

Silan/biopolymer microgels for functionalization of cotton fabric: dual responsive pH and temperature and antibacterial properties

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ABSTRACT

Biopolymer/chitosan/silan 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-glycidoxypolytrimethoxysilan (GPTMS) as a cross-linker. Characterisation of the prepared composites has been done through some measurements. FT-IR confirmed the chemical reactions between biopolymers, chitosan and GPTMS. TEM and particle size confirm that, the particles are in small size ranged from 20 - 200 μ m and have porous structure. Textural properties of the prepared composites were studied and provide that, the microgel with pullulan have the best texture properties than other gels, and gel with guar gum have a worst texture properties. Studying the pH effect found that, the microgels particle size was changing with increasing/decreasing the temperature. The flow properties of the chitosan based microgels at different concentrations and different temperatures were also determined. Treated fabrics with chitosan-based microgels were characterized for their morphological structure, antibacterial properties, water uptake for untreated and treated fabrics at different pHs and temperatures and it is confirmed that, the prepared composites impart a hydrophobicity property to the cotton fabrics.

INTRODUCTION

Cellulose is a natural polymer (Mohamed and Hassabo, 2015; Visakh and Arao, 2015) and it is useful to functionalize it to impart additional properties. Functionalization have been occurred through different methods such as surface functionalization through deposition and/or infiltration of polymeric materials. (Abo-Shosha *et al.*, 2009; Hassabo *et al.*, 2015; Ibrahim *et al.*, 2013; Mohamed *et al.*, 2013; Mohamed *et al.*, 2013; Waly *et al.*, 2009; Waly *et al.*, 2012) another way to functionalize natural fibres by a nano-coating methods.

(El-Zawahry *et al.*, 2016; Hassabo, 2011; Hassabo *et al.*, 2015; Hassabo *et al.*, 2014; Hassabo and Mohamed, 2016; Mohamed *et al.*, 2014) Therefore, to impart external properties to cotton fabric, like, flame retardancy, (Mohamed *et al.*, 2014; Waly *et al.*, 2008; Waly *et al.*, 2012) water/oil repellence, (Ibrahim *et al.*, 2013) antimicrobial, (Hassabo *et al.*, 2015; Mohamed *et al.*, 2016; Nada *et al.*, 2015) metal adsorption, (El-Zawahry *et al.*, 2016; Hassabo and Mohamed, 2016; Raj *et al.*, 2013; Singh *et al.*, 2014) gloss properties, (Hassabo *et al.*, 2014) rodent repellent, (Nada *et al.*, 2016) Stimuli-responsiveness pH and temperature, (Mohamed *et al.*, 2016) heat storage, (Hassabo, 2014; Hassabo *et al.*, 2015) it should be functionalised (S or z unify functionalized) with special finishing agents to have such properties and to obtain smart textile. Biopolymers have specific properties (biocompatibility and biodegradability) which make it very important in the improvement of environmentally coating (Mohamed and Hassabo, 2015).

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However, most biopolymers are not biocides. Therefore, antimicrobial activity has been improved by adding biocide materials during their processing, such as chitosan, quaternary ammonium groups and silan compounds (Hassabo *et al.*, 2015; Mohamed *et al.*, 2016; Mohamed and Hassabo, 2015). Chitosan is a copolymer of glucosamine and N-acetyl glucosamine and it has many properties such as biodegradability, biocompatibility and its nontoxicity (Crini *et al.*, 2014; Özen *et al.*, 2015; Wang and Chen, 2014). On its structure; chitosan has amine functional groups, which has strong affinity toward metal ions and other functional group. Pullulan is an important biopolymer compound have a repeated glucose unit linked as a (1/6) (Catley *et al.*, 1986; Zajic and LeDuy, 1973). Pullulan containing materials with biocide agents have a good antibacterial properties (Gniewosz and Synowiec, 2011). In addition, it has an excellent physical properties, such as, solubility in water, anti-inflammatory, antithrombotic, anticoagulant and adhesive properties. Therefore, pullulan is easily to utilise as flocculent, foaming and adhesive agent (Cheng *et al.*, 2011; Singh *et al.*, 2008). Furthermore, pullulan films, hydrogels and composites with antimicrobial properties can be prepared by incorporation of biocide agents. β -Cyclodextrin (CD) are cyclic oligosaccharides from seven cyclic maltose produced by enzymatic degradation of starch (El-Tahlawy *et al.*, 2006). It has a hydroxyl groups located at the top and bottom of the ring. Thus, the hydrophobic cavity of cyclodextrin can be include different hydrophobic compounds (Takashima *et al.*, 2004). Arabic gum is a branched-chain biopolymer and it can be either neutral or slightly acidic aqueous solutions (Ali *et al.*, 2009). It has an advantage to be used as flocculent agent to remove the toxic metals from water (Dauqan and Abdullah, 2013). Guar gum is a non-ionic, branched chain polymer, consisting of a mannose units joined by β -D (1–4) linkages with branched α -D-galactopyranose units joined by (1–6) linkages.

Presence of epoxysilanes such as 3-glycidylpropyloxytrimethoxysilan (GPTMS) on the surface of cotton cause increasing of the coating properties and enhancing the mechanical stability. This improving is due to chemical reactions between epoxy ring of GPTMS and hydroxyl groups on the cotton surface. (Abidi *et al.*, 2007; Mahltig *et al.*, 2005; Mohamed *et al.*, 2014; Park *et al.*, 1999; Schramm *et al.*, 2004)

Stimuli-responsive hydrogels are response hydrogels to external environment such as solvent composition, temperature, light, pH, mechanical force and magnetic or electrical field (Bonina *et al.*, 2004; Guo *et al.*, 2007; Mohamed *et al.*, 2016; Roy *et al.*, 2010; Santos *et al.*, 2010; Suwa *et al.*, 1998). Temperature and pH-responsive hydrogels have been studied more than others. It is swell or shrink according to changes in environmental pH and temperature. This phenomena is due to polymer protonation (Hariharan and Peppas, 1996).

This work aimed to functionalized cotton surface with a chitosan based microgel (biopolymer/chitosan/GPTMS) to improve its physical properties. Modification of chitosan to be able to react with biopolymers will occurred. Prepared composite will

reacted with GPTMS to be act as cross-linker. This composite will impart many properties to the surface such as antibacterial, temperature and pH-responsive. Therefore, the final prepared composite can impart new properties for multi textile usage.

EXPERIMENTAL

Materials

Chitosan high molecular weight (Cs), β -cyclodextrin (β -CD) epichlorohydrin and 3-glycidyloxypropyltrimethoxy silane (GPTMS) were purchased from Sigma–Aldrich and used as received without further purification. Pullulan was produced by Carbosynth Co. Arabic gum and guar gum were purchased from local market and used without further purification. sodium hydroxide (NaOH), acetone, hydrochloric acid (HCl), acetic acid were all of analytical grade.

