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Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties

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ABSTRACT

This research work deals with flame retardant and antibacterial finishing agent for cellulosic fabrics using TiO_2 nanoparticles and chitosan phosphate. TiO_2 nanoparticles were prepared by sol–gel method using titanium tetraisopropoxide. The size of TiO_2 nanoparticles was characterized using transmission electron microscope (TEM). The application of nano TiO_2 onto cellulosic fabrics (cotton 100%) was achieved in presence of polycarboxylic acid [1,2,3,4-butane tetracarboxylic acid (BTCA)] with sodium hypophosphite (SHP) as catalyst and chitosan phosphate through conventional pad-dry-cure method. The effect of the finishing on the physical properties, flammability and antibacterial properties of cross-linked fabrics are investigated. Thermal gravimetric analysis (TGA) was employed to investigate the thermal decomposition behaviour of the treated samples. Limited oxygen indexes (LOI) of the treated cotton fabrics were investigated. The treated cotton fabric also reveals excellent antibacterial properties.

1. Introduction

Cotton fabrics have been widely used in both military and civilian areas due to their excellent properties (Cullis & Hirschler, 1984; Dennis & Liu, 2002; Leslie, 2004).

Low thermal stability, easy ignition, and rapid combustion of cellulose fibres represent their weaknesses and limitations in the production of high-performance fire-protective textile products (Horrocks & Price, 2001). Thermal degradation of cellulose in air starts with cellulose pyrolysis at 300–400 °C through two competitive reactions: dehydration, which creates aliphatic char, and depolymerization, which creates levoglucosan. Levoglucosan decomposes and creates highly flammable, low-molecular-weight products that are further oxidized during exothermic combustion to support the pyrolysis process of cellulose. At higher temperatures (up to 800 °C), aliphatic char is converted to an aromatic form and oxidized to produce CH_4, H_2O, CO and CO_2 (Horrocks, 1983; Horrocks & Price, 2001; Price, Horrocks, Akalin, & Faroq, 1997).

To provide flame retardancy to cellulose fibres, several different inorganic and organic flame retardants have been synthesized and applied as one-component agents or as mixtures (Horrocks, 2011; Weil & Levchik, 2008). The most effective flame retardant is organophosphorus compounds. The mode of action of organophosphorus is complex; it includes the formation of phosphoric acid at lower temperatures, which has a catalytic effect on cellulose dehydration and char formation at the expense of cellulose depolymerization and the formation of levoglucosan (Horrocks, 1983; Horrocks, Price, & Akalin, 1996; Kandola, Horrocks, Price, & Coleman, 1996; Zhu, Sui, Wang, Sun, & Sun, 2004). Organophosphorus compounds that include N-methylol reactive groups in their structures can react with the hydroxyl groups of the cellulose fibres in a condensation reaction, which results in the formation covalent bonds that strongly increase the adhesion between the flame retardant and the fibre surface. Despite the high resistance of covalent bonds towards hydrolysis during multiple launderings, a methylolated melamine resin, such as trimethylolmelamine, is usually used as a co-reactant in the presence of a phosphoric acid catalyst to increase the number of covalent bonds to the cellulose fibres and to enhance the flame retardant (Lam, Kan, & Yuen, 2012; Wu & Yang, 2006, 2007).

Butane tetra carboxylic acid (BTCA) is one of the most efficient and expensive cross-linking agents (Yang, Chen, Guan, & He, 2010; Yang, Lu, & Lickfield, 2002; Yuen et al., 2007). BTCA gives cotton cellulose good crease recovery (Hsieh, Huang, Huang, & Tseng, 2004; Nazari, Montazer, Rashidi, Yazdanshenas, & Anari-Abasinejad, 2009; Schindler & Hauser, 2004; Zakaria, 2004).

TiO_2 nanoparticles have created a new approach for remarkable applications as an attractive multi-functional material. TiO_2 nanoparticles have unique properties such as high stability, long lasting, safe and broad-spectrum antibiosis. This makes TiO_2 nanoparticles applicable in many fields such as self-cleaning, antibacterial agent and UV protecting agent.

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Nano sized TiO_2 is well known photo-catalyst for many scientists due to its high chemical stability, non-toxicity and good heat resistance (Dastjerdi, Montazer, & Shahsavan, 2009; Dastjerdi, Mojtahedi, Shoshtari, & Khosroshahi, 2010; Dastjerdi, Montazer, & Shahsavan, 2010). TiO_2 nanoparticles are used as catalyst in cross-linking of cotton fabric with citric acid under the irradiation of UV light (Ki, Kim, Kwon, & Jeong, 2007; Li et al., 2008).

Chitosan, the second most abundant polysaccharide in the nature (Abou-Okeil & El-Shafie, 2011), is the deacetylated form of the polysaccharide chitin, which is mainly found in the exoskeleton of crustaceans and has received much attention due to its versatility, biodegradability, non-toxicity and antimicrobial properties (Lim & Hudson, 2003). The major problems of chitosan as an antimicrobial agent are its loss of the antimicrobial activity under alkaline conditions due to its loss of the cationic nature (El-Shafei & Abou-Okeil, 2011) and its poor durability on textile fabrics due to its poor adhesion to fabrics. Chemical modifications on chitosan can overcome the problems and enhance the properties of chitosan.

