) were used as co-monomer and initiator, respectively. All chemicals used directly without purification. Polymer synthesis was carried out in distilled water.

A 100 % cotton plain weaved fabric, which was scoured and bleached, supplied from Söktaş Textile Company (Turkey) was used to produce temperature responsive fabric. The weight of the fabric was 151 g/m^2 and it had 61 threads per cm in the warp direction and 38 threads per cm in the weft direction. 1,2,3,4-Butanetetracarboxylic acid (BTCA) as cross-linker and sodium hypophosphite (SHP) as its catalyst were used in order to fix the copolymer to the cotton fabric. They were purchased from Sigma-Aldrich company.

2.2. Method

2.2.1. *Synthesis of dual responsive copolymer*

Synthesis of the P(NIPAM-co-MAM) copolymer, expected to exhibit both thermo-responsive and pH-responsive properties was carried out using free radical addition polymerization method. The schematic representation of the polymerization reaction was given in Figure 1. In the synthesis of copolymer, NIPAM/MAM monomer ratios were chosen as 9/1, 9.5/0.5 and 9.75/0.25. NIPAM and MAM monomers were dissolved separately in 15 mL and 5 mL distilled water, respectively, and then the solutions were mixed. AMPA (1 % mole) dissolved in distilled water was added dropwise to the mixture of NIPAM and MAM monomer solutions. The reaction solution poured into glass tube was purged with nitrogen gas for 1 minute and then synthesis of the copolymer was carried out in a water bath for 5 hours at 80 ° C. The powder copolymer was obtained by removing water after the polymerization reaction was terminated. The copolymers synthesized with NIPAM/ MAM monomer ratios of 9/1, 9.5 / 0.5 and 9.75/0.25 were named as P(NIPAM-co-MAM)-1, P(NIPAM-co-MAM)-2 and P(NIPAM-co-MAM)-3, respectively.

2.2.2. *Application of the P(NIPAM-co-MAM)-2 polymer to the cotton fabric*

The P(NIPAM-co-MAM)-2 copolymer was chosen as a sample polymer to apply fabric because of its closest LCST value to human body temperature. Before polymer application, fabric was washed in the bath containing 2 g/L of nonionic surfactant (Span 20) at 60 ° C for 40 minutes in order to remove possible residues, rinsed and dried at room temperature. Polymer application was carried out via a double-bath impregnation method. In the first bath, fabric samples were impregnated with the first bath solution under a pressure of 2 bar and a speed of 2 m/min on laboratory type foulard machine and then dried at 80 °C for five minutes and cured at 160 °C for five minutes. The first bath contained 3.75 g BTCA cross-linker per 1 g polymer and ratio of the SHP catalyst to the cross-linker was 4/1. Fabric treated with the first bath was immersed in the aqueous polymer solution (the second bath at concentration of 30 g/L or 50 g/L) for 1 hour. At the end of 1 hour, the fabric was passed from foulard, dried at 80 °C and cured 160 °C for five minutes. The fabrics treated with polymer concentrations of 3% and 5% were termed as CF-P (NIPAM-co-MAM)-3 and CF-P (NIPAM-co-MAM)-5, respectively. In the study, fabrics treated by BTCA at the same amounts used in the polymer application baths were tested to examine the effect of BTCA application on the properties of the fabric. The abbreviations for these control fabrics were defined as BTCA-3 and BTCA-5.

2.2.3. *Characterization of the copolymer*

^{1}H NMR and Fourier Transform Infrared (FT-IR) spectroscopy analyses were used to investigate chemical structure of the synthesized P(NIPAM-co-MAM) copolymers. The ^{1}H NMR analysis was carried out on a Bruker 400 MHz instrument and deuterated dimethyl sulfoxide (DMSO) was used as solvent in the analysis. FT-IR spectroscopy analysis was performed using Perkin Elmer Spectrum BX instrument, on KBr disks, between wavenumbers of 4000 cm^{-1} and 400 cm^{-1}. The molecular weights of the synthesized copolymers were determined by cryoscopy method. The basis of this method is to determine the decrease in the freezing point of a solution in which organic matter is dissolved. Water was selected as solvent in the analysis and Equation (1) was used to calculate molecular weight of the polymer.

Where t_d is decrease in freezing point; M is molecular weight of the solute, W_1 is weight of the solvent (g), W_2 is weight of the solute (g) and K_d is freezing temperature drop constant)

$$\Delta Td = \frac{1000xKdxW_2}{M\ xW_1} \qquad \text{Equation (1)}$$

Thermo-responsive properties of the synthesized P(NIPAM-co-MAM) copolymers were examined by turbidity test. In the test, 1 % aqueous polymer solutions were used. The solutions were heated in 1 °C increment from 30 °C to 40 °C and taken their photographs at each temperature increment to observe the temperatures at which they begin to be turbid. The temperature at which the polymer solution began to be turbid was accepted as its LCST value. Additionally, LCST value of a selected copolymer was measured by Differential Scanning Calorimeter (DSC) analysis (Netsch Polyma instrument). DSC analysis was performed range of the temperatures of -10°C and 60 °C at 5 °C/min heating rate under inert nitrogen gas atmosphere at a flow rate of 60 ml/min.

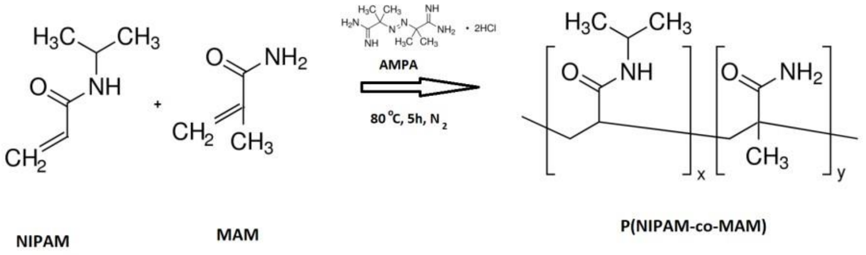

Figure 1. Schematic illustration for the synthesis of the P(NIPAM-co-MAM) copolymer

2.2.4. Characterization of the fabrics

Graft yield of the P(NIPAM-co-MAM)-2 copolymer onto the fabric was calculated using changes in the weights of fabrics before and after the grafting process. Morphology of the fabrics was investigated using Scanning Electron Microscopy (SEM, Phillips XL-30S FEG model). Their chemical structures were studied using FT-IR spectroscopy. The analyses were realized on KBr disk in the range of the wavelengths of 4000 cm^{-1} of 400 cm^{-1}.