Preparation

Preparation of Microgel based on Chitosan

Modification of the biopolymers

The biopolymers (β -CD, Arabic gum, guar gum and pullulan) have been synthesized by a limited polycondensation of biopolymer with epichlorohydrin. A typical synthesis procedure for a molar ratio of EP/ biopolymer = 10 was described as follows: a mixture of 5 g of biopolymer in NaOH solution (10%) (8 ml for β -CD and 30 ml for other biopolymer) was mechanically stirred overnight at room temperature. The mixture was heated to 50°C and 3.5 ml of EP was added. 20 ml acetone was added to stop the reaction after 3 h. After decantation, acetone was removed. After decreasing the pH of the aqueous solution to 12 with hydrochloric acid, it was kept at 50 °C overnight. Cooled, neutralized with hydrochloric acid and filtrated, the solution obtained was evaporated and the solid was washed with acetone to purify it. At last, the white product was isolated by filtration and dried.

Synthesis of Microgel based on chitosan

Chitosan–biopolymer microgels were prepared according to this method: chitosan powder was dissolved in 2.0% (v/v) aqueous acetic acid solution to prepare 1.5% chitosan solution. The solution was stirred at ambient temperature for overnight. GPTMS was added with 1:0.5 ratio (biopolymer: GPTMS) into this solution with vigorous stirring (500 rpm) at 50°C for 3 h. At the end of this period, 1 g of prepared modified biopolymer was added. Then the solution was kept on stirring at constant temperature for 1 h.

Incorporation of Microgels to cotton

Pad-dry-cure method was used to incorporate and cross-linked the Chitosan based microgels to cotton using butanetetracarboxylic acid (BTCA) as a crosslinking. The ratio of BTCA: Chitosan based microgels was maintained at 1:4 and of BTCA: SHP at 2:1. The treatment method was described as follow: BTCA (0.6 wt.%) and the catalyst SHP (0.3 wt.%) were

added to 10 ml Chitosan based microgels dispersion, then stirred for 15 min (5×5 cm) washed cotton fabric were dipped in the reaction mixture for 10 min and then padded (with 100% pick-up) using laboratory padder. Then samples were dried at 70°C and cured at 160°C. After that, the samples were washed for 45 min in an aqueous solution containing non-ionic detergent (2 g/l) with a liquor ratio of 25:1 at 60°C, and then rinsed twice in cold tap water.

Characterization

FT-IR spectra were recorded on a JASCO FT-IR spectrometer (ATR). Scanning Electron Microscopy HITACHI S-3000 microscope S, at 15-kV acceleration voltage, after gold coating was used to study the surface morphology of the composite films. Transmission electron microscopy (TEM) images of prepared microgels were recorded by a JEOL JEM-1200 EX transmission electron microscope operating at 120 KV. The size and potential of the synthesized microgels were further characterized by laser particle size analyser ZetaPAL/90plus (Brookhaven Instruments) equipped with a He-Ne laser (632.8 nm, 35 mW). 4 ml of dilute Ag colloid was added into quartz cuvette for the determination. The antibacterial examination was quantitatively evaluated against gram-positive bacterium (*S. aureus*) and gram-negative bacterium (*E. coli*) because the segels will be used in textile application. In order to study the antibacterial activity of the prepared gels, 1 ml of each prepared gel were prepared in aseptic manner. Each gram was placed in a sterile vial add 800 μ l distilled water then shaking for 10 min. Sterilized Tryptone soy broth (2.2 ml) was then added to each vial to make up a total volume of 3 ml. An aliquot (10 μ l) of *S. aureus* suspension was added to each vial (1.6×10^3 ml) containing the prepared gel. Control broths with and without bacterial inoculation were also included. The vials were then incubated with agitation at 35 °C, 220 rpm. Aliquots of 10 μ l broth were sampled at 24 h and serial dilution for the aliquots was prepared in broth. Duplicate aliquots (50 μ l) of the serially diluted samples were spread on to plates. The plates were incubated at 35 °C and bacterial counts were performed. The bacteriostatic activity was evaluated after 24 h and percent reduction of bacteria calculated using the following equation:

$$R\% = \left[\frac{A - B}{A} \right] \times 100$$

Where R = the reduction rate, A = the number of bacterial colonies from untreated fabrics, and B = the number of bacterial colonies from treated fabrics.

RESULT AND DISCUSSION

Characterization of Microgels based on Chitosan (CS-CDM) microgels

Four types of microgels based on chitosan with pullulan, β -CD, Arabic gum and guar gum were prepared. The FT-IR spectra of chitosan based microgel with pullulan, β -CD, Arabic gum and guar gum in the final microgel form are presented Fig. 1.

In addition, the FT-IR of each pure biopolymer and modified one (biopolymer/EP) beside the modified chitosan with GPTMS were also presented.

The characteristic bands of biopolymers appeared in the spectra of modified biopolymers. Peak around 2860 cm^{-1} is attributed to $-\text{CH}_2$ group, which also indicates that the modification of biopolymers have been prepared successfully. Moreover, in the modified biopolymers spectra, the characteristic peak for Chlorine and epoxy group were absence.

In addition, the FT-IR spectra of chitosan and modified chitosan with GPTMS are also illustrated in and provide that, the reaction between chitosan (NH_2) and GPTMS was observed near 1590 cm^{-1} (N-H bending vibration of the primary amine group). Absorption at 920 cm^{-1} , which is associated with Si-OH bonds. The broad band at 1000–1100 cm^{-1} owe to the absorption of the Si-O-C bonds. The peak at 800-920 cm^{-1} is the characteristic bands of β -(1,4) glucopyranose in biopolymers (García-Zubiri *et al.*, 2003).

