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The development of a novel smart material based on colloidal microgels and cotton

Natasa Majcen[1*], Reham Mohsen[1,2], Martin J. Snowden[1], John C. Mitchell[1], Bojana Voncina[3]

[1]Faculty of Engineering and Science, University of Greenwich, Medway, ME4 4TB, UK.

[2] Faculty of Biotechnology, October University for Modern Sciences and Arts, Cairo, Egypt

[3]University of Maribor, Gosposvetska 12, 2000 Maribor, Slovenia

[*]**natasa.majcen@gmail.com**

Abstract

Colloidal microgels are often described as "smart" due to their ability to undergo quite dramatic conformational changes in response to a change in their environmental conditions (e.g. temperature, pH). A range of novel smart materials were developed by the incorporation of colloidal microgels into cotton fabric. A series of microgels have been prepared by a surfactant free emulsion polymerisation based on N-isopropylacrylamide (NIPAM) monomer. Poly(NIPAM) is a thermosensitive polymer which undergoes a conformational transition close to the human skin temperature. Poly(NIPAM) was co-polymerized acrylic acid (AA), to prepare pH / temperature-sensitive microgels. Microgel particles were characterized by scanning electron microscopy (SEM), attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, and dynamic light scattering (DLS).

This research aims at coupling microgel particles onto cotton fibers and comparing between different attachment techniques. The coupling reactions between microgels and cotton cellulose are only feasible if they both have appropriate functionalities. For microgels, this was achieved by using different initiators which introduce different functional groups on the particle surface and different surface charges. Cotton samples were successfully modified by carboxymethylation, periodate oxidation, grafting of 1,2,3,4-butanetetracarboxylic acid, and chloroacetylation in order to target possible reactions with the terminal functional groups of the microgel particles. Microgels were attached to the cotton fabrics using different methods and the bonds formed were determined by ATR-FTIR spectroscopy and SEM. The reaction yields were quantified gravimetrically and the maximum weight increase of cotton samples due to the attached microgels was around 24% (w/w).

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1 Introduction

Colloidal microgels may be defined as a disperse phase of discrete polymeric gel particles, which are typically in the size range of 1nm to 1 µm uniformly dispersed in a continuous solvent medium, swollen by a good solvent [1-5].

Microgels behave like microsponges, absorbing solvated materials into the particles under one of set conditions, then undergoing rapid conformational changes, and releasing them again following environmental changes, such as temperature [1, 6, 7], pH [8], electric field [9], or ionic strength [10], i.e. the temperature responsive microgels display a rapid thermal and solution response. The rapidity of change comes about as a result of microgel particles having very high surface area to volume ratio which allows rapid diffusion of a given stimulus e.g. a reduction in environmental pH, to facilitate a response throughout the matrix of a microgel over very short time scales, typically of the order of a few seconds. They are of considerable academic and commercial interest because of their "sponge-like" properties and their ability to change molecular conformation i.e. shrink and swell in response to a number of different external stimuli [11].

Because of their "sponge-like" nature, they can hold a large volume of water within their open polymeric network structure. Water is held in interstitial sites between polymer chains. When swollen in water this conformation is retained by the presence of hydrogen bonds between polymer chains and water molecules. There is a balance of hydrophobic and hydrophilic interactions. When the microgel adopts a collapsed conformation the hydrophobic interactions become prevalent over the hydrophilic, and the particle as a whole becomes more hydrophobic in nature [3, 11].

Microgels are a two phase system consisting of a dispersed phase (i.e. the polymeric particles) dispersed throughout a medium (typically water). Unlike a single phase system, a microgel will display typical colloidal characteristics e.g. turbidity. They have similar properties to polymers and other water-swollen gels (bulk gels and hydrogels). Microgels are discrete particles with characteristics that are dependent on the method of preparation, cross-link density, monomer concentration, monomer composition and solvency conditions [7, 12, 13].

Poly(N-isopropylacrylamide) p(NIPAM) is one of the most widely studied microgels due to its different applications that include biological and non-biological ones [11]. p(NIPAM) is a temperature responsive microgel with a volume phase transition temperature around 34-35ºC which is close to the human body temperature (37 ºC). The addition of co-monomers can add different triggers and change the

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conformation of the particles. For example, adding acrylic acid (AA) as a co-monomer to p(NIPAM) particles adds pH responsiveness and produces temperature / pH responsive ones [3]. This combination of monomer and c-monomer seem to be suitable for delivering drugs to wounded tissues that have a different pH than healthy ones and so it was used in this work.

Different strategies for attaching p(NIPAM) onto cotton cellulose can be found in the literature. These include: grafting initiated by γ-irradiation [14, 15] and grafting initiated by ammonium cerium (IV) nitrate [16]. However, in these cases, NIPAM was attached to cotton cellulose only in the form of a hydrogel. The advantage of microgels over hydrogels is the speed at which the conformational change occurs. Conformational change occurs in the order of seconds for microgels, while conformational change occurs in order of hours or even days for hydrogels. The speed of the conformational change is of great importance where stimuli-responsive material should react instantly e.g. wound dressings (especially in severe wounds), clothes with incorporated actives. The attachment of microgels onto cotton fabric can be achieved using different approaches: grafting through initiator-activated cotton while simultaneously synthesizing microgels, modification of cotton cellulose to target specific reactions with terminal functional groups on microgels, attachment by hydrogen bonds formation, ionic interactions, or diffusion into cotton fabric using standard methods for fabric dying/modification in textile industry (i.e. exhaustion, thermofixation).

The aim of this project was to couple microgel particles onto cotton fibres. The coupling reactions are only feasible if both microgel and cotton have appropriate functionalities; for the microgels, this was achieved by using different initiators. One particular consideration in the microgel preparation was to prepare both pH- and temperature-sensitive particles and Poly(NIPAM) was therefore co-polymerized with acrylic acid. A range of colloidal microgels have been prepared by surfactant free emulsion polymerization (SFEP) [12, 17, 18]. These include poly(NIPAM), and poly(NIPAM)-co-acrylic acid (temperature / pH responsive) microgels. Different initiators with positive or negative surface charge were used and different terminal functional groups were incorporated some microgel particles. Different approaches were used for cotton modification in order to introduce appropriate functional groups for reactions with microgels. These are: periodate oxidation and 1,2,3,4-butaneteracarboxylic acid (BTCA)-grafting. Microgels were attached onto cotton samples to produce smart material using the following methods: physical mixing, exhaustion, thermofixation, and polymer grafting.

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2 Experimental Details

2.1 Materials

All chemicals were obtained from commercial and industrial suppliers and used without further purification: N-isopropylacrylamide 97% (Aldrich), acrylic acid (Aldrich), N,N'-methylenebisacrylamide 99% (Aldrich), Potassium persulphate 98% (BDH Laboratory Suppliers (GPR™), 4,4'-azobis(4-cyanovaleric acid) (Acros Organics), and 2,2'-azobis(2-methylpropionamidine) dihydrochloride 97% (Aldrich), sodium periodate (Aldrich), 1,2,3,4-butanetetracarboxylic acid (BTCA) (Aldrich), cyanamide (CA) (Aldrich), and ammonium dihydrogenphosphate (ADHP) (Aldrich). Dialysis tubing (molecular weight cut off = 12000 – 14000 Dalton) was obtained from Visking Medicell International Ltd. 100% bleached cotton fabric with a weight 167 g/m^2 was used.

