Indian Journal of Fibre & Textile Research
Vol. 39, December 2014, pp. 418-424

Multifunctional finishes on cotton textiles using combination of chitosan and polycarboxylic acids

Athisayam Edwin Sunder[1,a], Govindan Nalankilli[2] & N K Palani Swamy[3]

[1]Department of Textile Processing, SSM Polytechnic College, Komarapalayam 638 183, India

[2]Sri Ram College of Engineering, Permalpattu 602 204, India

[3]Department of Textile Technology, KSR College of Technology, Tiruchengode 637 215, India

Received 6 November 2013; revised received and accepted 15 January 2014

100% cotton fabric has been treated with suitable combinations of chitosan and polycarboxylic acids (PCAs) to impart multiple functional properties. It is found that irrespective of the type of PCA added, samples treated with all combinations of chitosan and PCAs exhibit very good protection against *Escherichia coli* and *Staphylococcus aureus* bacterial strains. Zone of bacterial inhibition ranges from 21mm to 25mm and 24mm to 27mm for these strains respectively. Addition of PCAs to chitosan helps to improve other functional properties, like crease recovery behavior, soil release property and flame retardency in addition to the antimicrobial property. Samples treated with the mixture of chitosan and PCAs show good thermal resistance with Class I flammability. Maleic acid with chitosan shows higher values of flame propagation time as compared to that of other PCAs combination with chitosan. Soil release property is also improved from grade 3 for parent sample to grade 5 for all combinations of PCAs + chitosan treated samples. The crease recovery angle of samples treated with chitosan and PCAs combination has increased upto 261^0 compared to 215^0 for parent sample. Loss of tensile strength and tearing strength is found to be lower in chitosan and PCAs combination samples than in resin treated samples. From the results, it is evident that all the combinations of PCAs and chitosan can impart multiple functional properties on cotton materials.

Keywords: Antimicrobial property, Chitosan, Cotton, Crease recovery angle, Flammability, Finishing treatment, Polycarboxylic acids, Soil release property

1 Introduction

Cotton, the most abundantly available natural fibre, possesses many functional properties such as high moisture regain with good absorbency, adequate strength, comfort feel during wear and easy dyeability[1]. For these reasons, cotton is preferred mainly for apparel end uses. Cotton fabrics, however, have problems of more tendencies to wrinkle badly due to the rupture and reformation of hydrogen bonds during laundering process, poor smooth drying properties, low dimensional stability, higher flexural rigidity among all textile fibres[2] and easy soiling characteristics. Cotton requires a combination of two or more functional properties like crease recovery behavior with higher strength retention, soil release characteristics, antimicrobial property and thermal resistance for applications like apparel use, laboratory and kitchen aprons, and hygiene wears. To impart such multifunctional properties on cotton textiles, specific chemical finishing treatments are required. Conventional crosslinking process uses methylol precondensate resins which gives excellent wrinkle recovery properties and durable press finish but the drawbacks[3] are more. Resin crosslinking prevents the movement of the fibre molecules causing severe (upto 50%) tensile strength and tearing strength loss and reduction in flexibility in the treated fabric. Further, most of these resins release formaldehyde which besides being a suspected human carcinogen, causes severe irritation to mucous membranes, induced cough and difficulties in breathing. Polycarboxylic acids (PCAs) are nowadays considered as a successful alternative crosslinking agent for resins, which can impart polyfunctional finishes in terms of improved crease recovery behavior with better strength retention, good soil release characteristic, reduced flexural rigidity and good whiteness retention properties. Combination of PCAs and chitosan is expected to impart many functional finishes by optimizing the advantages of both chemicals.