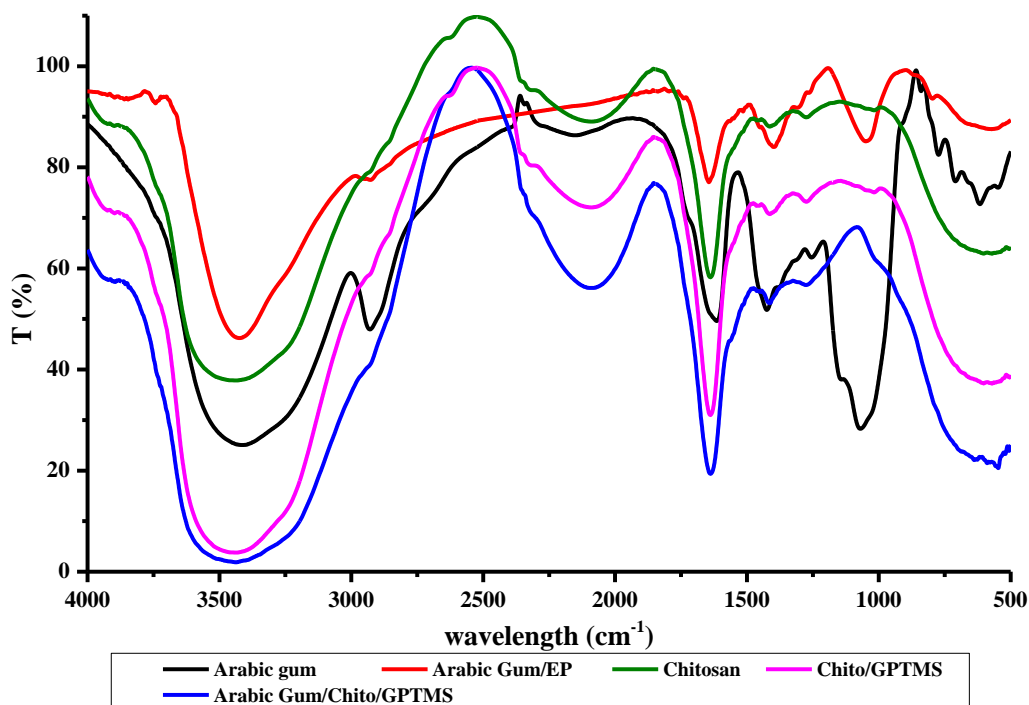
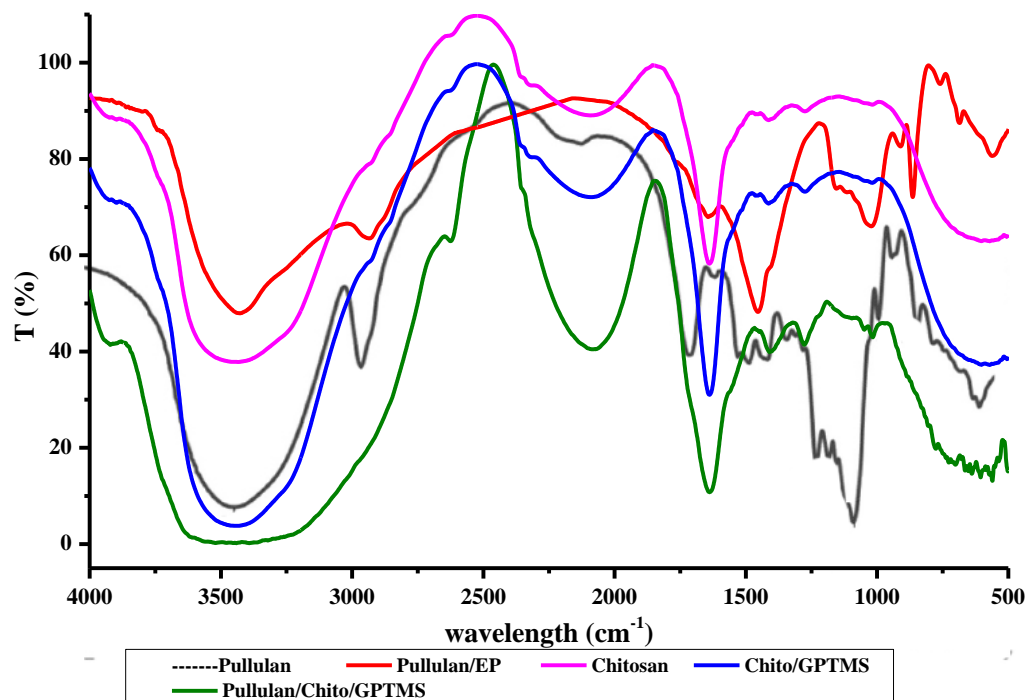
Fig. 2 illustrates the TEM images of different biopolymer/Chitosan/GPTMS, show that, the particles are smaller but tend to aggregate in bulk molecules. The obtained biopolymer/Chitosan/GPTMS have porous structure and size ranged from 20 - 200 μm . These data are provide agreed with the data from particle size analyser.

The results represented in **Fig. 3** show the particle size of the biopolymer/Chitosan/GPTMS. Obviously, this indicates that all the prepared microgels are in 138, 60, 138 and 208 μm for pullulan, β -cyclodextrin, Arabic gum and guar gum respectively. These different in the particle size is attributing to the particle size of the biopolymers.

Studying the pH effect (at 6.5) found that, the microgels particle size was changing with increasing/decreasing the temperature. The results show that microgels are swollen at 25 °C and have diameter average 190, 150, 195 and 180 μm , while at 40 °C the particles having average size 110, 25, 115 and 95 μm for pullulan, β -cyclodextrin, Arabic gum and guar gum respectively.

Fig. 4 show that gradual increasing in the temperature from 25 to 35°C makes the microgels (pullulan, Arabic gum and guar gum) particle size reduces gradually. Above 35 °C, the particles size does not vary significantly with increase in temperature. β -cyclodextrin/chitosan microgel shows a gradual reduction in microgels size by increasing the temperature from 25 – 40 °C.

Effect of pH on average diameter of prepared gels was studied using DLS at 25 °C (**Fig. 4**). At pH 10, microgels are in swollen state with average size of 150, 90, 155 and 290 μm for pullulan, β -cyclodextrin, Arabic gum and guar gum respectively. The microgels particle size was gradually decreased by decreasing pH (110, 25, 115 and 146 μm for pullulan, β -cyclodextrin, Arabic gum and guar gum respectively). As the biopolymers are in the microgel structure, so, they affect the swelling/de-swelling behaviour. Therefore, at high pH, the biopolymer act as cellulosic material (swelling).



