



Utilization of acrylates emulsion terpolymer with chitosan as a finishing agent for cotton fabrics

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ABSTRACT

Cotton fabrics were treated with finishing bath formulation containing emulsion lattices based on acrylate monomers, chitosan and polyethylene glycol (PEG) to provide cotton fabrics with antibacterial, UV-protection as well as improvement of dyeing properties with direct, acid and reactive dyes. The terpolymer emulsion, chitosan and PEG concentrations as well as fabric pretreatment with alkali significantly affected the performance properties, antimicrobial activity, UV-protection and dyeing behavior of treated cotton fabric. The finished fabrics were characterized in terms of FTIR, X-ray diffraction, scanning electron microscope (SEM) as well as mechanical properties such as tensile strength, elongation at break (%), abrasion resistance and air permeability. The obtained data showed that the tested fabrics have appropriate antibacterial activity with highly UV-protection properties with increasing chitosan concentration up to 3%. The mechanical properties expressed as tensile strength and abrasion resistance increased after finishing treatment. Moreover, the performance of the finished fabrics and dyeing properties with different dyes classes were greatly influenced by the action of alkali pretreatment of cotton fabrics, adding the polyethylene glycol to the finishing bath formulation as well as emulsion and chitosan concentrations.

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1. Introduction

Chitosan is the deacetylated derivative of chitin which is the second most abundant polysaccharide found on earth next to cellulose. Due to the characteristic properties of chitosan such as nontoxicity, biodegradability, antifungal activity, water-binding capacity, bioactivity, and biocompatibility, chitosan and its modified analogs have found many applications in pharmaceutical and medical applications, textile dyeing and finishing, fiber formation, waste water treatment, paper production, and cosmetics. (Hudson, 1998; Illum, 1998; Morimoto et al., 2001; Ngah, Ghani, & Kamari, 2005; Shantha, Bala, & Rao, 1995; Trung, Ng, & Stevens, 2003). The antibacterial activities of textile fabrics using chitosan were studied with respect to effect of chitosan's molecular weight, deacetylation and modification (Lim & Hudson, 2004a; Yoo, Shin, Kim, & Jang, 1997) as well as the types of crosslinking agents (El-tahlawy, El-bendary, Elhendawy, & Hudson, 2005; Kittinaovarat, Kantuptim, & Singhaboonponp, 2006).

Ultraviolet (UV) radiation is harmful to human health. Recently considerable attention has been paid to the barrier properties of textiles as a protection against UV-radiation (Hilfiker, Kaufmann, Reinert, & Schmidt, 1996; Ibrahim, Refai, Youssef, & Ahmed, 2005; Sharma & Singh, 2001). Ultraviolet-protection factor (UPF) is the scientific term used to indicate the amount of ultraviolet-protection provided to skin by fabric. The transmission of UV-radiation through fabrics is greatly influenced by different parameters such as fiber type and chemical composition, fabric construction, additives, textile processing aids, color, and fabric finish (Ghosh, Bajaj, & Kothari, 2003; Reinert, Fusco, Hilfiker, & Schmidt, 1997).

The present work aims to study the feasibility of applying freshly prepared terpolymer emulsion based on glycidyl methacrylate, styrene, and butyl acrylate (Nasr, 2005) as a crosslinking agent for chitosan-fabric bond formation. The performance properties of the finished fabric in presence or absence of alkali pretreatment as well as incorporation of polyethylene glycol were studied. Characterization of the finished fabrics was also studied in terms of FTIR, X-ray diffraction and scanning electron microscope (SEM). The work was further extended to include the antibacterial activities, UV-protection, dyeing performance and fastness properties of the finished fabrics.

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2. Experimental

2.1. Materials and chemicals

Cotton fabric of 150 g/m², supplied by Masr Helwan Company, treated with a solution containing 0.5 g/l soap and 0.5 g/l Na₂CO₃ at a temperature of 70 °C for 1 h, thoroughly washed and air dried at room temperature was used. Styrene (St), butyl acrylate (BuA) and glycidyl methacrylate (GMA) monomers were supplied by Merck-Schuchardt, Germany and redistilled before use and stored at –20 °C. Dodecyl benzene sodium sulphonate (DBSS) was a product of the Egyptian Starch, Yeast, and Detergent Company, Egypt. Polyoxyethylene monomethyl ether (MPOE) Union Carbide Company (USA) (M.wt. 5000 g/mol), was dried in a vacuum oven at 70 °C for 24 h prior to use. Potassium persulphate (KPS), polyethylene glycol (PEG) 300 & 600, sodium bisulphite (SBS) and sodium hydroxide NaOH were analytical grade chemicals. Chitosan of low molecular weight and 92% degree of deacetylation supplied by Fluka. The direct dye used was Optisal Scarlet BL.

2.2. Synthesis of terpolymer latex based on styrene, butyl acrylate and glycidyl methacrylate

Emulsion polymerization of terpolymer based on styrene (St), butyl acrylate (BuA), and glycidyl methacrylate (GMA) was prepared by semicontinuous technique (Nasr, 2005) with a solid content of ca 10 ± 1%. The following ingredients were mixed in a 250 ml three necked flask; mixture of dodecyl benzene sodium sulphonate (DBSS) (1 g) and polyoxyethylene monomethyl ether (MPOE) (1 g) were dissolved in distilled water (30 ml) and charged into mixture of St, BuA, and GMA. A redox initiation system composed of potassium persulphate (0.27 g) and sodium bisulphite (0.416 g) was dissolved in the remaining distilled water (30 ml) and added drop wise to the reaction mixture. The polymerization reaction was carried out at 70 °C under stirring at 300 rpm. The resultant emulsion latex was mixed with chitosan to be used for finishing.

2.3. Treatment of cotton fabrics with finishing agent

Cotton fabric was impregnated in NaOH solution (0.1–1 N) at a liquor ratio of 1/30, squeezed at a wet pick up of ca 100% and finally dried at 80 °C for 5 min. The alkali pretreated cotton fabric as well as untreated one were independently treated with finishing formulations containing chitosan [dissolved in acetic acid (w/w)] with concentration range (0.5–3%), the prepared terpolymer emulsion (0.5–3%), and polyethylene glycol (0–5%) using the pad-dry cure method. The finished fabric was dried at 80 °C for 5 min and cured at 130 °C for 6 min. After treatment, the fabrics were soaped using 2 g/l non-ionic detergent (Egyptol), washed with cold water and air dried.