In the study, to investigate thermo-responsive wetting properties of the copolymer incorporated fabrics, the fabrics at different temperatures were tested by various tests such as immersion test [7, 35], drop test and water uptake test. Besides, contact angle measurement on the fabrics and surface energy calculation were carried out at temperatures above and below LCST of the copolymer. The wetting times of the fabrics owning 20 °C and 40 °C fabric surface temperatures were determined according to the AATCC 79 test standard. The surface contact angles of the fabric samples were measured by a sessile drop method using a goniometer (Dataphysics OCA 15 plus model instrument) and a CCD camera. Measurements were realized on the fabric surface, the temperature of which was gradually increased from 25 to 35 °C in an air environment with 10-25% relative humidity. The surface temperature of the fabric was checked with a Fluke Ti100 Thermal Imager during measurements. Water uptake of the fabrics was determined at temperatures changing between 25 °C and 35 °C with 2 °C increments using gravimetric method. [7] In order to determine pH responsive behavior of the fabric samples, their water absorption capacity at different pH values (pH 3, pH 7, pH 10) were investigated. The pH of the distilled water was adjusted to pH 3 adding acetic acid and pH 10 adding sodium carbonate (Na_2CO_3). Distilled water at room temperature was used in the test. The sample fabrics were thrown into the water with different pH values and kept in the water for 1 hour. At the end of the test, water uptake value was calculated using gravimetric method. [36,37] In the study, thermo-responsive water vapor permeability of the fabrics treated with copolymer was measured in a drying oven according to the modified BS 3424 control dish method. [7,38] To determine the significant differences ($p < 0.05$) of the test results statistically, a Duncan Multiple Dispersion Tests were applied using SPSS 20.0 software package.

To assess durability of the thermo-responsive features of the fabrics against to repeated washings, fabrics were washed at 30 °C for 30 minutes according to test standard of TS EN 20105-C06: 2001. The washings were repeated ten times. Water uptake capacities of the washed fabrics were measured.

Antibacterial activity of the copolymer incorporated fabrics against gram positive bacteria was determined using ASTM E2149-01 test method. This test method is designed to evaluate the resistance of specimens to the growth of microbes under dynamic contact conditions. Antibacterial activity is determined by calculating the reduction rate in the number of microorganisms living in the solution. The same number of bacteria is inoculated to untreated (pure) and treated samples, and the decrease in the number of bacteria after 24 hours is calculated as a percentage. In the test, *S. aureus* (ATCC 29213) was used as test bacteria. In method, counting of bacterial colonies on the samples immediately after sowing (0 contact time) and after 1 hour, 3 hours and 24 hours' incubation was done using standard counting method and reduction rate in the number of bacteria was calculated using Equation (2). In the formula, A is the number of the bacteria obtained from test samples at contact time "0" and B is the number of the bacteria obtained from test samples incubated for a certain hour. [39]

$$Bacteria\ reduction\ rate\ \mathbf{(\%)} = \frac{(A-B)}{A} x100 \qquad \text{Equation (2)}$$

The effects of polymer application on mechanical properties of the fabrics were examined by tear strength and bending rigidity tests. Tear strength test was carried out according to TS EN ISO 13937-2 standard using a Lloyd LR5K Plus electronic tensile tester. Bending rigidity test was performed according to TS 1409 standard. Statistical analysis of the test results was carried out using the SPSS 20.0 statistical software, and Duncan Multiple Dispersion Tests was performed to determine significant differences ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Characterization of The P (NIPAM-co-MAM) Copolymer

3.1.1. FT-IR analysis results

The successful copolymerization of the NIPAM and MAM monomers were proved using FT-IR spectroscopy. As seen from FT-IR spectra given in Figure 2, the emerging C=C stretching peaks at 1620 cm^{-1} in the spectrum of NIPAM and at 1603 cm^{-1} in the spectrum of MAM disappeared in FT-IR spectrum of the P(NIPAM-co-MAM)-2. Disappeared C=C peak originated from addition reaction realized between NIPAM and MAM monomeric radicals, which were formed by opening of their double bonds by initiator. Moreover, the peaks at 1654 cm^{-1} and 1742 cm^{-1} in the spectrum of P(NIPAM-co-MAM)-2 were stretching vibrations of the C=O groups of the monomers. These two peaks showed the presence of the monomers in the copolymer molecule chain. The peaks at 1560 cm^{-1} and 1540 cm^{-1} in the P(NIPAM-co-MAM)-2 spectrum were characteristic bending vibrations of NH (amide II) group of the NIPAM monomer. The asymmetric and symmetric bending vibration of $-CH_3$ in isopropyl groups of the NIPAM monomer appeared at 1388 cm^{-1} and 1370 cm^{-1} in the spectrum of copolymer. The peaks at 2928 cm^{-1} and 2858 cm^{-1} in the spectrum of P(NIPAM-co-MAM)-2 were CH stretching peaks.

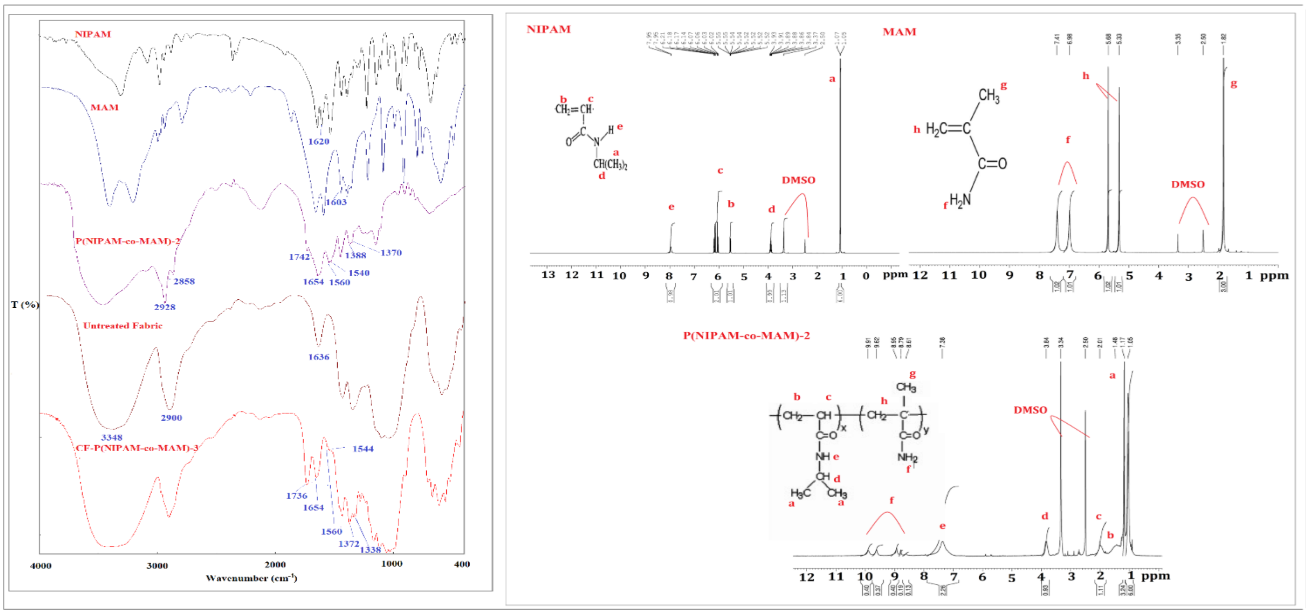

Figure 2. The FT-IR spectra (on the left) and ^{1}H-NMR spectra (on the right) of the NIPAM and PNIPAM