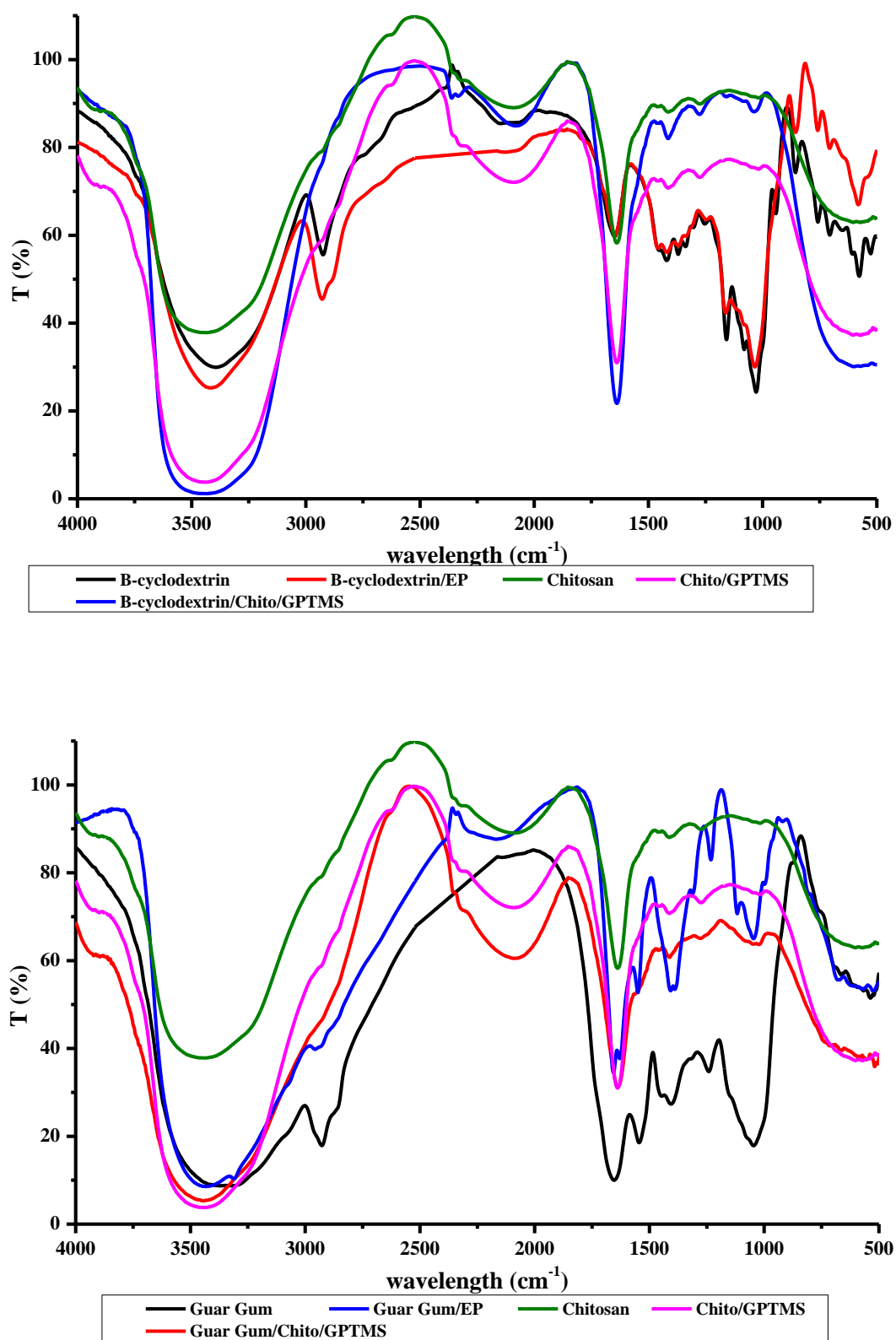


Fig. 1: FT-IR of chitosan based microgels.

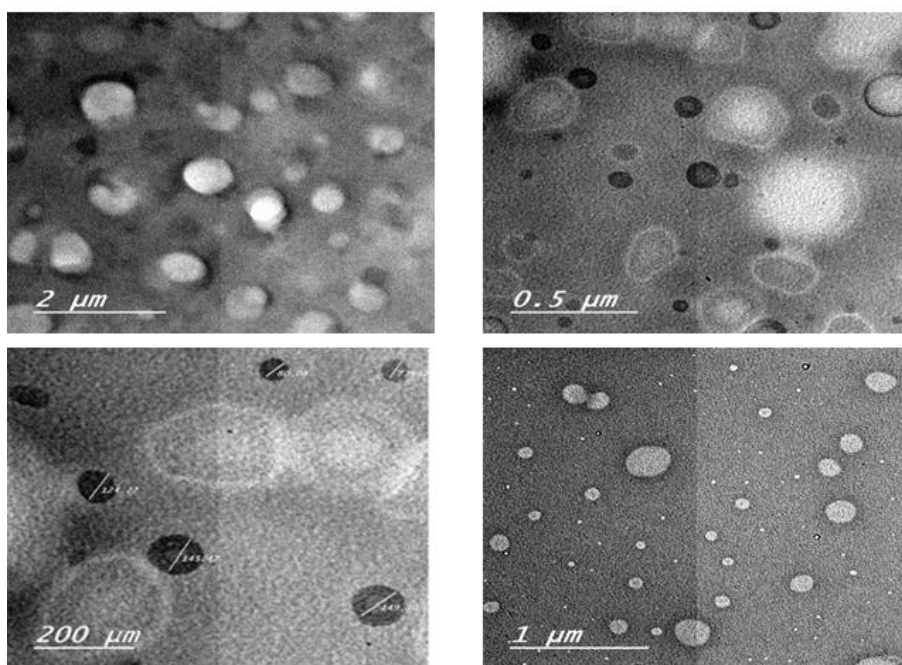


Fig. 2: TEM images of chitosan based microgel.

a) Pullulan

b) β -cyclodextrin

c) Arabic gum

d) Guar gum

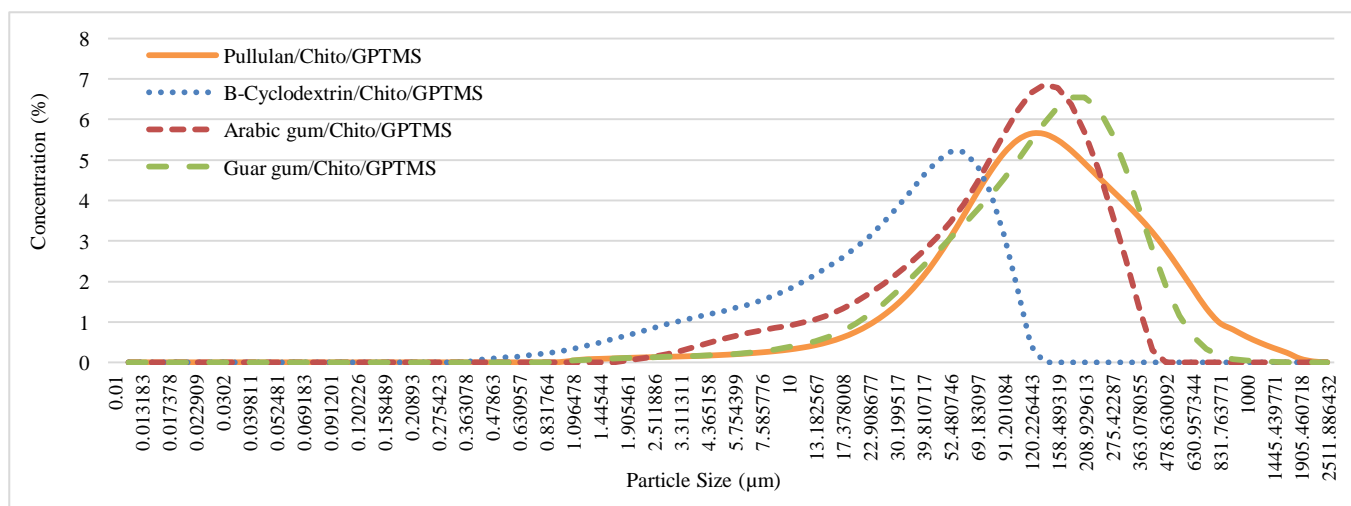


Fig. 3: Particle size analysis of Chitosan based microgel.

