Indian Journal of Fibre & Textile Research
Vol. 45, December 2020, pp. 475-481

Development of non-formaldehyde wrinkle resistant finish for cotton using carboxylic acids

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Received 30 March 2020; revised received and accepted 16 June 2020

A study has been conducted to develop a wrinke resistant cotton fabric using three carboxylic acids combination along with initiator and catalyst, at various *p*H and concentration, and to determine the effects of treatment on wrinkle recovery angle, wrinkle recovery appearance rating, and carboxyl group content of the treated fabrics. The amount of carboxylic acids on the fabric is determined by % weight gain of treated samples, carboxyl 'n' group content, wrinkle recovery angle and wrinkle recovery appearance rating. Furthermore, FTIR spectroscopic analysis has been conducted to study the attachment of acid groups for reducing the available free OH groups on the cotton cellulosic chains. The results show significant wrinkle resistance of treated samples. In order to evaluate the wash durability of the finish applied, the treated sample is laundered for 20 cycles and it is found that the wrinkle recovery property significantly persist even after washing.

Keywords: Carboxyl group content, Cotton fabrics, Wrinkle recovery angle, Wrinkle resistant finish

1 Introduction

Cotton is one of the most popular natural fibres due to its economic significance, apparently contributing to over 50% of apparel and textile products[1, 2]. Though cotton enjoys great popularity, there is stiff competition of cotton with other natural and man-made fibres, urging scientists to further enhance the performance of cotton fibres through research and innovations[2, 3]. Cotton is primarily composed of 90-95% cellulosic chains, which contain a collection of porous amorphous regions and tightly packed crystalline regions held in place by hydrogen bonds[4, 5]. Cotton readily absorbs moisture in the form of atmospheric moisture or perspiration, which acts as a lubricant and facilitates interpolymer chain movement[6]. Upon application of external forces, slippage and breakage of weak hydrogen bonds take place between these cellular chains in the amorphous region, which causes wrinkles in cotton textiles[7].

To improve properties of this natural cellulosic fibre, sometimes, a crosslinking agent or monomer is grafted onto the fibres to enhance the existing polymer chains[8]. This minimizes drawbacks of cotton such as wrinkling. Several technologies have been used to enhance the wrinkle recovery of cotton fabric, of which modified dimethylol dihydroxy ethylene urea (DMDHEU) has been the most traditional and prevalent finish due to its cost-effectiveness[9]. A cross-linking agent forms stronger covalent bonds which tend to bend rather than rupture upon stretching, thus giving the polymers more freedom to stretch and minimize wrinkling of the fabric[7]. A cross-linking agent can even react chemically with the hydroxyl groups of the cellulosic chain and thus reduce some number of hydroxyl groups, which modifies the chemical structure of the cellulosic polymer chain[10, 11, 12]. As some hydroxyl groups are reduced or masked, their moisture absorption tendency is also checked, and hence wrinkling is minimized[10, 11, 12].

Since 1900s, urea-based resins have been used in the chemical finish for cellulosic textiles, which release formaldehyde[13, 14]. Formaldehyde has been identified as a possible carcinogen and a strong allergen, resulting in rigorous efforts by researchers to find out formaldehyde-free cross-linking agents for cotton and other cellulosic textiles to replace the traditional N-methylol reagents[13,14]. Although several studies using polycarboxylic acids, such as butane tetra carboxylic acid (BTCA) and citric acid (CA), have been conducted in the past, but they did not turn out to be cost effective.