Chitosan is found to be the new range of chemicals used in imparting antimicrobial property on cotton textiles. Chitosan[4,5] is a polycation. The cationised

[a]Corresponding author.
E-mail: aedwinsunder69@gmail.com

amino group ($-NH_3^+$), present in chitosan, binds with negatively charged residues of the cell surface of bacteria and such interaction causes extensive changes in the cell surface and cell permeability, leading to the leakage of intracellular substances and thus inhibiting the growth of bacteria. Chitosan acts like a biocide. The antimicrobial activity of chitosan is influenced by a number of factors that include the type of chitosan, the degree of deacetylation, molecular weight, *p*H and other physicochemical properties. Shin[6] investigated the effect of molecular weight of chitosan on antimicrobial activity. Chitosan of higher molecular weight are found to be effective in inhibiting the bacterial growth even at low concentration. A fibre reactive chitosan derivative, *O*-acryl amido methyl-*N*-[(2-hydroxy-3-trimethyl ammonium)propyl] chitosan chloride (NMA-HTCC) was applied to cotton fabrics[7] by a cold pad-batch method in the presence of an alkaline catalyst to evaluate its use as a durable antimicrobial textile finish. Cotton fabrics treated with 1% NMA-HTCC (on weight of fabric) showed 100% bacterial reduction. Carboxymethyl chitosan (CMCTS) was applied to cationised cotton[8] in different concentrations. In comparison with untreated cationised cotton, the antibacterial property and physical properties were improved by increasing the concentration of CMCTS.

Huang *et al.*[9] studied the effect of low-molecular-weight chitosan (LWCS) on anti-creasing property of cotton fabric. The LWCS was mixed with dimethylol dihydroxyl ethylene urea (DMDHEU) and applied on cotton fabric. It was inferred that LWCS has increased the tensile strength retention and creasing resistance of the DMDHEU finished fabrics. Khaled Tahlawy[10] used chitosan phosphate to produce an eco-friendly flame retardant cotton textile. It was found that phosphate derivatives reduce the heat emitted by increasing the CO/CO_2 ratio, which reduces the rate of propagation and the afterglow. In another study[11], it was shown that chitosan could increase the efficiency of sodium stannate/phosphate flame retardants on cotton.

Tahlawy *et al.*[12] treated cotton fabrics with chitosan and two crosslinking agents 1,2,3,4 butane tetra carboxylic acid (BTCA) and Arcofix NEC (low formaldehyde resin). Fabrics treated with BTCA and chitosan were found to possess better antibacterial activity than the fabrics treated with Arcofix NEC only. Montazer and Afjeh[13] worked on simultaneous crosslinking and antimicrobial finishing of cotton fabric using chitosan and *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTCC) with different crosslinking agents including citric acid (CA), BTCA and glutaraldehyde. This treatment improved the laundering durability of antimicrobial treatment. Chung *et al.*[14] used HTCC as an antimicrobial agent for cotton fabrics. Crosslinkers such as DMDHEU, BTCA and CA were used with HTCC to improve the laundering durability of HTCC treatment. The polycarboxylic acid treatment was superior to the DMDHEU treatment in terms of prolonged antimicrobial activity of the treated cotton even after successive 20 laundry cycles.

In research works carried out so far using PCAs, the main objective was to use them as alternate crosslinking agents to improve crease recovery behavior and to impart durable press finish properties. Few researchers have reported improvement in one or two of the other functional properties like strength retention, dimensional stability and whiteness retention properties as additional benefits obtained. Similarly, chitosan has been used in many studies mainly to investigate their antimicrobial characteristics in the textile substrates. Few studies[8,10,11] have reported its effect on other characteristics like mechanical properties and flammability of the substrates. In the studies carried out so far using the combination of PCAs and chitoson, PCAs have been used only for making stronger bonds between chitoson and cellulose by way of formation of covalent bonds. The main objective of these studies was to improve the durability of antimicrobial activity. No earlier works have given importance for comprehensive analysis of the finished samples for all the functional properties like antimicrobial property, flame retardant property, soil release characters, crease recovery behavior and strength retention property in a single study.

In this work, three PCAs, viz. maleic acid, itaconic acid and citric acid were used along with chitoson with objectives of imparting multiple functionalities such as soil release property, resistance to flammability, crease recovery behavior with good strength retention in addition to antimicrobial activity, on cotton fabric in order to make it suitable for the production of regular apparels, sanitary wears, kitchen and laboratory aprons, hand gloves, etc.. The crosslinking characteristics of PCAs and antimicrobial property of chitosan have been effectively utilized to achieve maximum functionalities in cotton. The present study

has been carried out in two parts. In the first part, 100% cotton fabric samples are treated with combination of chitosan & single PCAs to find out which PCA+chitosan combination is much effective in imparting multifunctional properties. In the second part, binary combination of PCAs is mixed with chitosan and applied on cotton fabric samples to study the effect of combination of PCAs in contributing these functional properties as the PCAs selected for the study exhibit synergism in combination. All treated samples are tested for the functional properties as per international standards.