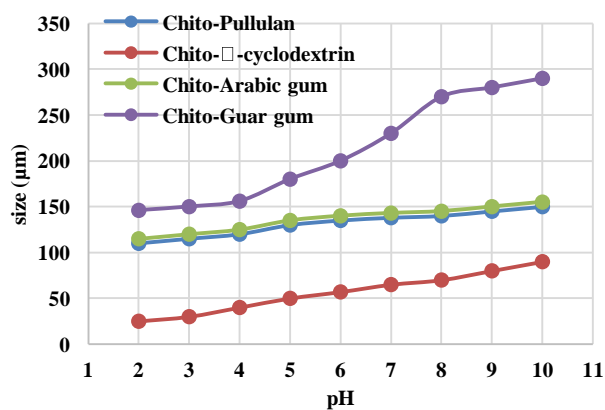
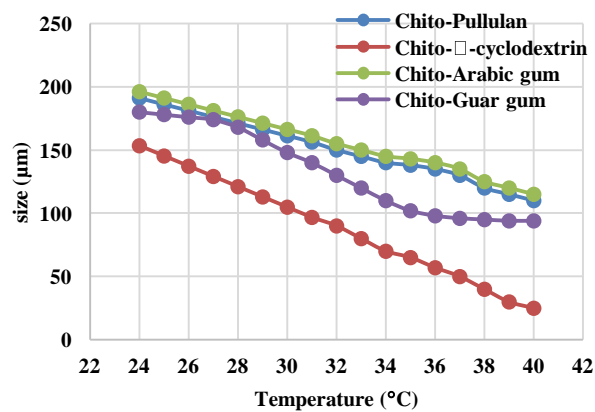


Fig. 4: Effect of temperature and pH on the particle size of chitosan based microgels.

At low pH, the biopolymer chain was affected by the acid medium and becomes soluble. Finally, it can be concluded that, due to pH sensitivity, microgels swell at high pH and deswell at low pH. Textural properties of the chitosan based microgels with different concentration (10, 15, 20, 25 and 30%, w/w) are presented in **Fig. 5**. It is noticed that, increasing in the gels concentration led to significant increasing in the gels hardness, stickiness and adhesiveness. It is realized that the deformability of swollen particles is the fundamental factor on the gel strength (Lii *et al.*, 1995). These results propose that, increasing in texture properties of microgels can be ascribed to the particles swelling. Lii *et al.* reported that, the particle structure and composition were central factors influencing the rheological properties of prepared microgels (Lii *et al.*, 1996). Furthermore, microgel with pullulan have the best texture properties than other gels, and gel with guar gum have a worst texture properties.

Fig. 6 shows the flow properties of the chitosan based microgels (pullulan, β -cyclodextrin, Arabic gum and guar gum) at different concentrations (a), different temperatures (b). At low concentration and high temperature ($>30^{\circ}\text{C}$), the microgels showed a Newtonian behaviour with a low shear viscosity. The effective volume of the microgels in solution was small due to insignificant degree of swelling caused by

the disruption of microgel hydrogen bonds, (Daly and Saunders, 2000) resulting in a constant viscosity-shear rate relationship. In addition, at high concentration and low temperature ($<30^{\circ}\text{C}$), increasing in the effective volume occupied by the particles may be due to the enhancing in osmotic pressure inside the polymeric network. In addition, the interaction forces between the swollen particles increased sharply, this is due to decreasing in the inter-particle distance, and that was resulting in shear-thinning behaviour.

Applying shear force to microgel dispersion led to flow and align the microgel particles in the shear direction. Furthermore, decreasing in the particle concentration and increasing temperature led to decreasing in the extent of shear thinning is due to the particles equilibrium. Similar shear rate dependent viscosity behaviour has been observed for the chitosan based microgels (pullulan, β -cyclodextrin, Arabic gum and guar gum) microgel systems (Senff and Richtering, 1999; Senff *et al.*, 1999; Stieger *et al.*, 2004). On the other hand, when the temperature was in the study run, at low temperature, the viscosity of the microgel can be arranged as follow: β -cyclodextrin > pullulan > Arabic gum > guar gum. At high temperature, the viscosity of the microgel can be arranged as follow: β -cyclodextrin > pullulan > Arabic gum > guar gum.