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Recently, cotton Incorporated have come up with a formaldehyde-free technology (PUREPRESS^{TM}) but the formulation of technique is unknown. There is not, yet, an optimum recipe, which has been commercialized, using a combination of mono- and dicarboxylic acid for a wrinkle recovery finish on cotton fabrics. Studies indicate that the recipes formulated using carboxylic acids, although producing good wrinkle recovery, fail to be cost-effective or durable in terms of strength and laundering[15 - 17]. Thus, the method needs to be optimized using processes and testing. Studies also provide evidence that prevalence of quantitative methodology to measure carboxyl group content on polycarboxylic treated cellulosic fabric, other than using FTIR, has not been sufficiently investigated[18 - 20]. The present study formulated and tested a recipe with a combination of mono and di-carboxylic acids to determine whether an improved material performance in cotton can be achieved. The finish treatment on the cotton fabric is quantitatively measured using titration method and qualitatively measured using FTIR spectroscopy. This study also investigates the durability of the finish for upto 20 laundry cycles.

2 Materials and Methods

Cotton fabric was procured online from Dharma Trading Co., California. A two-inch margin was left from the selvage of the fabric before randomly cutting the fabric with scissors and extracting the fabric specimens to be treated with the finish or used as a control. Six yards of mill bleached, plain weave 100% cotton fabric of 62 ends per inch and 52 picks per inch, 33.64 Ne for warp, 29.20 Ne for weft, and an average area density of 3.28 oz./yard^2 was used.

2.1 Fabric Treatment

The wrinkle-free finish (acid combinations) was applied at two different concentrations (6% and 8%), and three different *p*H levels (4, 5 and 6). Several tests were performed to check for esterification and cross-linking on the treated fabrics, using percentage weight gain values and iodometric titration to determine the carboxyl 'n'(where n is an integer) group content or COOH values, and subjective analysis using Fourier transform infrared (FTIR) spectroscopy. Performance of the treated samples was evaluated using wrinkle recovery appearance rating, and the wrinkle recovery angle (WRA) test procedure in comparison with an untreated cotton sample. Six specimens of treated cotton samples, that provided the best results at specific concentration and *p*H, were then subjected to 20 laundry cycles for studying wash durability. The WRA data, obtained after 20 laundry cycles, of the washed samples and the FTIR were then compared with the untreated sample' performance.

After the cotton fabric was scoured and line dried, it was then cut into 7 (6 for treatment and one control) pieces of approximately 23"×7". These were randomly picked for the finish with 6 recipes, while one sample served as the control group. Once all the cotton samples were treated with the various finish formulations, the templates for the wrinkle recovery angle (WRA) test, COOH value/carboxyl group content test, FTIR, and wrinkle recovery appearance tests were marked randomly on the warp (length wise) or the weft (cross wise) grain of the fabric, and cut as per the requirements of the standard test procedures. Before initiating the treatment, cut out fabric samples were conditioned at 65% relative humidity (RH), 21 $^{\circ}$C temperature for at least 4 h treatment time. The samples were then weighed to establish initial weights. Separate formulation was prepared for each of the six specimens.

The treated samples were also analyzed for % weight gain by weighing the sample before and after the treatment for dry add-on. The treated samples were subjectively analyzed for carboxyl and carbonyl peaks using an FTIR spectrometer. A Perkin Elmer FTIR Spectrometer Frontier (Universal ATR Sampling Accessory, LR64912C) was used where the wavelength range selected was between 3,500 and 900 cm^{-1}. Furthermore, FTIR analysis was conducted on the treated sample after twenty-laundry cycle to check the wash durability of the finish after 20 cycles.

The combination of three acids, viz maleic anhydride (MA 35%), itaconic acid (IA 35%), and methacrylic acid (MAA 30%), were used along with the 5% catalyst (sodium dihydrogen phosphate), and 5% initiator (potassium persulfate).