2 Materials and Methods

2.1 Fabric

100% cotton woven bleached fabric with the constructional parameters such as warp count 40Ne, weft count 40Ne, 106 ends per inch, 96 picks per inch and areal density 101 g/m^2 was selected for the study. A sample size of 50 cm x 50 cm was used for each finishing.

2.2 Chemicals

Chitosan (CHT, 98% deacetylated), maleic acid (MA, two carboxylic acid groups), itaconic acid (IA, two carboxylic acid groups), citric acid (CA, three carboxylic acid groups), acetic acid for dissolving chitosan and sodium hypophosphite (catalyst for PCAs) were purchased in analytical reagent grade.

2.3 Samples

Based on the results of the previous studies[15,16], the concentration of chitosan was fixed as 1% for all combination finishing and the concentration of PCAs was fixed as 4% and 5%, with an optimum curing at 170^{0}C for 3min in this study. Cotton fabric samples were treated with different combinations of chitosan and PCAs (Tables 1 and 2). The samples were padded in padding liquor containing necessary quantities of PCAs, catalyst, chitosan and acetic acid, squeezed in LABTEX laboratory padder[15,16] with 100% expression (100% wet pick up) using a pressure of 3kg/cm^2. These samples were dried at 80^{o}C for

Table 1—CRA and strength properties of combination of chitosan and single PCAs treated samples

Sample	Total CRA (W+F), deg	Tensile strength				Tearing strength			
		Warp-way, lb	Loss %	Weft-way, lb	Loss %	Warp-way g	Loss %	Weft-way g	Loss %
Untreated	215	75	*	60	*	1120	*	989	*
Resin treated	265	45	40.0	39	35.0	768	31.5	656	33.7
CHT + IA-4%	250	64	14.7	51	15.0	958	14.5	872	11.9
CHT + IA-5%	253	66	12.0	50	16.7	960	14.3	860	13.1
CHT + MA-4%	254	63	16.0	50	16.7	962	14.1	856	13.5
CHT + MA-5%	258	64	14.7	49	18.4	959	14.4	860	13.1
CHT + CA-4%	248	65	13.4	53	11.7	960	14.3	880	11.1
CHT + CA-5%	249	65	13.4	53	11.7	963	13.9	865	12.6

*Reference value based on which strength loss % is calculated.

Table 2—CRA and strength properties of combination of chitosan and mixed PCAs treated samples

Samples	Total CRA (W+F) deg	Tensile strength				Tearing strength			
		Warp-way, lb	Loss %	Weft-way, lb	Loss %	Warp-way g	Loss %	Weft-way g	Loss %
Untreated	215	75	*	60	*	1120	*	989	*
Resin treated	265	45	40.0	39	35.0	768	31.5	656	33.7
CHT + IA-2%,MA-2%	259	63	16.0	52	13.4	973	13.1	856	13.5
CHT+ IA-2.5%,MA-2.5%	261	64	14.7	51	15.0	975	13.0	850	14.1
CHT + IA-2%,CA-2%	261	66	12.0	53	11.7	965	13.7	862	13.0
CHT + IA-2.5%,CA-2.5%	260	65	13.4	52	13.4	963	13.9	855	13.5
CHT + MA-2%,CA-2%	259	65	13.4	52	13.4	980	12.5	878	11.3
CHT + MA-2.5%CA-2.5%	261	66	12.0	51	14.5	980	12.5	860	13.1

*Reference value based on which strength loss % is calculated.