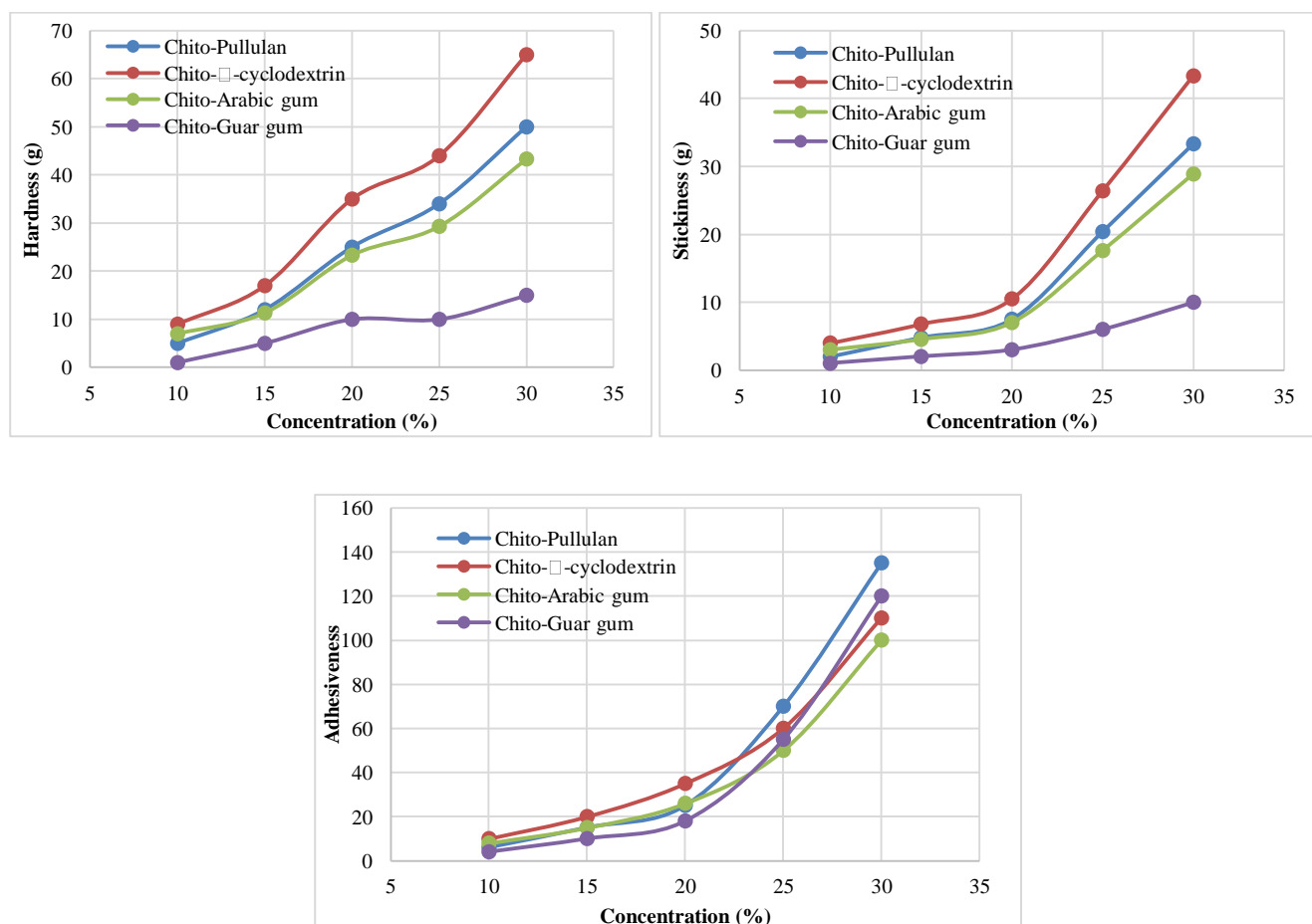


Fig. 5: Textural properties of the chitosan based microgels with different concentration.

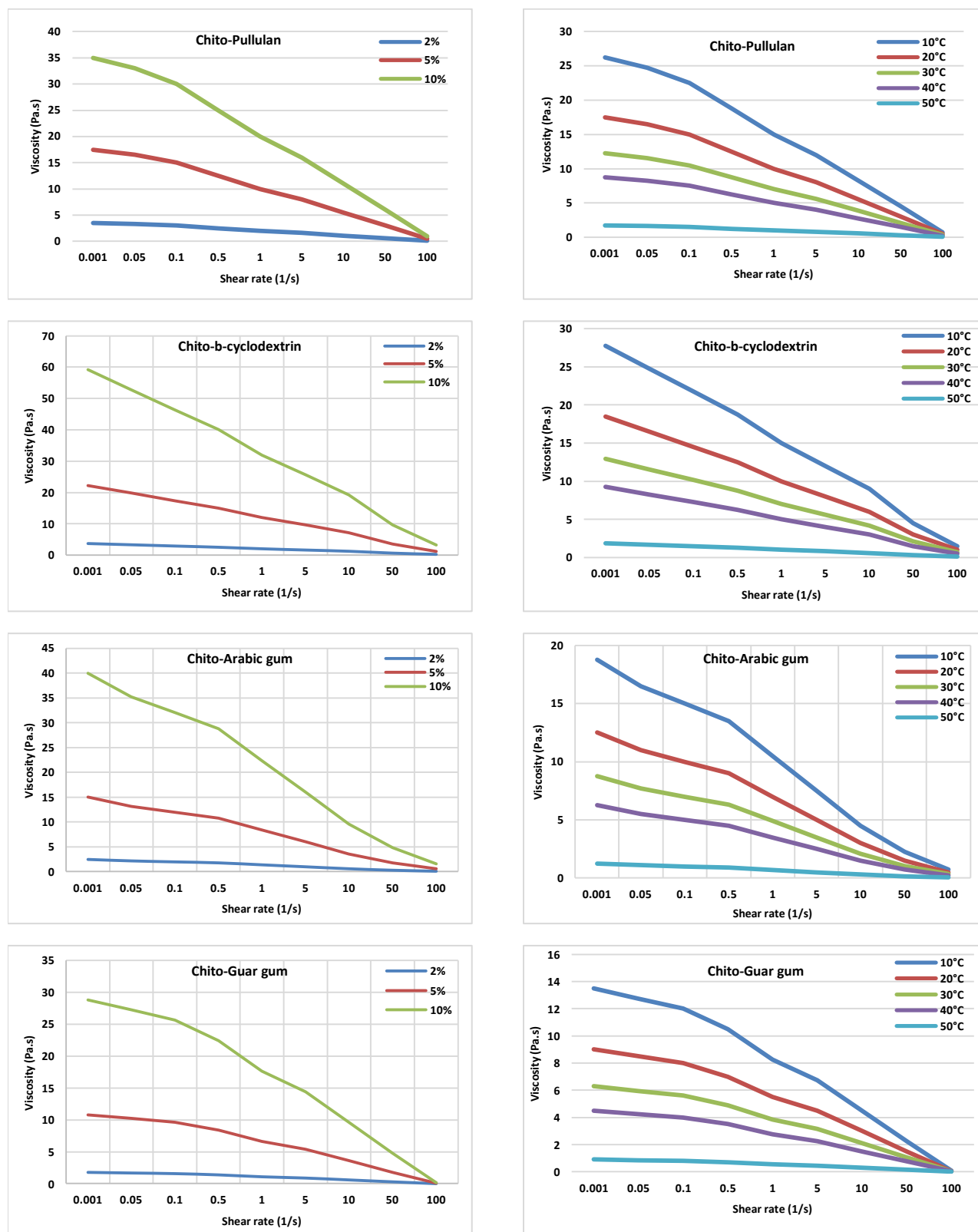


Fig. 6: Rheological properties of the prepared chitosan based microgel with different concentration and temperature a) Different concentration (2, 5 and 10 w/w %), temperature: 20°C b) Different temperature (10, 20, 30, 40 and 50°C), concentration: 5 w/w %.

Characterisation of Incorporated Microgels to Cotton

Fig. 7 shows the morphological behaviour of treated cotton fabrics with prepared microgels (a) pullulan/chitosan/GPTMS, b) β -cyclodextrin/chitosan/GPTMS, c) Arabic gum/chitosan/GPTMS and d) Guar gum/chitosan/GPTMS). One can notice that, whole cotton fibre surface was coated with thin film, and the microparticles was observed as clusters on the fibre surface. The antibacterial investigation was evaluated against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacterium because the segels will use in textile application. From the data displayed in Fig. 8, one can observe that all the treated fabrics with all chitosan based microgels have a good bacterial reduction effect for the two pathogenic bacteria, which mean that they have excellent antibacterial activity. The data obtained demonstrate that, treated fabrics had a higher antibacterial activity against gram-negative (*E. coli*) bacteria than gram positive (*S. aureus*) bacteria. It is known that, the cell walls of gram positive is thicker than

gram-negative bacteria which change the penetration behaviour of microgels to the cell wall bacteria (Hassabo *et al.*, 2015)(see

Fig. 9). pH sensitivity study provide that, from 22 - 27°C, the water uptake did not change, from 27 - 31°C, the water uptake was decreased, increasing temperature over 31°C did not affect in the water uptake values. In addition, comparing to the untreated one, treated fabric with all prepared composite have a significant response $\approx 25\%$. Furthermore, temperature sensitivity study at all pH medium provide that, the composite particles shrink and expels water with increasing the temperature, which may be due to presence of biomaterial part (pullulan, β -cyclodextrin, Arabic gum or Guar gum) which prevents the water molecules from migrating easily from composite network. Moreover, the water uptake is in a lower value due to increasing the temperature because the collapsing state of the prepared composites. Therefore, the prepared composites impart a hydrophobicity property to the cotton fabrics.