The aim of this study was to investigate the flame retardant action of SHP in the presence of nano TiO_2 and butane tetracarboxylic acid (BTCA) on cotton fabric in presence of chitosan phosphate. Various experiments with different concentrations of (BTCA), nano TiO_2, chitosan phosphate concentrations, and operation times are designed. Different response variables including char length in vertical flammability and char yield before and after five laundering cycles were studied. Also other testing including LOI and TGA on some samples were carried out. Evaluation of treated cotton efficiency against two pathogenic bacteria *Staphylococcus aureus* and *Escherichia coli*, and impacts on other physical features of cotton fabrics were done.

2. Experimental

2.1. Materials

Desized, scoured and bleached plain weave cotton fabric (230 g/m^2) was kindly supplied by Misr Company for spinning and weaving Mehala El-Kobra (Egypt). 1,2,3,4 butane tetra carboxylic acid (BTCA) and sodium hypophosphite (SHP) were supplied by Merck Chemical Co. (Germany). Titanium tetra-isopropoxide (TTIP) were purchased from Fluka Co. Chitosan, high molecular weight as determined by Brookfield viscometer (800.00 cps in 1% w/w chitosan aqueous 1% w/w acetic acid at 25 °C), degree of deacetylation 87% (Mukhopadhyay et al., 2013) was kindly supplied by Aldrich Chemical Company (Germany). Acetic acid, sodium nitrite, acetone, urea, orthophosphoric acid, DMF and isopropyl alcohol were of laboratory grade chemicals.

2.2. Depolymerization of chitosan

Solution of chitosan was prepared by dissolving 6 g of chitosan in 250 ml of 2% (w/w) aqueous acetic acid solution. A solution containing 0.085 g $NaNO_2$ in 50 ml distilled water was added slowly to chitosan solution with slow stirring for 2 h at 30 °C, then neutralized with dilute solution of sodium hydroxide, precipitated with excess acetone, filtered, and washed several times with acetone. The final product was dried at room temperature overnight. The N% and average molecular weight of prepared chitosan were as follows:

N%	Molecular weight
6.17	7.7×10^3

2.3. Preparation of chitosan phosphate (Chit-P)

Chitosan (23 g) was added to a solution of 40 g urea and 40 ml H_3PO_4 in 350 ml DMF. The temperature was raised to 100 °C and maintained at this temperature for 5 h. The final product was filtered, washed thoroughly several times with 50% (w/w) isopropyl alcohol in water, dried at 60 °C, and then subjected to analysis (Abou-Okeil, El-Shafie, & Hebeish, 2007).

2.4. Preparation of titanium dioxides nano particles

Nano TiO_2 sol–gel was prepared by dissolving 32 ml of isopropanol in 1 ml of titanium IV isopropoxide by vigorous stirring for ½ h then adding (0.05 g citric acid dissolved in 4 ml distilled water) then vigrous stirring for 2 h at 60 °C (Mahshid, Askari, & Sasani Ghamsari, 2007).

2.5. Cotton fabric treatment

The cotton fabric was first impregnated in a solution containing chitosan phosphate (0–10%) dissolved in 1,2,3,4 BTCA (0–8%), and SHP as catalyst (0–8%). The fabric was then passed through a laboratory padder with two dips and two nips, to wet pickup approximately 100%. The impregnated woven fabric was dried at 85 °C for 3 min and padded in solution containing different concentrations of TiO_2 nano particles (0–9%) after that dried and cured at a specified temperature (160 °C) for 2 min in a laboratory curing oven. All concentrations were presented as percent weight of bath (% w/w). The fabric properties were measured after the treated fabric was subjected to 10 home laundering and drying cycle according to technical report method AATCC 1999.

2.6. Testing

2.6.1. Transmission electron microscope (TEM)

TEM was measured using Zeiss-EM10-Germany, operating at power 60 kV. TEM samples were prepared by dispersing 2–3 drops of TiO_2-NPs solution on copper grid and dried at room temperature after removal of excess solution using a filter paper.

2.6.2. FTIR spectra

FTIR spectra of the fabric samples were recorded by KBr pellet technique, using Nexus 670 FTIR spectrometer from Nicolet, USA. The FTIR spectra were recorded between the range from 4000 cm^{-1} to 400 cm^{-1} with spectra resolution of 4 cm^{-1}

