DESIGNING BIOSHELLED MICROCAPSULES TO PRODUCE FABRIC WITH REVERSIBLE COLOR-CHANGING, THERMOREGULATION AND ANTIBACTERIAL PROPERTIES

SENA DEMIRBAĞ GENÇ,[*,**] MÜYESSER SELDA TÖZÜM[*,**] and SENNUR ALAY AKSOY[***]

[*]*Uşak University, Textile Engineering Department, Uşak 64200, Turkey*
[**]*Uşak University, Scientific Analysis and Technological Application and Research Center, Uşak 64200, Turkey*
[***]*Süleyman Demirel University, Textile Engineering Department, Isparta 32260, Turkey*
✉ *Corresponding author: M. Selda Tözüm, selda.tozum@usak.edu.tr*

Received September 23, 2024

This study presents the development of nontoxic thermochromic phase change microcapsules (TPCMs) using a complex coacervation technique. The shell materials of the microcapsules are chitosan and sodium alginate natural polymers. The microencapsulation technique employed in this study has the advantage of using natural, nontoxic, biocompatible, and biodegradable capsule materials. In addition, the method is both simple and versatile, making it applicable to various industries. The microcapsules exhibited spherical morphology and a high latent heat of 129.6 J/g. Furthermore, the microcapsules demonstrated good thermal stability and excellent thermochromic performance. Microcapsule-treated fabric exhibited thermochromic and antibacterial activity. The air and water vapor permeability of the microcapsule-treated fabric was lower than that of the untreated fabric. However, the application of microcapsules did not have any effect on the bending rigidity and tear strength of the fabric. Therefore, the produced microcapsules show promise for various applications, including medical textiles, wearable sensors and various consumer goods.

Keywords: chitosan, sodium alginate, thermochromic, complex coacervation, antibacterial

INTRODUCTION

Recently, research on thermochromic materials, which can change color with ambient temperature, has become highly popular and has been attracting great commercial interest.[1] Thermochromic materials have been widely used in various fields, such as smart windows,[2] packaging,[3] medical diagnostics,[4] wearable electronic devices, and sensors.[5,6] In the field of intelligent textiles, thermochromic materials are used for both functional and decorative purposes.[7] Thermochromic materials used in textiles are classified as liquid crystal and leuco dye based thermochromic systems (TSs). TSs are the most promising thermochromic materials due to their outstanding color-changing performance, with a wide range of colors and ease of use.[8,9,10]

A TS comprises a color former, a color developer, and an organic solvent. The color former provides coloring, while the color developer acts as a proton donor. The solvent creates the necessary environment for the interaction between the coloring former and the color developer. Additionally, the solvent is a phase change material and its phase transition temperature determines the color change temperature of the TS.[7] The thermochromic mechanism is a process that is activated by changes in temperature and is based on the interactions between the color former and color-developer components. The color former takes a proton and opens its ring structure and transforms into its colored form. This transformation is achieved by the color developer acting as a proton donor. At a temperature above the melting temperature of the solvent component of the system, a strong interaction between the color former and the color developer occurs and the system is colored. On the contrary, at a temperature below the melting temperature of the solvent component, the interaction between the color former and the color

developer disappears and the system loses its color.[11,12]

Thermochromic materials pose some basic problems in their application. TSs typically contain phenol and alcohol groups, making them sensitive to environmental conditions. However, the components of TSs can change and be lost, which limits their use.[13] Additionally, TSs are insoluble in water and can leak the solvent component when applied directly to textiles. Therefore, microencapsulation of TS is necessary.

In recent years, research on microcapsules with novel thermochromic properties has been a prolific topic. TSs have been selected as core materials for the preparation of temperature-sensitive thermochromic microcapsules.[1] Microencapsulation methods have been developed for the microencapsulation of TSs, including emulsion polymerization,[14-18] *in situ*,[7,19-31] suspension polymerization,[32] sol-gel[33,34] and interfacial polymerization.[35-37] It was found that the studies generally focused on the preparation of thermochromic microcapsules with synthetic polymer wall structure by chemical methods.

Nowadays, the complex coacervation method has become a common method for the preparation of microcapsules due to its easy and versatile application in industry and the fact that the materials forming the wall structure of the microcapsules are natural, environmentally friendly, renewable and biodegradable. Complex coacervation is the oldest and most widely used physico-chemical method. Coacervation occurs as a result of temperature change, addition of non-solvent or salt, addition of another polymer or polymer-polymer interaction. Li and Shen (2011) encapsulated a TS consisting of crystal violet lactone (CVL), bisphenol-A (BPA) and 1-hexadecanol in gelatin/gum arabic shells using the complex coacervation method.[38] Wu *et al*. (2017) fabricated thermochromic microcapsules with gelatin/gum arabic shells by the complex coacervation method. The TS consisting of CVL, BPA and 1-tetradecanol (TD) was used as the core material.[39] Guan *et al*. (2018) encapsulated cholesteric liquid crystal type thermochromic materials in gelatin/gum arabic using the complex coacervation method. The produced microcapsules were added to polyvinyl prolidone (PVP) solution, and the production of reversible thermochromic PVP fibres was carried out via electrospinning.[40] However, it was found that although all the above researchers mentioned microcapsules obtained by incorporating TS into the shell material, most of these studies focused on the morphology and particle size distribution of the microcapsules. In addition, BPA is the most commonly used color developer in the literature due to its low cost and high color contrast. However, BPA is known to have toxic and carcinogenic effects, causing various problems such as breast cancer, heart disease, infertility and neurodevelopmental disorders.[10] To avoid the effects of BPA, phenolphthalein can be used as a color developer.[16]

In contrast to the literature, this study focuses on the preparation of temperature-sensitive thermochromic microcapsules for the development of textile-based flexible temperature sensors or thermally adaptive clothing for use in medical fields. Thermochromic phase change microcapsules (TPCMs) containing TSs were prepared by the complex coacervation method and applied to cotton fabric. The microcapsules in this study were composed of a TS made from a fluoran dye, phenolphthalein (instead of BPA), and 1-tetradecanol (TD) as the core material, with chitosan/sodium alginate used as the wall material. A notable feature of this study is the natural, environmentally friendly, and biodegradable wall structure of the microcapsules produced. Chitosan is a natural polymer, with excellent biocompatibility, non-toxicity, biodegradability, and antibacterial properties.[41,42] This work presents the development of multifunctional textile fabrics that provide antibacterial activity, excellent color change, and latent heat storage properties through a single application. TSs can release and absorb latent heat energy during reversible color changes due to temperature changes. In this way, they are expected to impart both thermoregulation properties and reversible color change to the fabric to which they are applied. Thermo-regulating fabrics regulate heat transfer between the wearer's body and the environment to maintain a stable and comfortable temperature. Several studies have investigated fabrics incorporating synthetic walled thermochromic microcapsules,[43-46] but there is a lack of research on the application of natural walled thermochromic microcapsules. Protective medical products with antimicrobial activity play a crucial role in defending against bacterial infections.[47] Chitosan polymer, known for its antibacterial properties, was used in the wall structure of the thermochromic microcapsules designed for medical applications. The microcapsules prepared in the study are expected to provide antibacterial properties, as well as

thermochromic and thermal regulation to the fabrics they are applied to.

In summary, we produced TPCMs with a chitosan-sodium alginate shell and TS core using the complex coacervation method and characterized them within the scope of the study. We then applied the produced microcapsules to cotton fabric using the impregnation method to investigate their potential for use in medical fields. We investigated the morphology, thermochromic properties, and thermo-regulation properties of microcapsule containing fabrics. The fabrics that were prepared underwent evaluation for tear strength, bending rigidity, air permeability, and water vapor permeability.