The percentage of add-on is calculated by:

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

where

W₁, weight of fabric before treatment

W₂, weight of fabric after treatment

2.4. Dyeing procedure

Both finished and unfinished cotton fabrics were dyed with direct dye according to the conventional exhaustion method in a laboratory dyeing apparatus. The dye bath was applied at dye concentration 3% (owf), pH 8, liquor ratio of 1:50 and temperature

of 90 °C. The dyed samples were washed with a soap solution (2 g/L) at 50 °C for 30 min, rinsed with tap water and finally dried at ambient conditions.

2.5. Fabric characterization

IR Spectroscopy was carried out for treated and untreated fabrics using Nicolet 380 FTIR spectrometer in Attenuation Total Reflection (ATR) mode with a zinc selenide crystal, in the wavelength range 650–4000 cm^{–1}. Also samples have been investigated by X-ray diffraction was performed by Philips analytical X-ray B.V., the scanning electron microscopy (SEM) was conducted using Joel JSM-T20 Japan.

2.6. Fabric evaluation

The nitrogen content was determined using (Vogel, 1975). The thickness of the finished fabric was measured by using SLD Portable Thickness Gauges, England according to ASTM D1777-1996. The Air permeability according to ASTM D 737-1996, the abrasion resistance according to ASTM D 4158-1992, the fabric stiffness in terms of bending length in warp direction according to ASTM D 1388-1996, as well as the tensile strength and elongation at break according to ASTM D 5035-1995. The color strength (K/S) values of all examined dyed samples were determined using a SDL Opti-match Color Matching System, England. The fastness to washing and perspiration for the dyed fabrics were determined according to AATCC 61-1975 and ISO-105 E04-1994.

2.7. Antibacterial test

Microorganism used in this study is *Escherichia coli* as Gram-negative bacteria. Disc diffusion method was used for screening the cotton fabric samples for antimicrobial activity (Ericsson & Sherris, 1971).

2.8. Ultraviolet-protection factor (UPF)

UPF was measured using UV-vis double beam spectrophotometer (Perkin-Elmer, Lambda 35, Diffuse transmission technique) according to ASTM D-6603-2000 & AATCC 183-2000. The UPF was calculated using the following equation:

$$\text{UPF} = \frac{\sum_{280 \text{ nm}}^{400 \text{ nm}} E, S, \Delta\lambda}{\sum_{280 \text{ nm}}^{400 \text{ nm}} E, S, T, \Delta\lambda}$$

where

Eλ, relative erythermal effectiveness function,

Sλ, solar spectral irradiance in Wm^{–2} nm^{–1}

Tλ, spectral transmittance of fabric

Δλ, measured wavelength interval (nm)

The tested samples were classified according to their UPF values: <15 poor, 15–24 good, 25–39 very good, >39 excellent.

3. Results and discussion

3.1. Effect of sodium hydroxide concentration on the performance of finished fabrics

Sets of cotton fabrics were pretreated with different concentrations of sodium hydroxide (0.1–1 N). Both of untreated cotton fabric as well as previously alkali treated ones were padded in finishing bath formulation containing 2% terpolymer emulsion latex; 2% chitosan. After padding, the fabrics were

dried at 80 °C for 3 min, and then thermally cured at 130 °C for 6 min. Table 1 shows the effect of sodium hydroxide concentration on the fabric performances expressed as add-on, thickness, abrasion resistance, air permeability, nitrogen content and stiffness as well as tensile strength and elongation at break.

It is evident that the add-on of treated fabrics is significantly increased by increasing the alkali concentration in the studied range. For instance, the add-on value is increased by a value of 150% when the alkali concentration increased to 1 N. Also, the Nitrogen content increases from 0.82% for T1 (fabric without any alkali pretreatment) up to 1.29 for T6 (fabric pretreated with 1 N NaOH). Moreover, the abrasion resistance is pronouncedly increased from 82 cycle for the untreated sample to 127 cycle for the finished fabrics without alkali pretreatment (T1) and gradual increase in the abrasion resistance value is recorded when the finished fabrics is pretreated with NaOH to reach optimum conditions at pretreatment 0.75 N NaOH (T5). The tensile strength increased via finishing treatment by a value of 2.9% for sample T1 and further increase with a value of 10% for T6. It is important to mention that the most finishing treatment for cotton fabrics is accompanied by decreasing the mechanical properties expressed as tensile strength and elongation at break (El-tahlawy et al., 2005; Kittinaovarat et al., 2006). The elongation at break in this study is increased by increasing NaOH concentration from a value of 5.8% (untreated fabric) to 6.9% (T6). On the other hand, the air permeability of the finished fabrics decreases from 26 cm³/cm/s for the untreated fabric to 13 cm³/cm/s for the treated one T6.

Finally, the stiffness of the finished fabric, expressed as bending distance in cm, increases from a value of 1.36 cm for the untreated fabric to reach a value of 3.47 cm for treated one T6. So, we can say that all fabric performance is directly proportional to the alkali concentration except the air permeability tendency. In other words, we can say that the availability of interactions between the epoxy groups of the terpolymer and the alkali cellulose or abundant amino groups of chitosan is increased by increasing the alkali concentration. This ultimately leads to increase the amounts of reacted hybrid to cotton fabric giving positive action for either increasing the add-on, thickness, abrasion resistance, tensile strength and elongation at break or decreasing the porosity of the fabric i.e., decreasing the air permeability values.

The air permeability of the fabric is generally affected by many variables such as the fabric structure, thickness, and surface characteristics (Yipm, Chan, Sin, & Lau, 2002). Accordingly, the variation of the fabric thickness and/or add-on of a film formed polymeric hybrid composed of chitosan and terpolymer would certainly affect the magnitude of air permeability. The mentioned higher increase of stiffness values recorded by

increasing the alkali concentrations could be recognized to the growth of the crosslinking interaction between the epoxy of the formed hybrid terpolymer and cellulosic hydroxyl groups.

3.2. Effect of polyethylene glycol type and concentration on the performances of finished fabrics

Table 2 shows the effect of polyethylene glycol type and concentration on the performance properties of the finished cotton fabric in absence and presence of fabric pretreatment with sodium hydroxide (1 N), respectively. The untreated fabrics as well as alkali pretreated cotton fabrics are finished with finishing bath formulation containing 2% terpolymer emulsion latex and 2% chitosan.