2.6.3. Fabric performance evaluation

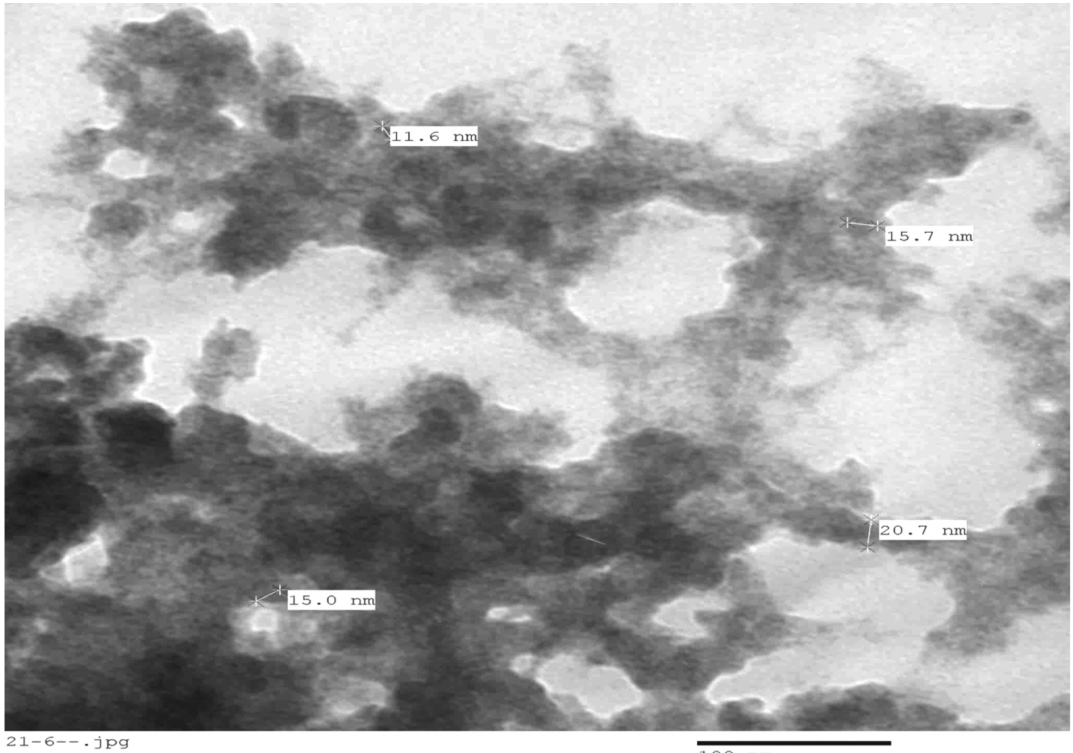
The treated samples evaluated for Breaking strength and tearing strength in accordance with ASTM D5035. The conditioned wrinkle recovery angles (WRA) were evaluated according to AATCC Test Method 66.

2.6.4. SEM

Scanning electron microscope (SEM), the samples were examined by a JEOL-840X scanning electron microscope, from Japan, magnification range 35–10,000, resolution 200 Å, acceleration voltage19 kV. All the samples were coated with gold before SEM testing.

2.6.5. Antibacterial

Antibacterial test: for antibacterial experiment, *S. aureus* (Gram-positive bacteria) and *E. coli* (Gram-negative bacteria) were used. The antibacterial activity of prepared cotton samples was measured by the inhibition zone method (Qin, Zhu, Chen, & Zhang, 2006).



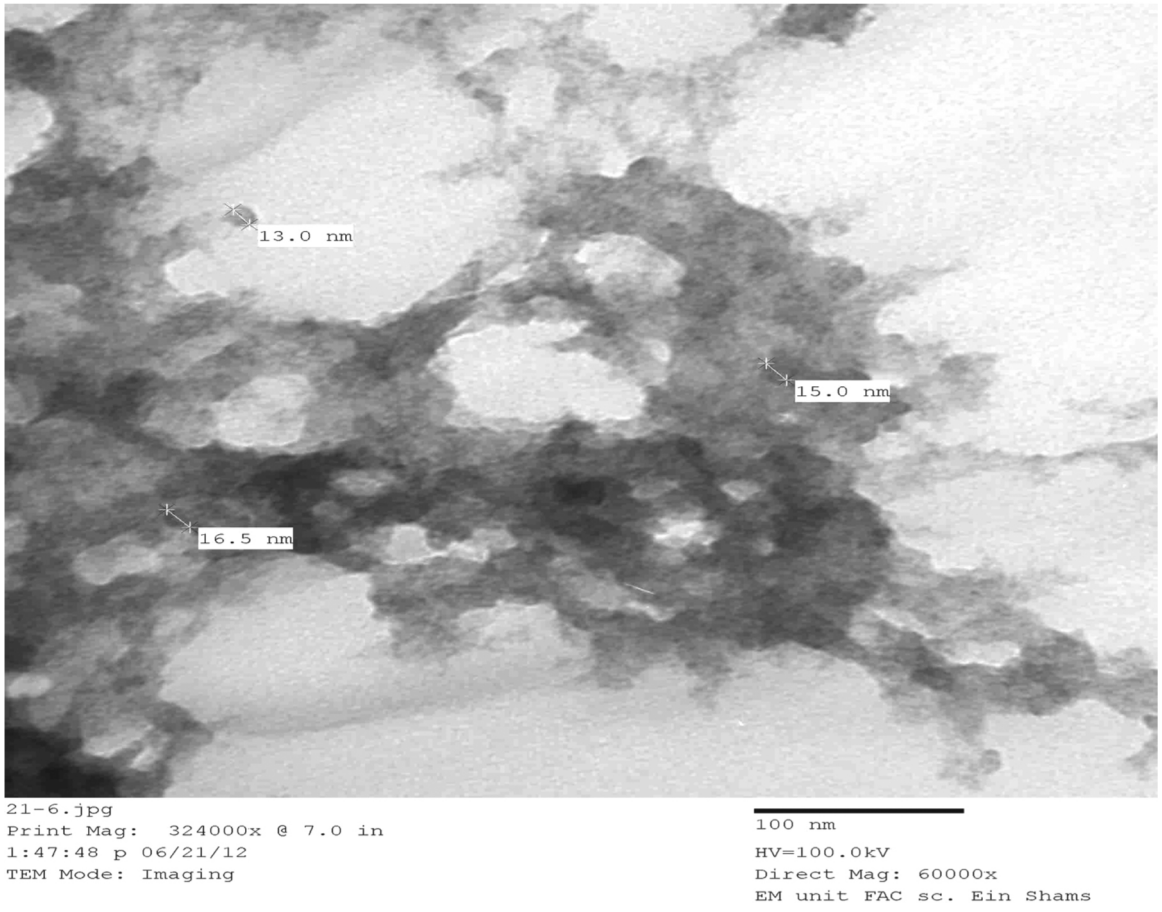


Fig. 1. TEM of the prepared TiO_2 nano particles.