3.1.2. ^{1}H NMR analysis results

Figure 2 showed NMR spectra and molecular formulas of the monomers and copolymer. The protons displayed as "b" and "c" in the molecular formula of the NIPAM monomer appeared in the range of 5.52-5.55 ppm and 6.02-6.21 ppm in the spectrum, respectively. The methyl groups in the isopropyl group were in the range of 1.05-1.07 ppm in the spectrum of NIPAM monomer. The single proton in the isopropyl group, displayed as "d" in the spectrum, appeared at 3.9 ppm. Besides, NH group proton, displayed as “e”, appeared at 7.95 ppm in the spectrum. According to the ^{1}H NMR spectrum of the MAM monomer given in Figure 2 methyl groups illustrated as "g" sharply appeared at 1.82 ppm. The peaks arose at 6.98 ppm and 7.5 ppm in the spectrum of the MAM comonomer were protons of the amine groups which displayed as "f" in the molecular formula. [40] In addition, vinylic hydrogen protons (= CH) illustrated with "h" in the molecular formula were observed at 5.33 ppm and 5.68 ppm. As seen from the spectrum of P(NIPAA-co-MAM)-2 copolymer, peaks of the monomer and comonomer were displaced in the spectrum of the copolymer and peaks of the vinyl groups disappeared. Methylene and methyl groups in the molecular structure of the MAM comonomer and methyl groups in the structure of the NIPAM monomer merged at 1.05 ppm and 1.17 ppm in the ^{1}H NMR spectrum of the copolymer. All these findings showed that the P (NIPAM-co-MAM) -2 copolymer has been successfully synthesized.

3.1.3. Determination of molecular weight

The number average molecular weight of the synthesized copolymers was determined by the cryoscopy method. The number average molecular weight was determined to be 4500 g/mole for P(NIPAM-co-MAM)-1 polymer, 4200 g/mole for P(NIPAM-co-MAM)-2 polymer, 4300 g/mole for P(NIPAM-co-MAM)-3 polymer. The synthesized copolymers were concluded to have low and close to each other molecular weights.

3.1.4. Turbidity test results

To investigate thermo-responsive properties and determine LCST values of the synthesized copolymers, turbidity test was carried out. The aqueous solutions of the copolymers were transparent at a certain temperature range because of their water solubility (Figure 3). As known, a thermo-responsive polymer exhibits hydrophilic property and is water soluble at temperatures below its LCST value. However, polymer is insoluble in the water at temperatures above its LCST value because of increasing interaction between hydrophobic groups in its macromolecule chains. The interaction between hydrophobic groups of the polymer causes phase separation and its solution becomes to be turbid. [5] Temperature at which the polymer solution began to cloudy is accepted as LCST value of that polymer. As seen from Figure 3 a, turbidity of P(NIPAM-co-MAM)-1 copolymer solution started at 41 °C and its LCST value was determined as 41 °C. According to Figure 3 b-c, LCST values of P(NIPAM-co-MAM)-2 and P(NIPAM-co-MAM)-3 were detected as 34 °C and 33-34 °C, respectively. According to turbidity test results, LCST value of the P(NIPAM-co-MAM)-2 copolymer was found close to human body temperature. Therefore, its LCST value was verified by DSC analysis before application to fabric. According to the DSC analysis, LCST value of the P(NIPAM-co-MAM)-2 copolymer was measured as 34 °C (Figure 4). It was concluded that LCST value of the synthesized copolymer increased as the amount of hydrophilic copolymer added to the structure increased. This result was attributed to increasing interaction between the water molecules and hydrophilic and charged groups of the copolymers. Moreover, the P(NIPAM-co-MAM)-2 copolymer was chosen as proper thermo-responsive copolymer to be applied fabric because its LCST value was quite close to the human body temperature.

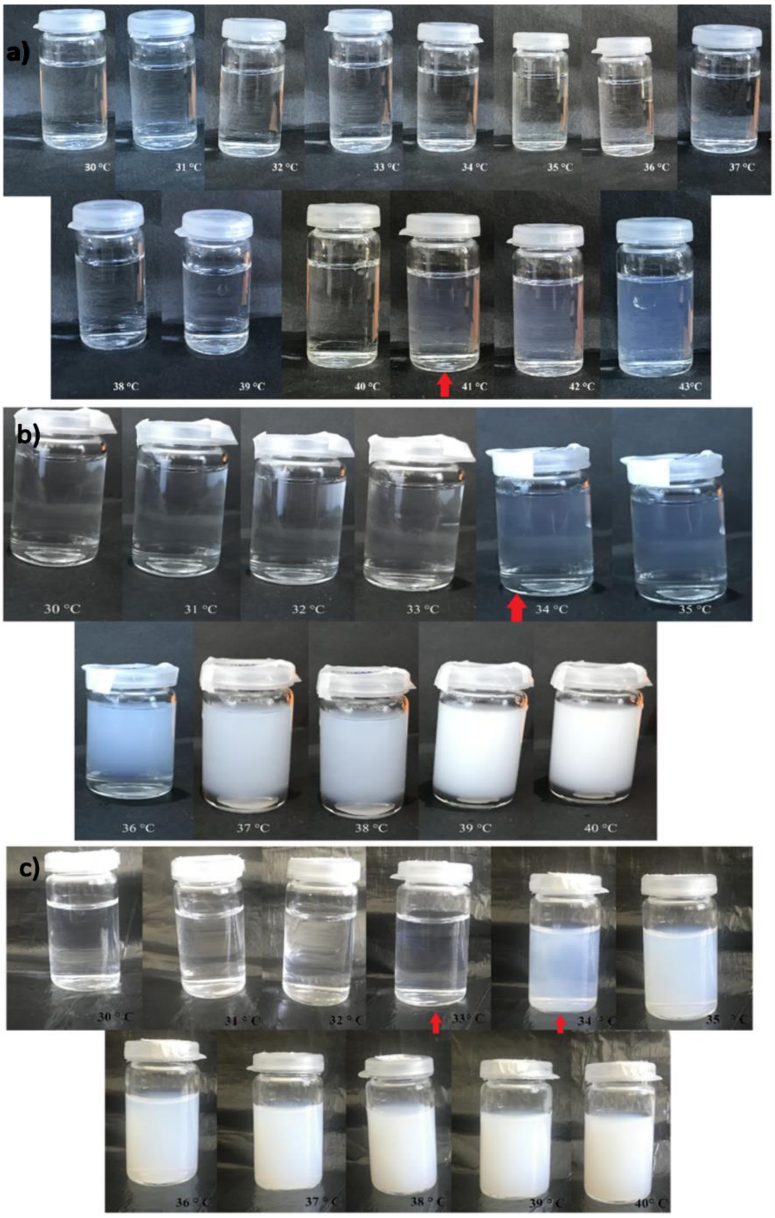

Figure 3. Images of the P(NIPAM-co-MAM)-1(a), P(NIPAM-co-MAM)-2 (b) and P(NIPAM-co-MAM)-3 (c) polymer solutions at different temperatures

