Core–shell titanium@silica nanoparticles impregnating in poly (itaconic acid)/poly (N-isopropylacrylamide) microgel for multifunctional cellulosic fabrics

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Abstract

A novel method for multi-finishing cellulosic fabrics is based on the consolidation of a thin layer of active material containing micro-gels, titanium nanoparticles and silica. The titanium@silica core–shell particles were synthesized and characterized for their morphological, structural, and compositional properties using X-ray diffraction and scanning electron microscopy. The nanoparticles are approximately 250 nm in size and have a spherical shape. A microgel/titanium@silica nanoparticles composite was prepared mixing with the gel produced from copolymerizing N-isopropyl acrylamide with itaconic acid and then it was characterized. The prepared gel is characterized to be pH and temperature-sensitive. Pad dry cure from the emulsion was used to applied the prepared gel with and without titanium nanoparticles to the cellulosic fabric. Fabric treated with a gel containing and without titanium nanoparticles was tested for antibacterial properties, ultraviolet protection, temperature, and pH sensitivity. According to the evaluation, treated fabric with titanium nanoparticles has better antibacterial, ultraviolet protection, and is more sensitive to pH and temperature than treated fabric without titanium nanoparticles, and both treated fabrics outperform the untreated one.

Keywords Titanium@silica nanoparticles · PNIPAAm/PIA · Cellulosic based materials · Antibacterial activity · pH – Temperature thermos-sensitive

Introduction

Cellulose is one of the natural organic polymers. Cellulosic fabrics have been functionalized to add properties such as flame retardancy [1–7], water/oil repellence [8–11], antimicrobial [12–17], metal adsorption [18–22], gloss properties [23], rodent repellence [24], anti-UV protection [10, 25], Stimuli-responsiveness to temperature, and pH [13, 26], heat storage, [27–30] via a variety of methods, including polymeric material deposition and/or infiltration [31–37], and nano-coating methods [4, 20, 21, 37–41].

Because of the common and easy-to-control temperature changes, thermo responsive hydrogels are one of the most

researched polymer architectures. The hydrogel transmission respond intelligently to temperature variation [42]. Hydrophobic and hydrophilic elements are frequently present in temperature-sensitive hydrogels, and the thermal response phenomena result from the delicate balance of the hydrophobic and hydrophilic parts [43, 44].

Temperature-sensitive component based on different monomer such as (N-isopropyl acrylamide; NIPAA), pH-sensitive (diethylaminoethyl methacrylate; DEAEMA) were produced as the hydrogen components utilised in the sample [17, 45]. As a hydrophobic component, such as copolymerisation of methyl methacrylate with acryloyl phenylalanine, [46] poly((2-dimethyl amino) ethyl methacrylate-co-butyl methacrylate), [47] has been synthesised as a pH sensitive component, with hydrophobic increases in mechanically stable gels [42, 48]. A poly(NIPAAm-co-BMA-co-DEAEMA) and Poly(acrylamide-co-DEAEMA) are shown to affect pH dependent inflation by the temperature [49]. Unconnected analogues of the gel were investigated on the Lower Critical Solution Temperature (LCST) to understand how ionisation

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impacts temperature-dependent swelling of the ionizable component [44, 50].

The most thoroughly investigated thermo-responsive polymer is poly(*N*-isopropylacrylamide) (PNIPAAm) exhibiting a volume-phase transition (e.g., side chain dehydration) in response to modest temperature fluctuations, especially in dyeing quantities [51]. Because of the extremely complicated polarity of the molecule, the transition between coil and globule takes place at a temperature of around 32 °C, named as a lower critical solution temperature (LCST) [52, 53]. Under the LCST the amide group links water molecules into an extended structure by hydrogen bonding (i.e., hydrates), which decomposed through destroying the hydrogen bonding of the LCST, and causing expelling water and precipitating polymer (i.e., its chains dehydrate to form a shrunken structure) [43, 44, 54].

