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Assessment of durable press performance of cotton finished with modified DMDHEU and citric acid

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Abstract

Cotton apparels possess inherent tendency to form wrinkles under external stress. Conventionally selective cross-linking agents in presence of specific catalyst are applied on cotton to supress formation of creases or wrinkles via pad-dry-cure technique at high curing temperature under acidic conditions imparting stability and elasticity to the fabric. Extensive research carried out in this field identifies invariable deterioration in mechanical properties of finished cotton. In this study, two different cross-linking agents, i.e. modified DMDHEU and citric acid working on etherification and esterification crosslinking reaction with cellulose respectively were applied on cotton through selection of factors using Box Behnken experimental design in conjunction with response surface analysis and regression methods to study their DP ratings as well as other mechanical properties. Significant factors were further drastically narrowed down to reach to most specific concentrations of cross-linker, catalyst as well as other chemicals along with finishing parameters. It was found that modified DMDHEU performed better in terms of DP rating as well as overall physical properties as compared to those obtained with citric acid.

Keywords: Cotton, Modified DMDHEU, Citric acid, DP rating, Box Behnken design, RSM

Introduction

Cotton fabric develops crease marks against external stress due to formation of new H-bonds deteriorating its look. Numerous approaches were developed to overcome this by applying different formaldehyde based cross-linking agents, viz. phenol formaldehyde resin, vinyl resin, dimethylol urea (DMU), dimethylol ethylene urea (DMEU), dimethylol-4,5-dihydroxyethylene urea (DMDHEU) etc. and non-formaldehyde products, such as 1,2,3,4-butane tetracarboxylic acid (BTCA), citric acid etc. (Andrews 1992; Harifi and Montazer 2012; Ramachandran et al. 2009). The most important and widely used chemical is DMDHEU and its derivatives because of their stability and durability (Cooke 1983; Holme 1993; Kittinaovarut 2003; Patricia 2012; Srivastava 1987; Srivastava and Kumar 1987; Voncina et al. 2002).

DMDHEU is manufactured from urea, glyoxal and formaldehyde, by reacting one molecule of urea with one molecule of glyoxal followed by reaction with two molecules of formaldehyde (Carr 1995; Schindler and Hauser 2004). Formaldehyde being toxic and carcinogenic in nature (Pastore and Kiekens 2001; Yang et al. 2000), various techniques were developed to minimize formaldehyde release by producing modified DMDHEU products i.e. partially or fully methylated DMDHEU (Patricia 2012). Reactivity is further reduced by reaction with methanol or diethylene glycol (producing ultra-low formaldehyde release) leading to ether modified DMDHEU products with low formaldehyde release (Holme 1993). These products possess improved stability and poor DP performance than that of its precursor but are acceptable due to comparatively less formaldehyde release because of end-caps present in it. The principle reaction of DMDHEU at elevated temperatures in presence of catalyst (a variety of acid or latent acid agents) with the cellulose is etherification of hydroxyl groups in the amorphous phase causing cross-linking of adjacent cellulose molecules preventing movement of fibre chains under stress thereby hindering wrinkle formation and shrinkage. Tensile and tear strength loss occur due to lack of molecular mobility in cross-links (Cooke and Weigmann 1982; Heywood 2003; Schindler and Hauser 2004; Tomasino 1992).

In this study, a commercial product called 'Fixapret F- ECO Plus' from BASF is used as modified DMDHEU. It is a clear aqueous solution with pH 4–5.5, confirms to the formaldehyde limits of Öko-Tex Standard 100 (75 ppm according to LAW 112) without washing after finishing of textile. It has high reactivity, extremely low formaldehyde release and is compatible with most of the finishing agents (Technical Information 2011).

Polycarboxylic acids form ester cross-links through esterification reaction with hydroxyl groups of cellulose, in the presence of selective weak catalysts such as alkali metal salts of phosphorous containing inorganic acids, e.g. sodium hypophosphite providing high level of resiliency when cured, imparting wrinkle resistance and smooth drying properties without producing any bad odour and stiff handle. Citric acid is the most extensively studied polycarboxylic acid having advantage of being inexpensive, wide availability, non-toxic and environmentally acceptable. It shows only moderate effectiveness as durable press finishing agent due to the presence of an α-hydroxyl group in its molecule which hinders its esterification with cellulose (Andrews 1990; Andrews et al. 1993; Bhattacharyya et al. 1999; Kittinaovarut 2003; Schramm and Rinderer 2000; Welch and Peters 1997; Yatagai and Takahashi 2005, 2006). Yellowing of fabric occurs at high curing temperatures (>175 °C) causing dehydration of the citric acid through formation of unsaturated polycarboxylic acids, such as aconitic acid, citraconic acid and itaconic acid; but exposing in open atmospheric moisture reverses the heat induced yellowing process to original whiteness (Choi 1993; Murray 1995; Schramm and Rinderer 1999; Welch and Peters 1999, 2000, 2002). During curing in presence of a catalyst, citric acid forms ester linkage (Welch and Peters 1997; Bhattacharyya et al. 1999); cross-links between two cellulose chains firstly by formatting a 5-membered cyclic anhydride as reactive intermediate and then the reaction between cellulose and anhydride intermediate, which is pH dependent (Yang et al. 2000).