EXPERIMENTAL

Material

A 2'-(Dibenzylamino)-6'-(diethylamino) fluoran ($C_{38}H_{34}N_2O_3$, color former), phenolphthalein ($C_{20}H_{14}O_4$, color developer, Sigma Aldrich) and 1-tetradecanol ($CH_3(CH_2)_{13}OH$ solvent, >97%, Alfa Aesar) were used to form a TS, which was the core material of the microcapsules. Chitosan and sodium alginate polymers used as microcapsules' wall materials were purchased from Sigma Aldrich. Cetyltrimethyl ammonium bromide ($C_{19}H_{42}BrN$, CTAB), supplied from Sigma Aldrich, was used as a cationic surfactant in the preparation of microcapsules. Glutaraldehyde ($OHC(CH_2)_3CHO$, 25%, Sigma Aldrich) was used as a cross-linking agent to stabilize the microcapsules. Acetic acid (10%) and sodium hydroxide (5%) solutions were used for pH adjustment during the microcapsule production steps. Setamordant T (a cationising agent, Setaş Company) was used to cationise the cotton fabric together with Triton X100 (a penetrating agent) and sodium hydroxide (20%) solutions. Fixapret Resin F-Eco as cross-linking agent was purchased from BASF Company. Other excipients used were magnesium chloride and sodium chloride as a catalyst and to increase the affinity of the microcapsules to the fabric, respectively.

Methods

Preparation of fluoran dye-based TS

Dye and color developer were added to 1-tetradecanol solvent, which was heated to approximately 90 °C. The mixture was stirred until the dye and developer were completely dissolved. The weight ratio of fluoran dye, phenolphthalein, and 1-tetradecanol was 0.055/0.09/6.42.[48] The prepared system was colorless above the phase change temperature of 1-tetradecanol, while it was dark green below the phase change temperature.

Microencapsulation of fluoran dye-based TS

Chitosan/sodium alginate microcapsules containing TS were prepared by the complex coacervation method. The core:shell ratio was 1:0.5. In the first step, the prepared fluoran dye-based TS (5 g) was emulsified in chitosan solution by adding 0.10 g CTAB surfactant. Sodium alginate solution was then added dropwise to the prepared solution and the pH of the solution was adjusted to 4 by adding acetic acid to initiate complex formation. In this step, a polyelectrolyte complex was formed between the anionic carboxyl group (COO^-) of sodium alginate and the cationic amino group (NH_3^+) of chitosan (Fig. 1).

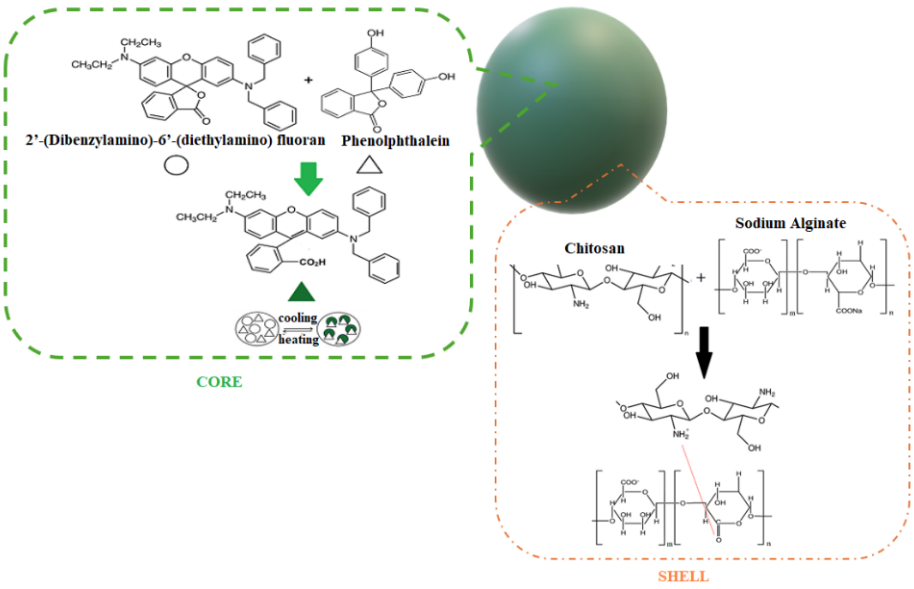

Figure 1: Schematic illustration of the core and shell structure of TPCMs microcapsule

Table 1
Conditions for applying microcapsules to textiles

Concentrations (g/L)				Drying temperature and duration	Fixing temperature and duration
Microcapsule	Cross-linker	Catalyst	Salt (NaCl)		
600	60	15	1%	80 °C, 5 minutes	120 °C, 1 minutes

After one hour, sodium hydroxide was added dropwise to reach a pH of 9, thereby stopping the complex formation. The temperature was maintained at 50 °C until the microcapsules were cross-linked. In the cross-linking step, the temperature was reduced to 4 °C and the microcapsules were cross-linked by adding glutaraldehyde solution (0.8 g). Finally, green solid microcapsules were obtained after filtration and then washed with distilled water at 70 °C and filtered. During the microcapsule production, the mixing speed was set to 1000 rpm, and the polymer concentration used to form the wall structure was 2.5%. The thermochromism mechanism of TS, which constitutes the core material, and the complex coacervation process are illustrated in Figure 1.

Application of the produced microcapsules to cotton fabric

The impregnation method was used to apply the microcapsules to the fabric. Prior to impregnation, the cotton fabric was cationized by the exhaustion method. The cationization process was carried out according to our previous study.[15,49,50] Then, the washed and filtered wet microcapsules were added to the fabrics. The microcapsule solution was prepared at the concentrations given in Table 1, using a Digital Weightlab WF-OD20 mechanical stirrer. Cotton fabric soaked in the prepared microcapsule solution for half an hour was impregnated using a foulard. Finally, the impregnated fabric was dried and cured.

Characterization of TPCMs and fabrics treated with TPCMs

Scanning electron microscopy (SEM) was used to observe the morphology and size of the microcapsules. The particle size and particle size distribution (PSD) of the microcapsules were measured using a particle size analyzer (Horiba LA-350). The shell materials, core material and microcapsules containing TS were chemically characterized by ATR-FTIR (Perkin Elmer) analysis in the range of wave numbers from 4000 to 400 cm^{-1}. The phase transition characteristics and thermal stability characterization of the microcapsules were investigated using a Perkin Elmer Jade DSC 400 instrument and a Perkin Elmer Diamond instrument, respectively. Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) measurements were performed under the conditions established in our previous studies.[15,49] The temperature-dependent color change behaviour of TS, microcapsules and microcapsule-treated fabrics was verified using photographs taken at 20 °C and 50 °C. In addition, the temperature-dependent color changes of the microcapsule-treated fabrics were verified using a spectrophotometer.[15,49]

In order to investigate the thermo-regulatory property of microcapsule treated fabrics, a T-history test was performed during their heating cycle.[49] The measurement was performed using an experimental setup consisting of an insulated box, a lamp with a thermostat (to fix the internal temperature), and a thermal camera (Fluke TiX 500). In this test, the conditioned fabric samples, cooled to a temperature below the crystallization temperature of the TS, were placed in the heated box and the change in their surface temperature was monitored with a thermal camera. The distance between the thermal camera and the sample was kept constant throughout the measurement and was approximately 30 cm. The measurements were carried out for the fabrics with and without microcapsules, and the graph showing the change in surface temperature over time was obtained.