Hydrogels that respond to external stimuli (pH, temperature, light, mechanical, magnetic, or electrical field) are referred to as "stimuli-responsive hydrogels" [55–59]. The sensitivity to temperature and pH are the properties that have received the most attention [60–62]. These polymers also inhibit both Gram-positive and Gram-negative bacteria effectively [63, 64]. In addition presence of metal oxides nanoparticle such as TiO₂, ZnO and SiO₂ are preferable to enhance the ultraviolet blockers and self-cleaning agents [65, 66].

Itaconic acid (ITA) is an unsaturated dicarboxylic acid. It is widely used in a variety of industries, including resin synthesis, textile dyeing, and finishing, biomedical fields, and papermaking [67, 68]. Choi was the first to report on the use of ITA as a cross-linking agent for cotton [69]. Cotton fabric was treated with maleic acid (MA) and itaconic acid (ITA) in the presence of free radical initiator potassium persulfate (K₂S₂O₈) and esterification catalyst sodium hypophosphite (NaH₂PO₂), and they discovered that copolymerization of MA/ITA was successfully impregnated on the cotton surface [69].

3- Glycidylpropyloxytrimethoxy silane (GPTMS) is an essential epoxy silicone cross-linker. The presence of this substance on the substrate surface improved mechanical stability. When the cotton surface is used as a substrate and GPTMS cross-linker is used, chemical interactions occur between the epoxy ring of GPTMS and the hydroxyl groups of the cotton substrate [70–72]. Biopolymer/chitosan/silane composite was synthesized in four forms by conjugating of chitosan with different biopolymer compounds namely, β-Cyclodextrin (β-CD), Arabic gum, Guar gum and pullulan in presence of 3-glycidoxypropyltrimethoxysilan (GPTMS) as a cross-linker. Treated fabrics with chitosan-based microgels were characterized and it is confirmed that, the prepared composites impart a hydrophobicity, pH and temperature thermo-sensitive properties to the cotton fabrics [26].

The goal of this research is to create a new microgel based on itaconic acid to functionalize cotton fabric and give it temperature and pH sensitivity. The addition of titanium@ silica nanoparticles to cotton fabrics adds an additional property to the main target property, such as antibacterial and UV protective properties.

Experimental

Materials

Sigma–Aldrich provided 3-glycidoxypropyltrimethoxy silane (GPTMS, 98%), tetraethoxysilane (TEOS, 99%), and *N*-isopropyl acrylamide (NIPAAm, 97%), sodium hydroxide (NaOH, 97%), ammonium persulphate ((NH₄)₂S₂O₈, 98%), sodium hypophosphite monohydrate (SHP, NaH₂PO₂·H₂O, 99%). Isopropyl alcohol ((CH₃)₂CHOH, 99.5%), ammonia solution (NH₄OH, 25%), butane tetracarboxylic acid (BTCA, [-CH(CO₂H)CH₂CO₂H]₂, 99%), itaconic acid (IA, HO₂CCH₂C(=CH₂)CO₂H, 99%), and titanium (IV) isopropoxide (Ti(OC₃H₇)₄, 97%) were purchased from Across, as were. All chemicals are used exactly as they are received, with no further purification.

Preparation

Preparation of TiO₂@SiO₂ nano-composites

In isopropyl alcohol, three different ratios of titanium (IV) isopropoxide Ti(OC₃H₇)₄ (3, 6, or 9) were added dropwise and stirred at pH 9. A corresponding ratio of tetraethoxysilane (3, 6, or 9, (12 ml) in 30 ml isopropyl alcohol) in isopropyl alcohol was added to these solutions and mechanically stirred for 30 min at 450 rpm to obtain a net volume of mixed oxides. Increasing the pH up to 9 of the solution with a drop-wise addition of 3 ml of ammonia solution resulted in the formation of the mixed oxide gel, which was then stirred for an additional 24 h. The residue was then washed three times with water and dried in the oven for 24 h. The precipitate was calcined for 3 h at 800 °C to remove organic residue and stabilize the materials (see Fig. 1) [73].