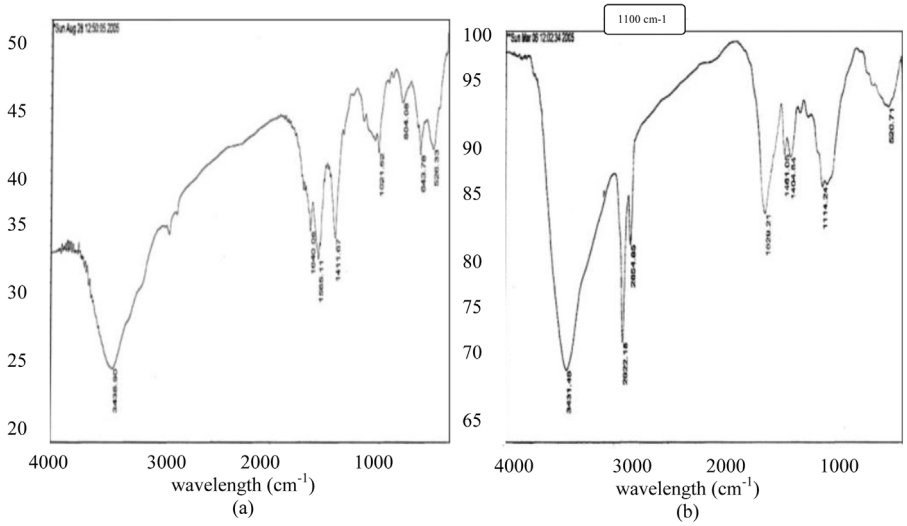


Fig. 2. FTIR spectra of (a) chitosan and (b) chitosan phosphate.

2.6.6. LOI

Limiting oxygen index (LOI) values of some samples were measured according to ASTM D2863-08 standard method. In this order, 5 specimens of each sample were prepared in 5 cm × 15 cm and a mixture of oxygen and nitrogen is passed up through a cylinder containing the fabric specimen supported vertically. The minimum fraction of oxygen in a mixture of oxygen and nitrogen in which one specimen will just sustain burning is determined and reported as the LOI value (Willard & Wondra, 1970).

2.6.7. Thermal analysis

Thermo gravimetric analysis (TGA) was carried out using a Perkin Elmer TG-DTA analyzer, model Pyris1, operating under nitrogen atmosphere with initial sample weights of 8 mg. Once the sample has been prepared, it should be placed into the TGA sample pan and distributed evenly across the pan bottom. The standard platinum sample pan (0319-0264) was used for this application. The runs were performed over a temperature range of 50–600 °C at a heating rate of 10 °C/min under a continuous N_2 flow of 100 ml/min.

2.6.8. N% content

The percent nitrogen of cationized sawdust was determined according to the micro Kjeldahl method (Vogel, 1975).

2.6.9. Phosphorus content

Phosphorus content was measured according to spectrophotometric method (Troug & Meyer, 1939).

2.6.10. Molecular weight

Molecular weight was determined viscosimetrically using the Mark–Houwink–Sakurada (Brandrub & Immergut, 1966; George Reports, 1992).

3. Results and discussion

A representative TEM micrograph of the final colloidal solution shows the visual evidence of the nanoparticles stabilization (Fig. 1). TEM shows that the particle size of TiO_2 nanoparticles was <25 nm.

3.1. FTIR

The IR spectra of chitosan and chitosan phosphate are shown in Fig. 2. Fig. 2(a) shows clearly the amide I band at 1643 cm^{-1} and the amide II band at 1565 cm^{-1}. Comparing this chitosan IR spectrum with the IR spectrum of chitosan phosphate Fig. 2(b), it is apparent that the IR spectrum of chitosan phosphate shows that the amide I band still remains, but shifted to 1629 cm^{-1}, while amide II band, which is at 1565 cm^{-1}, disappears. The peaks at 2922 and 2854 cm^{-1} are the characteristics of C—H stretching bands.

3.2. Flame retardant performance

3.2.1. Limited oxygen index LOI

Fig. 3(a)–(c) shows the limited oxygen index LOI values of different concentrations of TiO_2 nanoparticles, SHP and chitosan phosphate Chit-P. Fig. 3(a) studied the effect of different concentrations of TiO_2 nanoparticles for the treated cotton in presence of 6% Chit-P and 4% BTCA with 4% catalyst SHP. From the figure it is clear that the LOI values increase by increasing TiO_2 nanoparticles. This means that TiO_2 nano particles have a synergistic effect on the flame retardant cotton in the formulation bath.