The present study was aimed at formulating optimum durable press finish recipe to predict best durable press rating of cotton with two different types of anti-crease chemicals using Box–Behnken designs in conjunction with response surface analysis and regression methods. Thus finished cotton was evaluated for its DP rating followed by various other physical properties too.

Methods

Materials

Pre-treated plain woven cotton fabric possessing epi: 140, ppi: 72, warp: 40 s, weft: 40 s and gsm: 126 was used. Modified DMDHEU product 'Fixapret F- ECO plus' and 'Perapret PEB' (secondary polyethylene dispersion, having 9.4 pH) a polyethylene emulsion (PE) were obtained from BASF, India; Solusoft MW, a silicone softener (SS) which is an emulsion of amino modified silicone elastomer, non-ionic, having 6.46 pH was obtained from Clariant, India; reagent grade citric acid (CA) and $MgCl_2$ were obtained from SDFCL, Mumbai and sodium hypophosphite (SHP) was procured from Loba Chemie, Mumbai. Statistica 10, Systat 12 and Design Expert 9 softwares were used for sampling as well as analysis of data. Weight of catalysts ($MgCl_2$ and SHP) was calculated with respect to weight of modified DMDHEU and citric acid respectively.

Application of anti-crease finishes on cotton fabrics

Anti-crease finish liquor, prepared with desired factors (parameters) and levels based on the experimental design as mentioned in Table 1 was imparted to cotton on laboratory padder with 70–80% expression (owf) in modified DMDHEU and citric acid systems. All finished fabrics were dried at 80 °C and cured under stretched conditions at varying curing temperatures and times according to design.

Evaluation of properties of finished cotton

Finished cotton was evaluated for its DP (durable press)/smoothness appearance rating (AATCC test 124:2006). The best finished combinations were further evaluated for total crease recovery (AATCC Test 66-2003), tensile strength (ISO 13934-1:1999), tearing strength (ASTM D1424-09), bending length (ASTM D1388), air permeability (BS 5636) and whiteness index (Datacolor Check, Datacolor, USA).

Experimental design

Box Behnken factorial 6^3 research designs consisting of 54 runs with six replicates at central point were used to evaluate functional characteristics of modified DMDHEU and citric acid finished cotton. The characteristic of anti-crease finish was evaluated for durable press rating. Various parameters, viz, concentrations of modified DMDHEU, catalyst, silicone softener (SS), polyethylene emulsion (PE), curing temperature and time were included in the research design and their levels are mentioned in Table 1. Results

Table 1 Factors and levels in Box–Behnken design for finishing of cotton with modified DMDHEU and citric acid

	Independent variables #1 anti-crease chemical	Levels			Independent variables #2 anti-crease chemical	Levels		
		−1	0	1		−1	0	1
X1	Modified DMDHEU (gpl)	30	60	90	Citric acid (gpl)	40	60	80
X2	$MgCl_2$ (%) owf resin	10	20	30	SHP (%) owf CA	50	65	80
X3	SS (gpl)	5	12.5	20	SS (gpl)	0	10	20
X4	PE (gpl)	10	20	30	PE (gpl)	0	5	10
X5	Curing temperature (°C)	140	150	160	Curing temperature (°C)	150	160	170
X6	Curing time (min)	3	4	5	Curing time (min)	2	4	6

were analyzed with response surface plots and equations were formed for responses at 95% confidence level. The individual as well as interaction effect of the process factors on durable press rating was examined. Analysis of responses related with independent variables was done using quadratic polynomial equation (Eq. 1) and model accuracy was verified by the coefficient of determination (R^2). The P values of less than 0.05 were considered to be statistically significant.

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_{i^2} + \sum_{i=1}^{n} \beta_{ij} \chi_i \chi_j \quad \text{where n} = 3 \text{ or } 6 \tag{1}$$

where Y represents the response function (DP rating), β_0 is an intercept, β_i, β_{ii} and β_{ij} are the coefficient of the linear, quadratic, and interactive terms of regression equation; and χ_i, χ_{ii}, and χ_{ij} represent the coded independent variables, respectively.