The obtained results signify many interesting features (a) regardless of PEG type or the presence of alkali treatment of cotton fabric, the add-on, thickness, abrasion resistance and tensile strength as well as elongation (%) at break is significantly increased by the presence of PEG in the finishing bath formulation and such increase was independent of PEG concentration reflecting the characteristic action of PEG as a good film former with superior elastic properties (Ghosh & Das, 2000); (b) the nitrogen content, air permeability and stiffness values were decreased as the PEG concentration increased, which confirm the competitive interactions between the terpolymer epoxy functional groups with PEG or chitosan; (c) at fixed PEG concentration, PEG 300 gives the more pronounced fabric performance represented by higher nitrogen content percent, abrasion resistance, the add-on %, air permeability. Finished fabrics with higher nitrogen contents would reflect the presence of pronounced magnitude of chitosan content with its superior property as antimicrobial and or cationic character for improving dyeing behavior with reactive, acid and direct dyes. The PEG 600 gives a pronounced fabric performance in terms of stiffness as well as tensile strength and elongation % at break than PEG300. The need of higher magnitude of chitosan in the molecular structure of cotton fabrics is our target in the study to maintain the best antibacterial activity to the cotton fabrics. The suggested reaction mechanisms for the interaction between cotton fabric, terpolymer emulsion latex, chitosan, and PEG are shown by Eq. (1)–(4).

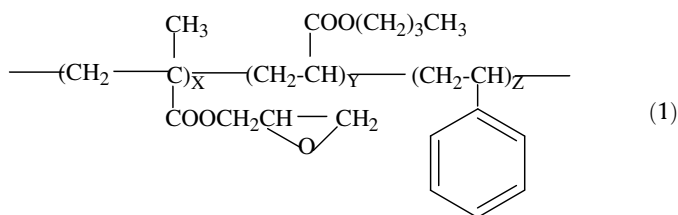


Table 1
Effect of sodium hydroxide concentration on the fabric performance

[NaOH] (N)	Code	Add-on %	Thickness (mm)	N%	Air permeability (cm ³ /cm/s)	Abrasion resistance (cycle)	T.S. (kg)	E (%)	Stiffness (cm)
Blank fabric	B	–	0.37	–	26	82	49	5.8	1.36
0	T1	4	0.40	0.82	24.8	127	50.4	6.0	3.02
0.1	T2	4.6	0.40	0.96	24	138	51.2	6.4	3.11
0.25	T3	5	0.40	1.02	22	141	51.7	6.7	3.18
0.5	T4	6.5	0.40	1.18	17.8	146	52.3	6.8	3.24
0.75	T5	9	0.40	1.25	16	150	53.1	6.8	3.35
1	T6	10	0.39	1.29	13	149	53.9	6.9	3.47

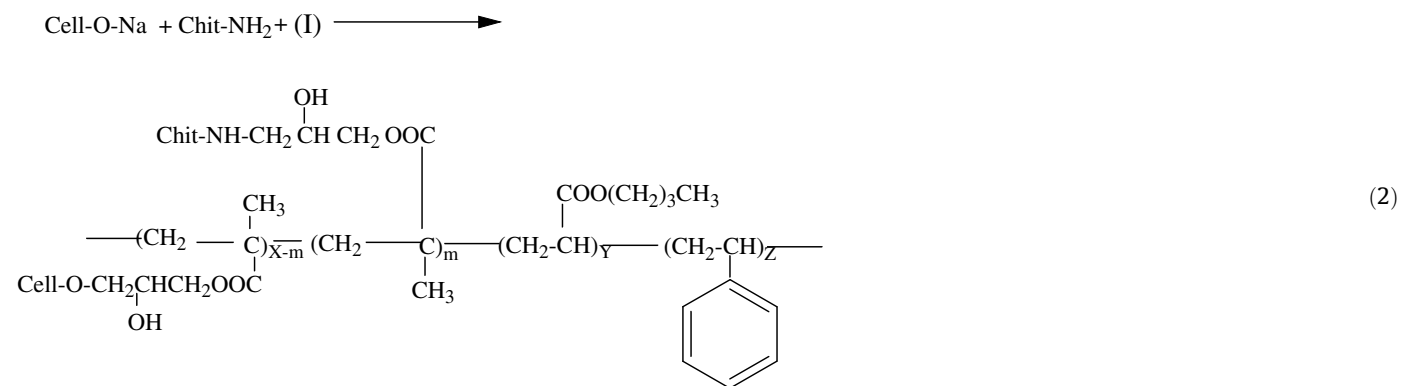
[Chitosan %], 2%; [Emulsion %], 2%; Drying temperature, 80 °C; Cure temperature, 120 °C.

Table 2

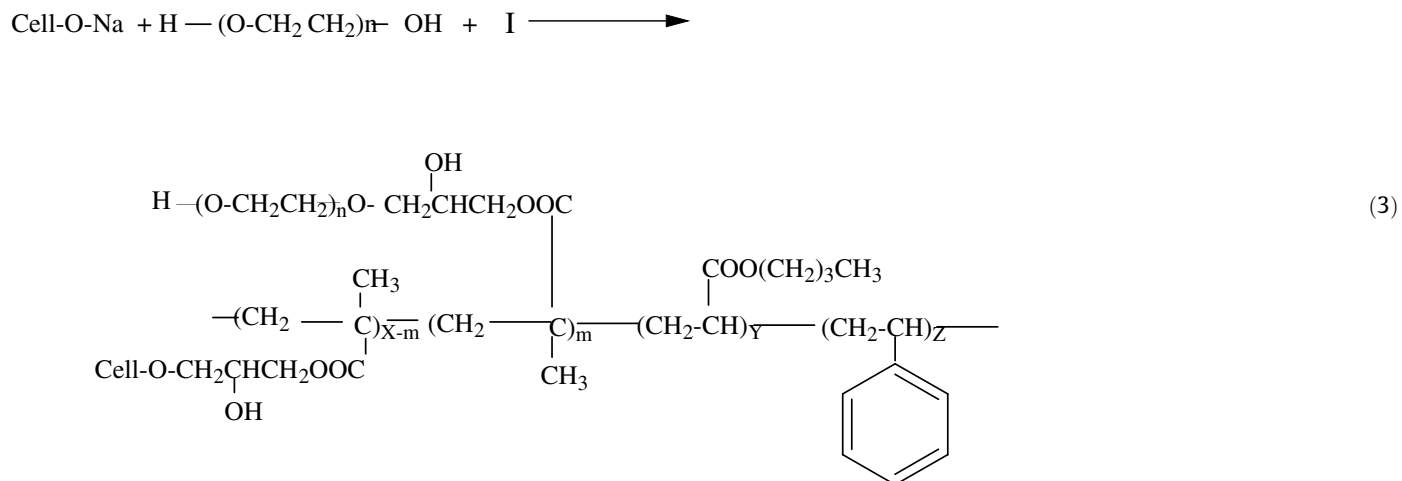
Effect of polyethylene glycol types and concentrations on the fabric performance