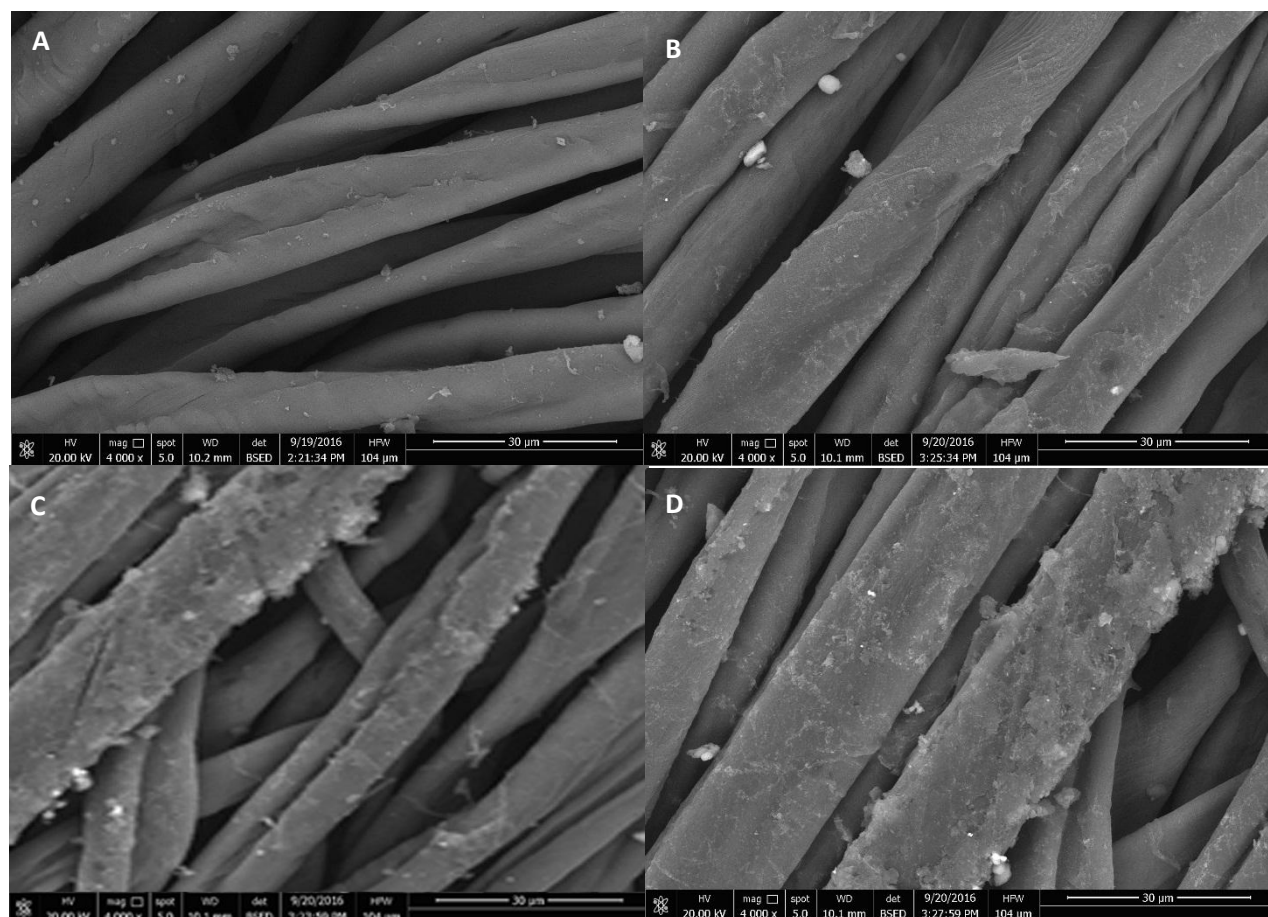


Fig. 7: morphological structure of treated fabric with prepared biopolymer/chitosan/GPTMS. a) Treated fabric with pullulan/chitosan/GPTMS. b) Treated fabric with β -cyclodextrin/chitosan/GPTMS. c) Treated fabric with Arabic gum/chitosan/GPTMS. d) Treated fabric with Guar gum/chitosan/GPTMS.

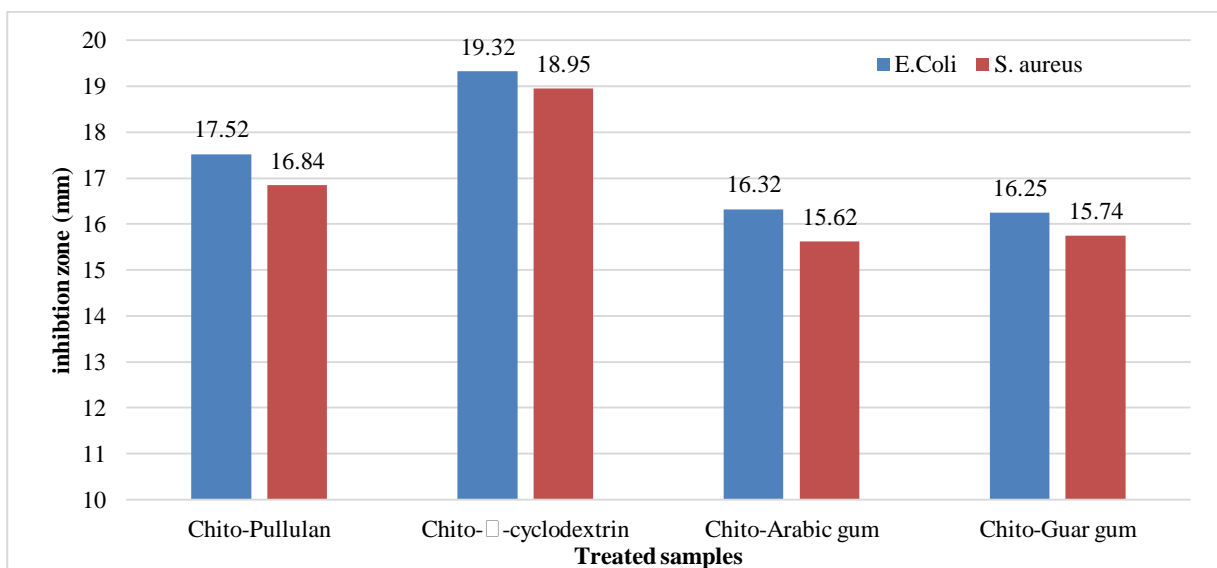


Fig. 8: Antibacterial activities for treating fabric with different microgels.