The antibacterial activity of the fabrics was determined according to ASTM E2149-01. The wetting times of the fabrics were determined using the AATCC79 test standard. The water vapour permeability of the fabrics was measured using the modified BS 3424 control dish method. The air permeability of the fabrics was determined using a Textest FX 3300 (TS 391 EN ISO 9237). The flexural strength and tear strength of the fabrics were tested according to TS 1409 and TS EN ISO 13937-1 respectively. Microcapsule-treated fabrics were washed up to 5, 10 and 20 times. The test was performed according to ISO standard 105-C06 in a Gyrowash machine for 30 minutes at 60 ºC. The surface and durability of the fabric after washing were observed by SEM analysis.

RESULTS AND DISCUSSION

Morphological study of TPCMs

SEM images of the TPCMs given in Figure 2a show that the microcapsules were spherical in shape. In addition, it was observed that the particle sizes of the microcapsules were smaller than 100 nm. According to the particle size distribution curve of microcapsules shown in Figure 2b, the microcapsules showed homogeneous distribution. Microcapsules had a mean particle size of 12.60 μm and their size varied extensively from 6.26 μm to 22.49 μm. When the results of SEM and particle

size analysis were evaluated together, the sizes of the microcapsules measured by PSD analysis were larger than those measured by SEM analysis. This variation in microcapsule size was due to agglomeration of nano-sized capsules, which were detected as a single particle during particle size measurement.[51,52] It is postulated that the attractive forces between the polymer molecules that comprise the microcapsule wall structures will also have an effect on the tendency of microcapsules to cluster. Indeed, this pronounced clustering phenomenon presents a significant challenge in the analysis of the SEM images of the capsules, as it hinders the ability to track the particles.

Chemical characterization of TPCMs by FT-IR analysis

Figure 3 illustrates the FT-IR spectra of chitosan, sodium alginate, TS and the resulting TPCMs. The observed peaks at 3324 cm^{-1} and 3229 cm^{-1} in the TPCMs spectrum were the result of a combination of hydrogen-bonded -OH stretching and -NH stretching peaks of the chitosan polymer, and -OH stretching peaks of sodium alginate. Moreover, these peaks were associated with the -OH stretching peaks of TD and phenolphthalein, which formed the TS. The amide I and amide II peaks of chitosan were observed at wavelengths of 1650 cm^{-1} and 1592 cm^{-1}, respectively.[53,54] Furthermore, these peaks were also observed in the TPCMs spectrum at the same wavelengths, although their intensity was diminished.[54] This decrease was attributed to the interaction of chitosan and sodium alginate within the TPCMs structure. The peaks at 2849 cm^{-1}, 2917 cm^{-1} and 2956 cm^{-1} in the spectra of TPCMs were characteristic C-H stretching peaks of TD, thereby proving the presence of TD in the structure. The sharp peaks observed at 1472 cm^{-1} and 1463 cm^{-1} in the TPCMs spectrum were identified as the C-H bending peak of TD in the TS. Additionally, the dual peak observed at wavelengths of 730 cm^{-1} and 720 cm^{-1} were identified as the characteristic wagging peaks of the TD solvent.

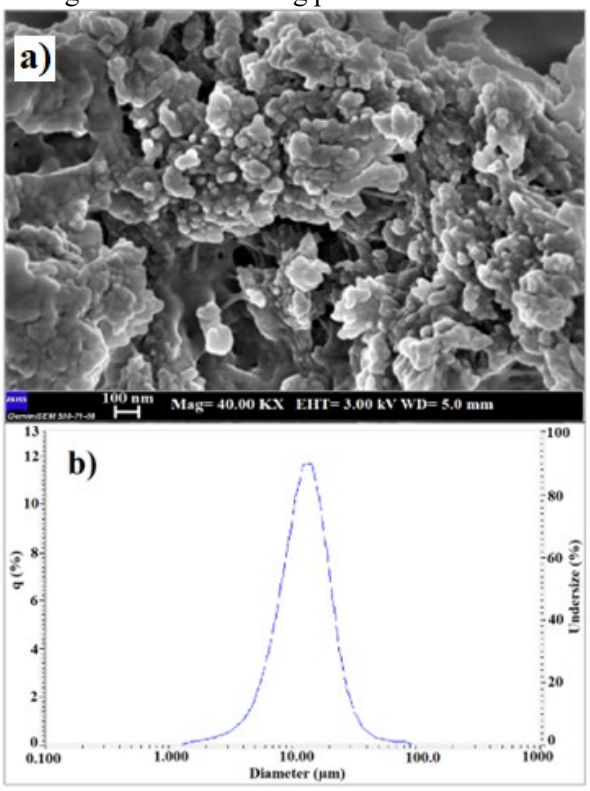

Figure 2: SEM images (a) and particle size distribution (b) of TPCMs

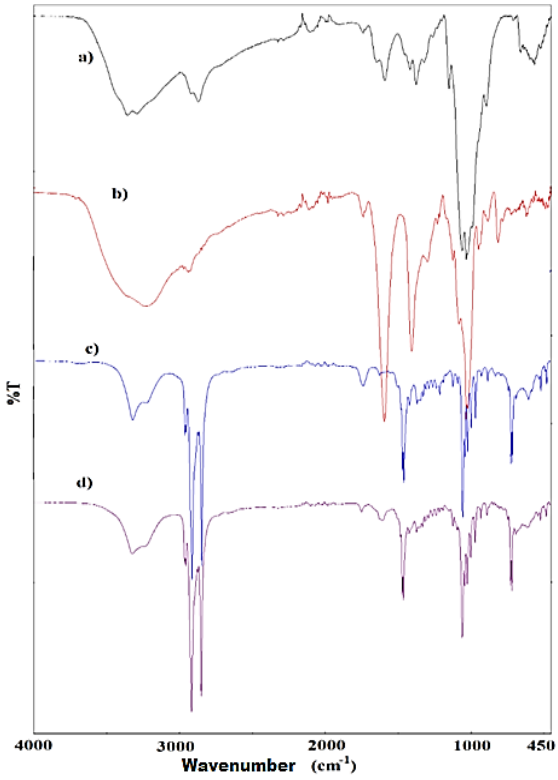

Figure 3: FT-IR spectra of chitosan (a), sodium alginate (b), TS (c), TPCMs (d)