PEG type	[PEG] %	Code	NaOH	Add-on %	Thickness (mm)	N%	Air permeability (cm ³ /cm/s)	Abrasion resistance (cycle)	T.S. (kg)	E (%)	Stiffness (cm)
Blank fabric		B			0.37	–	26	82	49	5.8	1.36
300	2	T7	Absence	5	0.38	1.24	23.5	125	62.2	14.6	2.93
	3	T8		4.3	0.38	0.93	21.2	133	63	14.8	2.81
	4	T9		4	0.376	0.87	20.5	152	65	14.9	2.78
	5	T10		4.4	0.375	0.80	19.7	150	66	14.8	2.71
600	2	T11	Absence	4.6	0.375	1.17	26.6	137	69	15.6	2.87
	3	T12		4.6	0.38	0.81	20.7	144	67	15.7	2.77
	4	T13		4.6	0.375	0.73	18.8	139	68	15.0	2.68
	5	T14		4.3	0.375	0.68	18.6	140	67	14.4	2.62
300	2	T15	Presence	8	0.385	1.27	11.1	129	63	14.3	3.27
	3	T16		7	0.40	1.18	11.5	152	65	14.5	3.06
	4	T17		5.6	0.40	1.06	12.3	145	66.2	15.1	2.98
	5	T18		6.7	0.40	0.91	11.6	143	68	15.4	2.91
600	2	T19	Presence	7	0.395	1.11	12.4	131	65	14.7	3.19
	3	T20		6.5	0.40	1.02	14.3	140	66.5	14.9	3.01
	4	T21		6.3	0.40	0.96	12.1	137	69	15.0	2.82
	5	T22		5.7	0.40	0.88	13.6	141	70	15.0	2.73

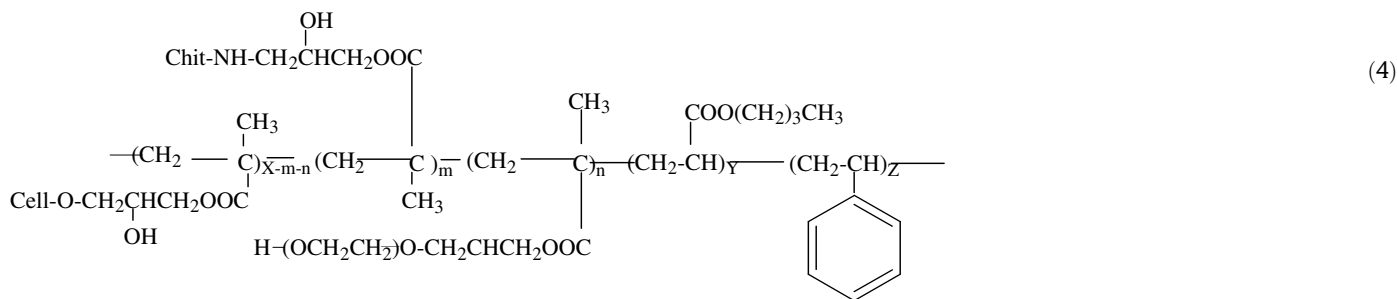
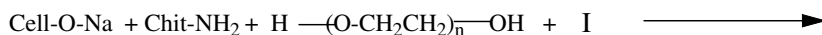
[Chitosan %], 2%; [Emulsion %], 2%; Alkali pretreatment with NaOH, 1 N; Drying temperature, 80 °C; Cure temperature, 120 °C.



and/or



and/or

**Table 3**

Effect of chitosan and terpolymer emulsion concentrations on the fabric performance for non-pretreated fabrics with alkali

[Emulsion] %	[Chitosan] %	Code	Add-on %	Thickness (mm)	N%	Air permeability (cm ³ /cm/s)	Abrasion resistance (cycle)	T.S. (kg)	E (%)	Stiffness (cm)
Blank fabric			–	0.37	–	26	82	49.0	5.8	1.36
0.5	0.5	T23	0.6	0.40	0.32	19.54	90	64.15	15.35	1.97
	1	T24	1.1	0.40	0.58	21.55	104	63.28	14.77	2.25
	2	T25	2.4	0.40	0.71	23.93	113	62.06	14.14	2.47
	3	T26	3.1	0.40	0.82	27.56	98	60.52	13.27	2.62
1.0	0.5	T27	1.3	0.40	0.41	18.7	102	63.72	15.41	2.02
	1	T28	1.2	0.40	0.66	21.8	108	62.71	14.93	2.31
	2	T29	2.5	0.40	0.80	24.7	118	61.02	14.23	2.50
	3	T30	3.3	0.40	0.96	25.55	107	60.11	13.23	2.71
2	0.5	T31	1.7	0.39	0.43	18.78	109	63.77	15.36	2.23
	1	T32	2	0.40	0.65	20.59	122	61.60	15.09	2.46
	2	T33	3.5	0.40	0.92	22.40	133	60.24	14.16	2.81
	3	T34	3.8	0.40	0.96	25.36	116	59.32	13.33	2.99
3	0.5	T35	3.0	0.40	0.49	18.21	117	63.22	15.40	2.60
	1	T36	2.1	0.41	0.77	19.45	136	61.37	15.00	2.84
	2	T37	4.4	0.40	0.89	21.83	145	60.27	14.45	3.11
	3	T38	4.4	0.40	1.02	23.65	123	58.77	13.23	3.32

[PEG 300 %], 3%; Drying temperature, 80 °C; Curing temperature, 120 °C.

Table 4

Effect of chitosan and terpolymer emulsion concentrations on the fabric performance for pretreated fabrics with alkali

[Emulsion] %	[Chitosan] %	Code	Add-on %	Thickness (mm)	N%	Air permeability (cm ³ /cm/s)	Abrasion resistance (cycle)	T.S. (kg)	E (%)	Stiffness (cm)
Blank fabric			–	0.37	–	26	82	49	5.8	1.36
0.5	0.5	T39	2.3	0.40	0.61	13.4	94	65	15.72	2.15
	1	T40	1.4	0.40	0.85	15.1	107	61.77	14.50	2.43
	2	T41	7.9	0.40	0.98	12.3	122	57.87	13.52	2.66
	3	T42	6	0.40	1.24	15.8	104	55.5	12.40	2.87
1.0	0.5	T43	3.8	0.40	0.73	11.6	109	64.8	16.23	2.32
	1	T44	2	0.40	0.91	12.9	119	60.8	14.77	2.61
	2	T45	9.9	0.40	1.07	9.79	137	58.1	14.00	2.84
	3	T46	7.6	0.40	1.34	13.7	116	55.5	12.70	2.96
2	0.5	T47	6	0.40	0.77	11.8	131	64.2	16.08	2.67
	1	T48	4	0.40	0.96	13	140	60.5	15.20	2.74
	2	T49	11.3	0.40	1.18	10.14	152	57.7	14.03	3.06
	3	T50	8	0.40	1.33	14.25	123	54.9	12.63	3.19
3	0.5	T51	9.06	0.41	0.86	9.47	142	64.4	16.23	2.92
	1	T52	5.7	0.41	0.98	10.1	153	61.2	14.97	3.14
	2	T53	12.6	0.41	1.30	8.74	159	56.9	14.12	3.37
	3	T54	10.6	0.41	1.41	12.72	136	54.2	12.86	3.69

[PEG 300 %], 3%; Drying temperature, 80 °C; Curing temperature, 120 °C; Alkali pretreatment with 1 N NaOH.