2.2 Methods

2.2.1 Microgel synthesis

The microgel dispersions were prepared by a surfactant free emulsion polymerization (SFEP), which was first described by Pelton and Chiabante [7]. The initiator was weighed and placed together with 800 mL of deonized water into a 1L reaction vessel to which a 3 neck lid was clamped. The reaction vessel then was placed onto a feedback hotplate stirrer and heated with constant stirring to 70°C. N-isopropylacrylamide (NIPAM), co-monomer (acrylic acid), and cross-linker (N,N'-methylene bisacrylamide) were weighed out according to table 1 and transferred into a beaker together with 200 mL of deionized water and stirred gently with a magnetic stirrer. Once the reagents were dissolved they were transferred into the reaction vessel containing the initiator. The reaction was carried out under an inert atmosphere of nitrogen with continuous stirring for 6 hours. When the reaction was complete the microgel dispersion was cooled to room temperature, filtered through glass wool and transferred to dialysis tubing. The dialysate was changed at least 3 times daily until the conductivity of the dialysate was below 1μS cm^{-1}. The microgel dispersions were stored in a fridge at 3°C until further use.

Anionic microgel dispersions with terminal -SO$_4^-$ groups were prepared using potassium persulphate initiator. Similarly, the second anionic microgel dispersions with terminal -COO$^-$ groups were prepared by using 4,4'-azobis(4-cyanovaleric acid) as an initiator. Cationic microgel dispersions with -NH$_3^+$ groups

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were prepared using 2,2'-azobis(2-methylpropionamidine) dihydrochloride as the initiator. The microgel particles produced contain fixed charged groups on their surface from the ionic initiator.

For the synthesis of cationic microgels it is important to pre-treat all glassware before use in order to prevent the adhesion of material to the glass. For this reason all glassware was rinsed with a silanisation solution (dichlorodimethylsilane 2% (v/v) in 1,1,1-trichloroethane) and oven dried over night at 100°C.

The actual masses of reagents used for the synthesis of each microgel are shown in table 1:

Table 1: Mass of reagents used for the preparation of microgel dispersions

Name of sample	Mass of NIPAM mono-mer [g]	Mass of co-monomer [g] AA	Ratio of NIPAM: co-monomer [w/w %]	Mass of initiator [g] CA	PA	Mass of cross-linker MA [g]	Nature of resultant microgel particles
M1	5.0	-	100:0	-	0.5	0.5	Temperature-sensitive, cationic.
M2	4.75	0.25	95:5	0.5	-	0.5	Temperature- and pH-sensitive, anionic.

Where:AA = acrylic acid, CA = 4,4'-azobis(4-cyanovaleric acid), PA = 2,2'-azobis(2-methylpropionamidine) dihydrochloride, and MA = N,N'-methylenebisacrylamide*.*

2.2.2 Cotton modification

Cotton fabric was cut into pieces with an approximate weight of 1g (~ 2 x 5 cm). For each cotton modification, samples were prepared in 5 replicates and then oven dried at 104°C before and after

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treatments until constant weight was obtained (~ 4 hours). Where applicable, standard deviation of weight increase due to modification was calculated. Cotton samples were weighed (using a six digit balance) before and after grafting / attachment of microgels to determine the added weight.

2.2.2.1 Periodate oxidation

For the preparation of oxidized cotton, the cotton fabric was placed in a 250mL round bottom flask fitted with a magnetic stirrer. To this 0.877g sodium periodate was added for each 1g of cotton fabric. 50 mL distilled water was added per 1g of cotton fabric and the solution was stirred in dark for 4 hours at a room temperature. The samples were rinsed in running water for 10 min and then dried at 104°C until a constant weight was obtained.

2.2.2.2 Modification with BTCA

Cotton samples were immersed in treating baths on a Mathis foulard. The aqueous treating solution contains 100 mL deonized water, 6g BTCA, the curing catalysts CA (5g) and ADHP (1g). The fabric was passed through the pad mangle squeeze rollers, immersed again with treating solution, and again passed through squeeze rollers to give a wet pick up of ~ 95 - 105%. The fabric was then suspended in a forced draught oven and predried at 90°C for 5 min. After curing at 130°C for 3 min, the samples were rinsed in running water for 10 min and then dried at 104°C until a constant weight was obtained.

2.2.3. Strategies for attachment

Samples for each experiment of microgels attachment onto cotton were prepared in 5 replicates. Samples were oven dried at 104°C before and after experiments until constant weight (~ 4 hours). The standard deviation of weight increase was calculated.

2.2.3.1 Physical mixing

Cotton sample was placed into 50 mL microcentrifuge tube and mixed with 30 mL of microgel dispersion for 48 hours using a Denley Spiramix 5 rollerbed mixer. Microcentrifuge tube was then placed in a water bath at 70°C for 2 hours. Samples were then put into an ultrasonic bath (Decon FS 300). After the treatment, the samples were rinsed in running water for 10 min and then dried at 104°C until constant weight was obtained.

2.2.3.2 Exhaustion method

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Cotton sample was placed into a 100 mL beaker with 30 mL of microgel dispersion and mixed on a Mathis labomat BFA-12 for 4 hours at 70°C. After the treatment, the samples were rinsed in running water for 10 min and then dried at 104°C until a constant weight was obtained.

Mathis labomat BFA-12 is a beaker dyer for textile sample dyeing at elevated temperatures. This apparatus is commonly used for mimicking the treatment conditions used in textile industry on small textile samples. The beakers are under constant rotation, and are heated from above by infrared radiators. The angle of inclination of the beakers to the disc is chosen in such a way as to get a good liquor circulation by the rotation of the disc. The temperature of the sample is monitored by a sensor in one of the beakers. The programmable process controller Mathis Univision Touch S is used to control the time and temperature of the treatment.

2.2.3.4 Thermofixation method

Cotton samples were immersed in treating baths containing microgel dispersions (30 mL of dispersion per 1g cotton) on a Mathis foulard. The pH of treating solutions was adjusted with dilute HCl or NaOH. The fabric was passed through the pad mangle squeeze rollers, wetted again with treating solution, and again passed through squeeze rollers to give a wet pick up of ~ 95 - 105%. Samples were suspended in a Mathis forced draught oven and predried at 90°C for 5 min. After curing at 130°C for 3 min, the samples were rinsed in running water for 10 min and then dried at 104°C until a constant weight was obtained.

2.2.3.5 Polymer grafting

Cotton samples (5g) were placed in the reaction vessel together with 1 L deionized water with monomer, initiator, and cross-linker at the beginning of the polymerization. The reaction was carried out according to the microgel synthesis detailed earlier. After grafting, the samples were rinsed in running water for 10 min and then dried at 104°C until a constant weight was obtained.

2.2.4 Characterization methods

2.2.4.1 Scanning electron microscopy (SEM)

SEM of the microgel particles were obtained using a Stereoscan 360 scanning electron microscope operated at 15 kV. Microgel particles were supported on carbon grids by micropipetting ~10μL of dispersion onto the grids and allowing them to dry.

2.2..4.2 Dynamic light scattering (DLS)

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DLS measurements were performed using a Malvern Zetasizer Nano SZ. All samples were diluted with distilled water to an appropriate concentration before the measurements: 1mL of microgel dispersion was diluted with 3 mL of distilled water. The temperature of the dispersion was controlled by a Peltier thermocouple. The samples were equilibrated at each temperature for 15 minutes before data collection. Samples were analyzed over the range 10-60°C. Three measurements were made at each temperature, each consisting of 10 sub-runs in order to obtain an average hydrodynamic diameter. The pH of the samples was adjusted with diluted HCl and NaOH. Measurement parameters were set to be optimized at each temperature in order to take into account the changes in particle size (and therefore count rate) and hence the turbidity of the sample. Optimization was carried out by automatic changes in the attenuator settings and measurements position. The data were analyzed using the Malvern Zetasizer Nano software.

2.2.4.3 IR-spectroscopy and mapping

IR measurements were performed with a Perkin Elmer Spectrum GX FT-IR spectrometer equipped with a Golden Gate ATR with a diamond crystal. Samples were forced into almost perfect optical contact with the diamond using a sapphire anvil assembly mounted overhead on a unique swing bridge. Reproducible loads of 3 kbar can be applied using a special torque wrench supplied with the unit. The data were analyzed by the Perkin Elmer Spectrum Life software.