2.2 Preparation and Application of Finish Formulation

Carboxylic acids, initiator and catalyst, procured from Sigma Aldrich, were used without further purification. The three acid combinations were used for the preparation of finish in the presence of a catalyst (sodium phosphate monobasic) and an initiator (potassium persulfate) at two different concentrations (6% and 8%) and three different *p*H (4, 5, 6) levels. The initiator generated the free radical

for the polymerization of acid monomer with the cellulosic components of textiles. The ratio of fabric weight to formulation volume was kept 1:25. The concentrations of catalyst and initiator were kept constant at 5% for all recipes. The synthesis was carried out step by step. The chemicals and deionized water were stirred at 250 rpm till a clear solution was obtained. The first step was to soak the sample in the solution prepared using deionized (DI) water and half concentration of the initiator (2.5% i.e. 2.5 g in 100 mL DI water) and Triton-X^{TM} (0. 015%) in the bath for 20 min at 35 ^{0}C. In the next step, a separate solution was prepared which used the remaining half of the initiator (2.5%), including 5% catalyst, and either 6% or 8% of acid concentration along with 0.015% surfactant to create the finish formulation. After steeping in the initiator (step1) bath for 20 min, the samples were immediately transferred to the second solution bath where they were steeped for 30 min at 44 ^{0}C in the finish formulation.

The sample steeped in the second step was then passed through a padding machine (LAB-PRP GmbH; CH-4806 Wikon) using 5-nip-dip to produce 100% wet pickup. The pressure of the padding machine was adjusted to 0.1 Mpa, which enabled a wet pickup between 100% and 125%. The padded specimens were then subjected to drying in an oven at 95 ^{0}C for 5 min followed by curing at 140 ^{0}C for 5 min. The cured samples were cooled under ambient conditions and then rinsed with 2% sodium carbonate followed by a thorough wash with Tide Free & Gentle^{TM} laundry detergent until the *p*H of the residual water was neutral. The samples were then line-dried overnight at ambient conditions and dried percentage add-on for treated samples was calculated.

2.3 Testing of Treated and Untreated Samples

Wrinkle recovery angle was measured using the AATCC 66-1990 test method, which works on the principle that crease is imparted to a textile fabric of dimensions 15 × 40 mm, upon application of a predetermined load of 500 g for 5 min. Samples were then inserted into an apparatus attached to a rotating disc and protractor. The value of the angle was recorded from the protractor. The appearance of the wrinkled specimen was measured using AATCC 128-1999 test method. For this test, samples were cut out in the dimension of 27.94 cm × 28 cm and wrapped around the top and bottom flange of the AATCC Wrinkle Tester, and then the predetermined load of 3500g was placed for 20 min to impart wrinkles. The specimen were hung by clips on a cloth hanger for 24 h and then evaluated against standard replicas that ranged from a rating of 1-5 representing poorest to smoothest appearance.

Carboxyl 'n' group content analysis was performed using an Iodometric titration method (IS: 1560 part I-1974) to check the amount of COO^- functional group content ('COOH value') in the text. The procedure has been substantiated to estimate carboxylic acid groups in cellulosic textile materials. After being made cation free, treated and untreated cellulose textile materials are steeped and suspended in potassium iodide, potassium iodate, and sodium chloride solution. To this solution, which has a pre-weighed textile material of 0.5 g, sodium thiosulfate is added to capture the iodine from vaporizing and hence disappearing. Thiosulfate solution also facilitates the completion of the reaction by reacting with any liberated iodine. The excess thiosulfate is then titrated with a standardized iodine solution. The amount of iodine solution used to titrate the thiosulfate solution with the cellulose material (treated or untreated) was used to calculate the carboxylic content per hundred grams of sample. A blank titration without specimen is also observed to help in the calculations.

3 Results and Discussion

3.1 Effects of Finish Application on Fabric Weight Gain

Acid concentration and *p*H level influence the weight gain of the treated fabric samples as seen in Table 1. It is further observed that with the increase in *p*H level from 4 to 6, the dry add-on decreases, indicating an inverse relationship between weight gain and *p*H.