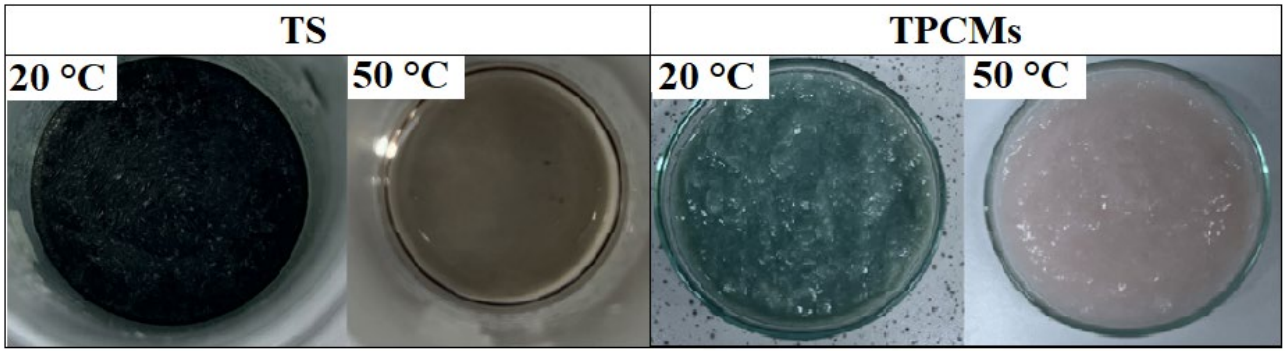

Figure 4: Photographs of TS and TPCMs at 20 °C and 50 °C

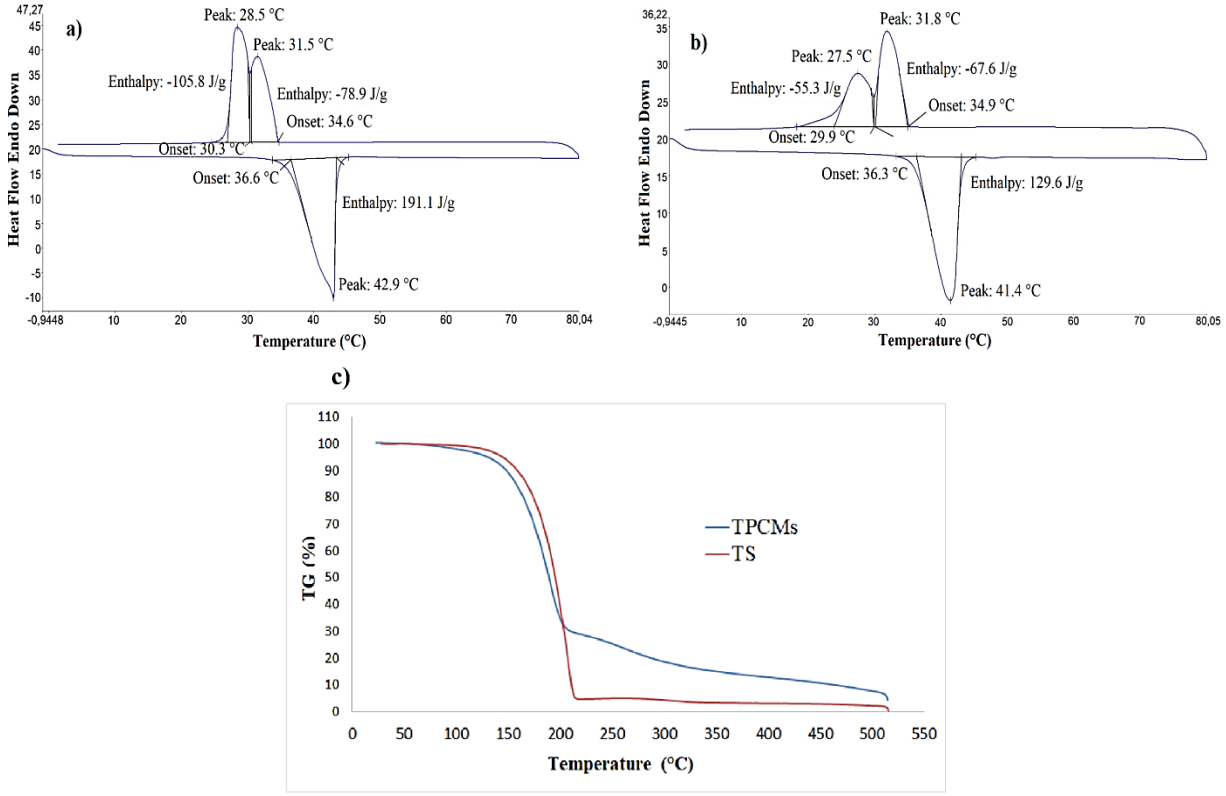

Figure 5: DSC thermograms of TS (a), TPCMs (b), and TGA curves of TS and TPCMs (c)

The peaks at 1426 cm^{-1} and 1372 cm^{-1} in the spectra of TS were the result of symmetric stretching peaks opening the ring structure of the dye, which had been colored in a cold medium. Furthermore, these peaks were also observed at the same wavelengths in the spectrum of the TPCMs.

Thermochromic behavior of TS and TPCMs

The photographs of TS and TPCMs were captured using a digital camera at two distinct temperatures: 20 °C (cold) and 50 °C (hot). As illustrated in Figure 4, the TS that were green in a cool medium lost their color completely when exposed to hot medium. At 20 °C, TPCMs exhibited a range of colors, from green to colorless, as the temperature increased.

Determination of thermal properties of TPCMs

The phase change temperatures and latent heat storage capacities of TS and TPCMs were quantified by differential scanning calorimetry (DSC). The resulting DSC thermograms are presented in Figure 5. As illustrated in Figure 5 (a and b), the phase change behaviour of the TPCMs exhibited similarities to that of TS. Both the TS and TPCMs exhibited a single endothermic peak

during the heating process. The latent heat stored by TS was found to be 191.1 J/g at 36.6 °C, while that stored by TPCMs was 129.6 J/g at a melting temperature of 36.3 °C. The cooling thermograms of TS and TPCMs revealed exothermic peaks at 30.3 °C and 29.9 °C, respectively, which were assigned to the crystallization temperatures of the β-form crystals in the solid-solid transition of 1-tetradecanol. The solid-solid crystallization enthalpies were determined to be -105.8 J/g for TS and -55.3 J/g for TPCMs. Furthermore, it was observed that a small shoulder was present at higher temperatures, which was attributed to the crystallization temperature of α-crystals in the liquid-solid transition of TD. The liquid-solid crystallization enthalpies were -78.9 J/g at 34.6 °C for TS and -67.6 J/g at 34.9 °C for TPCMs.

The thermogravimetric analysis curves of the TS and TPCMs are presented in Figure 5 (c). The curve of TS demonstrated that its thermal degradation commenced at 150 °C, with the weight loss reaching a plateau at 217 °C. The initial weight loss ratio of the microcapsules was 60.39% within the temperature range of 150 °C to 220 °C. In this step, the weight loss of the microcapsules was found to be lower than that of the TS, which serves to demonstrate that the shell material acts to provide a superior degree of protection for the core material by means of enclosing it. During the application of microcapsules to textile fabrics, the capsules are typically subjected to temperatures below 150 °C. Consequently, it is crucial that the TS retained within the capsules remains in high amount within the capsule structure at these temperatures. The results of the TG analysis indicate that, in light of the minimal mass loss observed in microcapsules at temperatures approximating 150 °C, the microcapsule structure is capable of withstanding the processing conditions typically encountered during the application of microcapsules to fabric. The second decomposition step, which was attributed to the degradation of the polymeric shell, occurred between 220 °C and 400 °C, with a weight loss of 16.07% for TPCMs. In conclusion, the TG results indicated that TPCMs exhibited sufficient thermal stability for potential applications in the textile industry.

Morphologies of fabrics treated with TPCMs

SEM analysis was carried out to analyze the morphology of fabrics treated with TPCMs before and after repeated washing. According to the SEM image in Figure 6 (a), the adhesion of many spherical microcapsules to the fiber surface is confirmed.

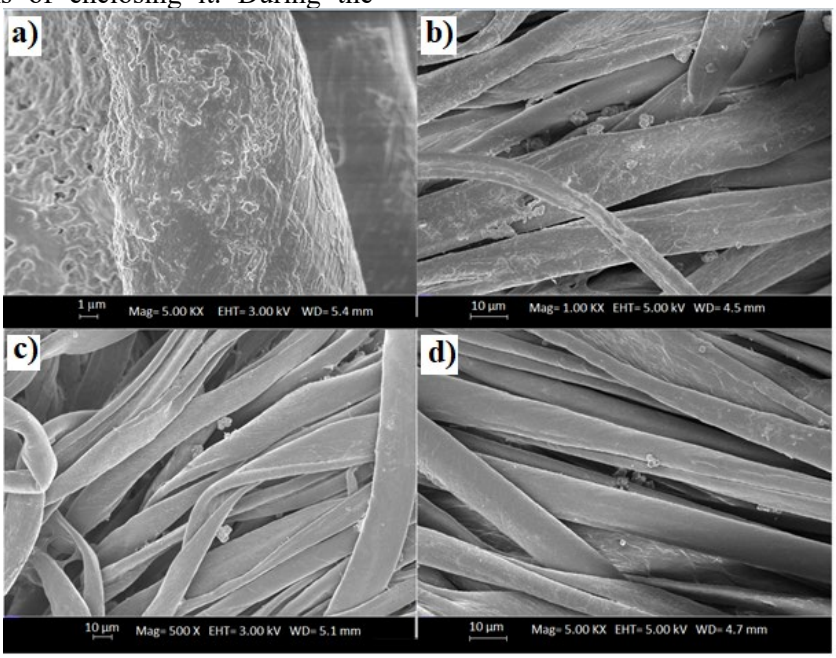

Figure 6: SEM images of fabric treated with TPCMs before washing (a), and after 5 (b), 10 (c) and 20 washing cycles (d)

It can also be observed that the microcapsules were clustered together due to the affinity of the surface of the particles to each other. The effect of washing cycles on microcapsule treated fabrics

was also studied to determine the durability of microcapsules on textiles against washing. Although there was a significant reduction in the amount of microcapsules on the fabric after 10 wash cycles, the microcapsules remained on the fabric even after 20 wash cycles (Fig. 6 (c,d).