Preparation of PNIPAAm/PIA microgel

Five grams of dry NIPAAm were placed in a 10% w/w aqueous IA solution and rested at 4 °C for 24 h to achieve equilibrium swelling. The swollen NIPAAm microspheres was then transferred to a closed round flask contain a cross-linker (GPTMS) for the polymerization process. After 30 min of nitrogen gas passing through the mixture, the temperature was raised to 70 °C. The mixture was treated

Fig. 1 Suggesting mechanism for synthesis of Titanium@silica nanoparticles

with ammonium persulphate. The polymerization process then continued for another 30 min. The grafted PNIPAAm microspheres with PIA were washed with excess water after polymerization to remove any unreacted IA. Finally, the product was vacuum-dried to achieve a constant weight. Titration of the extract against NaOH (0.1 N) to the phenolphthalein endpoint was used to determine the IA content of the PNIPAAm/PIA copolymer microspheres. The suggesting mechanism for preparation of PNIPAAm/PIA microgel was illustrated in Fig. 2.

Incorporation of microgels into cotton

The pad-dry-cure method was used to apply the prepared gel to cotton fabric. After stirring for 15 min, prepared gel

(10 g/l) with and without $\text{TiO}_2/\text{SiO}_2$ nanoparticles were suspended in water, and stirred for 15 min. The pre-treated cotton fabric with butane tetracarboxylic acid (BTCA; 5 g/l) and sodium hypophosphite (SHP; 5 g/l) were then immersed in the prepared solution for 3 min before being padded with an 80 percent wet pickup, dried at 100°C for 5 min, and cured at 130°C for 3 min. The suggesting mechanism for reaction between PNIPAAm/PIA/ $\text{TiO}_2/\text{SiO}_2$ with cellulosic fabric Fig. 3. The treated fabrics were washed and dried at room temperature using the same procedure as for the pre-treatment method.

The actual pickup and add-on of the prepared gel transferred to the treated and untreated fabrics were weighed and calculated using the equations below:

Fig. 2 Suggesting mechanism for preparation of PNIPAAm/PIA microgel

$$\% \text{ Pickup} = \frac{W_2 - W_1}{W_1} \times 100 \quad \% \text{ Add-on} = \frac{W_3 - W_1}{W_1} \times 100$$

where W_1 is the dry fabric weight before padding, W_2 is the wet fabric weight after padding, and W_3 is the dry fabric weight after curing.

Fig. 3 Suggesting mechanism for reaction between PNIPAAm/PIATiO₂@SiO₂ with cellulosic fabric

Characterization

The FT-IR spectra were captured using a JASCO FT-IR spectrometer (ATR). Scanning Electron Microscopy (HITASHI S-3000 microscope) was used to examine the morphological behavior of the treated samples. A JEOL JEM-1200 EX transmission electron microscope operating at 120 kV was used to capture TEM images of prepared nanoparticles and microgels. The laser particle size analyzer ZetaPAL/90 plus was used to further characterize the size and potential of the synthesized microgels (Brookhaven Instruments).

The dry crease recovery angle (CRA) was determined using the AATCC Test Method 66 – 2014 [74]. A SE 1700 Surface Roughness Measuring Device and ASTM Test Method D 7127 – 13 were used to measure fabric roughness [75]. Tensile strength and elongation at a break were determined using ASTM Test Method D 5035–2011 [76]. The given results were calculated using the average of three measurements.

The UV-protection factor (UPF) for untreated and treated samples of cotton fabric was determined by the Australian/New Zealand standard (AS/ NZS 4366–1996). Using a UV spectrophotometer, the UV-protecting factor (UPF) of the treated fabrics was studied by absorption spectroscopy [77].