3.2 Effect of Finish Treatment on the COOH Values

As the *p*H level of the finish decreases, carboxyl '*n*' (*n* is an integer) group content value/COOH values increase in the treated samples, which also result in fabric weight gain (dry add-on), as seen in Table 1. The mean COOH values for all treated cotton samples is found to be 62.24 milliequivalents per 100 grams (mL. eq. /100g), and the mean COOH values for untreated cotton samples is 2.11 mL. eq. /100g of sample. Data for both 6% and 8% concentrations exhibit a significantly large change in the COOH values of the treated cotton samples arising from the esterification between the cellulose chains in the cotton and the carboxylic acid groups. This causes an increase in weight of the treated cotton specimens.

This phenomenon supports the attachment of the wrinkle recovery finish on the fabric.

The schematic diagrams of the chemical reaction taking place between the cotton cellulose and the various acids due to esterification reaction, chain polymerization, and cross-linking are illustrated in Figs 1 and 2. The weight gain of treated specimen, (Table 1) further supports the attachment of carboxyl groups on the fabric. The acid combination of (IA, MA, and MAA) causes the addition of higher levels

Table 1 — Properties of untreated and treated samples at different acid concentrations and *p*H

Acid concentration %	*p*H	Mean COOH value mL. eq. /100g	% weight gain	WRA in deg		WRA after 20 washes deg		Appearance rating
				Warp	Weft	Warp	Weft	
Untreated	-	2.11	-	78.67	84.83	-	-	1
6	4	76.02	8.80	117.17	128.17	-	-	4
6	5	59.45	6.40	109.50	127.33	-	-	4
6	6	47.87	5.70	97.00	109.67	-	-	3.5
8	4	83.11	10.0	127.83	149.83	102.83	101.17	4
8	5	64.63	6.62	122.33	120.50	94.67	94.50	4
8	6	42.37	5.0	97.50	102.33	80.00	80.67	3.5