Thermal analysis results of the fabrics

The thermoregulation property of the microcapsule treated fabric, resulting from the latent heat absorbed by the TS was investigated by T-history analysis. Figure 7 shows the time-dependent temperature change curve of the fabrics during the heating cycle. The surface temperature of the untreated fabric was higher than that of the fabric treated with TPCMs throughout the measurement. Within two minutes, the surface temperature of the microcapsule treated fabric rose rapidly to around 34 °C, while the surface temperature of the untreated fabric rose to 36.7 °C with a similar increasing trend. The difference between the surface temperatures of the two fabrics continued for about nine minutes, after which the temperatures stabilized at the same level (38.6 °C). The maximum temperature difference between the untreated fabric and the microcapsule treated fabric was calculated to be 4.9 °C. This difference between the fabric surface temperatures is due to the heat absorbed during the melting of the encapsulated TS system, which is a cooling effect. This result, as well as similar research results in the literature, shows that the TS can delay the temperature change of the fabric in case of sudden temperature changes and show a significant temperature regulating function for a certain period of time.[15,49,50,55]

Determination of color changing properties of fabric

The color changes of the fabrics treated with TPCMs were observed with a camera. The thermochromic effect was clearly visible to the naked eye on the fabrics photographed at 20 °C and 50 °C (Fig. 8). It could be seen that the color of the fabrics, which was green at 20 °C, became completely white as the temperature increased. In addition to the sensory evaluation, the colorimetric parameters (L*, a*, b*) were measured using the CIELab color space and the total color difference (ΔE) value was calculated from these values (Table 2). The calculated total color difference was indicative of the change that occurred with temperature change.

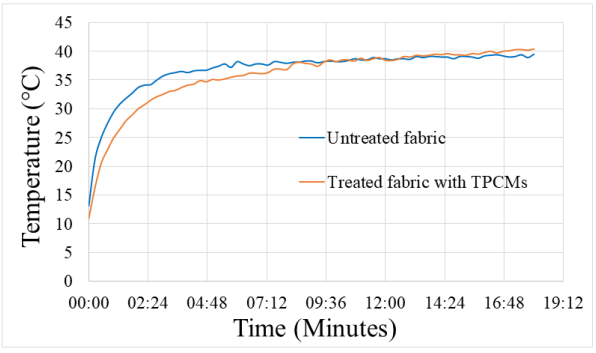

Figure 7: T-history results of the fabrics during heating

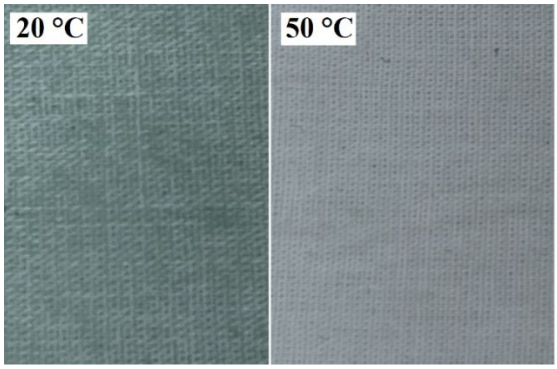

Figure 8: Photographs of fabric treated with TPCMs at 20 °C and 50 °C

Table 2
Color measurement results of fabric treated with TPCMs

Temperature of fabric sample	L*	a*	b*	ΔE
20 °C	63.94	1.48	-24.74	27.92
50 °C	80.54	-1.11	-2.43	

Antibacterial activity tests of fabrics

Antibacterial textiles are products that are effective against bacterial infections that threaten human health.[56] Nowadays, the development of antibacterial textiles for medical use is becoming increasingly important. This can be achieved by applying antibacterial finishes to textile materials.[57] The application of antibacterial chemicals, such as silver, triclosane, ZnO materials and quaternary ammonium salts, to the fabrics has

been used to incorporate antimicrobial properties.[58] Several natural, biocompatible and environmentally friendly polymers, such as chitosan, gum arabic and sodium alginate, have also been investigated for their antimicrobial activity.[59-61] Furthermore, smaller nanoparticles have been found to have stronger antimicrobial activity and their application in nanoparticle form is more effective than direct application.[62]

The antibacterial activity of the untreated and TPCM-treated fabrics was determined against *Escherichia coli* bacteria. Table 3 shows the bacterial reduction/increase rates of the fabrics after incubation for 6 and 24 hours. According to Table 3, at the end of 24 hours, the bacterial increase for the untreated fabric was 23.26%, while the bacterial decrease for the fabric treated with TPCMs was 99.51%. This result indicated that the fabric treated with TPCMs had strong antibacterial activity against *Escherichia coli* bacteria.

The antibacterial activity of microcapsules is thought to be related to the antibacterial activity of glutaraldehyde, which is a cross-linking agent in their structure, and chitosan, which is used as a shell material. The antibacterial effect of glutaraldehyde, which is commonly used for sterilization and as a disinfectant in hospitals, is due to its strong binding to the outer membrane of *Escherichia coli*.[63] On the other hand, chitosan polymer, known for its antibacterial properties, has a broad inhibition spectrum against gram-positive and gram-negative bacteria, as well as the ability to sterilize some yeasts and moulds.[64] The antibacterial activity of chitosan is thought to be due to the electrostatic interaction between chitosan and bacterial cells. The protonated amino group of chitosan interacts with the negatively charged molecules on the surface of bacterial cells, causing permeabilisation of the cell surface and leakage of intracellular substances. This ultimately leads to the death of the bacteria.[65,66] In addition, the hydrophilic nature of the microcapsule shell structure is thought to influence antibacterial performance. Literature studies have shown that bacteria attach to hydrophobic surfaces. The hydrophilic polymers in the microcapsule shell structure are thought to provide antibacterial properties by preventing bacteria from attaching to the surface.[61]

Table 3
Antibacterial test results of fabrics

Sample	6 h		24 h	
	Reduction/rise of bacteria			
	(%)	log	(%)	log
Untreated fabric	+44.19	+0.16	+ 23.26	+ 0.09
Fabric treated with TPCMs	-98.95	-1.98	-99.51	-2.31

Notes: The bacteria concentration transferred to each sample weighing 1 gram was calculated as 3.9 x105 (log 5.59) cfu/mL (cfu: colony forming unit); Values given as (+) indicate an increase in the number of bacteria, and those given as (-) indicate a decrease in the number of bacteria

Hydrophilicity of fabrics

Hydrophilicity is one of the most important properties affecting water vapor permeability and, as hydrophilicity increases, water vapor permeability increases.[67,68] The water vapor permeability of fabrics is important for the thermal comfort of garments. Ensuring a high-water vapor transfer rate from the fabric structure allows the transfer of body heat and maintains thermal comfort.[69] The interaction of functional groups (hydroxyl, amine, carboxylic acid) in the polymeric wall structures of microcapsules in the fabric structure with water molecules provides the hydrophilic character of fabrics. In this study, a water absorption test was used to evaluate the effect of the wall structure of microcapsules with different functional groups on the water absorbency/hydrophilicity of fabrics. According to the water absorption test, fabrics are considered hydrophilic when the absorption time of the fabric is less than 5 seconds. While the water absorption time of the untreated fabric was recorded as 3.63 seconds, the microcapsule treated fabric completely absorbed the water in 0 seconds, thus both the untreated fabric and the microcapsule treated fabric had hydrophilic character. It was concluded that the hydrophilicity of the fabrics increased with the application of microcapsules and this was due to the functional groups of the polymers forming the shell structure of the microcapsules.