The presence of 4% BTCA, 4% Chit-P and 9% TiO_2 increasing the concentration of SHP from (3–8%) in the finishing solution as seen in Fig. 3(b), is accompanied by increase of the LOI value from 17.4 to 22.7 representing the effect of presence of phosphorous compound. Similar also true, as increasing the chit-P concentrations from 2–6% in presence 4% BTCA, 6% SHP and 9% TiO_2 accompanied by an increasing in LOI from 17.4 for blank to 23.

Fig. 4 shows a comparison for the fabric formulation with individual component and after combination all formulation ingredients. The figure shows that the presence of TiO_2 along with chit-P more effective as flame retardant fabric than every component alone. The LOI value in the absence of TiO_2 and presence of the other ingredient is lower than its presence as seen in Fig. 4.

It is clear that the presence of BTCA, TiO_2 and chit-P is playing an important role in the thermal stability of cotton fabric. This finding may be attributed to the ability of BTCA to crosslink the cellulose chains, this crosslinking increases in presence of TiO_2 which promotes the crosslinking of cellulose chains by BTCA. It is apparent that the crosslinking of cellulose chains leads to the stability of cotton structure which enhances the thermal stability of cotton fabrics. The other factor is the presence of P-containing compounds (SHP and chit-P) which has an incremental effect on the thermal stability.

3.2.2. Thermal decomposing behaviours

Thermo gravimetric analysis (TGA) is an important means to study the thermal behaviours of materials (Yuen et al., 2007). TGA

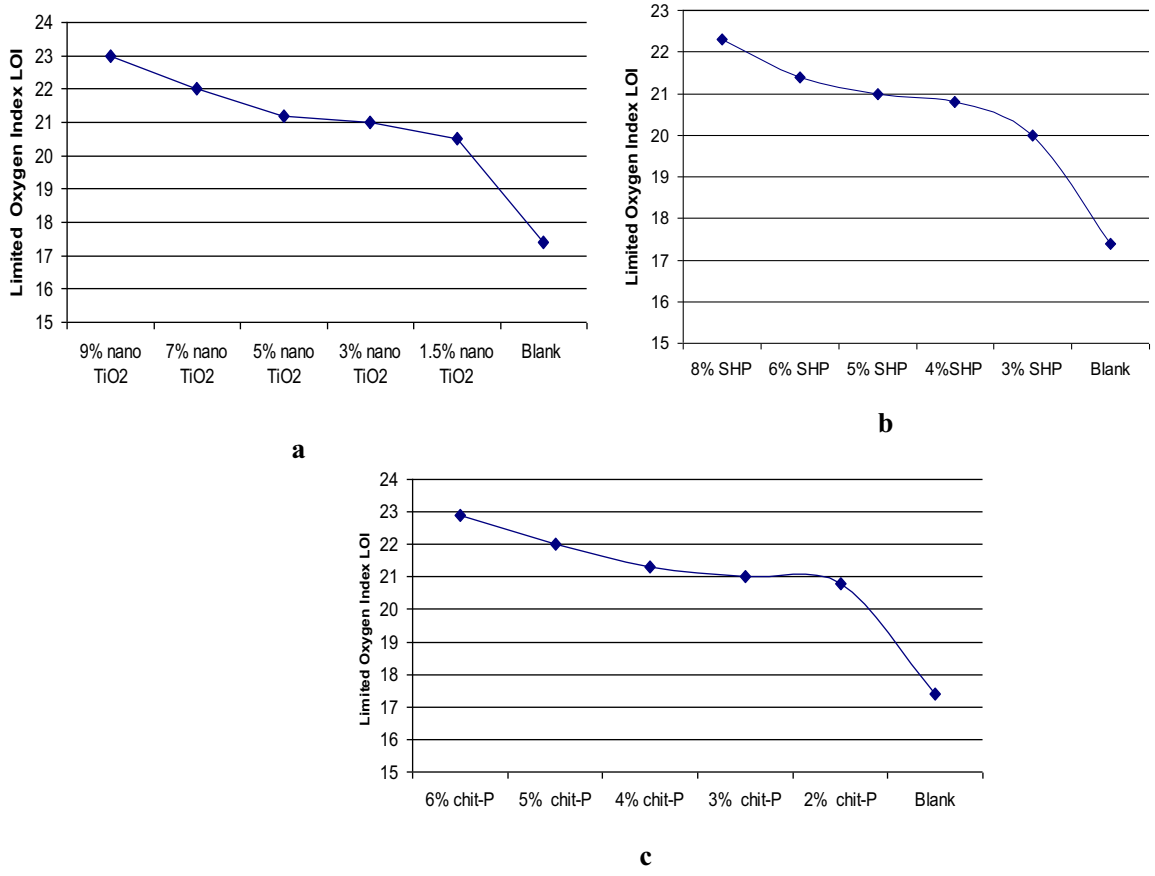


Fig. 3. (a) Effect of TiO_2 nano particles concentration on the limited oxygen index of the treated fabric; (b) effect of SHP concentrations on the limited oxygen index of the treated fabric; (c) effect of chitosan phosphate (chit-P) concentration on the limited oxygen index of the treated fabric.

curves of treated and untreated cotton fabric samples are shown in Fig. 5.