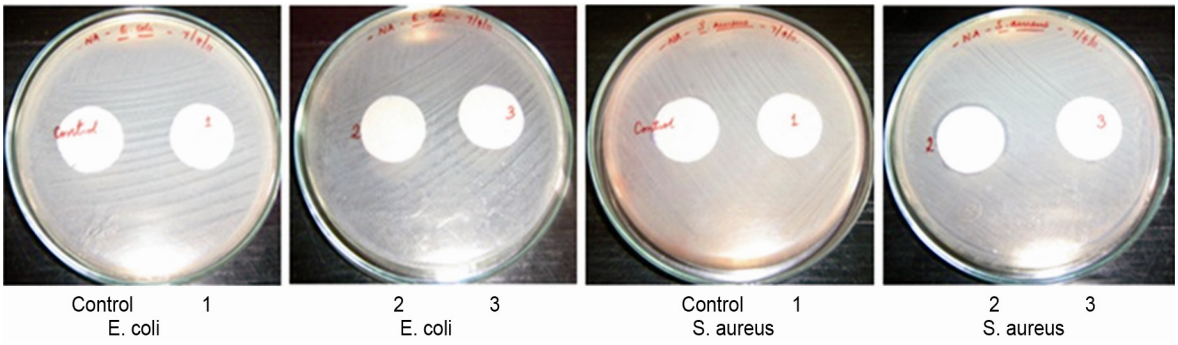


Fig. 1—Photographs showing antimicrobial test results for *E.coli* and *S.aureus*

10 min and curing was carried out at 170°C for 3min in RBE hot air curing oven. After curing, the samples were washed and dried.

To compare the chitosan and polycarboxylic acid combination finishing with standard finishes, DMDHEU based crease resistant finish and THPC based flame retardant finish were prepared as follows. For crease resistant finish, cotton fabric was padded in a solution containing 100 g/l DMDHEU resin, 20 g/L $MgCl_2.6\ H_2O$, 25 g/L polyethylene emulsion, 30 g/L acrylic emulsion and 3 g/L non-ionic wetting agent. Padded fabric was squeezed for 100% expression at 3 kg/cm^2 pressure, dried at 80°C for 10 min followed by curing at 160°C for 5 min, washed and dried.

For flame resistant finish, cotton fabric was padded in a solution containing 16.0% THPC, 9.5 % methylol melamine, 3.0% triethanol amine and 9.0% urea. Padded fabric was squeezed for 100% expression at 3 kg/cm^2, dried at 80°C for 10 min followed by curing at 140°C for 5 min, washed and then dried.

2.4 Testing Methods

All the samples were conditioned for 8 h at 65%±2% RH and 20°±2°C in a conditioning chamber. Functional properties, viz. antimicrobial activity (AATCC 147), flammability (45° Flame test ASTM D 1230- 94) , soil release properties (AATCC 130 :2000), crease recovery angle (AATCC 66-2008), tensile strength (ASTMD 5035–06–2008) and tearing strength (ASTMD 1424–09) of finished and unfinished cotton samples were evaluated.

3 Results and Discussion

3.1 Antimicrobial Activity

Antibacterial activity in terms of zone of inhibition (mm) for all samples treated with chitosan and PCAs was evaluated as per AATCC 147, parallel streak method. *Escherichia coli* ATCC 11229 (*E. coli*) and *Staphylococcus aureus* ATCC 6538(*S. aureus*) were

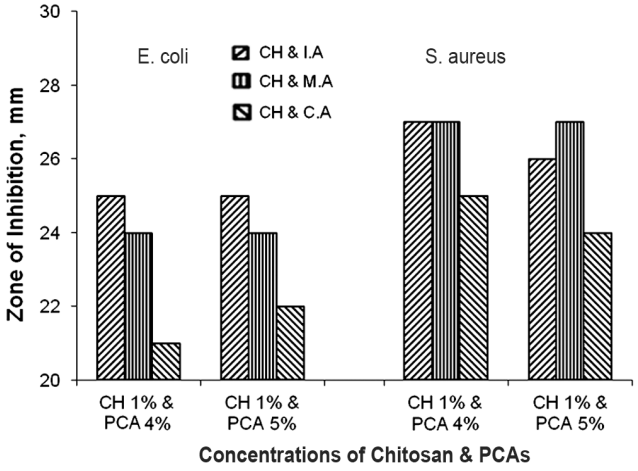


Fig. 2—Zone of inhibition for *Escherichia coli* and *Staphylococcus aureus*

the bacterial strains used. The zone of inhibition is "0 mm" for parent sample against both the strains.