The measurement of the control reference was as air. The efficiency of UV (UPF) treated fabric was determined by calculating the absorption, transmission, and reflection of UV. The UPF value was determined using the following equation from the transmission spectra of the fabric samples within the range 280–400 nm [15, 37, 61, 72, 78].

$$UPF = \frac{\int_{\lambda_2}^{\lambda_1} E(\lambda) \times S(\lambda) \times \Delta(\lambda)}{\int_{\lambda_1}^{\lambda_2} E(\lambda) \times S(\lambda) \times T(\lambda) \times \Delta(\lambda)}$$

The control relation was calculated as the air where λ_1 and λ_2 were equivalent to 280 and 400 nm respectively, $E(\lambda)$ being the relative erythral spectral effectiveness, $S(\lambda)$ being the solar spectral irradiance in $\text{W} \cdot \text{m}^{-2} \cdot \text{nm}^{-1}$ (λ) and $S(\lambda)$ were derived from the National Oceanic and Atmospheric Administration (NOAA) database, $T(\lambda)$ being the spectral transmission of the sample obtained from UV spectrophotometric experiments and $\Delta(\lambda)$ is the difference between measurable wavelengths.

Because these gels will be used in the textile industry, their antibacterial activity was tested against both gram-positive and gram-negative bacteria (*S. aureus* and *E. coli*). As a result, the samples were tested for antimicrobial activity by measuring the diameter of the inhibition zone (IZD) using the agar diffusion technique modified by Bershteein et al. [79, 80].

Fig. 4 FT-IR sand spectra of $\text{TiO}_2/\text{SiO}_2$ prepared at different $\text{TiO}_2/\text{SiO}_2$ ratios; TS1, TS2, and TS3 for 3:9, 6:6, and 9:3, respectively

45 ml of previously sterilized media was poured to make nutrient agar. A cork borer was used to make holes in treated fabrics (0.9 mm). Each plate was seeded with 0.5 ml of suspension (24 h old) and allowed to solidify and dissolved in sterilized water to obtain a bacterial suspension with a concentration of 100 mg/ml. A portion of each tested bacteria's 100 μ l was added to a petri dish containing treated fabrics. The test plates are incubated for 24 h at 37 °C. The diameter of the inhibition zone (IZD) was measured in millimeters.

Rheological property measurements were carried on a Carri-Med-CSL 100 Rheometer (TA Instruments Ltd., Surry, England) equipped with parallel plate geometry, small amplitude oscillatory rheological experiments were performed (20 mm, diameter).

Textural measurements for the gel paste were measured at a TA-XT2i Texture Analyzer (Stable Micro Systems, England) with an aluminum plate probe was used to measure the freshly created gel (5.0 mm dia.). The following compression mode parameters were set: Pretest speed was 2.0 mm/s, test speed was 1.0 mm/s, and posttest speed was 2.0 mm/s, with a trigger force of 15 g at a distance of 50% of the starting sample. The test yielded a force time curve, which was used to calculate the textural findings. The maximal compressive force that exhibits significant resistance to deformation is characterised as hardness (g force). The maximal force required to overcome the attraction forces between the surface of the sample and the surface of the

probe with which the sample comes into contact is known as stickiness (g force). The negative force area after the initial compression, which represents the work required to draw the compressing plunger away from the sample, was used to determine adhesiveness [81].

Result and discussion

Characterization of silica-coated TiO₂ nanoparticles (TiO₂@SiO₂)

FTIR analysis of TiO₂/SiO₂ particles

The FT-IR spectra of the sol-gel TiO₂@SiO₂ nanocomposite are shown in Fig. 4. The peaks in the spectra at 3396 and 1599 cm^{-1} are caused by the stretching and bending vibration of the -OH group. The weak peak at 3396 $^{-1}$ for TS3 (which contain more TiO₂ nanoparticles) is observed as a result of the decrease the intensity of hydroxyl group which consumed in the chemical reaction between formed nanoparticles to produce the core shell particles and also in calcination process. This decreasing was also confirm the suggesting mechanism. Furthermore, the asymmetric Si-O-Si stretching vibration is represented by the strong observed band at 1079 cm^{-1} . This peak was increased as the ratio increased from TS1 to TS3 as result of the chemical

Fig. 5 XRD pattern of TiO₂@SiO₂

reaction [82]. The peak at 465 cm^{-1} represents the stretching vibration of Ti–O, while the peak at 949 cm^{-1} represents the overlapping vibrations from Si–OH and Si–O–Ti bonds [83]. These findings indicate that a $\text{TiO}_2@\text{SiO}_2$ nanocomposite was created by combining TiO_2 nanoparticles with SiO_2 nanoparticles.