Air and water vapor permeability of fabrics

To determine the effect of microcapsules on the air and water vapor permeability of fabrics in relation to the thermal comfort properties of garments, the air and water vapor permeability test was carried out. The test results are shown in Figure 9. The air permeability, in other words, porosity is an important criterion for evaluating and simulating garment performance in terms of thermo-physiological comfort.[70] Several factors, such as the size, shape, volume and number of pores in the fabric structure, affect the air permeability of fabrics.[71-73] According to the air permeability test results of the fabrics, the application of microcapsules significantly affected the air permeability properties of the finished product ($p<0.05$). This is because the microcapsules fill the pores between the fibers, closing the pores of the fabric and reducing air permeability.[74-78]

Another parameter that affects thermo-physiological comfort properties is water vapor permeability. Water vapor permeability is related to the porosity and interfiber space in the fabric structure. A review of the literature shows that the application of microcapsules reduces the water vapour permeability of fabrics.[79,80] Similarly, in this study, as can be seen from the results in Figure 9, the application of microcapsules significantly reduced the water vapor permeability of the fabrics. This reduction is the same factor that caused the reduction in air permeability, *i.e.* the microcapsules filled the pores of the fabric and reduced the porosity of the fabric. However, the decrease in water vapor permeability was not as great as the decrease in air permeability. This is thought to be due to the increase in hydrophilicity of the fabric after microcapsule application. It is known that the more hydrophilic character of the fabric allows more water permeability.[67,68,79,81,82,83] However, as shown by the results of the fabric hydrophilicity test, this small increase in fabric hydrophilicity was not sufficient to compensate for the water vapor permeability caused by the decrease in porosity.

Evaluation of mechanical properties of fabrics

Bending rigidity is an important property that affects the handle and comfort of clothing.[84-86] The effect of microcapsule application on the bending rigidity of the fabrics was investigated and the test results are shown in Table 4. The test results showed that the application of microcapsules did not have a statistically significant effect on the bending rigidity of the fabrics ($p>0.05$).

On the other hand, to determine the change in the tenacity values of the fabrics after the application of microcapsules, a tear strength test was performed.

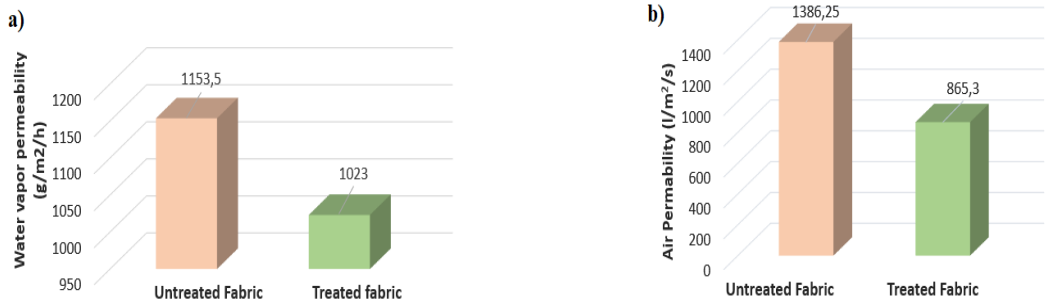

Figure 9: Water vapor (a) and air permeability (b) test results of fabrics

Table 4
Test results of bending rigidity and tear strength of fabrics

Sample	Bending rigidity (mg.cm) [SD]	Warp tear strength (N) [SD]	Weft tear strength (N) [SD]
Untreated fabric	107.51 [4.52]	11.941 [0.78]	6.236 [0.20]
Treated fabric with TPCMs	108.28 [6.79]	10.82 [1.00]	6.216 [0.31]

As can be seen from the results in Table 4, the application of microcapsules had almost no effect on the tear strength in the weft direction, while the tear strength in the warp direction decreased slightly ($p>0.05$). The bending rigidity of the fabric is related to the tear strength of the fabric, and increasing the bending rigidity decreases the tear strength by causing the threads to break one by one.[87] The results obtained were consistent with this finding and in general, it was concluded that the application of microcapsules did not adversely affect the mechanical properties of fabrics.

CONCLUSION

In this study, TPCMs with natural polymer shells that reversibly change color upon temperature variation were developed. These microcapsules were successfully prepared by microencapsulating TS as the core material in chitosan/sodium alginate shells via the complex coacervation method. The resulting microcapsules exhibited not only clear spherical morphology, but also a very high latent heat capacity (129.6 J/g) and good thermal stability.

The cotton fabric was treated with TPCMs to impart thermochromic, temperature regulating and antibacterial properties. The thermochromic cotton fabrics prepared by the impregnation process showed a fully reversible thermochromic performance individually with a high color contrast value ($\Delta E = 27.92$, calculated value between fabrics measured at 25 °C and 50 °C). They had excellent thermochromic reversibility and their color changed reversibly from green to colorless between 25 °C and 50 °C during the heating-cooling cycle. In addition, the antibacterial activity of fabrics treated with TPCMs against *Escherichia coli* bacteria was calculated to be 99.51%. SEM images of the fabrics before and after washing showed that a large number of spherical clustered microcapsules were firmly attached to the surface of the cotton fabrics. Even after 20 wash cycles, the microcapsules remained on the fabric, demonstrating their durability. The application of microcapsules caused a significant decrease in the air and water vapor permeability of the fabric, while it had no significant effect on the flexural rigidity and tear strength of the fabric.

As a result of the study, it has been shown that fabrics with thermochromic and thermoregulation functions, and antibacterial activity can be successfully produced with the application of the developed microcapsules. It is believed that the developed fabrics can be evaluated in the design of products that appeal to different areas, especially medical textiles, with their antibacterial properties, sensor feature that can visualize temperature changes and temperature regulating functions.

ACKNOWLEDGEMENTS: The authors are thankful to the TÜBİTAK (Project No. 221M773) for financial support.