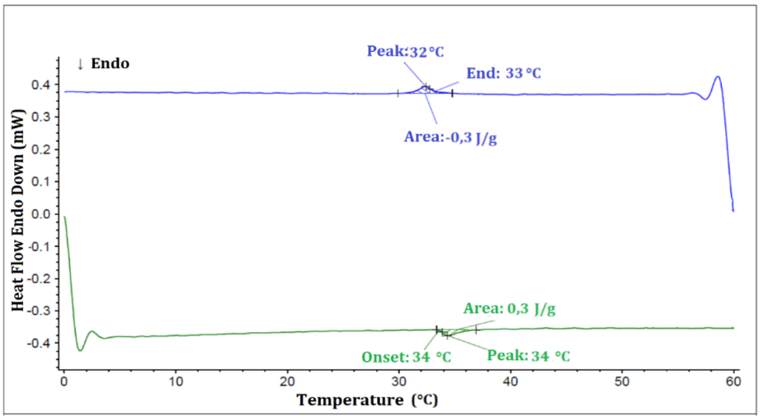

Figure 4. DSC thermogram of PNIPAM-co-MAM-2 copolymer

3.2. Characterization of Dual Responsive Fabric

3.2.1. Determination of grafting yield

Amount of the polymer added on the fabric structure was determined as grafting yield. The values were calculated as 19.24 % for the CF-P(NIPAM-co-MAM)-3 fabric and 20.6% for the CF-P(NIPAM-co-MAM)-5 fabric. According to the results, increase in the polymer concentration impregnated to the fabric slightly increased amount of the polymer transferred to the fabric.

3.2.2. SEM analysis results

Figure 5 indicated SEM micrographs of the untreated fabric and the fabrics treated with P(NIPAM-co-MAM)-2 copolymer. According to the images, fiber surfaces in the structure of the CF-P(NIPAM-co-MAM)-3 and CF-P(NIPAM-co-MAM)-5 fabrics were completely covered by polymer. Besides, the polymeric fractions forming the inter-fiber connections was observed on the CF-P(NIPAM-co-MAM)-3 fabric. However, a smoother and homogeneous coating was formed on the CF-P(NIPAM-co-MAM)-5 fabric surface because of increasing polymer concentration (Figure 5c) and this polymeric coating completely filled the spaces among the fibers.

3.2.3. Chemical analysis results by FT-IR spectroscopy

The chemical structure of the fabrics treated with copolymer was studied by FT-IR spectroscopy to confirm cross-linking of the P(NIPAM-co-MAM)-2 copolymer on the cotton fabric. In FT-IR spectrum of the untreated fabric, the peak at 3348 cm^{-1} corresponded to hydrogen-bonded OH stretching. Besides, the C-H stretching peak at 2900 cm^{-1} and C-H wagging peaks at 1315 -1373 cm^{-1} were observed. The peak appeared at 1636 cm^{-1} was due to absorbed water molecules. [41,42] Compared to the FT-IR spectrum of the untreated fabric in Figure 2, the characteristic peaks of the P(NIPAM-co-MAM)-2 copolymer were observed in the FT-IR spectrum of the CF-P(NIPAM-co-MAM)-3 fabric. The typical amide I and II stretch vibrations of the copolymer were arisen at 1654 cm^{-1}, 1560 cm^{-1} and 1544 cm^{-1}. In addition, the characteristic peaks of the isopropyl groups of the copolymer were observed at 1372 cm^{-1} and 1338 cm^{-1} wavelengths. A peak appeared at 1736 cm^{-1} corresponding to the ester carbonyl group formed between BTCA and the hydroxyl groups (OH) of cotton fabric. [43, 44]

3.2.4. Determination of the thermo-responsive wetting property

The change in hydrophilic property of the fabrics as a function of the temperature was examined by sinking behavior of the fabrics in the water and wetting time tests. Untreated fabric and copolymer-applied fabrics sank in the water at 20 °C because of their hydrophilic character. When the temperature of the water increased to 40 °C, copolymer-applied fabrics moved to the water surfaces while the untreated fabric kept its position in the water (Figure 6). The upward movements of the copolymer-applied fabrics in hot water and their settling on the surface of the water were indicators of their hydrophobic character. The fabrics exhibited hydrophobic character at temperature above