XRD analysis of $\text{TiO}_2/\text{SiO}_2$ particles

Figure 5 depicts the results of XRD studies on titanium-modified silica nanoparticles. $\text{TiO}_2@\text{SiO}_2$ nanoparticles exhibited multiple diffraction peaks that can be attributed to TiO_2 's anatase phase (JCPDS File No. 21–1272) at 25.31° ; 31.4° ; 35.2° ; 38.3° , 56.6° , and 62.8° which are typical for anatase TiO_2 and SiO_2 structure [84]. Furthermore, the TS nanocomposite particles' crystallite type was pure anatase. These findings are consistent with those of Venkateshet al. [85]. The results confirmed the transformation of the TiO_2 shell from amorphous to anatase phase. The peaks were recognised using 2θ , confirming that at $2\theta = 25.31^\circ$, an

anatase structure of SiO_2 was created. The peaks recorded for TiO_2 particle reflection were extremely close to those previously reported [86]. The d-spacing values of 3.4, 2.3, 1.8, 1.68, and 1.65, as well as their relative intensities at 2θ locations 31.4° , 35.2° , 38.3° , 56.6° , and 62.8° , correspond to Anatase data [86].

TEM of $\text{TiO}_2@\text{SiO}_2$ nanoparticles

Figure 6 shows TEM images of prepared core/shell $\text{TiO}_2@\text{SiO}_2$ nanoparticles at various Ti and Si salt concentrations. The TEM images clearly show that the as-prepared $\text{TiO}_2@\text{SiO}_2$ nanocomposite (Fig. 6a) at the $\text{TiO}_2:\text{SiO}_2$ (3:9) ratio has a definite shape with the smallest size compared to the other $\text{TiO}_2:\text{SiO}_2$ concentrations of 6:6 and 9:3. Figure 6a also shows that the TiO_2 nanoparticles were surrounded by SiO_2 nanoparticles, forming the so-called core shell. The distance between two crystal lattices is indicated by the TEM magnification of Fig. 6.

Fig. 6 TEM images for $\text{TiO}_2@\text{SiO}_2$ nanoparticles at different ratios of $\text{TiO}_2:\text{SiO}_2$ nanocomposite; **a)** 3:9, **b)** 6:6, **c)** 9:3 and **d)** crystal lattice at high magnification of (a)

Particle size distribution of TiO₂@SiO₂

The particle size distribution of SiO₂ nanoparticles modified with TiO₂ nanoparticles is shown in Fig. 7. Particles of TiO₂@SiO₂ with a lower TiO₂ concentration have a smaller particle size and particle distribution index (PDI) than SiO₂ particles modified with a high TiO₂ concentration. Understandably, nano-particulate systems with lower PDI are more transparent. In conclusion, the SiO₂:TiO₂

concentration of 3:9 is more suitable for further characterization and application in terms of particle size and distribution particle size.

Zeta potential of TiO₂@SiO₂ nano-composite

The zeta potential (surface charge) measurements are an indirect measure of their physical stability because they

Fig. 7 Particle size analyzer, polydispersity, and histogram of TiO₂@SiO₂ nanoparticles prepared using different ratios of TiO₂: SiO₂; a) 3:9, b) 6:6, c) 9:3

Fig. 8 Zeta potential of $\text{TiO}_2/\text{SiO}_2$ nanocomposite

measure the electric charge at the surface. Figure 8 depicts the zeta potential of a $\text{TiO}_2/\text{SiO}_2$ nanocomposite prepared at a $\text{TiO}_2:\text{SiO}_2$ (3:9) ratio. It is worth noting that the zeta potential value is -31.3 mV. The obtained negative values for $\text{TiO}_2:\text{SiO}_2$ (3:9) Zeta potential can be explained by a negatively charged surface created by a large number of hydroxyl groups available in SiO_2 molecules.

The higher value of zeta potentials implies that the nanoparticle may show good stability in aqueous solutions. There is a specific zeta potential value ($\approx \pm 30$ mV) that determines the stability of nanoparticles because of the presence of high electrostatic repulsive forces between the nanoparticles exhibiting this value.