For IR mapping an image was generated by scanning a cotton sample point by point and a spectrum was obtained for each point. In this project, a grid of the size 75 x 75 µm was created with 16 pixels of the size 25 x 25 µm. Finally, a spectrum was systematically collected from each pixel of the grid. The intensity of the band at 1550 cm^{-1} was used for plotting a map with Origin Pro 7.0 after the intensity of the same band for blank cotton was deducted. For all IR maps the same color scheme was used from black areas with low band intensity to red areas with high band intensity.

2.2.4.4 Dry weight

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The dry weight of a colloidal dispersion is a measure of the solids content of the particles in the dispersion medium expressed as (w/w) %. Samples were weighed in triplicates before and after drying in the oven set at 100°C until a constant weight was obtained. The effective concentration of the microgel dispersion was then calculated from the weight difference following equation 1:
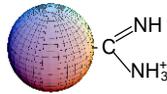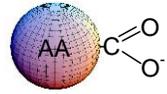
Equation 1: $$\frac{\text{Residual weight after drying}}{\text{Total weight of dispersion before drying}} \times 100 = \% \text{ solids content}(w/w)\%$$

3. Results and discussion

3.1 Microgel synthesis and characterisation

Microgel dispersions with different functional groups and different co-monomers were prepared. Reaction yield, pH of prepared microgel dispersions and particle size are sumarised in table 2. With variation of the composition of the microgels, the dry weight does not significantly change. The average dry weight for all microgels was approximately 0.5% (5g/1000mL). The reaction yield was calculated from the total weight of reagents (6g = 100%). The average reaction yield was 83.3%, which illustrates the efficiency of SFEP. The pH of microgels dispersions was measured after dialysis.

Table 2: Reaction yield, pH of dispersions, particle size and schematic representation of microgel particles

Microgel (composition detailed in table 1)	Reaction yield (total weight = 6g) [%]	pH of dispersion	Particle size at 20 °C [nm]	Particle size at 50 °C [nm]	Schematic representation
M1 (100%poly(NIPAM), cationic-PA)	92	5.9	708 ± 11	163 ± 3	
M2 (95/5 (w/w %))	75	5.5	639 ± 5	375 ± 4	

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poly(NIPAM)-co-AA, anionic-KP)					

Where: AA = acrylic acid, KP = potassium persulphate, and PA = 2,2'-azobis(2-methylpropionamidine) dihydrochloride.

Figure 1 shows an SEM image of the M1 microgel particles. This method was used for determination of particle morphology. The presence of discrete sphere shaped particles is evidence of successful polymerization of microgels which was consistent for microgels M1 – M2.
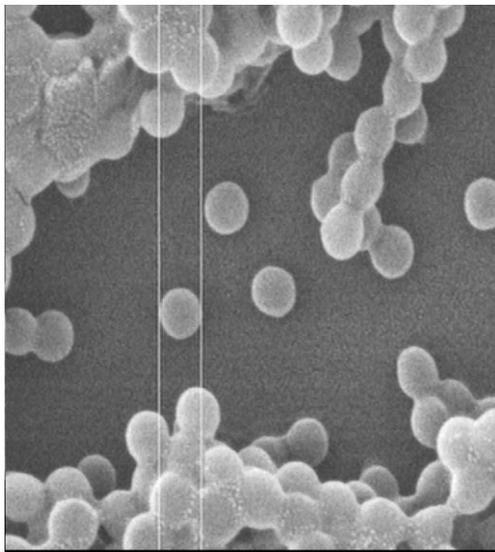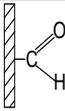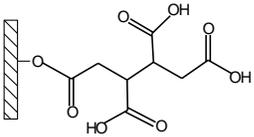

Figure 1: SEM of M1 microgel

3.2 Cotton modification

Cotton samples are summarized in table 3. Cotton C1 is blank cotton, samples C2 and C3 are modified as explained in experimental section.

Table 3: Schematic representation and sample names for cotton and modified cotton

COTTON NAME	SCHEMATIC REPRESENTATION	SAMPLE NAME
Blank cotton		C1
Peroidate oxidized cotton		C2
1,2,3,4-butanetetracarboxylic acid (BTCA) grafted cotton		C3

ATR-FTIR analysis of untreated cotton (C1), oxidized cotton samples (C2) and cotton modified with BTCA (C3) is complicated because of the high affinity of the samples with water (figure 2). In fact, one of the bands of absorbed and bonded water is in the region of the carbonyl group (between 1635 and 1670 cm^{-1}) and can often mask the bands of carbonyl groups. Moreover, in the oxidized samples the identification of the functional groups is complicated because aldehyde, keto and carboxyl groups of oxycellulose absorb in a very narrow region of the spectrum, between 1720 and 1780 cm^{-1}. For samples oxidized with metaperiodate, the identification of the aldehydic group is even more difficult, since dialdehyde cellulose can exist in partially or completely hydrated form, i.e. under forms that do not present a classical peak of the aldehydic carbonyl [19]. IR spectroscopy does not show the presence of aldehyde groups, however, the evidence of the treatment can be found in SEM images (figure 3). For C3 samples modified with BTCA , the absorption band at 1718 cm^{-1} could be due to stretching vibration of C=O in BTCA which suggests successful cotton modification.
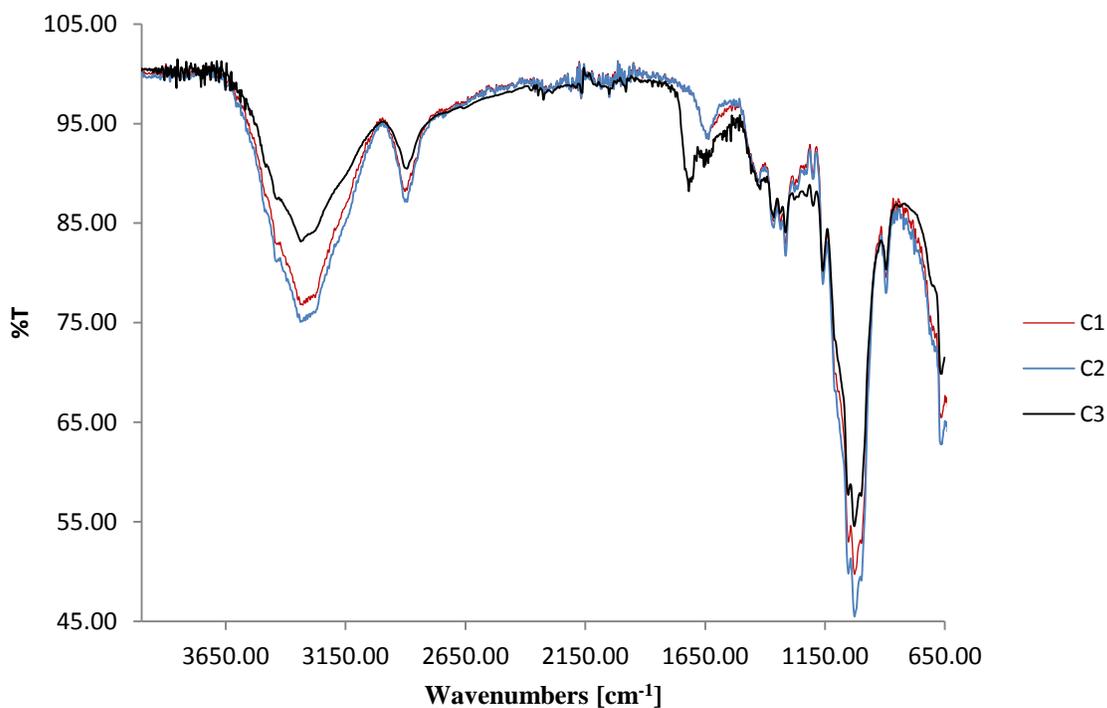
Figure 2: ATR-FTIR spectra of C1, C2 and C3