It is shown that (Fig. 5) the decomposition temperature of untreated cotton fabric which is 310 °C, this is against 300 °C, 310 °C, 290 °C, and 260 °C. For cotton fabric treated with depolymerised chitosan, depolymerised chitosan + 9% TiO_2, chitosan phosphate + 9% TiO_2 and chitosan phosphate in presence of BTCA and SHP respectively. It is clear that treatment of cotton fabric with depolymerised chitosan has almost no effect on the decomposition temperature. Adding 9% TiO_2 to this bath leads to the decrement in the decomposition temperature to 300 °C. Using chitosan phosphate instead of depolymerised chitosan lowers the decomposition temperature to 290 °C. The higher influence on the decomposition temperature (260 °C) is achieved by using 6% chitosan phosphate along with BTC, SHP and TiO_2 nanoparticles.

Fig. 5 reveals also the results of weight loss, the weight loss was found to be 66.6%, 77.35%, 63.834%, 44.85% and 40.91% for untreated cotton fabric, cotton fabric treated with depolymerised chitosan, cotton fabric treated with depolymerised chitosan + 9% TiO_2, cotton fabric treated with chitosan phosphate + 9% TiO_2, and cotton fabric treated with chitosan phosphate and BTCA and SHP, respectively. The results indicate the importance of presence of TiO_2 and chitosan phosphate in presence and absence of BTCA which have the lower

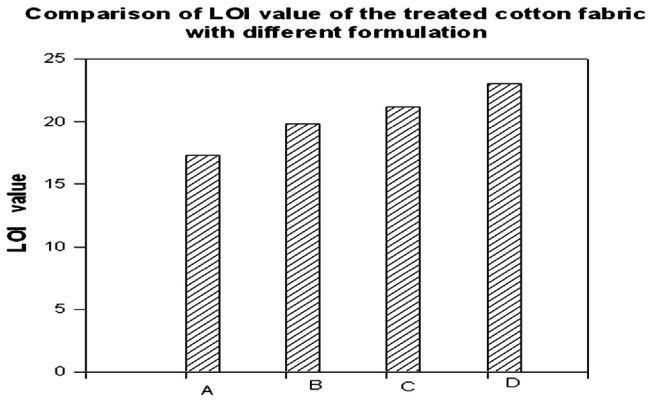


Fig. 4. (a) Cotton blank; (b) cotton fabric treated with BTCA 4%; SHP, 4%; (c) cotton fabric treated with BTCA 4%; SHP, 4%, Chit-P, 6%; (d) cotton fabric treated with BTCA 4%; SHP, 4%, Chit-P, 6% and TiO_2 nanoparticles, 9%.

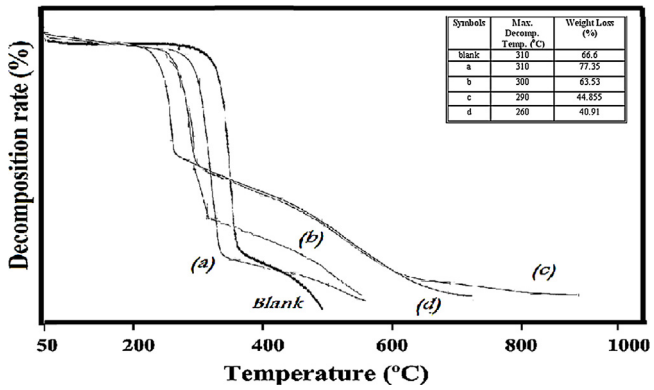


Fig. 5. TGA for: blank cotton, (a) 2% depolymerized chitosan; (b) 2% depolymerized chitosan + 9% nano TiO_2; (c) 6% chitosan phosphate + 9% nano TiO_2, 4% BTCA + 4% SHP; (d) 6% chitosan phosphate + 4% BTCA + 4% SHP.

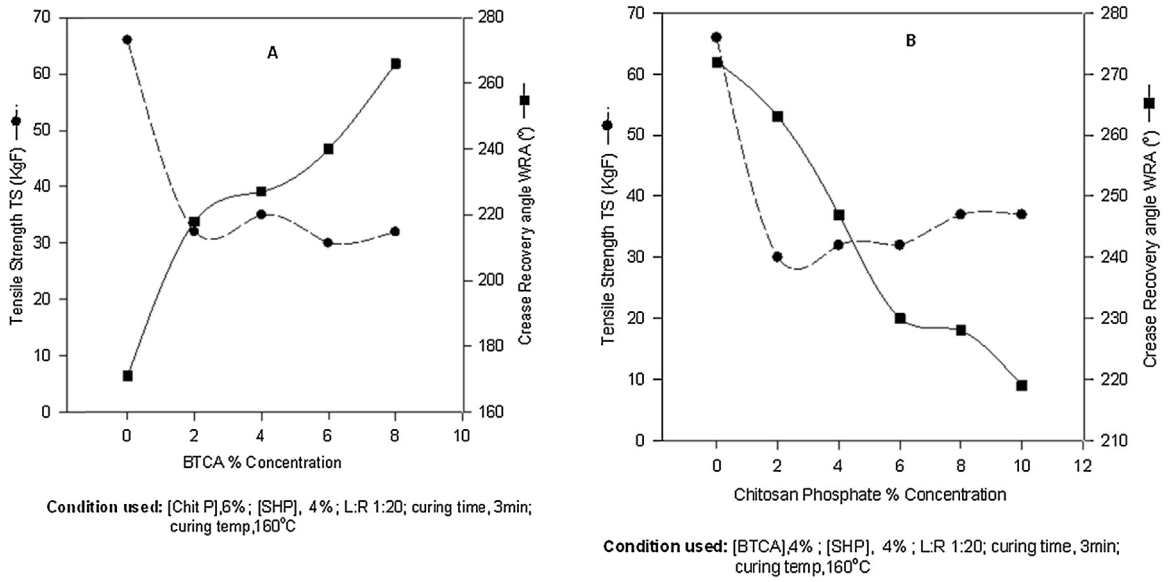


Fig. 6. Effects of the BTCA (a) and chitosan phosphate (b) concentrations on the crease recovery angle and tensile strength of the treated cotton.