Characterization of microgels

Figure 9 depicts the swollen size distribution of PNIPAAm/PIA microspheres. This graph confirmed that approximately 65 percent of the particles were in the 150–250 nm range.

Fig. 9 Size distribution of PNIPAAm/PIA microspheres

The grafting of PIA into the PNIPAAm network was investigated using FT-IR spectroscopy. The FT-IR spectra of pure PNIPAAm microspheres and PNIPAAm/PIA graft copolymeric microspheres are shown in Fig. 10. Figure 10 shows pure PNIPAAm microspheres with a characteristic amide I band at 1640 cm^{-1} ($\text{C}=\text{O}$ stretching) and an amide II band at 1564 cm^{-1} ($\text{N}-\text{H}$ bending). In addition, only one $\text{N}-\text{H}$ stretching band, typical of secondary amides, can be seen at 3435 cm^{-1} in the PNIPAAm spectrum. The FT-IR spectrum of the graft copolymer with IA (Fig. 10) shows a stretching band at 1720 cm^{-1} for the carbonyl group ($\text{C}=\text{O}$) of acid. This indicates that the modification of PNIPAAm was successful.

The effect of temperature on the diameter of PNIPAAm/PIA microgel was studied at pH 6.5 and confirmed that the particles are swollen at room temperature with a diameter of around $230\text{ }\mu\text{m}$, but have an average size of $50\text{ }\mu\text{m}$ at 40°C . Figure 11 shows that increasing the temperature from 25 to

Fig. 10 FT-IR spectrum of pure PNIPAAm (A) and PNIPAAm/PIA (B)

40 °C gradually reduced the PNIPAAm/PIA microgel size, which was observed at 40 °C.

The effect of pH on the size of PNIPAAm/PIA microgels was investigated using dynamic light scattering at 20 °C (Fig. 11). At high pH (pH 10), the PNIPAAm/PIA microgel was swollen and had a size of 140 (m. When the pH is reduced, the PNIPAAm/PIA microgel size gradually decreases, eventually reaching 50 μm . As a result of the pH sensitivity, PNIPAAm/PIA microgels swell in basic medium and de-swell in acid medium with fine size.

Figure 12 depicts the textural properties of the PNIPAAm/PIA microgel at various concentrations (10, 15, 20, 25, and 30% w/w). It was discovered that increasing the gel's concentration resulted in a significant increase in the gel's hardness, stickiness, and adhesiveness. The deformability of swollen granules is known to be a major factor contributing to gel strength [87]. These findings indicate that the less mobile state was associated with granular remnants and that the increase in texture properties of the PNIPAAm/PIA micro-particles can be attributed to granule swelling. According to reports, the structure and composition were major factors influencing the rheological behaviour [88].

Figure 12 depicts the flow properties of the PNIPAAm/PIA microgel at various concentrations and temperatures. The samples exhibited Newtonian behaviour with low shear viscosity at temperatures greater than 30 °C and low

Fig. 11 Effect of temperature and pH on the diameter size of PNIPAAm/PIA microgel

Fig. 12 Textural and rheological properties of PNIPAAm/PIA microgel with different concentration and temperature

concentration. The effective concentration of the microgel is small due to the disruption of microgel hydrogen bonds, which causes a minor amount of swelling in a constant viscosity-shear rate relationship [89].

Furthermore, at temperatures below 30 °C and high concentrations, an increase in the effective concentration occupied by the particles is caused by an increase in osmotic

pressure in the polymeric network. Furthermore, as the inter-particle distance between swollen particles decreased, so did the interaction forces, resulting in the observed shear-thinning behavior. When shear force was applied to the microgel dispersion, the particles tended to flow and align themselves in the shear direction. Any increase in shear force indicates that more particles are aligned in the shear direction.

Evaluation of treated cotton fabrics

The pad-dry-cure method was used to treat cotton fabrics with prepared microgel. At 160 °C, the hydroxyl groups on cellulose and the amine groups from the prepared microgel undergo the esterification and amidation with the carboxyl groups from BTCA, respectively.