SEM images of untreated cotton (C1) and oxidized cotton (C2) are shown in figure 3. The presence of cracks in the cotton fiber is the consequence of the oxidation. The pore size of blank cotton is approximately 3 nm [20]. The size of cracks on the SEM image is in the range of µm which could allow the penetration of microgel particles into fibers.
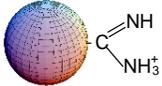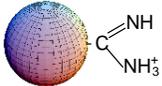
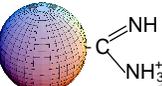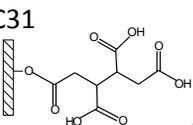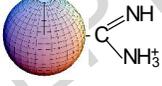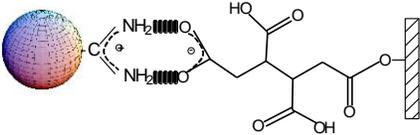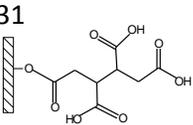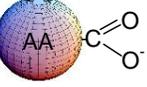Novel smart material based on colloidal microgels and cotton fabric
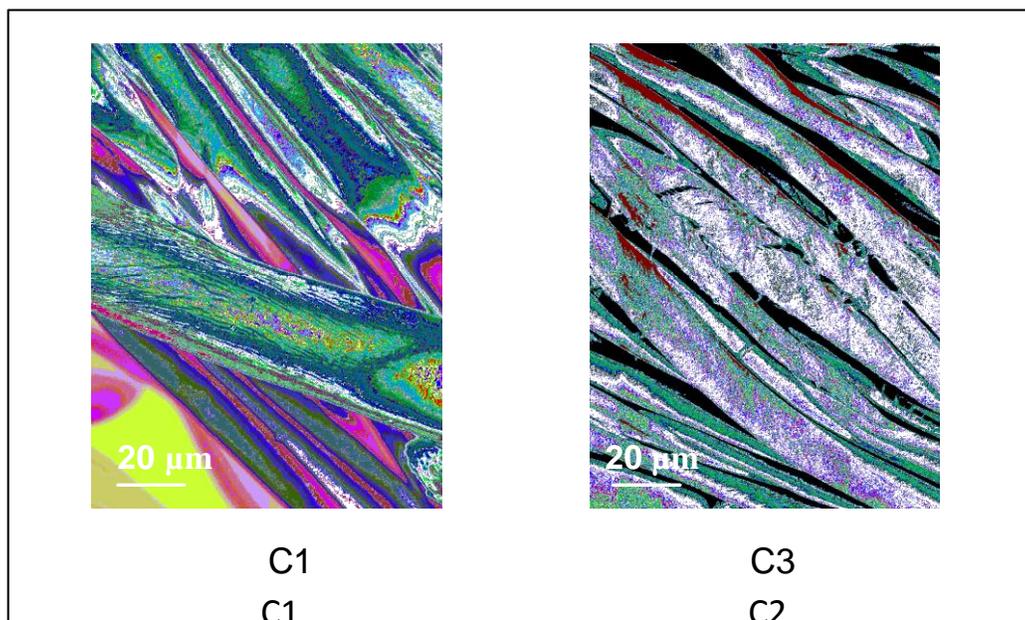
Figure 3: SEM images of C1 and C2

3.3 Strategies for attachment

3.3.1 Physical mixing

The combinations of cotton samples and microgels are summarized in table 4. The incorporation of microgels with this method is mainly driven by the diffusion of microgel particles into the fabric structure when cotton cellulose swells and absorbs water. After drying, the microgel particles are located in the interstitial spaces between the fibers. When the material is immersed in water, fibers swell and close the interstitial areas through which the microgel particles could be washed out. Ionic interactions and H-bonds between cationic microgel and hydroxyl groups of cotton cellulose could also contribute to successful incorporation of microgel particles. To increase the entrapment of particles, the fabric was exposed to ultrasound.

Table 4: Illustration of the microgel, cotton fabric and attachment method used for the preparation of each sample.

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Sample name	Cotton	Microgel	Treatment conditions	Interaction	Average weight increase [w/w %]	SD
D1	C1	M1	2 hours, 70°C, pH 6, ultrasound 30 min	**Physical mixing**: Physical attachment due to diffusion into fabric, ionic interactions, H-bonds	4.11	0.19
D2	C2	M1	2 hours 70°C, pH 6, ultrasound 30 min	**Physical mixing**: Physical attachment due to diffusion into fabric, ionic interactions, H-bonds	3.98	0.12
D3	C1	M1	4 hours 70°C, pH 6	**Exhaustion:** Physical attachment due to diffusion into fabric, ionic interactions, H-bonds	5.1	0.31
D4	C31	M1	pH = 6.0 130°C 3min	**Thermofixation:**	2.22	0.40
D5	C31	M2	pH = 2.7 130°C 3min	**Thermofixation:**	3.02	0.40

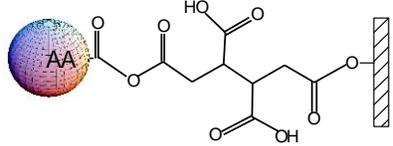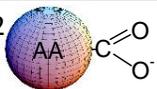Novel smart material based on colloidal microgels and cotton fabric

D6	C1	M2	pH = 2.7 CA, ADHP 130°C 3min	**Thermofixation:**	3.71	0.20
D7	C1	M1	one pot reaction, 70°C, 8h, under N_2	**Polymer grafting:**	23.51	0.29
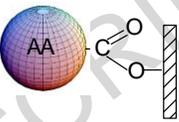
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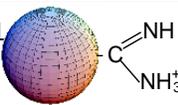Figure 4 shows ATR-FTIR spectra of blank cotton C1, sample D1, C2 and D2 (to compare the effect of using different cotton fibres (C1 and C2) with M1. Comparing the spectra of C1 and D1, it can be concluded that the additional bands in the spectrum for D1 are due to the presence of microgels: C-H stretching vibrations at 2970 cm^{-1}, amide I and II bands at 1650 and 1550 cm^{-1}, and the isopropyl bending vibrations at 1465 cm^{-1}.
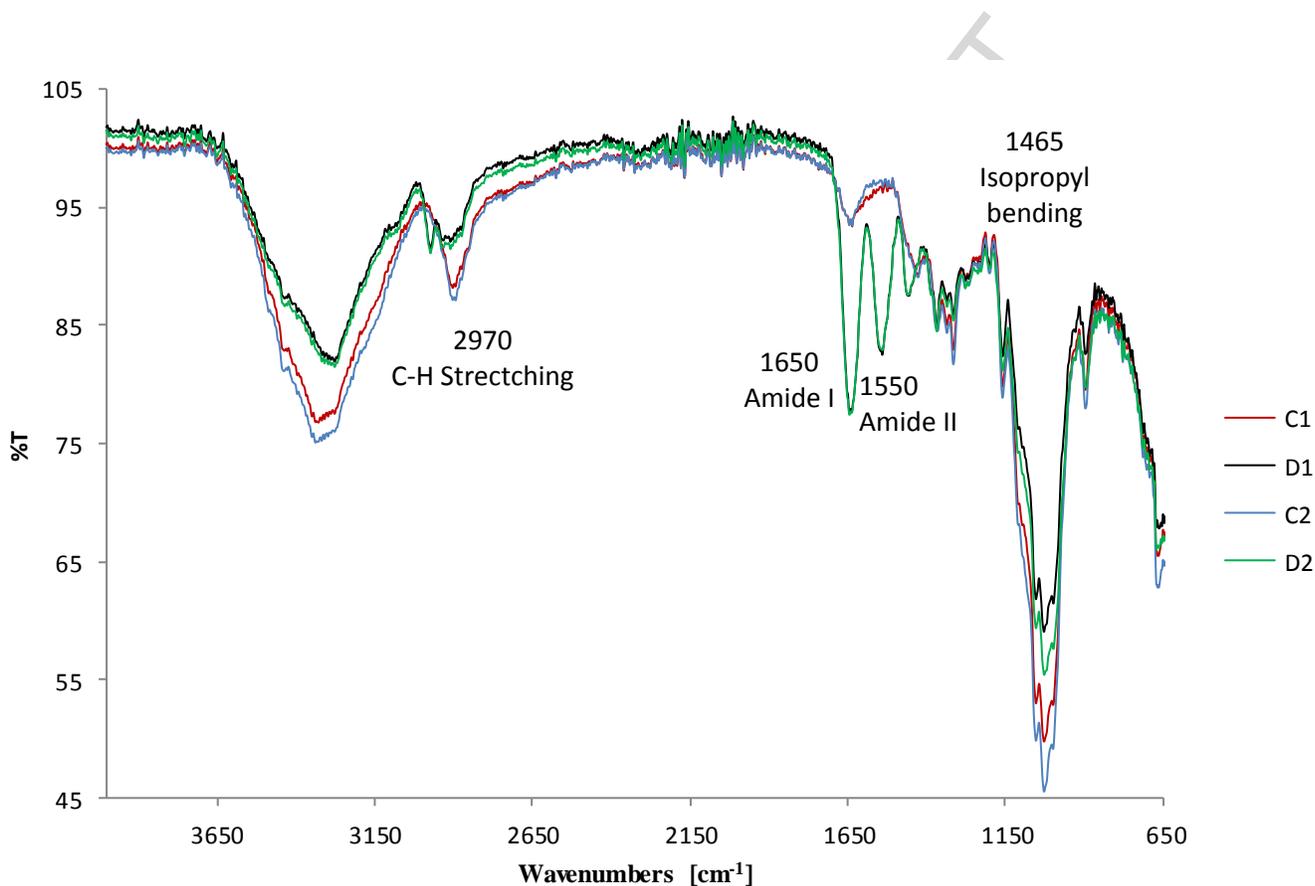
Figure 4: ATR-FTIR spectra of C1, D1, C2 and D2