Chitosan with PCAs combination finishing imparts good antibacterial property on cotton fabric. Zone of inhibition for samples treated with chitosan and PCAs is found to be 21 - 25mm for *E.coli* and 24 - 27mm for *S. aureus* (Figs 1 & 2). The improvement in antibacterial property may be due to the presence of cationised amino groups ($-NH_3^+$) in the chitosan and not influenced by the PCAs present. This is evident from the observation that there is no significant difference between the inhibition values of 100% chitosan treated samples[15] and the chitosan based combination samples. Nevertheless, among the three PCAs combinations, the inhibition values for itaconic acid + chitosan and maleic acid + chitosan are found to be slightly better than the citric acid + chitosan, which may be due to the better crosslinking exhibited by itaconic acid and maleic acid[16] that helps in more bonding of chitosan with the cellulose. The zone of inhibition is higher for Gram positive bacterium

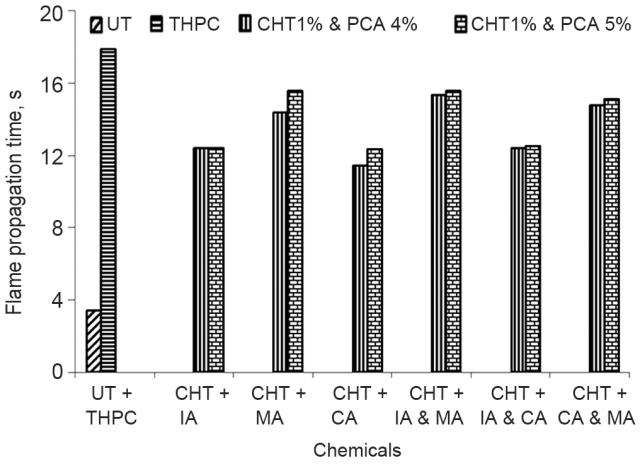
S.aureus than that for gram negative bacterium *E.coli*, which is well in agreement with findings of Rajendran *et al*.[17].

The mechanism of antimicrobial activity[4,5] exhibited by chitosan can be explained in the following manner. Chitosan is a polycation. The amine groups present in chitosan are bound with negatively charged residues of the cell surface of bacteria and such interaction causes extensive changes in the cell surface and cell permeability, leading to leakage of intracellular substances, which inhibits the growth of bacteria. Thus, chitosan acts like a biocide.

3.2 Flammability

Samples were tested for flammability using test method ASTM D1230-94. Based on the flame propagation time and degree of flammability, samples can be categorised into three classes by the Consumer Product Safety Commission of USA, viz. Class I-normal flammability (>7 s), these textiles are considered by the trade to be generally acceptable for apparel, Class II - intermediate flammability (4 s–7 s), these textiles are considered by the trade to have flammability characteristics for apparel intermediate between Class I and Class III fabrics and Class III-rapid flammability (<3.5 s), these textiles are considered by the trade to be unsuitable for apparel [18,19].

It is observed that degree of flammability follows Class III for parent sample with a flame propagation time of 3.4s and Class I for the THPC treated control sample with flame propagation time of 17.89 s. Chitosan and PCAs treatment reduces the degree of flammability from Class III to Class I which is due to the nitrogen source of chitosan[3]. Maleic acid and chitosan treated samples produce a maximum protection with a flame propagation time of 16.54s, which is almost close to control sample. Maleic acid/sodium hypophosphite system[20] has been found to possess good flame resistant characteristics by retaining more phosphorous in cellulose. Therefore, in combination with chitosan, nitrogen present in the chitosan when combined with phosphorous, has synergic effect[3] in improving thermal resistance of the maleic acid and chitosan treated samples (Fig. 3). Interestingly, maleic acid both in single PCA and mixed PCAs combination with chitosan was found to exhibit better flame resistance than other PCAs combinations. A similar trend of improved flame resistance for maleic acid treated samples was reported in the literature[18,19].