Scanning electron microscope

The morphological behavior of treated and untreated cotton fabrics with prepared microgel containing core-shell nanoparticles is depicted in Fig. 13. The surface has changed, and the nanoparticles appear to be embedded in the cross-linker coated film. Furthermore, the entire cotton fiber surface is coated with a thin film, and the nanoparticles are visible as clusters on the fiber surface.

Evaluation of the antibacterial properties

Table 1 shows the results of a study on the effect of treated fabrics on two bacteria, *Escherichia coli* (Gram-negative)

and *Staphylococcus aureus* (Gram-positive). When compared to untreated cotton fabric and treated cotton fabric with prepared microgel, treated cotton fabric with TiO_2NPs demonstrated strong antibacterial activity against both tested bacteria.

The antimicrobial activity of the produced gel was influenced by modified silicon and TiO_2NPs , which affect the mode of interaction with the bacteria's cytoplasmic membrane [90].

Evaluation of the mechanical and physical properties

Table 1 compares the mechanical and physical properties of treated cotton fabrics to those of untreated cotton fabrics. The results show that the treated fabrics have a significant decrease in tensile strength and elongation at break. Furthermore, the treatment causes a slight increase in roughness values. This is due to microgel and TiO_2NPs being deposited on the surface of cotton fabrics. Furthermore, the application of the produced film to the cotton surface resulted in an improvement in the crease recovery angle (CRA) of all treated fabrics.

Fig. 13 SEM image of untreated and treated fabric. **a)** untreated fabric, **b)** treated fabric with PNIPAAm/PIA, **c)** treated fabric with PNIPAAm/PIA/ $\text{TiO}_2\text{@SiO}_2$

Table 1 UPF, antibacterial activities, mechanical and physical properties for both untreated and treated cotton fabrics

Sample	Antibacterial activities				Mechanical and physical properties					UPF				
	Zone of inhibition diameter in mm				Tensile Strength (kg)	Elongation at a break (%)	Roughness (μm)	CRA (°)		Before washing	After washing			
								warp	weft					
	E. coli													
	24 h	48 h	72 h		24 h	48 h	72 h							
Untreated	0	0	0	0	0	0	0	41	15	11.65	50	45	11.12	11.08
Treated with microgel	18.2	18.4	18.5	16.1	16.3	16.3	16.3	38.3	13.95	14.895	89	85	32.45	32.33
Treated with microgel and TiO ₂ @SiO ₂	22.3	22.5	22.6	20.3	20.4	20.4	20.4	38.7	14.02	16.16	98	91	255.36	250.66

Evaluation of the UPF factor

The UV-protective properties of treated fabrics were investigated. The control reference was assumed to be air. The UV absorption, transmission, and reflection of treated fabric were measured to demonstrate its protective properties. The samples were measured four times and the average was calculated. Using the following equation, the ultraviolet protection factor (UPF) was calculated from the transmission data.

$$UPF = \frac{\int_{\lambda_2}^{\lambda_1} E(\lambda) \times S(\lambda) \times \Delta(\lambda)}{\int_{\lambda_1}^{\lambda_2} E(\lambda) \times S(\lambda) \times T(\lambda) \times \Delta(\lambda)}$$

The UPF values for both untreated and treated samples with produced microgel with/without TiO₂NPs were reported in Table 1 before and after washing. The UV-protection values of treated fabric with produced microgel and TiO₂@SiO₂ were higher than those of untreated and treated fabric with produced microgel but no TiO₂@SiO₂. According to [91], the UPF of a UV-protected garment should be at least 40–50. As a result, fabric treated with prepared microgel and TiO₂@SiO₂ provides excellent UV protection. Furthermore, the UPF values of the treated fabric did not decrease significantly after washing, confirming the treatment's durability even after washing.

CRA crease recovery angle.

Estimation of the temperature and pH sensitivity of treated fabrics

The temperature and pH sensitivity of treated fabrics was investigated by measuring water uptake of treated fabrics with PNIPAAm/PIA in the presence and absence of TiO₂@SiO₂ nanoparticles at various temperatures (24–40 °C) and pH (3, 7, and 10) (see Fig. 14). Water uptake values for untreated fabrics ranged from 95 to 100% for each measured pH and total tested temperature.