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The vibrational band at 1550 cm^{-1} which corresponds to amide II band was used for IR mapping experiments. An image was generated by scanning a cotton sample point by point and 16 spectra were obtained forming a grid of the size 75 x 75 µm. Figure 5 shows an IR map of D1 which gives the information about the microgel distribution on cotton fabric. Black areas on the map would indicate that there is no microgel on the fabric. The IR map for D1 show the dark blue area with the lowest microgel concentration, large light blue area with higher microgel concentration, and green area with the highest microgel concentration on cotton fabric. The IR map is a proof of microgel coating over the area of interest on the cotton fabric.
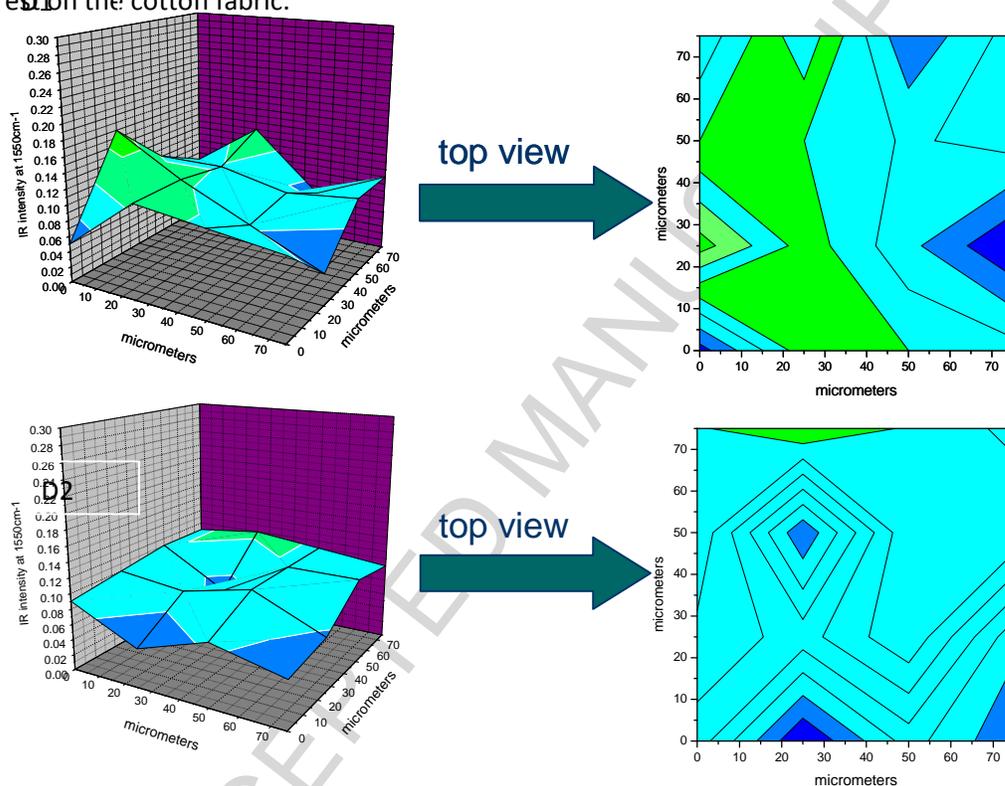

Figure 5: IR mapping of samples D1 and D2

ATR-FTIR spectra of D2 and oxidized cotton C2 are also shown in figure 4. Similar to the spectrum of D1, the additional bands in the spectrum of D2 are due to the presence of microgels. Figure 5 also shows IR map of D2. The only difference between D1 and D2 is the cotton: C2 has aldehyde functional groups and cracks in fibres while C1 is blank cotton. The IR map for D2 is very similar to the map of D1. There are no black areas on the map which is a proof that the microgel particles coat the whole area under investigation. IR map

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for D2 consists mainly of light blue areas, which suggests more equal distribution of particles on cotton fabric than in the case of D1.

Figure 6 shows the SEM images of D1 and D2. It can be seen in both images that the microgel is coating cotton fibers.
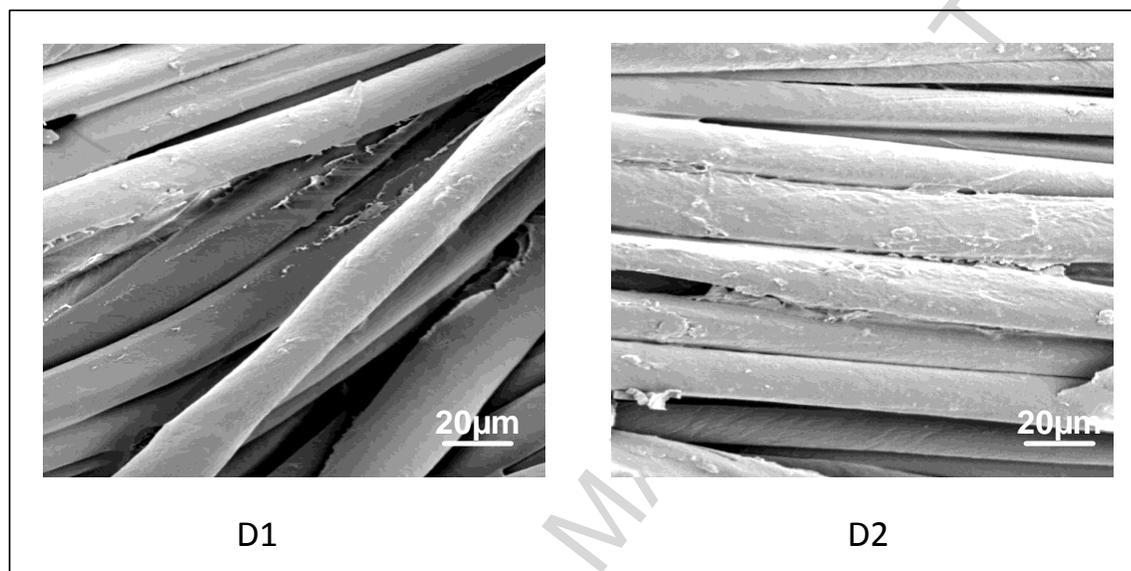
Figure 6: SEM of D1 and D2