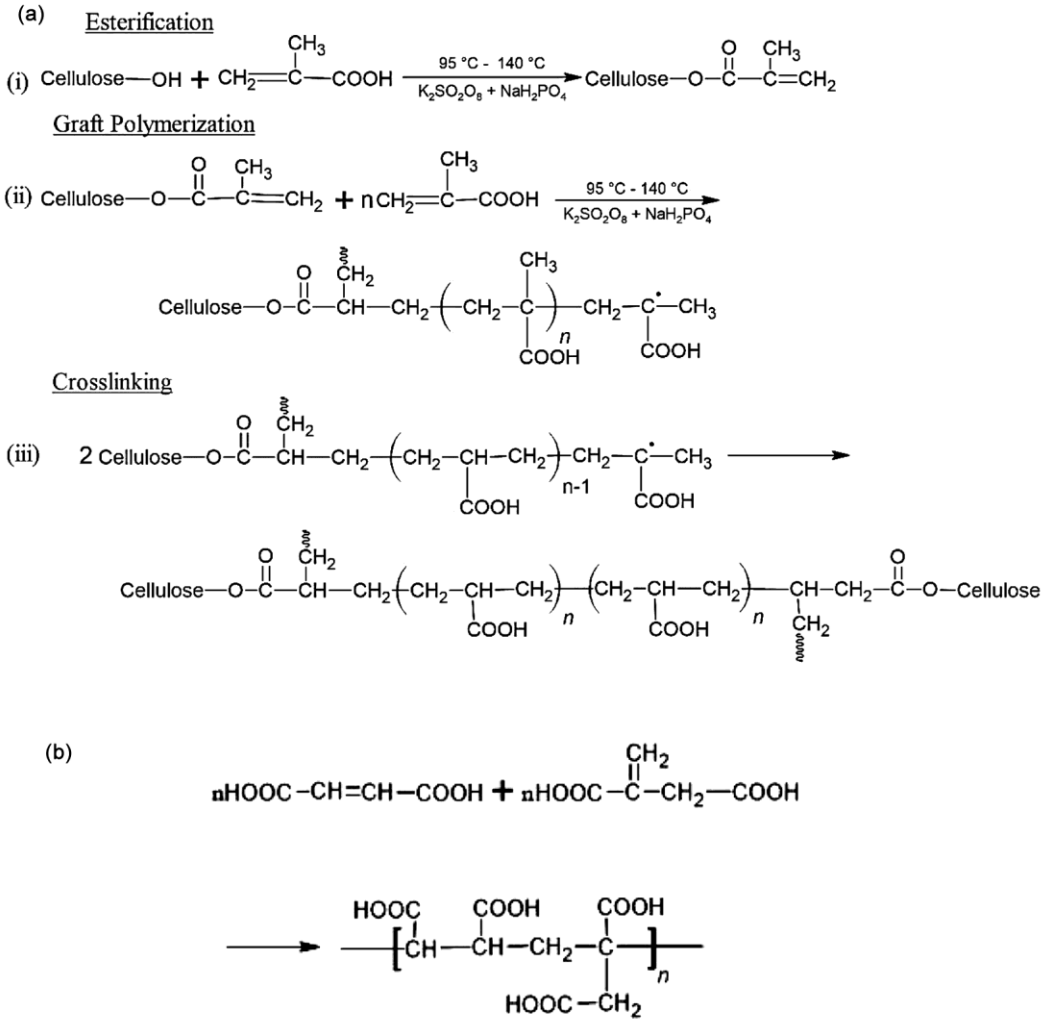

Fig. 1 — (a) Free radical polymerization and chemical reaction between cellulose and methacrylic acid[27]; and (b) comonomer of maleic acid and itaconic acid [19]

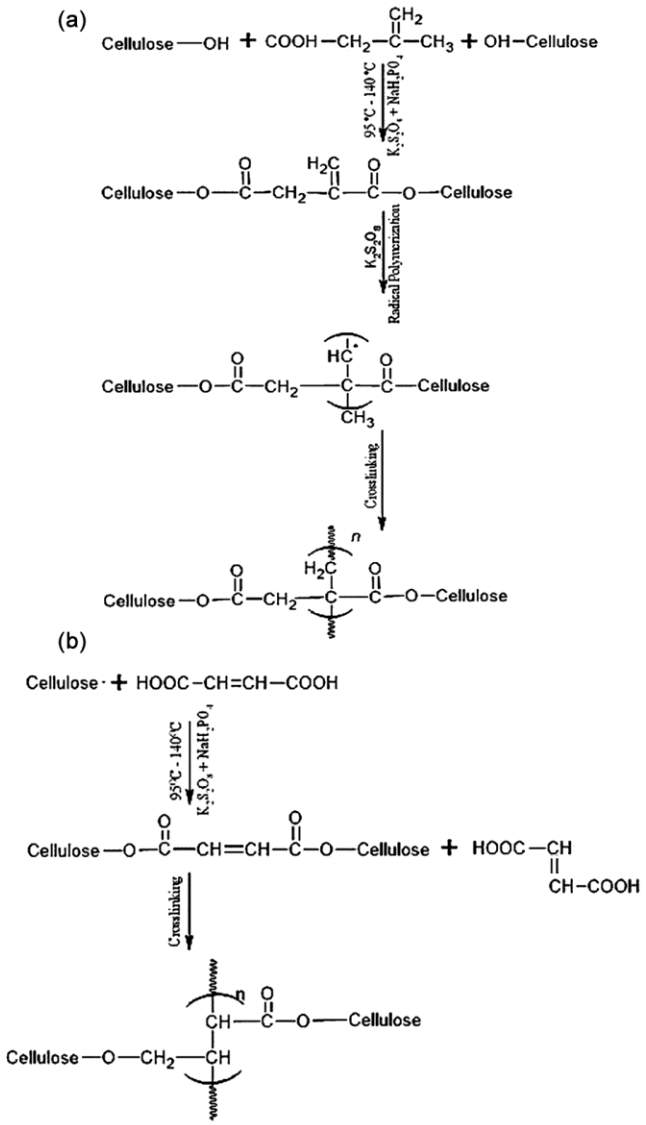

Fig. 2 — (a) Chemical reaction between cellulose and itaconic acid; and (b) chemical reaction between cellulose and maleic anhydride

of carboxyl groups in the fabric owing to more availability of carboxyl groups through the chosen acid combinations.