The pH sensitivity of treated cotton fabrics is studied, and it is discovered that water uptake decreases steadily from 24 to 33 °C. Furthermore, as the temperature rises, the water uptake remains constant. Furthermore, when compared to untreated fabric, the treated one has a significant response of around 10%.

PNIPAAm/PIA with and without TiO₂@SiO₂ microparticles are slightly collapsed at lower pH. As a result, at 24 °C, pH 3 has a lower water uptake than pH 7 and pH 10. In any case, at 30 °C, PNIPAAm/PIA with and without TiO₂@SiO₂ microparticles are in the collapsed state, so the measured water uptake over 30 °C is nearly the same for each of the three measured pH.

Fig. 14 Effect of temperature and pH on the water uptake for both untreated and treated cotton fabrics with PNIAAm/PIA with and without TiO₂@SiO₂

The temperature sensitivity at all pH mediums was studied, and it was discovered that increasing the temperature causes the nanoparticle to shrink and expel water, owing to the network of prepared microgel that prevents water molecules from migrating.

When compared to the untreated fabric, it is clear that the loss percent of water uptake is lower due to the collapsing state of the prepared microgel, which is due to the prepared microgel imparting a hydrophobicity property and thus increasing the fabric's hydrophobicity properties.

It is fascinating to note that when the surface changing framework is collapsed, the water uptake is consistently lower than when it is untreated. This perception confirms that once the transition temperature is reached, the surface adjusting framework becomes hydrophobic, giving the treated fabric increased hydrophobicity.

When the temperature is raised, poly-NIPAAm collapses, resulting in a sharp change in polymer adaptation due to the harmony of hydrogen bonding and hydrophobic accumulation of isopropyl groups [92].

As a result, groups of bound water exist along the chain. When the polymer chain is heated, the hydrogen bonds are broken and the polymers become dehydrated overall, causing the chain to abruptly collapse due to the hydrophobic cooperation among the isopropyl groups. Furthermore, because of its hydrophilic nature, which is influenced by the pH of the medium, the incorporation of PIA with a high concentration of hydrophilic groups (carboxyl groups) into the PNIPAAm network is approved.

Conclusion

A polyitaconic acid-based microgel has been synthesized and characterized. TiO₂@SiO₂ nano-composites were synthesized using titanium (IV) isopropoxide Ti(OC₃H₇)₄ and tetraethoxysilane and characterized via different techniques such as particle size, zeta potential, FT-IR, XRD, and TEM. The results confirmed that the TiO₂ nanoparticles were surrounded by SiO₂ nanoparticles, which formed the so-called core-shell, with lower PDI and being uniformly distributed with a zeta potential value of -31.3 mv. A different technique was used to prepare and characterize the PIA/PNIPAAm microgel such as size and distribution. The TEM image and particle size show that the microgel particles have a porous and smaller structure. The effect of temperature on diameter was studied at different pH levels and confirmed that at high pH, the microgel behaves similarly to cellulosic material, whereas at low pH, the acid medium attacks the microgel backbone and becomes soluble. The rheological properties of the PIA/PNIPAAm microgel were also determined, and it was confirmed that at low microgel concentration and high temperature, Newtonian behavior with low shear viscosity was provided.

Finally, the prepared microgel was incorporated into the cotton fabric using the pad-dry-cure method, and the treated fabrics had a thin film coating the entire surface fiber surface and nano titanium clusters on the fiber surface. Further investigation for the treated fabrics was going on for its antibacterial activities against both gram-positive and

gram-negative bacteria (*S. aureus* and *E. coli*), and it is provided that treated fabrics with prepared microgel have an excellent bacterial reduction. Furthermore, the water uptake behavior of untreated and treated fabrics was investigated, and it was confirmed that treated cotton fabrics have a hydrophobicity property.

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Declarations

Conflict of interest We confirm that there is no conflict of interest.

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