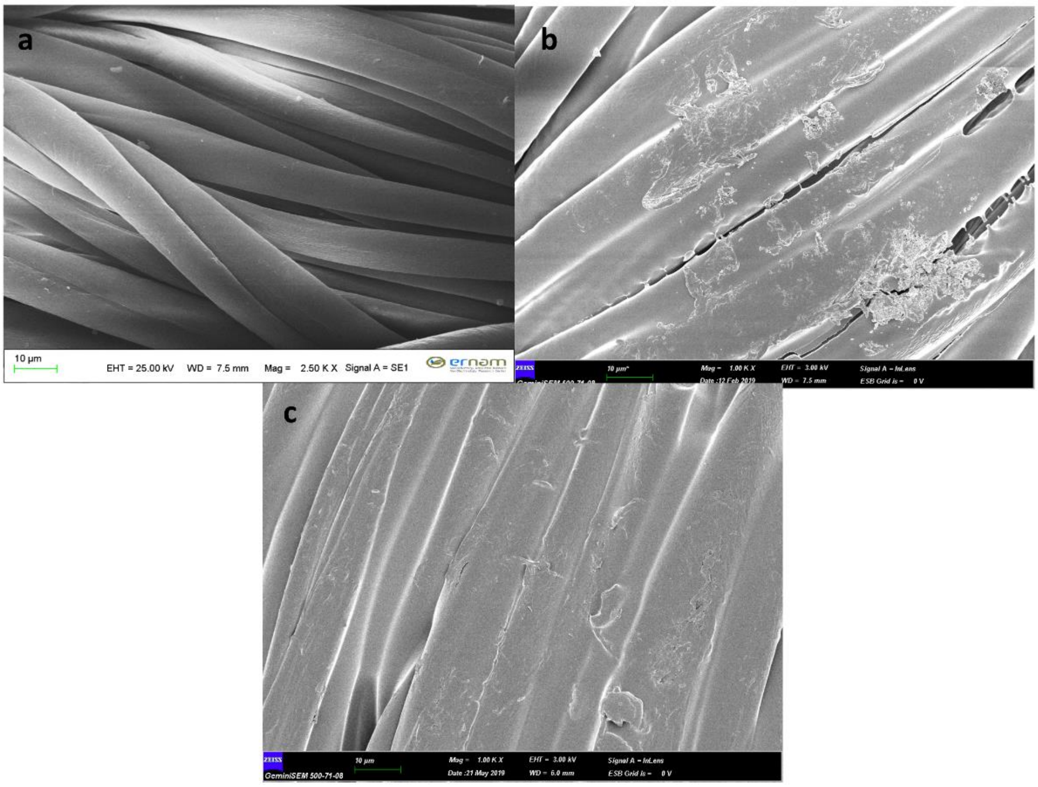

Figure 5. SEM micrographs of untreated cotton (a) [7], CF-P(NIPAM-co-MAM)-3 (b) and CF-P(NIPAM-co-MAM)-5 (c) fabrics.

LCST of the copolymer resulting with decreasing the adhesion force between the copolymer and the water molecules· [7] The wetting time test confirmed these results. Wetting time of the untreated fabric at 20°C and 40°C was determined to be 0 s. Unlike, as the fabric surface temperature increased from 20°C to 40°C, the wetting time rose from 2.40s to 26.60s for the CF-P(NIPAM-co-MAM)-3 and from 3.9 s to 39 s for the CF-P(NIPAM-co-MAM)-5. This result showed that hydrophilic character of the CF-P(NIPAM-co-MAM)-3 and CF-P(NIPAM-co-MAM)-5 fabrics altered depending on change in temperature.

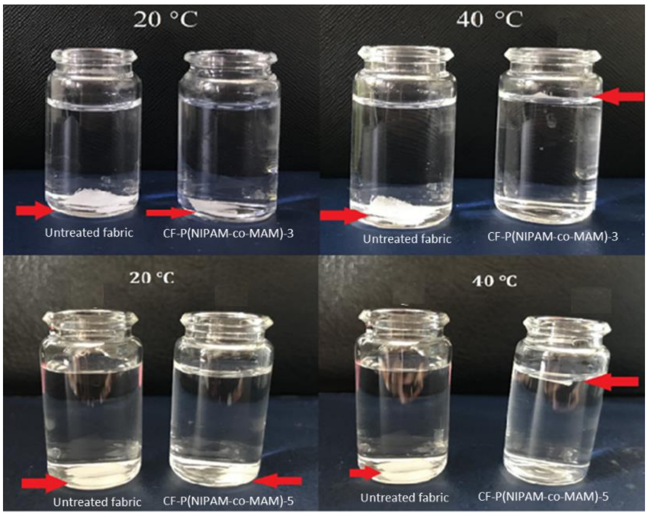

Figure 6. Sinking behavior of the untreated cotton fabric and treated fabrics in distilled water

In the study, thermo-responsive wettability behaviors of the fabrics were examined by measuring contact angle. Figure 7 a showed contact angles of the fabrics measured at different temperatures ranging from 25°C to 50°C. The contact angle of the untreated fabric was accepted to be 0° at each temperature due to the fact that the contact angle value cannot be measured as a result of instant absorption of the water drop. The contact angle of the copolymer-applied fabrics was measured almost 30° at temperature of 25°C. This showed unimportant decrease of the hydrophilic character of fabrics due to crosslinking of the cellulose molecules by BTCA. However, unlike untreated fabric, there was a sudden increase in contact angles of CF-P(NIPAM-co-MAM)-3 and CF-P(NIPAM-co-MAM)-5 fabrics in temperature range of 30 °C to 45 °C. LCST value (34°C) of the copolymer was in this temperature range. The maximum contact angle was determined to be 72.65° for CF-P(NIPAM-co-MAM)-3 and 63.98° for CF-P(NIPAM-co-MAM)-5. It was found the contact angle values measured for the CF-P(NIPAM-co-MAM)-5 fabric sample were lower than that of the CF-P(NIPAM-co-MAM)-3 because of decreasing surface roughness (Figure 7 a). The increment in the contact angle confirmed that the fabrics incorporated with copolymer transformed from the hydrophilic character to the hydrophobic character due to the temperature increase and had a thermo-responsive wetting property. However, the contact angles of the CF-P(NIPAM-co-MAM)-3 and CF-P(NIPAM-co-MAM)-5 fabrics were not measured high enough to explain the hydrophobic character. As seen from SEM images given in Figure 5, application of the polymer caused to reduce the fabric surface roughness because of filling inter-fiber gaps by polymer molecules. This has prevented the contact angle value from reaching the desired angles (θ> 90 °) at high temperatures.

3.2.5. Determination of the thermo-responsive water uptake property

In the study, water uptake values of the fabrics left in water with temperatures changing in the range of 25 °C to 40°C were measured to investigate thermo-responsive water uptake properties of the fabrics. The water uptake values of the pretreated fabrics and copolymer-applied fabrics were presented in Figure 7b. According to the results, water uptake behaviors of the untreated fabric, BTCA-3 fabric and BTCA-5 fabric were not significantly affected by change in temperature. However, crosslinking of cotton cellulose with BTCA caused to decrease in water uptake value compared to the untreated fabric. The cotton fabrics absorb water molecules by forming H bonds between hydroxyl (-OH) groups of the cellulose molecules and water molecules. In the esterification of cellulose molecules with BTCA, hydroxyl groups, which ensure the absorption of water molecules, react with the carboxylic acid groups of BTCA.[44] Consequently, water uptake of the fabric is reduced because of the decreasing free -OH groups of cellulose. However, temperature rise affected water uptake values of the copolymer-applied fabrics. An important reduction in water absorption capacities started at 27 °C for the CF-P(NIPAM-co-MAM)-3 fabric and 29 °C for the CF-P(NIPAM-co-MAM)-5. The water absorption capacity diminished from 200% at 25 °C to 70% at 40 °C for the CF-P(NIPAM-co-MAM)-3 fabric. The value decreased from 90.75% to 65 % for the CF-P(NIPAM-co-MAM)-5 fabric. Decreasing water absorption capacity was more pronounced for the CF-P(NIPAM-co-MAM)-3 fabric. The high difference was due to the fact that P(NIPAM-co-MAM)-3 fabric had higher hydrophilicity at 25 °C. This decrease in water uptake was related to the predominance of hydrophobic groups in the P(NIPAM-co-MAM) macromolecule on the fabric surface with increasing temperature. As mentioned earlier, around their LCST value, the temperature sensitive polymers get hydrophobic character and their molecules shrinkage. The CF-P(NIPAM-co-MAM)-3 fabric had higher hydrophilic character at temperatures below LCST compared to CF-P(NIPAM-co-MAM)-5 fabric because of usage the less BTCA during polymer application. These results revealed that fabrics changed their hydrophilic character depending on increase in temperature and they exhibited temperature sensitive water absorption ability.