3.3. Effect of chitosan and terpolymer emulsion concentration on the performances of finished fabrics

Tables 3 and 4 show the effect of different terpolymer emulsion/chitosan concentrations on the performance of the finished fabric in absence and presence of alkali pretreatment, respectively. The obtained results clarify the following aspects: (a) regardless of alkali pretreatment, increasing the chitosan concentration at fixed terpolymer emulsion concentration is accompanied by increasing of nitrogen contents, add-on, fabric stiffness and abrasion resistance (in the range studied) meanwhile, the mechanical properties maintain its pronounced higher values than the untreated one; (b) increasing the terpolymer emulsion concentration, at fixed chitosan concentration is associated with increasing the add-on, nitrogen content, abrasion resistance and fabric stiffness, reflecting the higher extents of epoxy groups available for interaction and crosslinking with either cotton hydroxyl groups in one side or chitosan as well as PEG in the other side; (c) the alkali pretreat-

ment of cotton fabric increases the fabric add-on, nitrogen content, abrasion resistant and stiffness while the air permeability was distinctly decreased.

From the above findings, we can conclude that the finishing of pretreated fabrics with finishing bath containing concentration greater than 1% of chitosan and terpolymer emulsion is satisfied to obtain finished fabrics with the best performance suitable to mention antibacterial properties due to exist of considerable amount of chitosan expressed as obtained N%.

3.4. Characterization and evaluation of finished fabrics

3.4.1. FTIR spectroscopy

Fig. 1 (a and b) shows the FTIR spectra of untreated fabric and cotton fabric treated with finishing bath formulation containing chitosan (2%); terpolymer emulsion (2%); PEG (3%), respectively. In the IR spectra of untreated fabric (Fig. 1 a) the characteristic

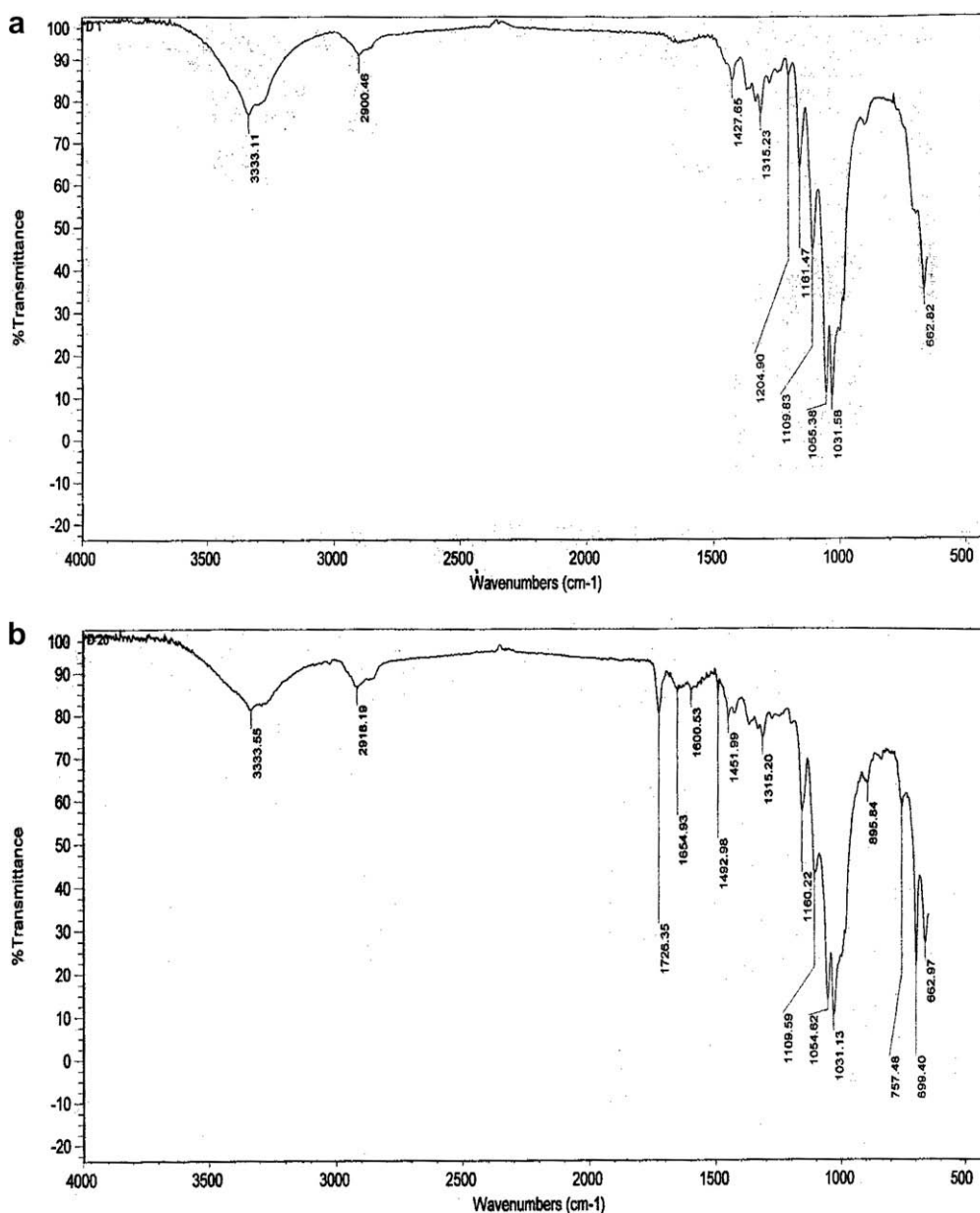


Fig. 1. FTIR spectra for untreated fabric (a) and finished fabric (b).

vibration bands were observed at 1427, 1160, 1109, 1054, and 1031 cm^{-1} characteristic for cellulosic structure. In IR spectra of the finished fabrics (Fig. 1b), the spectrum reveals 1726 cm^{-1} for carbonyl ester group of acrylates and 1600, 1492, 1451, 757, and 699 cm^{-1} for polystyrene confirming the presence of terpolymer functional groups (Nasr, 2005). Moreover, the absorption peak at about 1492–1600 cm^{-1} is due to characteristic N–H bending vibration for chitosan (Shin & Yoo, 1998) (overlap with the polystyrene bands). The presence of absorption bands at 3333 cm^{-1} for –OH stretching and 1109 cm^{-1} for C–O stretching of primary alcohols confirm the presence of PEG (overlap with –OH) and C–O function groups of cotton and chitosan.