3.3.2 Exhaustion method

The combination of cotton and microgels is shown in table 4. Sample D3 was prepared by attaching M1 to blank cotton C1 using exhaustion method (Table 4). Similar to physical mixing, the attachment is mainly driven by diffusion of microgel particles into the fabric structure while cotton cellulose swells and uptakes water. The additional contributions to microgels incorporation are also ionic interactions and H-bonds between cationic microgel and hydroxyl groups of cotton cellulose. Figure 7 shows ATR-FTIR spectra of D3 in comparison to blank cotton C1. The additional vibrational bands in the spectrum of D3 are due to the presence of microgels on cotton fabric.
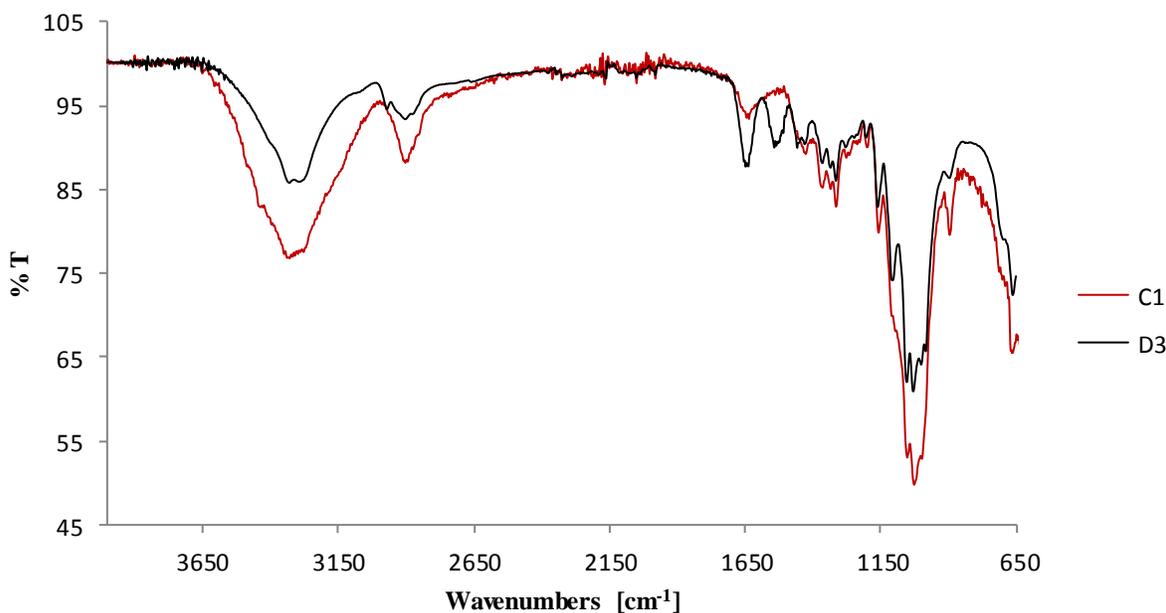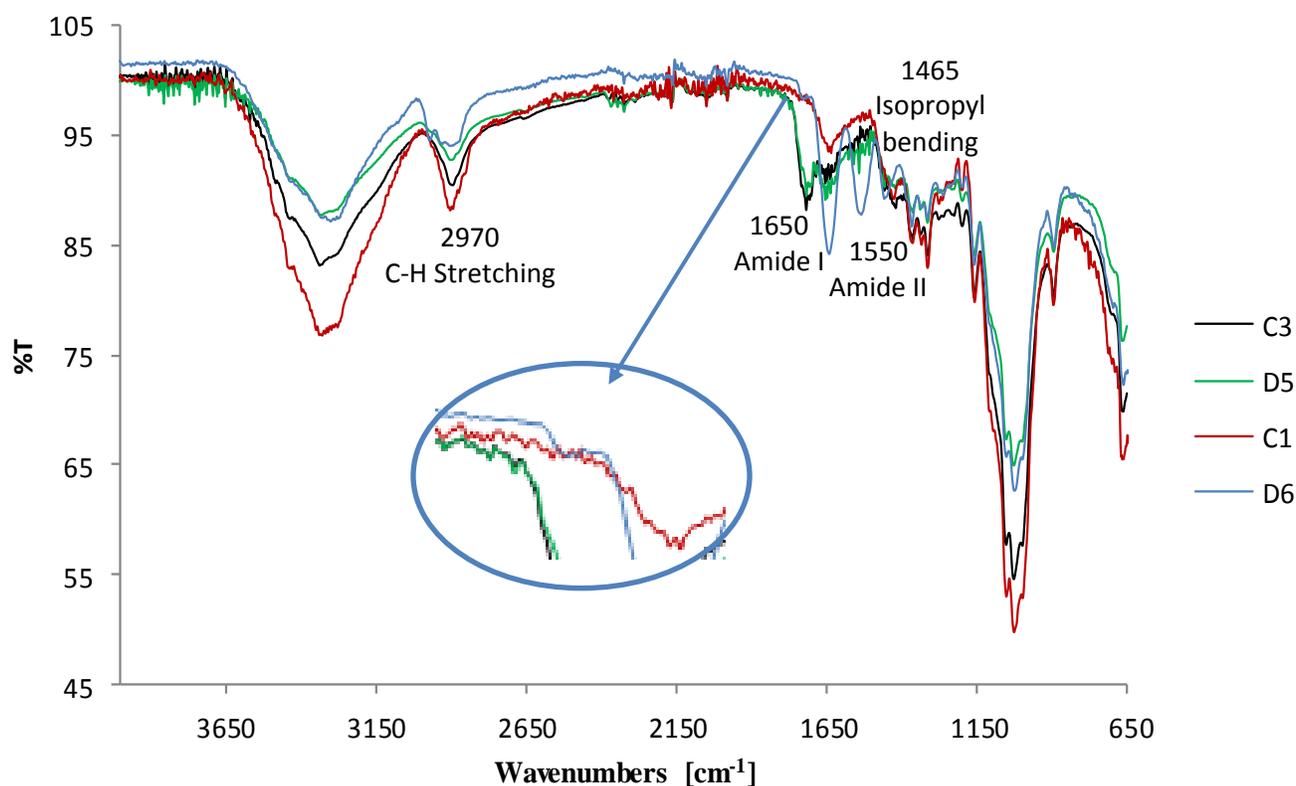
Figure 7: ATR-FTIR spectra of C1 and D3

3.3.3 Thermofixation method

Table 4 shows the composition of the samples prepared using thermofixation. Amidine functional groups of the microgel can form salt bridges with the carboxylic acid of modified cotton as shown for D4 [21]. The pH of the treating baths in this experiment was in the range of 2.7 – 9. However, the interactions occur only at pH 4 and 6. An anhydride can be formed by dehydrating a carboxylic acid and elimination of water between two carboxylic acid molecules. An anhydride formation was targeted as an interaction between BTCA-grafted cotton and microgel with carboxylic acid terminal functional groups (D5). The reaction was more successful under more acidic conditions (pH = 2.7). After modification with microgel dispersions, cotton samples were rinsed with running water. At this stage water molecules could hydrolyze the formed anhydride and break the bond between the microgel and the cotton. However, in the case of D5 the average weight increase of cotton fabric due to modification with microgels was 3% after rinsing with running water.