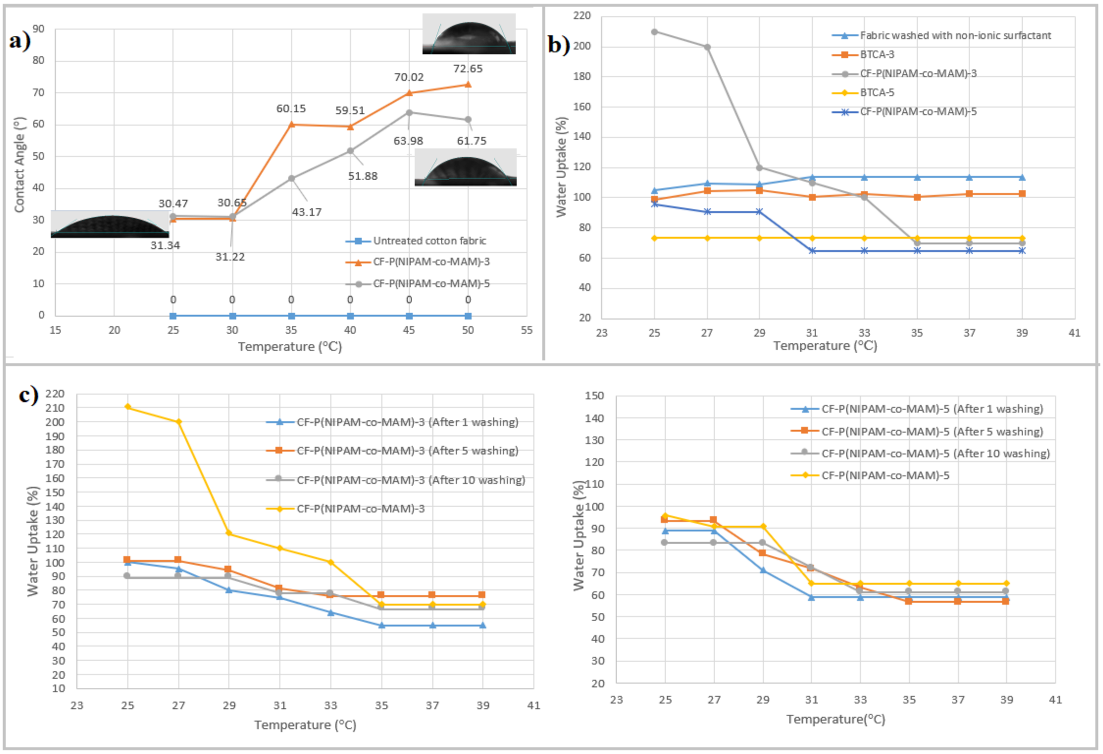

Figure 7. Test results of the fabrics (contact angle at different temperature (a), water uptake at different temperature (b), water uptake after repeated washings (c)

In the study, durability of the fabric thermo-responsive property against to repeated washings was examined by determining the changes in water uptake values of the washed fabrics. For this aim, water absorption capacities of the fabrics at temperature below and above LCST were measured after repeated washings. Water uptake values of the CF-P(NIPAM-co-MAM)-3 and CF-P(NIPAM-co-MAM)-5 fabrics after 1, 5 and 10-times washings were presented in Figure 7 c. According to the results, difference between the water absorption capacities measured above and below LCST started to decrease even if the first washing for the CF-P(NIPAM-co-MAM)-3 fabric and the CF-P(NIPAM-co-MAM)-5 fabric. After each wash cycle, the difference between water absorption capacity values measured above and below LCST value has closed. It was concluded that thermo-responsive property of the CF-P(NIPAM-co-MAM)-3 was weakened after especially first washing. However, the difference did not close completely even after 10 washes and was over 20% for the CF-P(NIPAM-co-MAM)-3 fabric. Based on this finding, it was concluded the fabrics kept their thermo-responsive properties even after 10 washes. However, it was concluded that increasing in the molecular weight of the synthesized polymer and developing the binding of the polymer to the fabric could positively change the permanence of the thermo-responsive property of the fabric.

3.2.6. Determining of the thermo-responsive water vapor permeability

To study temperature sensitive moisture management property of the copolymer-applied fabrics depending on changes in the hydrophilicity and molecules conformation of the thermo-responsive polymer, water vapor permeability of the fabrics was measured at temperature below and above LCST of the copolymer. Water vapor permeability test results of the fabrics and statistical analysis results were shown in Figure 8 and Table 1, respectively. According to the results measured at 20°C, the fabrics treated with BTCA transferred less water vapor compared to untreated fabric. As described earlier, BTCA application reduces free OH groups in the cellulose molecule resulting decline in water vapor permeability by absorption. However, water vapor permeability increased after copolymer application to the fabrics pretreated by BTCA. Water vapor permeability of the CF-P(NIPAM-co-MAM)-3 and the CF-P(NIPAM-co-MAM)-5 fabrics was measured as higher compared to fabrics treated with BTCA because of increase in their hydrophilic character. Although the pores in the fabric structure were closed by polymer layer formed on the fabric surface after the copolymer application as seen from SEM images (Figure 5), the water vapor permeability increased. It was thought that increase was resulted from increasing hydrophilic feature of the copolymer grafted to the fabric surface at temperature below LCST. However, their water vapor permeability was lower compared to untreated fabric because the fabric pores were blocked by swollen hydrophilic copolymer molecules at temperatures below LCST (20°C). Increase in the amount of polymer transferred to the fabric significantly promoted this reduction in the water vapor permeability ($p<0.05$). Regarding to the results measured at 40°C, evaporation of more water molecules at high temperature caused to rise in water vapor permeability values of all fabrics. Application of the copolymer at concentration of 3% positively affected water vapor permeability. As expected, water vapor permeability of the CF-P(NIPAM-co-MAM)-3 fabric was statistically higher than other fabrics ($p<0.05$) (Table 1). Shrinkage of the copolymer at 40°C (above the LCST) because of the increasing interaction between its hydrophobic groups resulted opening of the fabric pores and increasing water vapor permeability. However, unexpectedly, water vapor permeability of the CF-P(NIPAM-co-MAM)-5 was lower significantly compared to untreated fabric. This was due to limitation of opening of the pores resulted from shrinkage of polymer molecules because of high amount of the polymer transferred to the fabric. As known, the water vapor permeability is related to porosity and hydrophilicity [45] and the water vapor permeability of the fabrics can be controlled by a thermo-responsive smart polymer application which exhibits changeable porosity and hydrophilicity depending on change in temperature.