Fig, 3—Effect of concentration of chitosan and PCAs on Thermal Resistance

3.3 Crease Recovery

Crease recovery behavior has been measured in terms of total crease recovery angle (CRA), which is the sum of crease recovery angle measured in warp way and weft way. CRA is only 215° for untreated fabric and for all chitosan and PCAs treated fabrics the values range from 248° to 261° which is comparable to that of resin treated control sample. Increase in CRA is mainly due to the crosslinking of cellulosic chains. PCAs form ester cross - links with cellulose through esterification reaction and therefore are able to mask –OH groups of cellulose polymer and impart crease recovery behavior[21]. As 100 % chitosan treated samples show only a marginal increase in CRA values[15] in the range of 225° - 230°, it is inferred that chitosan cannot improve the crease recovery property of cotton fabric significantly, but addition of PCAs helps to improve this behavior through molecular crosslinking and makes the fabric more functional[16].

The crease recovery angle of the treated samples increases with the increase in concentration of PCAs and accordingly 5% concentration of PCA along with chitosan show greater values of CRA than the values of samples with 4% PCA conc. (Table 1). Similar trend is observed in samples treated with combinations of mixed PCAs and chitosan and almost all samples show good CRA of around 260^0 (Table 2). This observation is in accordance with the earlier findings that better crosslinking leads to better CRA[21].

When mixed PCAs are combined with chitosan, difference in CRA values among different combinations is very meager. Combinations of CA with other PCAs has shown better CRA values than when applied

alone. Though citric acid, when applied in single, is found to have difficulties in crosslinking due to its hydroxyl group, CA exhibits synergic effect[22] in crosslinking cellulose when combined with other PCAs. Combinations of CA with other PCAs increase the functionality of PCAs in terms of increased number of carboxylic acid groups.

3.4 Strength

Since there is no crosslinking between chitosan and cellulose, loss in strength of cotton fabric is low[15] because of chitosan treatment. When combined with PCAs, significant strength loss from 11% to 18% is observed in samples treated with different combinations of chitosan and PCAs. The reason may be due to the formation of inter-molecular and intra-molecular crosslinks by PCAs which reduce the possibility of equalizing the stress distribution among all molecules, causing reduction in the capacity to withstand load[23]. In comparison with the strength loss of resin crosslinked fabric, the PCAs finished samples have shown good strength retention properties. This is due to the fact that PCAs crosslinking is softer than resin treated one and allows more stress to be borne[22]. Chitosan and 5% maleic acid show maximum strength loss and chitosan + citric acid combination shows minimum strength loss both in tensile and tearing strength properties (Table 1).

Though maleic acid has only two carboxyl groups, its structure is linear and when polymerized can form stronger crosslinks. Further it can copolymerize easily with other PCAs enhancing its crosslinking capacity by increasing the number of carboxyl groups[23]. Maleic acid samples show higher strength loss in all combinations. However, the strength loss values are still lower than DMDHEU resin treated fabrics and further its performance in terms of functional properties like improved CRA, soil release characteristics, low flammability values is better than other samples and therefore reduction in strength retention could be tolerated.

3.5 Soil Release

Soil release of grade 3 is obtained for untreated fabric, it has increased to maximum grade of 5 for samples treated with combinations of PCAs and chitosan. Surface property alteration of cellulose towards hydrophilic / hydrophobic nature affects the soiling characteristics of the fabrics[24]. All chitosan and PCAs treated samples have shown the same level of soil release property, irrespective of the type of PCAs added. The uncrosslinked carboxyl groups[25] (hydrophilic polar groups) present in the PCAs and the amine group present in chitoan[2] are the reasons for increasing hydrophilic nature as well as soil release characteristic of the treated samples. Since the soil release grade of all treated fabric samples has increased from grade 3 to grade 5, and so all finished fabrics acquire very good soil release nature to make it more of easy care nature.

4 Conclusion

100% cotton fabric has been finished with combinations of chitosan and polycarboxylic acids (PCAs) to impart multiple functional properties. All combinations of chitosan and PCAs finished samples show great level of inhibition against both bacterial strains, viz. *E. coli and S. aureaus* with a zone of inhibition ranging from 21 mm to 25 mm and from 24 mm to 27 mm respectively. The values are not much influenced by the type of PCA added. In all chitosan and PCAs combinations finishing, the flammability rating is Class I and flame propagation time of maleic acid combination with chitosan is found to be better than that of other PCAs combinations with chitosan.