weight loss which imparts to the cotton fabric the ability to give off less volatile components than does the untreated samples when the fabrics were thermally decomposed. This effect can be attributed to the ability of TiO_2, chitosan phosphate and BTCA to stabilize the structure of cotton fabric and directs the thermal decomposition to the way which give less volatile and nonflammable components which is favoured by lowering the maximum decomposition temperature.

3.3. Tensile strength and crease recovery angle (CRA)

The CRA of the cotton fabric treated with the combination of Chit-P and BTCA in addition to TiO_2 nano particles and that treated with BTCA, and cured at 160 °C for 3 min was plotted against BTCA concentration in Fig. 6. Dastjerdi et al. (2009) the CRA of the cotton fabric treated with Chit-P/BTCA was significantly lower than that treated with BTCA (Fig. 6). These results lead us to say that part of BTCA was consumed in esterification and crosslinking of Chit-P instead of cellulose chains which reflected on the results of CRA. Cotton fabric lost 51% of its original strength when it was treated with 5% BTCA, whereas the fabric lost only 31% of its strength when 6% chit-P was present together with 5% BTCA. The data presented here clearly demonstrate that the cotton fabric lost significantly less tensile strength in presence of Chit-P along with BTCA.

The relation between the amounts of chitosan phosphate incorporated in the finishing bath and performance properties (physical

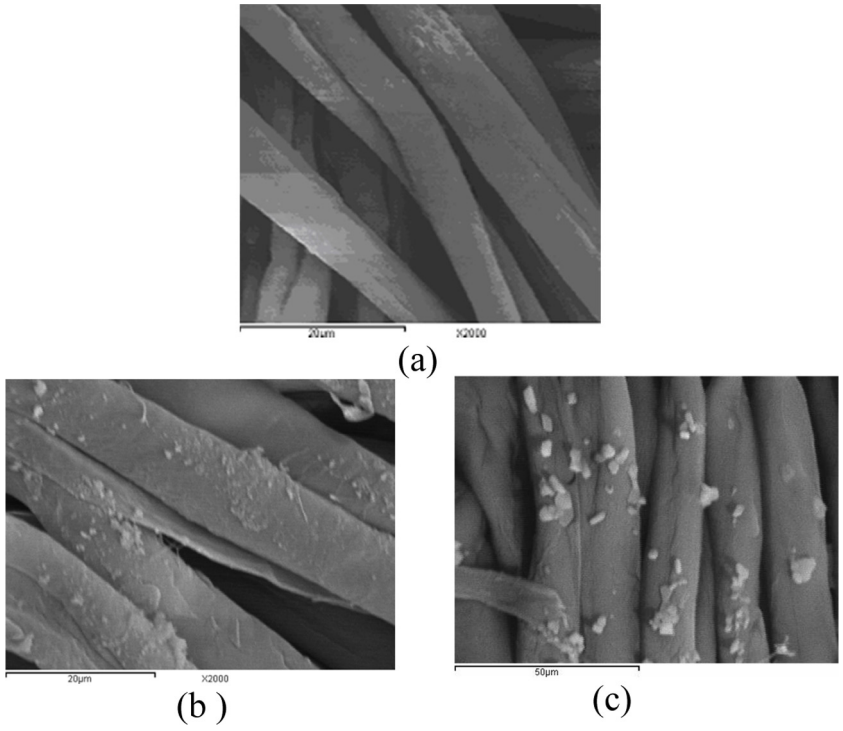


Fig. 7. SEM of the (a) untreated cotton; (b) chitosan phosphate + BTCA; (c) chitosan phosphate + BTCA + TiO_2 nano.