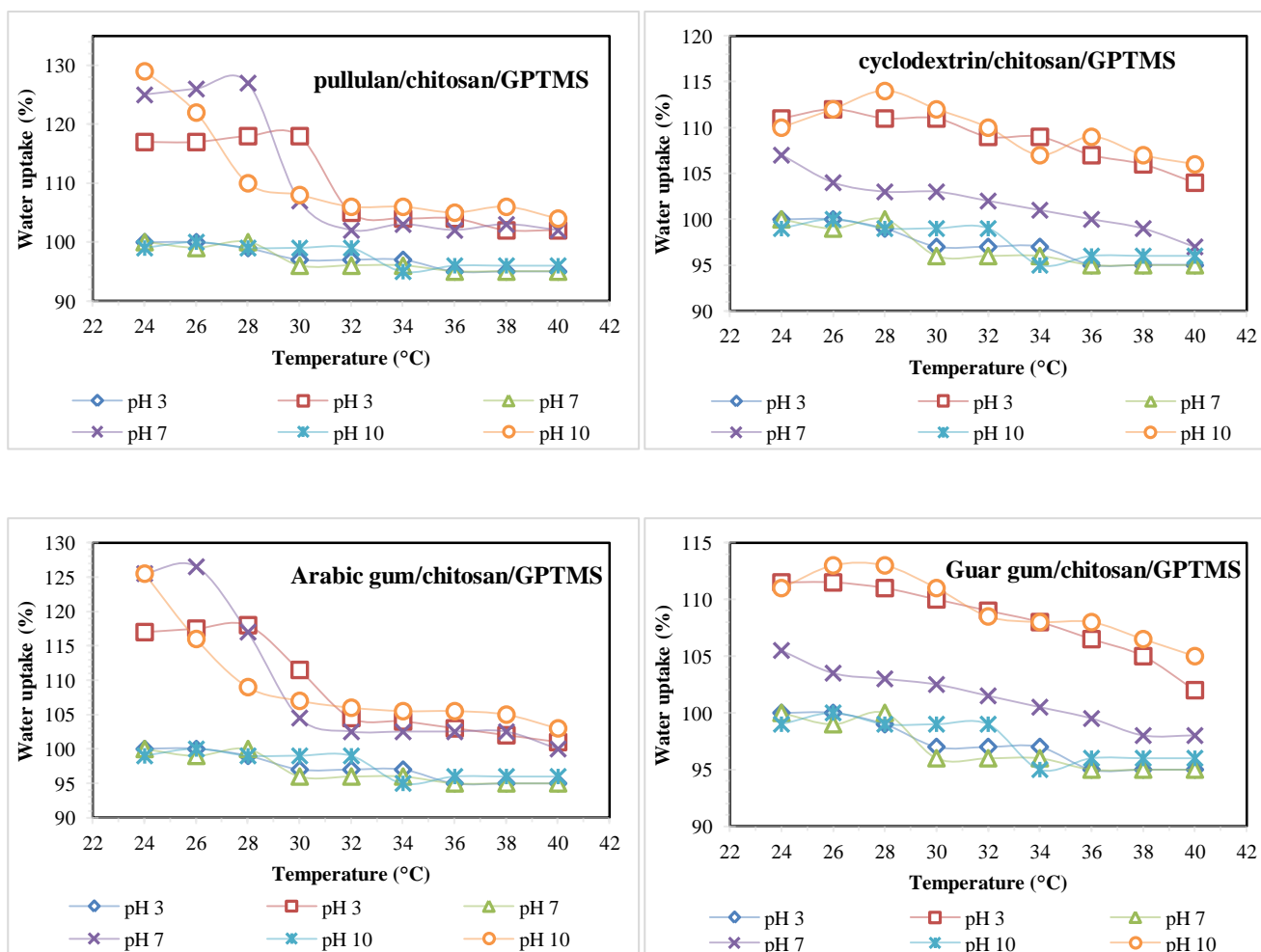


Fig. 9: pH and temperature effect on the water uptake of untreated and treated cotton fabrics.

CONCLUSION

Four microgel based on chitosan have been synthesized and characterized during this research. Firstly, four biomaterials namely, β -cyclodextrin (β -CD), Arabic gum, guar gum and pullulan were modified with epichlorohydrin. Then, chitosan-biopolymer microgel (CS-CDM) were sensitized using 3-glycidoxypropyltrimethoxysilan (GPTMS) as cross linker. Characterisation of prepared composite (pullulan/ chitosan/ GPTMS, β -cyclodextrin/chitosan/GPTMS, Arabic gum/chitosan/ GPTMS and Guar gum/chitosan/GPTMS) was occurred through some analysis. FT-IR of modified biopolymer (biopolymer/EP) beside the modified chitosan with GPTMS were confirmed the chemical reactions. Also, the reaction between chitosan (amine groups) and GPTMS (oxirane groups) was observed. TEM image and particle size of different biopolymer/Chitosan/GPTMS particle size, show that, the particles are smaller ranged from 20 - 200 μ m and have porous structure. The effect of temperature on particle size diameter of prepared microgels have been studied at different pH. Data confirmed that, at high pH, the biopolymer act as cellulosic material (swelling). At low pH, solution acid medium act the rest of biopolymer chain and becomes soluble. Thus, due to pH sensitivity of biopolymer, the microgels swell in basic medium and de-swell in acid medium. Textural properties of the chitosan based microgels with different concentration (10, 15, 20, 25 and 30%, w/w) were studied. So, increasing in the gels concentration led to significantly increasing in the gels hardness, stickiness and adhesiveness. The microgel with pullulan have the best texture properties than other gels, and gel with guar gum have a worst texture properties. The flow properties of the chitosan based microgels (pullulan, β -cyclodextrin, Arabic gum and guar gum) at different concentration (a), different temperature (b) were also determined and confirmed that, a) At low concentration and high temperature ($>30^{\circ}\text{C}$), the microgels showed a Newtonian behaviour with a low shear viscosity, b) at high concentration and low temperature ($<30^{\circ}\text{C}$), increasing in the effective volume occupied by the particles may be due to the enhancing in osmotic pressure inside the polymeric network, c) at low temperature, the viscosity of the microgel can be arranged as follow: β -cyclodextrin $>$ pullulan $>$ Arabic gum $>$ guar gum, and d) at high temperature, the viscosity of the microgel can be arranged as follow: β -cyclodextrin $>$ pullulan $>$ Arabic gum $>$ guar gum. Incorporation of Microgels to cotton fabric was occurred and the treated fabrics were characterized.

The morphological behaviour of treated cotton fabrics with prepared microgels provide that, whole cotton fibre surface was coated with thin film, and the microparticles was observed as clusters on the fibre surface. In addition, the antibacterial investigation was evaluated against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria and it is confirmed that, all the treated fabrics with all microgels have a good bacterial reduction. Further investigation was occurred to determine the water uptake for untreated and treated fabrics at different pH and

temperature and it is confirmed that, the prepared composites impart a hydrophobicity property to the cotton fabrics.

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