When PCAs are combined with chitosan, crease recovery properties of the fabric are also improved in addition to the antimicrobial property. CRA for samples treated with combination of PCAs and chitosan is almost comparable to that of resin treated control samples, while the strength loss is only about 10%-15%. Binary combinations comprising CA with other PCAs and chitosan treated samples show a maximum CRA of 261^0 because of the synergic effect exhibited by CA with other PCAs. Soil release characteristics of all finished samples are rated as grade 5 against grade 3 for untreated fabrics. Addition of PCAs with chitosan has helped to improve the hydrophilic nature of cellulose, resulting in improved soil release property. Among the finishing combinations, 1% chitosan + 5% maleic acid and 5% of maleic acid + itaconic acid (total concentration is 5%) + 1% chitosan finishing combinations are found the optimum combinations for achieving the multifunctional properties in an efficient manner on cotton textiles.

References

1 John Shore, *Cellulosics Dyeing* (Society of Dyers and Colourists, Bradford), 1995, 48, 367 & 368.

2 Morton W E & Hearle J W S, *Physical Properties Textile Fibres* (The Textile Institute, Manchester), 1997, 406.

3 Schindler W D & Hauser P J, *Chemical Finishing of Textiles* (Woodhead Publishing Limited, Cambridge), 2004, 105.

4 Yuan Gao & Robin Cranston, *Text Res J,* 78(2008) 60.
5 Anjali Karolia & Snehal Mendopara, *Indian J Fibre Text Res,* 32(2007) 99.
6 Shin Y, Yoo D I & Jang J, *J Appl Polym Sci,* 80(2001) 2495.
7 Sang-Hoon Lim & Samuel Hudson M, *Carbohydr Polym,* 56(2004) 227.
8 Amira El-Shafei M Fouda M G & Knittel D, *J Appl Polym Sci,* 110(2008) 1289.
9 Kuo-Shien Huang Wei-Jang Wu Jeong-Bor Chen & Huey-Shan Lian, *Carbohydr Polym,* 73(2008) 254.
10 Khaled Tahlawy E L, *J Text Inst,* 99(2008) 185.
11 Khaled Tahlawy E L, Roshdi Eil & Samuel Hudson, *J Text Inst,* 99(2008) 157.
12 Khaled Tahlawy E L, Magda A, Bendary E l, Adel Elhendawy G & Samuel Hudson *Carbohydr Polym*, 60(2005) 421.
13 Majid Montazer & Gorbanali Afjeh M, *J Appl Polym Sci*, 103(2007) 178.
14 Yong-Sik Chung, Kwang-Keun Lee & Jin-Woo Kim, *Text Res J*, 68(1998) 772.
15 Edwin Sunder A & Nalankilli G, *Asian Dyer* (in press) 2014.
16 Edwin Sunder A & Nalankilli G, *Indian J Fibre Text Res*, 37(2012) 364.
17 Rajendran R, Radhai R, Balakumar C, Hasabo A, Mohammad Ahamed, Vigneswaran C & Vaideki K, *J Eng Fibre Fabrics,* 7(2012) 136.
18 Xinying Cheng & Charles Q Yang, *Fire Materials*, 33(2009) 365.
19 Xialing Wu & Charles Q Yang, *J Fire Sci,* 27(2009) 431.
20 Xialing Wu & Charles Q Yang, *AATCC Rev*, 7(2007) 35.
21 Xiaoqun Qiu & Charles Q Yang, *AATCC Rev*, 5(2005) 34.
22 Charles Q Yang, Lan Xu Shiqi Li & Yanqiu Jiang, *Text Res J*, 68(1998) 457.
23 Weilin Xu & Yi Li, *Text Res J*, 70(2000) 588.
24 Mamiko Yatagai & Yui Takahashi, *AATCC Rev,* 6(2006) 44.
25 Olivera Sauperl, Kleinchek K S & Volker Ribitsch, *Text Res J,* 79(2009) 780.