Esters can be synthesized in a condensation reaction between an acid and an alcohol. In case of cotton, an ester bond will form by reaction of cellulose hydroxyl groups with polycarboxylic acids through an anhydride intermediate [22, 23]. Udomkichdecha *et al.* [24] showed that acrylic acid co-polymerized with maleic acid can form an ester bond with cotton cellulose. Similar conditions for the esterification

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reaction can be achieved by using microgel particles with incorporated acrylic acid and cyanovaleric acid initiator with cotton fabric (D6). Reaction was catalyzed by CA and ADHP and was more successful at acidic conditions (pH = 2.7).
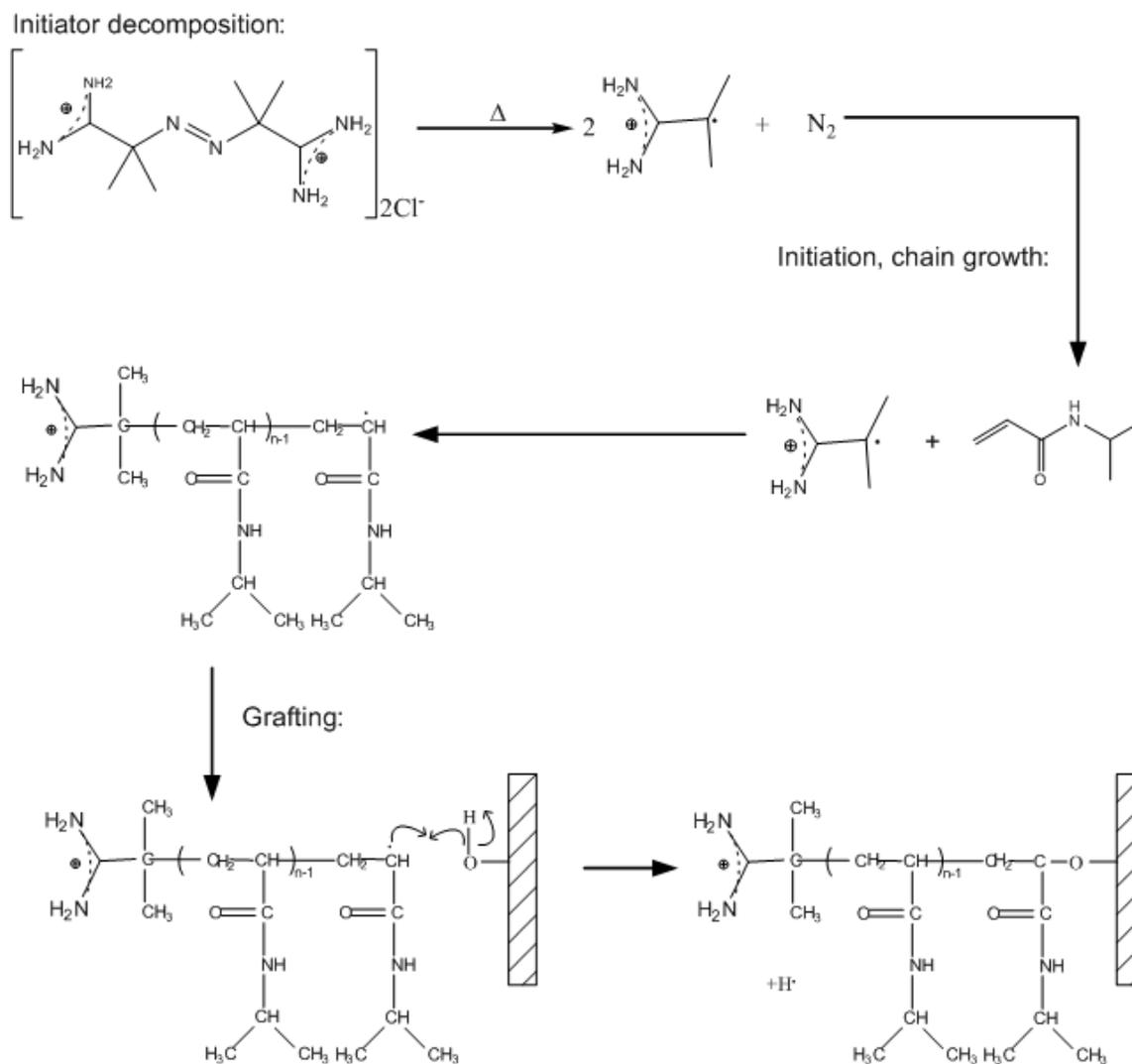
Figure 8 shows ATR-FTIR spectra of D5 in comparison to BTCA-grafted cotton C3. The additional vibrational bands in the spectrum of D5 are due to the presence of microgels on cotton fabric. However, there is no evidence for the anhydride bond in the spectra. Figure 8 also shows ATR-FTIR spectra of D6 in comparison to blank cotton C1. In the spectrum of D6 there are additional vibrational bands due to the presence of microgels on the cotton fabric and a vibrational band at 1741 cm^{-1} which can be ascribed to C=O stretching vibration of an ester.

Figure 8: ATR-FTIR spectra of C3, D5, C1 and D6

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3.3.4 Polymer grafting

The cotton and microgels used are shown in table 4. The average weight increase of cotton fabric due to modification with microgels was the highest among all methods of modification. This is expected when comparing a chemical grafting method with other physical ones such as physical mixing and thermofixation (Table 4). The proposed mechanism of the grafting reaction is shown in figure 9. The decomposition of the amidine initiator is followed by initiation of both cotton and NIPAM monomer. After the initiation, NIPAM polymer chains grow and grafting of poly(NIPAM) chain onto cotton fabric occurs. The application of stirring allows the movement of polymer chains in the reaction flask and the ionic repulsion due to amidine initiator forces the polymer chains to adopt a spherical shape. The cross-linker irreversibly connects the polymer chains in a sphere shaped particle. Ghosh and Das [25] carried out similar work on cotton modification based on potassium persulphate initiator and acrylic acid as a monomer.

Initiator decomposition:

Initiation, chain growth:

Grafting:

Figure 9: Reaction scheme showing the modification of cotton cellulose with microgels by grafting

The surface morphology of microgel-grafted cotton D7 was examined by SEM (figure 10). In the SEM image of D7 it can be seen that the fabric is coated with microgels (right). At a higher magnification the sphere shaped microgel particles can be clearly seen in the micrograph (left).
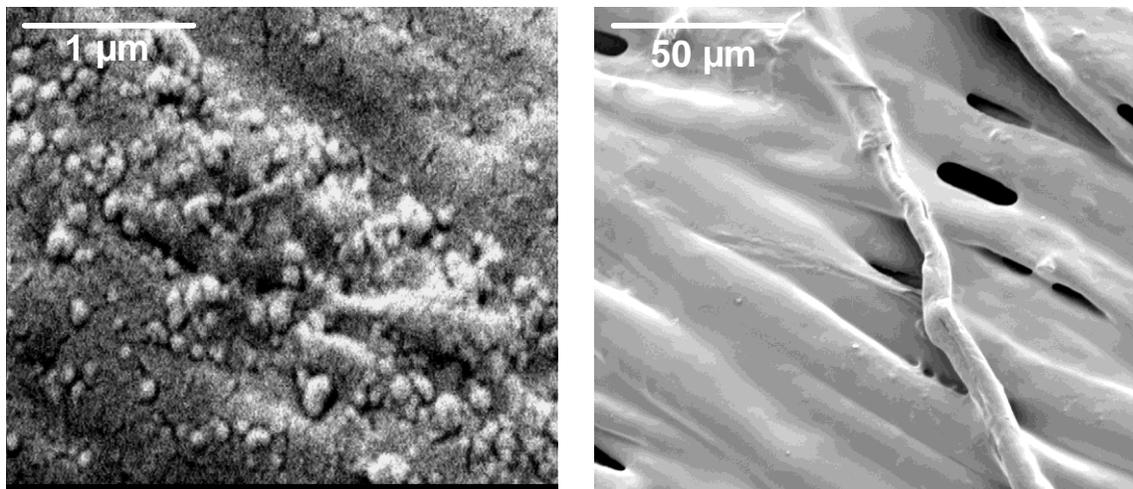
Figure 10: SEM images of D7

Figure 11 shows ATR-FTIR spectra of D7 and blank cotton C1. Additional vibrational bands in the spectrum of D7 are due to the presence of microgels on the cotton. The most prominent band for ether would be due to C-O stretch, 1300-1000 cm^{-1}. However, there is no evidence of the new ether bond that links microgels with cotton.