3.4.2. X-ray diffraction

The results represented in Fig. 2 showed some selected results of Wide Angle X-Ray (WAXS) diffractograms of the unfinished (blank) and finished cotton fabrics using different formulation conditions. It is evident that all studied samples show remarkable crystalline peak at $2\theta = 22^\circ$, which is generally characteristic for cotton fabrics (Marchessault & Sundararajan, 1982, chap. 2). Moreover, there are significant changes in the peak intensity due to finishing treatment. By increasing alkali pretreatment, chitosan and terpolymer emulsion concentrations the crystalline size markedly decreased, also the size of their lateral dimension and crystalline index almost changed. These observations demonstrate that the

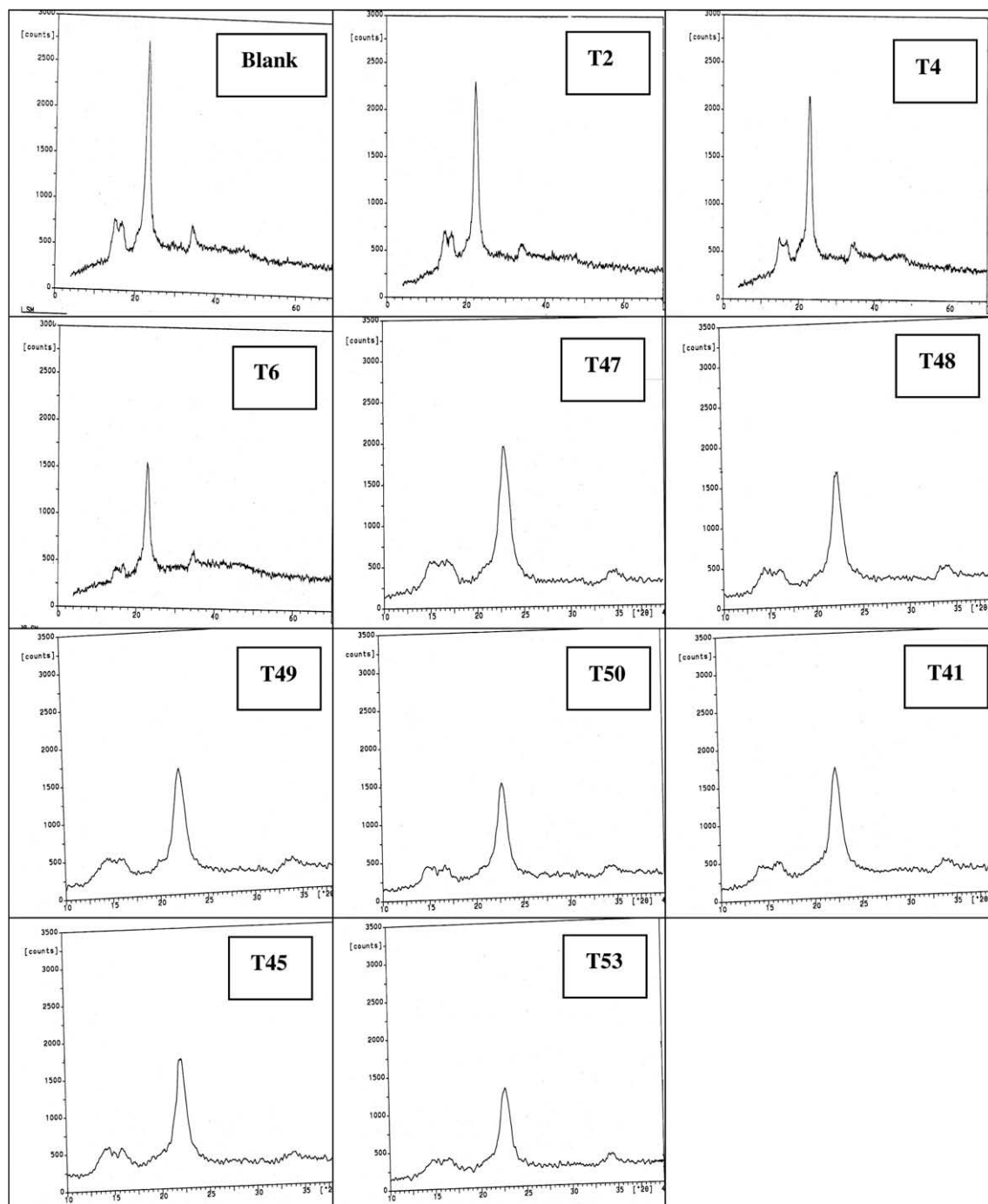


Fig. 2. Wide Angle X-Ray of untreated cotton (blank); different alkali pretreated finished fabric (T2, T4 & T6: 0.1, 0.5 & 1 N); different chitosan concentrations (T47, T48, T49 & T50: 0.5, 1.0, 2.0 & 3%) and different emulsion concentrations (T41, T45, T49 & T53: 0.5, 1.0, 2.0 & 3%).