REFERENCES

[1] H. Liu, Y. Deng, Y. Ye and X. Liu, *Materials*, **16**, 1 (2023), https://doi.org/10.3390/ma16145150
[2] T. Xue and Y. Yin, *J. Sol-Gel. Sci. Techn.*, **108**, 1 (2023), https://doi.org/10.1007/s10971-023-06232-5
[3] Y. Pu and J. Fang, *Colloids Surf. A*: *Physicochem. Eng. Asp.*, **653**, 1 (2022), https://doi.org/10.1016/j.colsurfa.2022.129889
[4] S. Siddiqui, A. Saeed and M. Abiodullah, *Pak. J. Social Sci.*, **43**, 381 (2023), https://doi.org/10.5281/zenodo.8424320
[5] Y. Wu, R. Sun, Y. Han, S. Zhang and S. Wu, *Chem. Eng. J.*, **451**, 1 (2023), https://doi.org/10.1016/j.cej.2022.139075
[6] S. Duzyer Gebizli, N. Guclu, M. Tiritoglu, S. Tezel and M. Orhan, *Fiber. Polym.*, **24**, 3393 (2023), https://doi.org/10.1007/s12221-023-00323-4
[7] L. Zhou, J. Ye, Q. Cai, G. Liu, M. Dadgar *et al.*, *Particuology*, **88**, 89 (2024), https://doi.org/10.1016/j.partic.2023.08.016
[8] L. Civan and S. Kurama, *Mater. Chem. Phys.*, **305**, 127977 (2023), https://doi.org/10.1016/j.matchemphys.2023.127977
[9] M. Hussain, M. A. Sikandar, A. Nasir and W. Ahmed, *J. Build. Eng.*, **35**, 102019 (2021), https://doi.org/10.1016/j.jobe.2020.102019
[10] J. Liu, J. Tan, H. Liu, Y. Yin and C. Wang, *Ind. Crop. Prod.*, **204**, 117254 (2023), https://doi.org/10.1016/j.indcrop.2023.117254
[11] M. A. Chowdhury, M. Joshi and B. S. Butola, *J. Eng. Fiber. Fabr.*, **9**, 1 (2014), https://doi.org/10.1177/155892501400900113
[12] I. Malherbe, R. D. Sanderson and E. Smit, *Polymer*, **51**, 22 (2010), https://doi.org/10.1016/j.polymer.2010.09.018
[13] X. Zhu, Y. Liu, Z. Li and W. Wang, *Sci. Rep.*, **8**, 4015 (2018), https://doi.org/10.1038/s41598-018-22445-z
[14] M. S. Tözüm, S. Alay Aksoy and C. Alkan, *Fiber. Polym.*, **19**, 660 (2018), https://doi.org/10.1007/s12221-018-7801-3
[15] M. S. Tözüm, C. Alkan and S. Alay Aksoy, *J. Appl. Polym. Sci.*, **137**, 1 (2020), https://doi.org/10.1002/app.48815
[16] M. S. Tözüm, S. Alay Aksoy and C. Alkan, *Int. J. Energ. Res.*, **45**, 7018 (2021), https://doi.org/10.1002/er.6287

[17] S. Özkayalar and S. Alay Aksoy, *Text. Appar.*, **31**, 156 (2021), https://doi.org/10.32710/tekstilvekonfeksiyon.761461
[18] I. J. Kim, M. Ramalingam and Y. A. Son, *Dyes. Pigm.*, **151**, 64 (2018), https://doi.org/10.1016/j.dyepig.2017.12.047
[19] D. Xue and T. Zhao, *Colloids Surf. A*: *Physicochem. Eng. Asp.*, **678**, 132458 (2023), https://doi.org/10.1016/j.colsurfa.2023.132458
[20] X. Wang, W. Lei, F. Zou, Y. Zhong, G. Guo *et al.*, *Appl. Surf. Sci.*, **630**, 157431 (2023), https://doi.org/10.1016/j.apsusc.2023.157431
[21] J. Zhang, C. Wang, F. Liu and C. Dong, *J. Therm. Anal. Calorim.*, 1 (2022), https://doi.org/10.1007/s10973-021-11082-w
[22] Y. Li, A. Yang, Y. Li, Z. Jiang, F. He *et al.*, *Colloids Surf. A*: *Physicochem. Eng. Asp.*, **677**, 132333 (2023), https://doi.org/10.1016/j.colsurfa.2023.132333
[23] W. Zhao and X. Yan, *Polymers*, **14**, 1393 (2022), https://doi.org/10.3390/polym14071393
[24] X. Yan, W. Zhao and L. Wang, *Polymers*, **13**, 3109 (2021), https://doi.org/10.3390/polym13183109
[25] E. Arman Kandirmaz, A. Ozcan and D. Er Ulusoy, *Pigm. Resin. Technol.*, **49**, 273 (2020), https://doi.org/10.1108/PRT-12-2019-0116
[26] X. Ma, L. Wang, L. Li, L. Bian, W. F. Yan *et al.*, *J. Macromol. Sci. A.*, **56**, 588 (2019), https://doi.org/10.1080/10601325.2019.1590125
[27] X. Ma, S. Zhao, L. Wang and H. Zhou, *J. Text. Inst.*, **111**, 1097 (2020), https://doi.org/10.1080/00405000.2019.1684224
[28] X. Yan and Y. Chang, *Prog. Org. Coat.*, **136**, 105262 (2019), https://doi.org/10.1016/j.porgcoat.2019.105262
[29] X. Geng, W. Li, Y. Wang, J. Lu, J. Wang *et al.*, *Appl. Energ.*, **217**, 281 (2018) https://doi.org/10.1016/j.apenergy.2018.02.150
[30] X. Geng, W. Li, Q. Yin, Y. Wang, N. Han *et al.*, *Energy*, **159**, 857 (2018), https://doi.org/10.1016/j.energy.2018.06.218
[31] Z. Wu, X. Ma, X. Zheng, W. Yang, Q. Meng *et al.*, *J. Text. Inst.*, **105**, 398 (2014), https://doi.org/10.1080/00405000.2013.814753
[32] H. Wang, J. Luo, Y. Yang, L. Zhao, G. Song *et al.*, *Sol. Energ.*, **139**, 591 (2016), https://doi.org/10.1016/j.solener.2016.10.011
[33] M. C. Burt and B. C. Dave, *Sensor. Actuat. B-Chem.*, **107**, 552 (2005), https://doi.org/10.1016/j.snb.2004.11.015
[34] W. Zhang, X. Ji, C. Zeng, K. Chen, Y. Yin *et al.*, *J. Mater. Chem. C.*, **32**, 8169 (2017), https://doi.org/10.1039/C7TC02077E
[35] Y. Li, Z. Jiang, F. He, Z. Chen, X. Li *et al.*, *J. Energ. Storag.*, **72**, 108674 (2023), https://doi.org/10.1016/j.est.2023.108674
[36] J. Gao, P. Guan, X. Hu and M. Cao, *Key. Eng. Mat.*, **501**, 231 (2012), https://doi.org/10.4028/www.scientific.net/KEM.501.231
[37] Y. Zhang, H. Liu, J. Niu, X. Wan and D. Wu, *Appl. Energ.*, **264**, 114729 (2020), https://doi.org/10.1016/j.apenergy.2020.114729
[38] D. M. Li and L. P. Shen, *Adv. Mat. Res.*, **332**, 1443 (2011), https://doi.org/10.4028/www.scientific.net/AMR.332-334.1443
[39] B. Wu, L. Shi, Q. Zhang and W. J. Wang, *RSC Adv.*, **7**, 42129 (2017), https://doi.org/10.1039/C7RA06764J
[40] Y. Guan, L. Zhang, D. Wang, J. L. West and S. Fu, *Mater. Design.*, **147**, 28 (2018), https://doi.org/10.1016/j.matdes.2018.03.03039
[41] X. Li, R. Xing, C. Xu, S. Liu, Y. Qin *et al.*, *Carbohyd. Polym.*, **264**, 118050 (2021), https://doi.org/10.1016/j.carbpol.2021.118050
[42] E. A. El-Hefian, M. M. Nasef and A. H. Yahaya, *J. Chem. Soc. Pak.*, **36**, 1 (2014)
[43] K. Iqbal, A. Khan, D. Sun, M. Ashraf, A. Rehman *et al.*, *J. Text. Inst.*, **110**, 625 (2019), https://doi.org/10.1080/00405000.2018.1548088
[44] J. Tabor, K. Chatterjee and T. K. Ghosh, *Adv. Mater. Technol.*, **5**, 1901155 (2020), https://doi.org/10.1002/admt.201901155
[45] Y. Peng and Y. Cui, *Joule*, **4**, 724 (2020), https://doi.org/10.1016/j.joule.2020.02.011
[46] D. G. Prajapati and B. Kandasubramanian, *Polym. Rev.*, **60**, 389 (2020), https://doi.org/10.1080/15583724.2019.1677709
[47] R. Paul (Ed.), "High Performance Technical Textiles", John Wiley & Sons, 2019, pp. 1-9
[48] S. Özkayalar, E. Adıgüzel, S. A. Aksoy and C. Alkan, *Mater. Chem. Phys.*, **252**, 123162 (2020), https://doi.org/10.1016/j.matchemphys.2020.123162
[49] M. S. Tözüm, C. Alkan and S. Alay Aksoy, *J. Ind. Text.*, **51**, 1964S (2022), https://doi.org/10.1177/1528083720980831
[50] M. S. Tözüm, S. Alay Aksoy and C. Alkan, *J. Text. Inst.*, **113**, 2159 (2022), https://doi.org/10.1080/00405000.2021.1972645
[51] C. Alkan, S. Alay Aksoy and R. Altun Anayurt, *Text. Res. J.*, **85**, 2051 (2015), https://doi.org/10.1177/0040517514548751
[52] S. Alay Aksoy, C. Alkan, M. S. Tözüm, S. Demirbağ, R. Altun Anayurt *et al.*, *J. Text. Inst.*, **108**, 30 (2017), https://doi.org/10.1080/00405000.2015.1133128
[53] J. S. Ahn, H. K. Choi and C. Chong-Su, *Biomaterials*, **22**, 923 (2001), https://doi.org/10.1016/S0142-9612(00)00256-8
[54] E. Genç and S. Alay Aksoy, *Text. Appar.*, **26**, 180 (2016), https://dergipark.org.tr/en/download/article-file/218331
[55] Q. Zhang, L. Ma, T. Xue, J. Tian, W. Fan *et al.*, *Compos. B. Eng.*, **248**, 110377 (2023), https://doi.org/10.1016/j.compositesb.2022.110377
[56] W. Fan, Y. Zhang, Y. Sun, S. Wang, C. Zhang *et al.*, *Chem. Eng. J.*, **455**, 140917 (2023), https://doi.org/10.1016/j.cej.2022.140917