Figure 12 shows an IR map of D7 based on an amide II band. The IR map shows the distribution of microgels on cotton fabric. Red area has the highest and dark blue area has the lowest microgel concentration on the fabric.
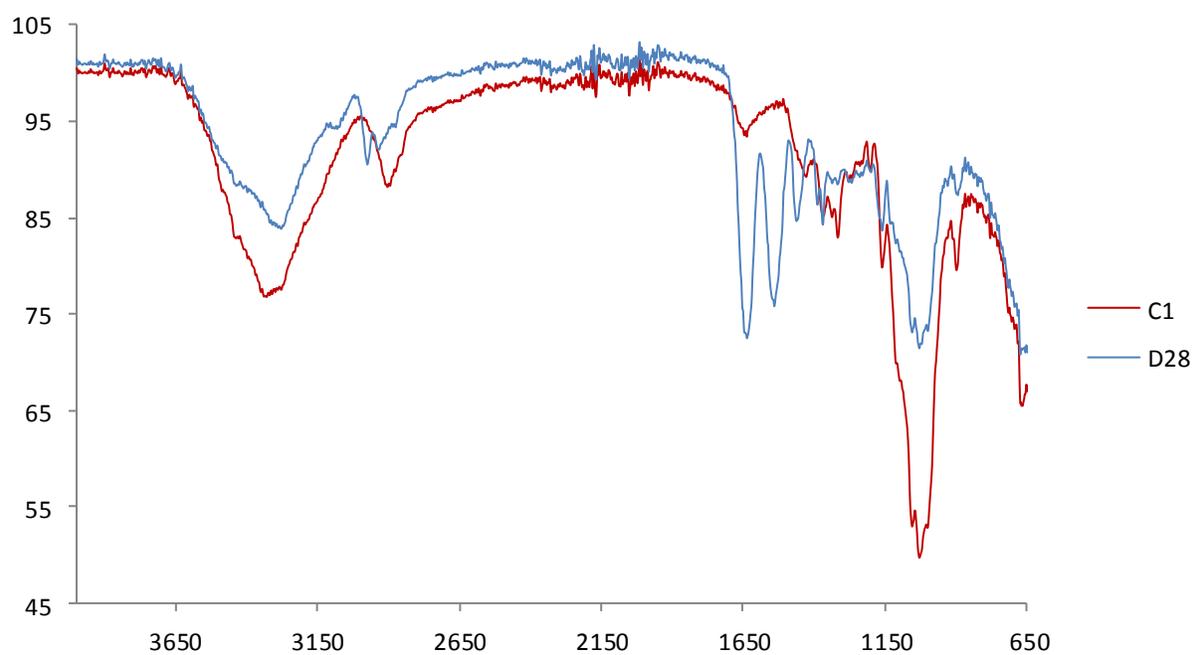
Figure 11: ATR-FTIR spectra of C1 and D7

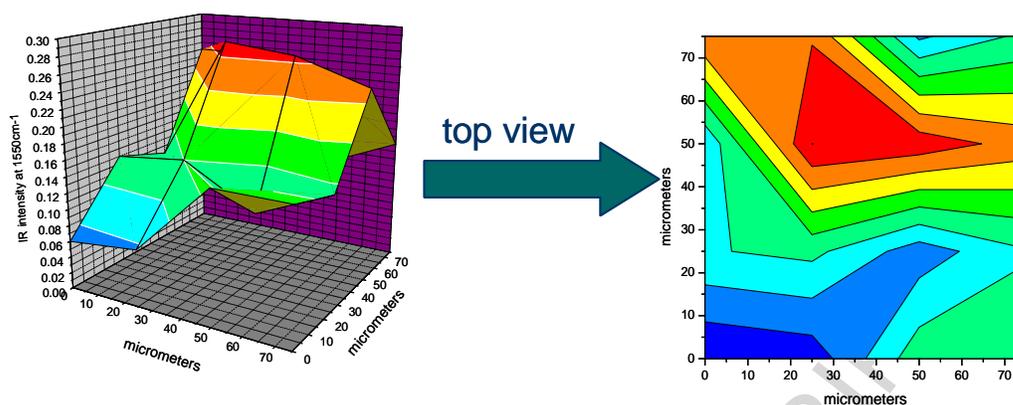Novel smart material based on colloidal microgels and cotton fabric

Figure 12: IR mapping of the sample D7

Conclusion

Cotton cellulose was successfully modified by periodate oxidation and BTCA-grafting. By cotton modification, new functional groups were introduced to cellulose prior to microgel attachment in order to target possible reactions with terminal functional groups on the microgel surface.

SEM results suggest cotton modification by periodate oxidation. ATR-FTIR spectrum of BTCA-grafted cotton displays a new absorption band for stretching vibration of C=O functional group which is a proof of cotton modification with BTCA.

Microgels were attached to cotton fabric using different methods: physical mixing, exhaustion method, thermofixation method, and polymer grafting.

By using these methods, attachment of microgels onto cotton fabric can occur due to: grafting through initiator-activated cotton during microgel synthesis, specific reactions of modified cotton cellulose with terminal functional groups of the microgels, hydrogen bonds, ionic interactions, or diffusion into cotton fabric using standard methods for fabric dying/modification in textile industry (i.e. exhaustion, thermofixation).

Microgel attachment on cotton fabric by physical mixing is based on weak interactions (hydrogen bonds, ionic interactions, or entrapment in the fabric network when water emerges) and the maximum weight increase of cotton samples due to microgels was ~ 4 %. With prolonged reaction time and improved

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water circulation (exhaustion method) the maximum weight increase of cotton samples due to microgels was ~ 5 %. When the attachment occurred through water elimination (thermofixation method), the weight increase of samples due to microgels was slightly lower (~ 3.7 %). This could be due to water elimination or due to insufficient time of the fabric treatment with microgels prior to thermofixation (cotton fabric was dipped into microgel dispersion on foulard). Polymer grafting was the most successful method of attachment and results in the highest weight increase of cotton fabric due to microgels (~ 23 %).

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Graphical Abstract
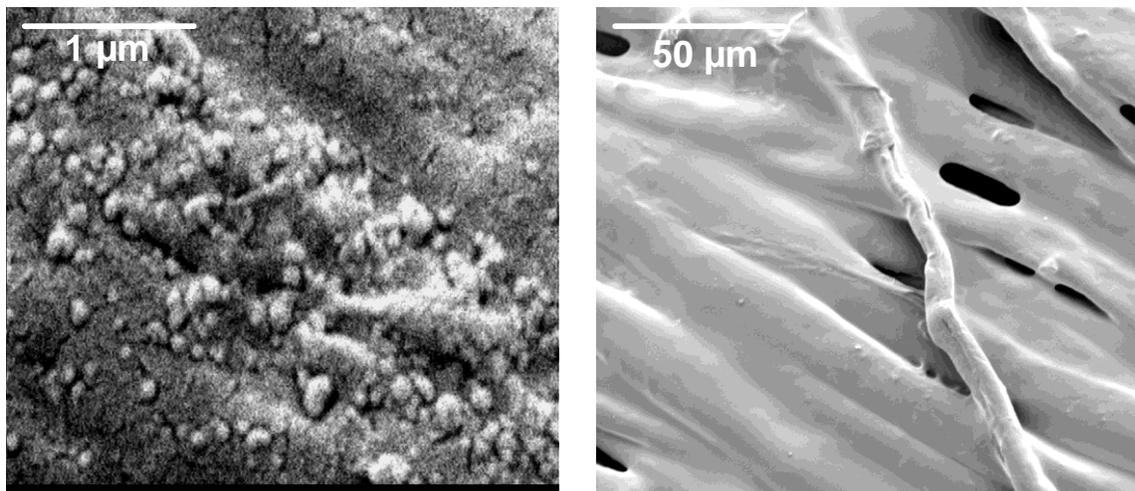
SEM images of cationic p(NIPAM) attached to blank cotton using polymer grafting.

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Highlights

- Smart materials

- Modified cotton

- Wound dressings and Biomaterials

- Microbes

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