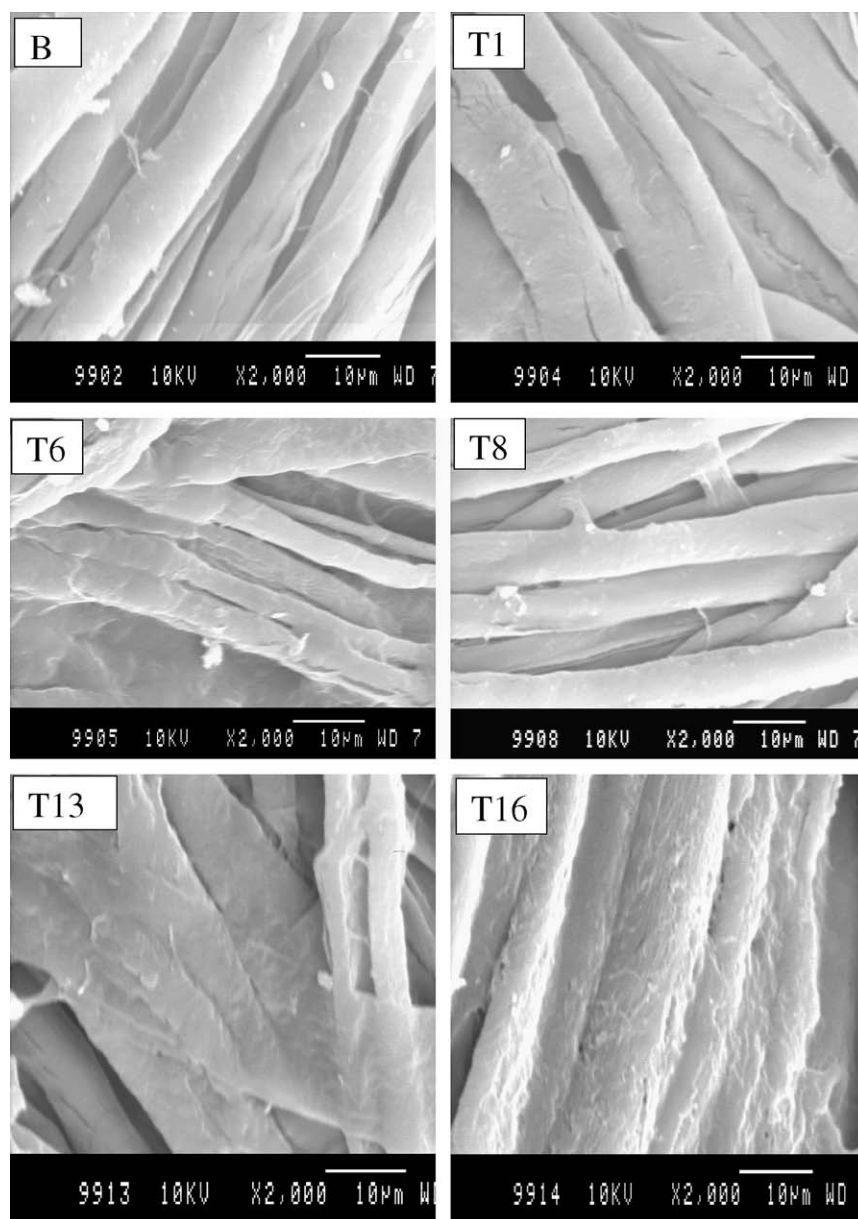


Fig. 3. SEM of untreated cotton (B); and treated cotton fabric using different application conditions.

finishing treatment of cotton fabrics (under the given conditions) proceeds in the crystalline regions of cotton fabrics.

3.4.3. Scanning electron microscope

Fig. 3 represents the scanning electron microscope graphs of untreated cotton (B) and treated cotton fabric using different application conditions. The graph of the finished fabrics (T1–T16) showed deposition of the polymer hybrid between the fiber chains. Moreover, the graphs show higher fiber swelling and more of the polymer film network present on the fiber thread when the fabric was firstly alkali pretreated (T6). Higher extent of fiber coating with more film uniformity was observed by using PEG and alkali pretreatment (T16).

3.5. Evaluation of the finished cotton fabric for antibacterial activities, UV-protection, dyeing performance and fastness properties

Some selected finished samples were evaluated for different properties such as antibacterial, UV-protection, dyeing behavior expressed as color strength values (K/S) and fastness to washing

and perspiration (acidic and alkali) and the data are given in Table 5. It is evident that the untreated fabric shows no antibacterial activity and the finished fabrics manifest different extent antibacterial activity depending on chitosan concentration in the finishing bath, i.e. higher antibacterial activities of the finished fabrics were observed as the chitosan concentrations increased in the finishing bath. This reflects the effect of the terpolymer emulsion as a good crosslinking agent available to fix chitosan and PEG in the molecular structure of cellulose. Many literatures demonstrate that the antimicrobial activity of chitosan could be originated from its polycationic nature which can interact with the anionic components (lipopoly-saccharides and proteins of microorganism surface) resulting in changes in permeability which causes death of the cell by inducing leakage of intracellular components (Helander, Nurmi-aho-Lassila, Ahvenainen, Rhoades, & Roller, 2001; Lim & Hudson, 2004b).

The UV-protection of untreated and finished fabrics was assessed for previously dyed samples with a direct dye. The UPF results showed that the dyed untreated fabric have a protection range of 12.4. The finished fabrics showed much more

Table 5
Antimicrobial activity; UV-protection factor (UPF), color strength value (K/S) and fastness performances (washing and perspiration) of the cotton fabrics treated with different chitosan/emulsion concentrations

Code	Antimicrobial activity expressed as inhibition zone <i>E. coli</i> (mm)	UPF	K/S	Washing			Acidic perspiration			Alkali perspiration		
				Alt.	Stain.		Alt.	Stain.		Alt.	Stain.	
Blank	0	12.4	14.21	3	3	3/4	3/4	3	3	3/4	3/4	3
T39	3	16.4	15.57	5	5	5	4/5	5	4/5	4/5	4/5	4/5
T40	4	20.2	16.25	5	5	5	5	5	5	5	5	4/5
T41	5	26.5	17.35	5	5	5	5	5	4/5	5	5	4/5
T42	6	31.7	18.24	5	5	5	5	5	4/5	4/5	4/5	4/5
T43	4	19.9	15.68	5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
T44	5	24.5	16.37	5	5	5	5	4/5	4/5	5	5	4/5
T45	7	35.0	17.12	5	5	5	5	5	4/5	5	4/5	4/5
T46	8	39.8	18.98	5	5	4/5	5	5	4/5	5	4/5	4/5
T47	4	18.0	16.09	5	5	5	5	5	4/5	5	5	5
T48	5	22.1	17.22	4/5	5	5	5	5	5	5	4/5	4
T49	8	31.4	18.69	5	5	5	5	4/5	5	4/5	5	4/5
T50	9	33.6	19.33	4/5	5	5	5	4/5	4/5	5	4/5	4/5
T51	4	15.6	15.84	4/5	5	5	5	5	5	5	5	4/5
T52	5	19.2	17.31	5	5	5	4/5	5	5	4/5	4/5	4/5
T53	8	26.6	17.95	4/5	5	4/5	4/5	4/5	4/5	5	4/5	4/5
T54	9	30.0	18.69	4/5	4/5	4/5	5	4/5	4/5	5	5	5

pronounced UPF range and such increment is directly dependent on the chitosan concentration in the studied range as well as emulsion concentration up to 1%, then it begins to decrease. The improvement of UV-protection property of direct dyed untreated fabric could be related to the high bulky structure effect of the direct dyes to cause blocking the holes in the fabric to avoid the holes effect. This criteria minimizing the transmission of UV-radiation through the fabric structure, i.e. better UPF rating (Ghosh et al., 2003; Reinert et al., 1997). The high extent of UV-protection in terms of UPF by finishing treatment may be attributed to the formation of uniform film covering and coating the inter-fiber structure and this could be also seen via SEM graphs (Fig. 3). At lower emulsion concentration and increasing the chitosan concentration in presence of constant PEG concentration the extent of penetration and crosslinking magnitude would be available for forming non-brittle uniform film available for much more blocking the holes in the fabric.