Finish formulation with *p*H 4 has a higher number of COOH groups available to react with the OH groups of cotton cellulose. Thus, the data obtained upon quantitative testing of the treated specimen using titration confirm that a chemical reaction, as described in Figs 1 and 2, occur between the cotton cellulose and carboxyl groups, providing more attachment of the finish to the fabric at low *p*H. The blocking of the free hydroxyl groups, on the cellulose chain, occurs due to the esterification reaction with the carboxyl group in the finish that elevates the wrinkle resistance tendency of the fabric.

3.3 FTIR Analysis of Treated and Untreated Cotton

The FTIR spectrum are illustrated in Fig. 3 both for the untreated and treated sample with acid combinations at 8% concentration and 4 *p*H. The FTIR spectrum of untreated cotton shows a prominent band at 1643 cm^{-1} attributed to O-H bending in the presence of adsorbed moisture[21, 23]. The same peak at 1643 cm^{-1} with reduced intensity becomes wider and transformed into three distinct peaks in the treated sample. The band at 1715 cm^{-1} indicates an aromatic C=O stretching originating from (ester/acid) carbonyl group[6, 23]; and band at 1640 cm^{-1} associates with C=C stretching[24, 22]. The third band at 1578 cm^{-1} indicates the asymmetric stretching mode of carboxylate carbonyl[25, 26]. It is also observed that the intensity of the peak at 3340 cm^{-1} is arising from OH stretching in both treated and untreated samples[3]. The reduction in the hydroxyl band intensity in the treated sample may be due to the reaction between the hydroxyl and the acid group's esterification process, indicating an

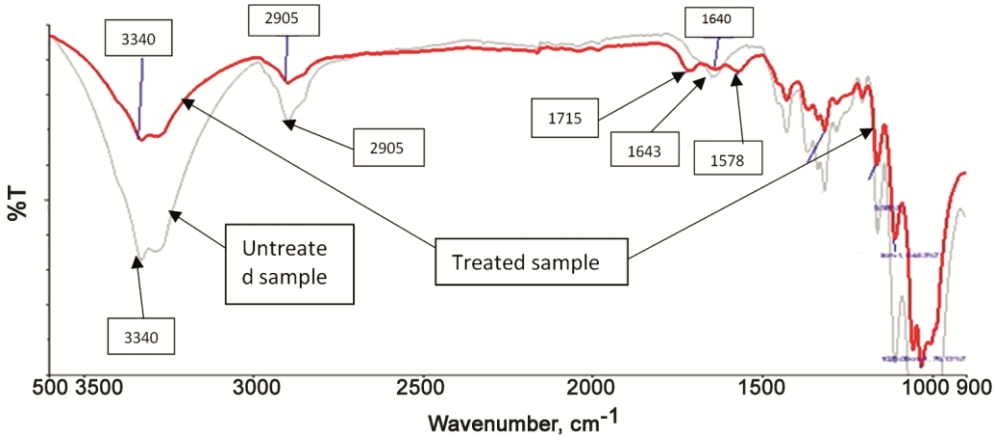

Fig. 3 — FTIR spectra of treated and untreated cotton fabrics wave length, cm^{-1}

expected change in the spectra of the treated fabric sample. It is further observed from the spectra (Fig. 3) that the intensity of the peak at 2905 cm^{-1}, attributed to C-H stretch[8], in both treated and untreated samples, show a reduction in intensity for the same in the treated sample. A reduction in the intensity of the bands between 1400 cm^{-1} and 900 cm^{-1} is also observed due to the expected change in the cellulosic structure of cotton upon application of the treatment.