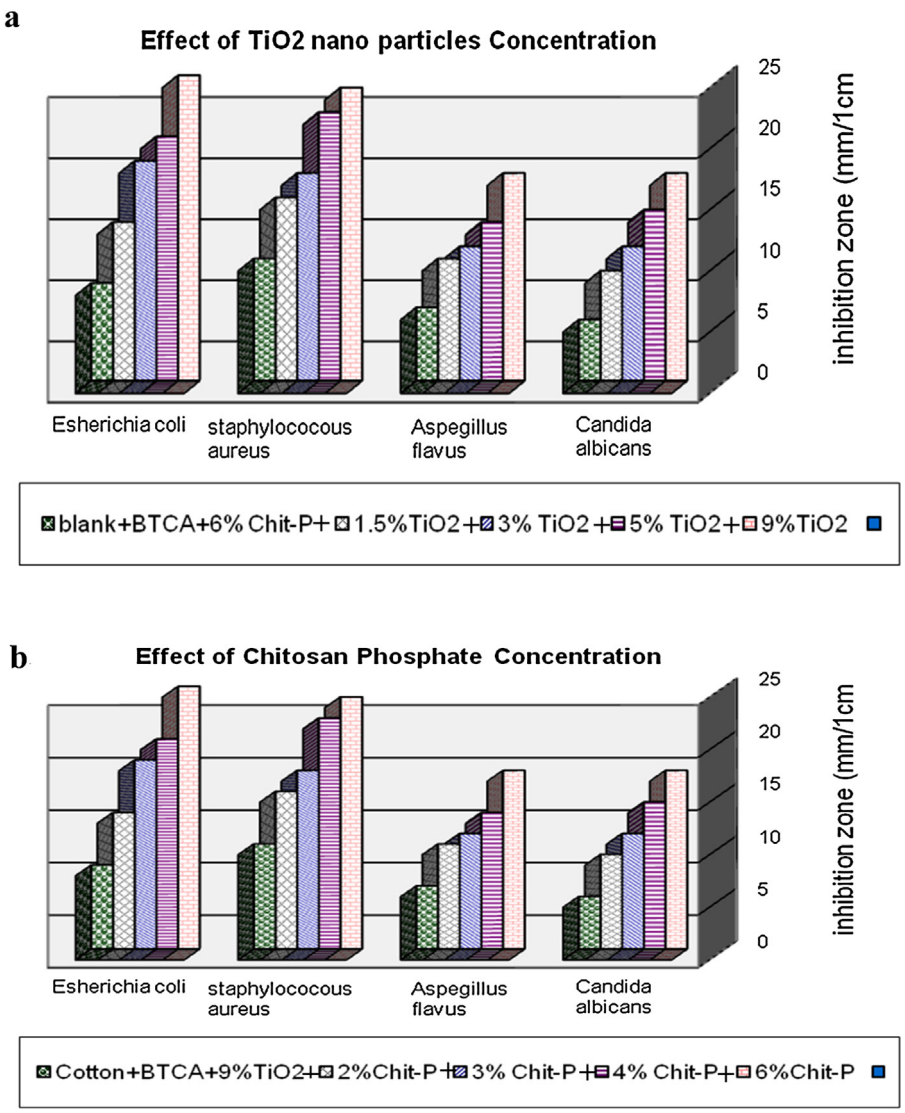


Fig. 8. (a) Effect of TiO_2 nanoparticles concentration on the antibacterial properties of the treated cotton; (b) effect of chitosan phosphate concentration on the antibacterial properties of the treated cotton.

and chemical properties) increasing concentration of chitosan phosphate from 0 to 10% is accompanied by decrement in the CRA (Fig. 6(b)), such a decrease in the CRA may be due to the following reasons: (1) increasing the viscosity of the finishing ingredients which in turn and (2) decrease the penetration of the finishing formula and consequently decrease in the efficiency of the polycarboxylic acid as crosslinking agents.

3.4. Scanning electron microscope SEM

Fig. 7(a)–(c) illustrates the SEM of untreated cotton fabric (a), cotton treated with BTCA and chitosan phosphate (b), and cotton treated with BTCA and chitosan phosphate in addition to TiO_2 nanoparticles (c) (magnification = 1000×). The morphology of cotton fibre with smooth surface is shown in Fig. 7(a). The morphological changes in the appearance of cotton fibres treated with either chitosan phosphate and BTCA in absence and presence of nano TiO_2 are shown Fig. 7(b) and (c).

3.5. Antibacterial properties of treated fabrics

We investigated the effect of changing the concentration of chitosan phosphate and the concentration of the TiO_2 nano particles on the antibacterial activities of finished fabrics to obtain effective antibacterial textiles. The treated cotton fabric samples with BTCA as non formaldehyde finishing agents in presence of 9% TiO_2 nano particles and with different concentrations of chitosan phosphate (2–10%) were shown in Fig. 8(b) also same holds true, for cotton fabric treated with finishing formulation in addition to different concentrations of TiO_2 nano particles (1.5–9%) at 6% Chit-P were shown in Fig. 8(a). The antimicrobial activities of treated fabrics were tested against staphylococcus aureus (G +ve), *E. coli* (G −ve), *Aspergillus flavus* (fungus) and *Candida albicans* (fungus).

The tested results are shown in Fig. 8(a) and (b). It can be seen from the figures that all treated fabrics possess good antimicrobial activity under the optimum finishing conditions. Fig. 8(b) shows the antimicrobial activity increased with the increase of the concentration of chitosan phosphate at constant concentration of TiO_2 nano particles. Fig. 8(a) shows that by increasing the TiO_2 nano particles at constant concentration of chitosan phosphate there is increase in the antibacterial activity. These results demonstrate that the combination of TiO_2 nano particles and chitosan phosphate improve the antibacterial properties of cotton treated fabrics.

4. Conclusion

In this work cotton fabric was treated with nano TiO_2 in presence of polycarboxylic acid [1,2,3,4-butane tetracarboxylic acid] with sodium hypophosphite as catalyst and chitosan phosphate through conventional pad-dry-cure method. This treatment was established to achieve flame retardant and antibacterial cotton fabric. It is concluded from the results obtained that presence of 1,2,3,4-butane tetracarboxylic acid, TiO_2 and chitosan phosphate is important to increase the thermal stability antibacterial properties of treated cotton fabrics.

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