The dyeing and fastness performances of the untreated and finished fabrics show that the color strength and fastness properties increased after finishing. It seen that, chemical treatment of cotton fabrics with cationizing agent increase the interaction between the direct dye and pretreated fabrics giving rise for higher color strength value and fastness properties (Shin & Yoo, 1998).

4. Conclusion

Terpolymer emulsion latex composed of butyl acrylate, styrene and glycidyl methacrylate is used as a crosslinking finishing agent and to bind chitosan with cotton fabrics. The extent absorption of each of terpolymer emulsion latex and/or chitosan greatly influenced via alkali pretreatment of cotton fabric before the finishing process. The fabric performance expressed as abrasion resistance, air permeability, tensile strength and elongation at break as well as stiffness is improved via incorporation of PEG in the finishing bath. The IR spectra demonstrate the chemical interaction between the finishing bath ingredient (terpolymer emulsion, chitosan, and PEG) and cotton fabric. The X-ray diffraction clarified that the chemical crosslinking reaction proceeds in the crystalline structure of the cotton fabric. SEM shows more uniformity and good film forming via adding PEG to the finishing bath. The finished fabrics acquire appropriate antibacterial activity for *E. coli*, and good to

very good ultraviolet-protection as well as excellent dyeing performance expressed as color strength and fastness properties.

References

- El-tahlawy, Kh. F., El-bendary, M. A., Elhendawy, A. G., & Hudson, S. M. (2005). The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. *Carbohydrate Polymers*, 60, 421–430.
- Ericsson, H. M., & Sherris, J. C. (1971). Antibiotic sensitivity testing. Report of an international collaborative study. *Acta Pathologica Scandinavica Section B Supplement*, 217.
- Ghosh, P., & Das, D. (2000). Modification of jute by some low molecular weight glycols and a polyol under thermal treatment. *European Polymer Journal*, 36, 2147–2157.
- Ghosh, S. B., Bajaj, P., & Kothari, V. K. (2003). Effect of dyes and finishes on UV protection of jute/cotton fabrics. *Indian Journal of Fibre & Textile Research*, 28, 431.
- Helander, I. M., Nurmiaho-Lassila, E. L., Ahvenainen, R., Rhoades, J., & Roller, S. (2001). Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria. *International Journal of Food Microbiology*, 71, 235–244.
- Hilfiker, R., Kaufmann, W., Reinert, G., & Schmidt, E. (1996). Improving sun protection factors of fabrics by applying UV-absorbers. *Textile Research Journal*, 66, 61–70.
- Hudson, S. M. (1998). The Applications of Chitin and Chitosan to Fiber and Textile Product's. In R. H. Chen & H.-C. Chen (Eds.). *Advances in Chitin Science* (Vol. III, pp. 80). Rita Advertising Co., Ltd.
- Ibrahim, N. A., Refai, R., Youssef, M. A., & Ahmed, A. F. (2005). Proper finishing treatments for sun-protective cotton-containing fabrics. *Journal of Applied Polymer Science*, 97, 1024–1032.
- Illum, L. (1998). Chitosan and its use as a pharmaceutical excipient. *Pharmaceutical Research*, 15, 1326–1331.
- Kittinaovarat, S., Kantupim, P., & Singhaboonponp, T. (2006). Wrinkle resistant properties and antibacterial efficacy of cotton fabrics treated with glyoxal system and with combination of glyoxal and chitosan system. *Journal Applied Polymer Science*, 100, 1372–1377.
- Lim, S. H., & Hudson, S. M. (2004a). Synthesis and antimicrobial activity of a water-soluble chitosan derivative with a fiber-reactive group. *Carbohydrate Research*, 339, 313–319.
- Lim, S. H., & Hudson, S. M. (2004b). Application of a fiber-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish. *Carbohydrate Polymers*, 56, 227–234.
- Marchessault, R. H., & Sundararajan, P. R. (1982). In G. O. Aspinall (Ed.). *The Polysaccharides* (Vol. II). New York: Academic Press.
- Morimoto, M., Saimoto, H., Usui, H., Okamoto, Y., Minami, S., & Shigemasa, Y. (2001). Biological activities of carbohydrate-branched chitosan derivatives. *Biomacromolecules*, 2, 1133–1136.
- Nasr, H. E. (2005). Preparation and characterization of some terpolymer latices and its application as finishing agent for cotton fabric. *Polymer Plastic Technology and Engineering*, 44, 389.
- Ngah, W. S. W., Ghani, S. A., & Kamari, A. (2005). Adsorption behaviour of Fe (II) and Fe (III) ions in aqueous solution on chitosan and crosslinked chitosan beads. *Bioresource Technology*, 96, 443450.
- Reinert, G., Fuso, F., Hilfiker, R., & Schmidt, E. (1997). UV-protecting properties of textile fabrics and their improvement. *Textile Chemist and Colorist*, 29, 36–43.

- Shantha, K. L., Bala, U., & Rao, K. P. (1995). Tailor-made chitosans for drug delivery. *European Polymer Journal*, 31, 317–382.
- Sharma, D. K., & Singh, M. (2001). Effect of dyeing & finishing treatments on Sun protection of woven fabric – A study. *Colourage Annul*, 48, 69.
- Shin, Y., & Yoo, D. I. (1998). Use of chitosan to improve dyeability of DP-finished cotton (II). *Journal of Applied Polymer Science*, 67, 1515–1521.
- Trung, T. S., Ng, C. H., & Stevens, W. F. (2003). Characterization of decrystallized chitosan and its application in biosorption of textile dyes. *Biotechnology Letters*, 25, 1185–1190.
- Vogel, A. I. (1975). *Elementary Practical Inorganic Chemistry* (2nd ed.). London: Longman. Part 3, p. 652.
- Yipm, J., Chan, K., Sin, K. M., & Lau, K. S. (2002). Low temperature plasma-treated nylon fabrics. *Journal of Materials Processing Technology*, 123, 5–12.
- Yoo, D. I., Shin, Y., Kim, K., & Jang, J. I. (1997). Functional finishing of cotton fabrics by treatment with chitosan. In A. Domard, G. A. F. Roberts, & K. M. Vårum (Eds.). *Advances in Chitin Science* (Vol. II, pp. 763–770). Lyon, France: Jacques André Publisher.