3.2.7. Determination of the pH responsive water uptake value

Presence of basic amino groups in the chemical structure of the MAM monomer of the synthesized copolymer provides to copolymer pH sensitivity. The dissociation constant (pKb) of the MAM co-monomer is pH 8. MAM molecule is found in ionic form at pHs less than pKb. It exhibits hydrophobic property in alkaline environments (pH> pKb). [25,46] It was expected that gaining hydrophobic character of the MAM molecules of the copolymer at pH 10 resulted reduction in the water absorption of the fabrics. In the study, to examine pH responsive properties of the copolymer-applied fabrics, water absorption ability of the fabrics at different pH values at temperature of 20 °C was measured. As seen from Figure 9, no significant difference in the water absorption ability of the untreated fabric was observed depending on change in pH. Although there was no significant difference between water uptake values of the fabrics measured at acidic pH and neutral pH, water uptake values of the copolymer-applied fabrics decreased prominently when the pH increased from 3 to 10. The water absorption capacity decreased from 105.53% at pH 3 to 80.14% at pH 10 for the CF-P(NIPAM-co-MAM)-3 fabric. The value decreased from 90.46% to 72.67% for the CF-P(NIPAM-co-MAM)-5 fabric. Consequently, the water uptake capacities of the copolymer-applied fabrics changed significantly depending on change in pH and the fabrics exhibited pH sensitive water uptake property as well as temperature sensitive water uptake property.

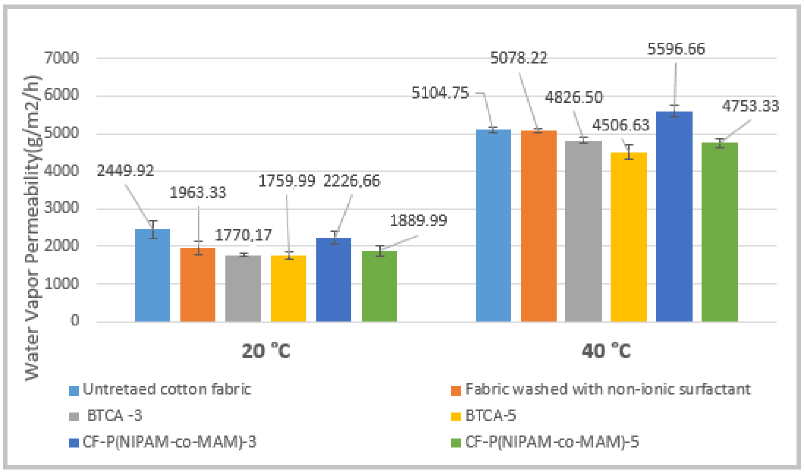

Figure 8. Water vapor permeability of the fabrics measured at 20 °C and 40 °C

Table 1. Statistical analysis results of the water vapor permeability, bending rigidity and warp tear strength test results

Sample	**Water Vapour Permeability**						**Bending Rigidty**				**Warp tear strength**				
	20 °C		**40 °C**												
	Subset for alpha = 0.05														
	1	**2**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**5**
Untreated fabric		2449.92			5104.75		170.74								4.94
Fabric washed with non-ionic surfactant	1963.33				5078.22		-	-	-	-	-	-	-	-	-
BTCA-3	1770.17			4826.50			193.36	193.36						2.51	
BTCA-5	1759.99		4506.63					209.43	209.43				1.98		
CF-P(NIPAM-co-MAM)-3		2226.66				5596.66			225.97			1.36			
CF-P(NIPAM-co-MAM)-5	1889.99			4753.33						542.58	1.05				
Sig.	0.151	0.091	1.000	0.493	0.803	1.000	0.066	0.184	0.172	1.000	1.000	1.000	1.000	1.000	1.000

3.2.8. Determination of the antibacterial activity

Antibacterial activity of the CF-P(NIPAM-co-MAM)-3 fabric was investigated under dynamic conditions using *S.aureus* bacteria by a quantitative method (ASTM E2149-01 test method). In the Table 2, bacterial reduction rates (%) of the untreated fabric and CF-P(NIPAM-co-MAM)-3 fabric after 3-hours, 6-hours and 24-hours incubation were given. According to the test results, a gradual decrease in the number of bacterial colonies in the control group and untreated fabric was observed. After 24 hours, there was a 98.71% reduction for the control group and 99.87% for the untreated fabric in the number of bacteria colonies. The reason of decreasing was to die of the bacteria in the solution depending on time. On the other hand, 100% bacteria reduction was detected at the end of the 3-hours incubation for the CF-P(NIPAM-co-MAM)-3 fabric. It meant that all bacteria in the environment died during this period. This finding indicated that CF-P(NIPAM-co-MAM)-3 fabric had strong antibacterial activity against the *S.aureus* bacteria. Antibacterial activity of the synthesized copolymer, resulting in bacterial death might be due to the interactions between the positively charged groups on the polymer chains and negatively charged carboxylic acid groups of the macromolecules of the bacterial cell wall. The copolymerization of NIPAM with MAM increases cationic centers on the macromelecules, consequently, the net positive charge of the molecules is strengthened because of the protonated C=O and NH groups. [47,48]

3.2.9. Determining mechanical properties

Bending rigidity and warp tear strength tests were carried out in order to examine the effect of copolymer application on the mechanical properties of the fabrics and test results were presented in Table 3. Bending rigidity is associated with fabric stiffness and fabric stiffness rises as bending rigidity increases. [49] According to the test results, the bending rigidity increased after treatments with the BTCA and copolymer compared to untreated fabric. Moreover, increase in polymer concentration caused the bending stiffness to be significantly higher (CF-P(NIPAM-co-MAM)-5 fabric) ($p<0.05$) (Table 1). Covering of the fiber surfaces and filling gaps between the fibers by the copolymer molecules as well as crosslinking of the fiber elements by BTCA cross-linker limited the movement of fibers and yarns and caused to increase of the bending resistance of the fabrics. [50] Besides, tear strength of the fabrics decreases as increasing bending rigidity because increased bending resistance causes the threads to break one by one. [51] Additionally, treatment by chemical finishes which restricts movement of the yarns in the fabric results in low tear strength. This decrease in tear strength may be attributed to acidic pH of the application bath as well as reduced yarn slippages. [52] The results of warp tear strength in Table 3 overlapped with this information. Each pretreatment and copolymer application caused to reduce in warp tear strength of the fabric significantly ($p<0.05$) (Table 1).