[57] S. Chandrasekar, S. Vijayakumar and R. Rajendran, *Biomed. Aging Pathol.*, **4**, 59 (2014), https://doi.org/10.1016/j.biomag.2013.10.007
[58] N. Arshad, K. M. Zia, M. T. Hussain, M. Zuber and M. M. Arshad, *Polym. Bull.*, **79**, 7711 (2022), https://doi.org/10.1007/s00289-021-03871-y
[59] X. Zhao, Y. Xia, Q. Li, X. Ma, F. Quan *et al.*, *Colloids Surf. A: Physicochem. Eng. Asp.*, **444**, 180 (2014), https://doi.org/10.1016/j.colsurfa.2013.12.008
[60] E. Kılık, Master's Thesis, Sakarya University, 2018
[61] S. Asim, M. Wasim, A. Sabir, M. Shafiq, H. Andlib *et al.*, *J. Hazard. Mater.* **343**, 68 (2018), https://doi.org/10.1016/j.jhazmat.2017.09.023
[62] A. Lange, E. Sawosz, M. Wierzbicki, M. Kutwin, K. Daniluk *et al.*, *Materials*, **15**, 3122 (2022), https://doi.org/10.3390/ma15093122
[63] S. K. Sehmi, E. Allan, A. J. MacRobert and I. Parkin, *Microbiologyopen*, **5**, 891 (2016), https://doi.org/10.1002/mbo3.378
[64] M. Kong, X. G. Chen, C. S. Liu, C. G. Liu and X. H. Meng, *Colloid. Surf. B. Biointerfaces*, **65**, 197 (2008), https://doi.org/10.1016/j.colsurfb.2008.04.003
[65] Y. Ni, X. Shi, J. Ma, Z. Jia, H. Qiu *et al.*, *J. Polym. Environ.*, **32**, 2988 (2023), https://doi.org/10.1007/s10924-023-03135-y
[66] J. Li and S. Zhuang, *Eur. Polym. J.*, **138**, 109984 (2020), https://doi.org/10.1016/j.eurpolymj.2020.109984
[67] S. Demirbağ Genç, S. Alay Aksoy and C. Alkan, *Cellulose*, **30**, 2467 (2023), https://doi.org/10.1007/s10570-022-04934-7
[68] S. Demirbağ Genç and S. Alay Aksoy, *Int. J. Cloth. Sci. Tech.*, **34**, 852 (2022), https://doi.org/10.1108/IJCST-08-2021-0105
[69] S. Garg, M. P. Sikka and V. K. Midha, *Res. J. Text. Appar.*, **206** (2022), https://doi.org/10.1108/RJTA-03-2022-0034
[70] M. Havlová, *Fibres Text. East. Eur.*, **2**, 84 (2013)
[71] R. T. Ogulata, *J. Text. Appar. Technol. Manag.*, **5**, 1 (2006)
[72] D. Haroglu, *J. Text. Inst.*, **114**, 265 (2023), https://doi.org/10.1080/00405000.2022.2028361
[73] L. Sabantina and A. Ehrmann, *Comm. Develop. Assembl. Text. Prod.*, **4**, 164 (2023), https://doi.org/10.25367/cdatp.2023.4.p164-170
[74] S. Alay, C. Alkan and F. Göde, *J. Text. Inst.*, **103**, 757 (2012), https://doi.org/10.1080/00405000.2011.606982
[75] M. S. Tözüm and S. Alay Aksoy, *J. Text. Inst.*, **107**, 1203 (2016), https://doi.org/10.1080/00405000.2015.1099374
[76] L. Li, L. Song, T. Hua, W. M. Au and K. S. Wong, *Text. Res. J.*, **83**, 113 (2013), https://doi.org/10.1177/0040517512454184
[77] F. Salaün, E. Devaux, S. Bourbigot and P. Rumeau, *Thermochim. Acta*, **506**, 82 (2010), https://doi.org/10.1016/j.tca.2010.04.020
[78] Y. Shin, D. I. Yoo and K. Son, *J. Appl. Polym. Sci.*, **97**, 910 (2005), https://doi.org/10.1002/app.21846
[79] R. Rathinamoorthy and G. Thilagavathi, *Int. J. Pharmtech. Res.*, **5**, 894 (2013)
[80] M. S. Stan, L. Chirila, A. Popescu, D. M. Radulescu, D. E. Radulescu *et al.*, *Materials*, **12**, 2029 (2019), https://doi.org/10.3390/ma12122029
[81] S. Demirbağ Genç and S. Alay Aksoy, *Text. Appar.*, **32**, 193 (2022), https://doi.org/10.32710/tekstilvekonfeksiyon.979303
[82] A. Marmarali, *Comm. Develop. Assembl. Text. Prod.*, **4**, 42 (2023), https://doi.org/10.25367/cdatp.2023.4.p42-50
[83] N. S. Save, M. A. Jassal and K. Agrawal, *J. Ind. Text.*, **34**, 139 (2005), https://doi.org/10.1177/1528083705047905
[84] S. D. Tohidi, A. A. Jeddi and H. Nosrati, *Int. J. Text. Sci.*, **2**, 73 (2013), https://doi.org/10.5923/j.textile.20130204.01
[85] L. Fridrichová, *Text. Res. J.*, **83**, 883 (2013), https://doi.org/10.1177/0040517512467133
[86] G. Süle, *Text. Res. J.*, **82**, 810 (2012), https://doi.org/10.1177/0040517511433152
[87] Y. Bulut and V. Sülar, *J. Text. Eng.*, 70, **5** (2015)