These changes in the spectra with increase in carboxyl band intensity while reduction in the hydroxyl band intensity is due to the esterification reaction of the cotton cellulose with the applied acid solution, which provide the wrinkle free properties to the fabric.

3.4 Effect on WRA Values of Cotton Fabric for Warp and Weft Directions

Wrinkle recovery angle is a measure of wrinkle resistance performance of the treated sample. A large increase in the mean WRA values in both warp and weft directions of cotton sample occurs because of the finish application, as shown in Table 1, for cotton untreated (CU) and treated at various concentrations and *p*H. This increase in WRA mean values for samples treated at different concentrations and *p*H is ranging from 97^0 to 127.83^0 for the warp direction, as compared to 78^0 mean WRA values for untreated samples. Similarly, in the weft direction the mean values of treated sample range from 109.67^0 to 149.83^0, which is significantly higher than that of untreated samples.

It has been reported in prior studies[27 - 29] that cotton textile fabric, when treated with carboxylic acid or a combination of carboxylic acids in the presence of an initiator and a catalyst, undergoes an esterification and graft polymerization reaction, followed by cross-linking upon curing of the treated sample.

The first indication of the component attachment on treatment is the % weight gain of the treated fabric samples (~4-10%), which is more than the weight of the untreated sample. Any higher level may lead to an interference with the fabric properties, related to hand, stiffness, and strength. It is also observed that the samples with higher COOH values show high WRA values and wrinkle recovery appearance rating.

3.5 Effect on Wrinkle Recovery Appearance Rating

The overall treated cotton samples wrinkle recovery appearance rating is found to be 3.75, whereas untreated samples show a rating of 1, which is a significant difference (Table 1). Higher ratings strongly indicate that wrinkle recovery resistance property has been induced to the treated cotton fabric samples.

3.6 Effect on WRA after 20 Laundry Cycles

All three cotton samples that are treated with the same acid combination and same concentration (8%) but at different *p*H levels (4, 5 and 6) show higher WRA value in warp directions as compared to WRA values before finish treatment.

Samples treated at *p*H 4 and *p*H 5 maintain a significant amount of WRA angle even after 20 washing cycles (Table 1), which imply that better esterification reaction takes place between the cotton cellulose and the finish formulation at *p*H 4 and *p*H 5 due to more attachment of COOH groups. There is, however, a significant loss in the finish applied to the sample treated at *p*H 6.

A similar trend for WRA is observed in the weft direction also, where the WRA of cotton samples treated at *p*H 4 and *p*H 5 supports the fact that there is still a significant amount of finish retained by samples to provide higher WRA values after 20 washes as compared to that of untreated fabric sample, as indicated in Table 1.

The loss in the finish during laundry may be due to the fact that some carboxyl groups do not react to form esters; rather, they form oxycellulose, where the primary or secondary hydroxyl groups of the cellulose are converted to carboxyl groups. Further, the loss of finish also implies that the new bonds that are formed upon treatment with the finish, break under the laundry conditions, owing to the spinning action of the laundry machine, water pressure and use of alkaline detergent, resulting in a reverse chemical reaction.

4 Conclusion

Cotton fabric has been treated with IA, MA, and MAA along with indicator and catalyst to impart wrinkle resistant properties. Chemical reaction takes place between the carboxylic acids and the hydroxyl groups of the cellulosic chains resulting in the alteration of the chemical structure of the cellulosic chain. The treatment time of 40 min is found sufficient for 100% take-up. Concentration of 8% and *p*H 4 are found to be the optimum values for the process. Samples treated at *p*H 4 and *p*H 5 are able to retain the finish even after 20 laundry cycles. The test results further support the conclusions that a

combination of mono and dicarboxylic acids in the presence of an initiator and a catalyst can be successfully used in finishing cotton textiles fabrics without causing any evident physical damage to the textile fabric. Cotton fabric when treated with carboxylic acids shows increase in carboxyl group values, resulting in higher wrinkle resistance property.

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