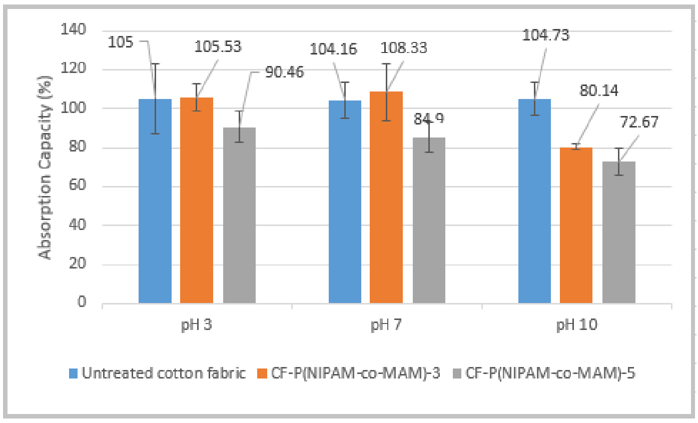

Figure 9. Water uptake test results at different pH values

Table 2. Antibacterial activity test results

Sample	Bacteria Reduction					
	3 hours		6 hours		24 hours	
	%	log	%	log	%	log
Control group	-7.69	-0.03	-42.31	-0.24	-98.71	-1.89
Untreated fabric	-19.23	-0.09	-79.62	-0.69	-99.87	-2.87
CF-P(NIPAM-co-MAM)-3	-100.00	-5.37	-100.00	-5.37	-100.00	-5.37

* The bacteria concentration transferred to each sample weighing 1 gram was calculated as 2.36 x105 (log 5.37) cfu * / ml.

** (cfu: Colony forming unit).

*** Bacteria values given as (+) indicate an increase in the number of bacteria, and bacteria values given as (-) indicate a decrease in the number of bacteria. The value of (-) 100% indicates that all bacteria on the surface have been killed.

Table 3. The bending rigidity and warp tear strength test results

Sample	Bending rigidity test results (mg.cm) [SD]	Tear strength test results (N) [SD]
Untreated fabric	170.74 [21.81]	4.94 [0.01]
BTCA-3	193.36 [11.39]	2.51 [0.00]
BTCA-5	209.43 [7.00]	1.98 [0.06]
CF-P(NIPAM-co-MAM)-3	225.97 [8.83]	1.36 [0.15]
CF-P(NIPAM-co-MAM)-5	542.58 [36.61]	1.05 [0.01]

4. CONCLUSION

In this study, synthesis of a random PNIPAM copolymer containing components responsible for temperature/pH sensitivity and antibacterial activity and fabrication of cotton fabric having active comfort regulation and antibacterial activity were aimed. For this aim, a random copolymer of N-isopropylacrylamide with methacrylamide (P(NIPAM-co-MAM)) was synthesized via free radical addition copolymerization method and applied to the cotton fabric. The copolymer exhibited temperature sensitivity because of the presence of the NIPAM monomer and pH sensitivity because of the presence of the MAM monomer. The chemical structure of the copolymer was described by FT-IR spectroscopy and ^{1}H NMR analyses. Its thermo-responsive property was proved by turbidity test and DSC analysis. LCST values of the copolymers were detected in the range of the 34 °C and 41 °C depending on the change in MAM co-monomer ratio. The addition of hydrophilic MAM monomer to the polymer backbone increased LCST value of the synthesized copolymer compared to PNIPAM homopolymer because of increasing interaction between the water molecules and hydrophilic and charged groups of the copolymers. Thus, it was possible LCST value of the thermo-responsive PNIPAM polymer closer to the body temperature. In the study, synthesized copolymer (P(NIPAM-co-MAM)-2) with NIPAM/MAM monomer ratio of 9.5/0.5 had LCST of 34 °C and was chosen as polymer to be applied to fabric.

P(NIPAM-co-MAM)-2 copolymer was applied to the cotton fabric using a double-bath impregnation method. SEM analysis showed that copolymer covered fiber surfaces and filled gaps between the fibers. The smoother and uninterrupted coating on the fabric surface which completely filled spaces among the fibers was formed as the copolymer concentration increased in the bath. According to the fabric wetting and water absorption test results, copolymer-applied fabrics exhibited hydrophobic character at temperatures above LCST and their water absorption capacities decreased as a result of decreasing the adhesion forces between the molecules of the copolymer and water molecules. However, the fabrics at temperatures below LCST exhibited hydrophilic character and their water absorption capacities increased. Additionally, it was concluded that fabrics kept their thermo-responsive properties even after 10 washes. However, it is thought increasing in the molecular weight of the synthesized polymer and developing the binding of the polymer to the fabric can positively change the permanence of the thermo-responsive property of the fabric. The fabrics treated with the thermo-responsive copolymer could manage their water vapor permeability by means of altering their porosity and hydrophilicity depending on change in temperature. The water vapor permeability of the copolymer-applied fabrics was lower compared to untreated fabric because the fabric pores were blocked by swollen hydrophilic copolymer molecules at temperatures below LCST. The decreasing in the water vapor permeability was insignificant for the lower polymer concentration (CF-P(NIPAM-co-MAM)-3 fabric) ($p>0.05$). However, increase in the concentration of the copolymer caused to significant decrease in the water vapor permeability compared to untreated fabric. Shrinkage of the copolymer on the fabric surface at 40°C (above LCST) resulted the opening of the fabric pores and increasing water vapor permeability. Although the presence of the polymer coating on the surface of the fabric, their water vapor permeability at high temperatures was found to be higher significantly than the untreated fabric ($p<0.05$). However, this effect was limited by the high amount of the polymer transferred to the fabric. Consequently, the CF-P(NIPAM-co-MAM)-3 fabric was found as a suitable thermo-responsive fabric capable of smart water vapor management. The copolymer-applied fabrics exhibited pH sensitive water uptake property. Their water uptake values decreased at basic pH, which was above the value of pkb (pH 8) of the MAM co-monomer, compared to acidic and neutral pH values because decreasing hydrophilicity of the copolymer molecules.

In conclusion, in the study, dual stimulus sensitive cotton fabrics were produced successfully. It was concluded that fabrics produced in this study could be used to design smart thermo-responsive and pH sensitive textile products. Besides, fabric treated with copolymer had strong antibacterial activity against *S.aureus* bacteria. It is concluded this feature of the fabrics will be beneficial in terms of protecting both the cotton fabric and the user from the harmful effects of the bacteria in question. In addition, it is thought that developed fabric structures will be promising in the production of medical textile structures where antibacterial activity and thermophysiological comfort are important.

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