After studying the response surface plots, the conditions for DP rating ≥3.5 were analyzed; significant factors were considered further and their levels were varied for design accordingly, in order to develop DP rating ≥3.5 with more effective optimum conditions. From these runs, sets of runs (combinations) developing maximum DP rating were selected for further study based on their physical properties.

Results and discussion

Finishing with modified DMDHEU and citric acid

According to the experimental design runs were performed (Table 1), DP rating was evaluated and results were analysed by response surface methodology to obtain the response surface equation for modified DMDHEU. DP rating of control fabric was found to be as poor as 1.5. Cotton finished with modified DMDHEU showed DP rating of >3 and close to or 3.5 against that with citric acid around 3. All those sets of runs (combinations) with modified DMDHEU resulting in DP rating close to or ≥3.5 are mentioned in Table 2. However, levels of factors in citric acid finish were subsequently further modified to obtain better DP rating.

Influence of finishing parameters on DP rating and its statistical analysis

Modified DMDHEU anti crease finish

Concentration of anti-crease agent, catalyst, curing temperature and time are the important parameters (factors) for crosslinking with cellulose to obtain better DP rating and fabric properties. Magnesium chloride being a latent acid provides stability to the bath and initiates the crosslinking during curing. Silicone softener reduces strength loss of the fabric. Incorporation of polyethylene emulsion helps in retaining the tear strength properties.

Considering DP rating as response (dependent variable), the response surface plots are shown in Figs. 1a–h and 2a–g to see the effect of each independent factor mentioned in Table 1, as a function of two factors, whilst rest four factors were kept at a constant centre level to study their interaction on the DP ratings.

Initially concentration of cross-linker, catalyst, softener, PE emulsion and finishing parameters were selected with wider range to see their impact on DP rating. Response surface analysis shows that at higher concentration of cross-linker (60–90 gpl), DP rating

Table 2 Selective sets of runs resulting maximum DP rating with modified DMDHEU

Run no.	Independent variables					
	X1: modified DMDHEU (gpl)	X2: $MgCl_2$ (%)[a]	X3: SS (gpl)	X4: PE (gpl)	X5: curing temperature (°C)	X6: curing time (min)
4	90	30	12.5	10	150	4
14	60	30	5	20	160	4
15	60	10	20	20	160	4
16	60	30	20	20	160	4
26	90	20	12.5	10	140	4
30	90	20	12.5	10	160	4
32	90	20	12.5	30	160	4
36	60	30	12.5	20	160	3
39	60	10	12.5	20	160	5
40	60	30	12.5	20	160	5
42	90	20	5	20	150	3
43	30	20	20	20	150	3

[a] $MgCl_2$ (% ow modified DMDHEU)

was better, with minimum catalyst concentration at 15% (Fig. 1a). At resin concentration of 60 gpl along with increased curing temperature i.e. above 150–160 °C and longer curing time (4 min) adequate crosslink formation took place showing better and acceptable DP rating (Fig. 1d, e); further increase in time didn't show substantial effect on it. At lower concentration of catalyst but increase in resin concentration, curing temperature and time did not increase the contribution of magnesium chloride to enhance the DP rating, while, at a higher concentration of it, the increase in resin concentration and curing temperature as well as time increased the effect of magnesium chloride to form more crosslinks with better DP rating (Figs. 1a, h, 2a). Concentration of softeners and polyethylene emulsion (Figs. 1b, c, f, g, 2b–f) didn't have much impact on DP rating, although these two at higher concentrations may attribute to hinder in crosslinking of chains (Fig. 1b, c); maximum effect of softener was at 18 gpl, PE in between 5 and 25 gpl or beyond and 60 gpl for modified DMDHEU. It can be concluded that concentration of modified DMDHEU, $MgCl_2$ and curing temperature were the major factors and showed direct influence on the DP ratings whereas, curing time showed negligible effect while silicone softener (Figs. 1b, f, 2b–d) and polyethylene emulsion (Figs. 1c, g, 2b, e, f) were not contributing significantly much towards the DP rating. From the obtained results and analysis the best DP rating were achieved at resin concentrations of 60–90 gpl, $MgCl_2$ (20–30%) and curing temperature beyond 160 °C.

Statistical analysis for durable press rating shows that out of six independent factors only three, i.e. concentrations of modified DMDHEU, $MgCl_2$ and curing temperature showed significant influence on DP rating. Regression equation for DP rating is mentioned in Table 3. From this analysis only significant factors were taken into consideration for next design runs to obtain more precise conditions to achieve effective DP rating. The regression model obtained was significant with F value of 6.45 implying that the model is significant as F value is less than that of the calculated one. The model showed statistically insignificant lack of fit, as is evident from the P value of 0.088. The

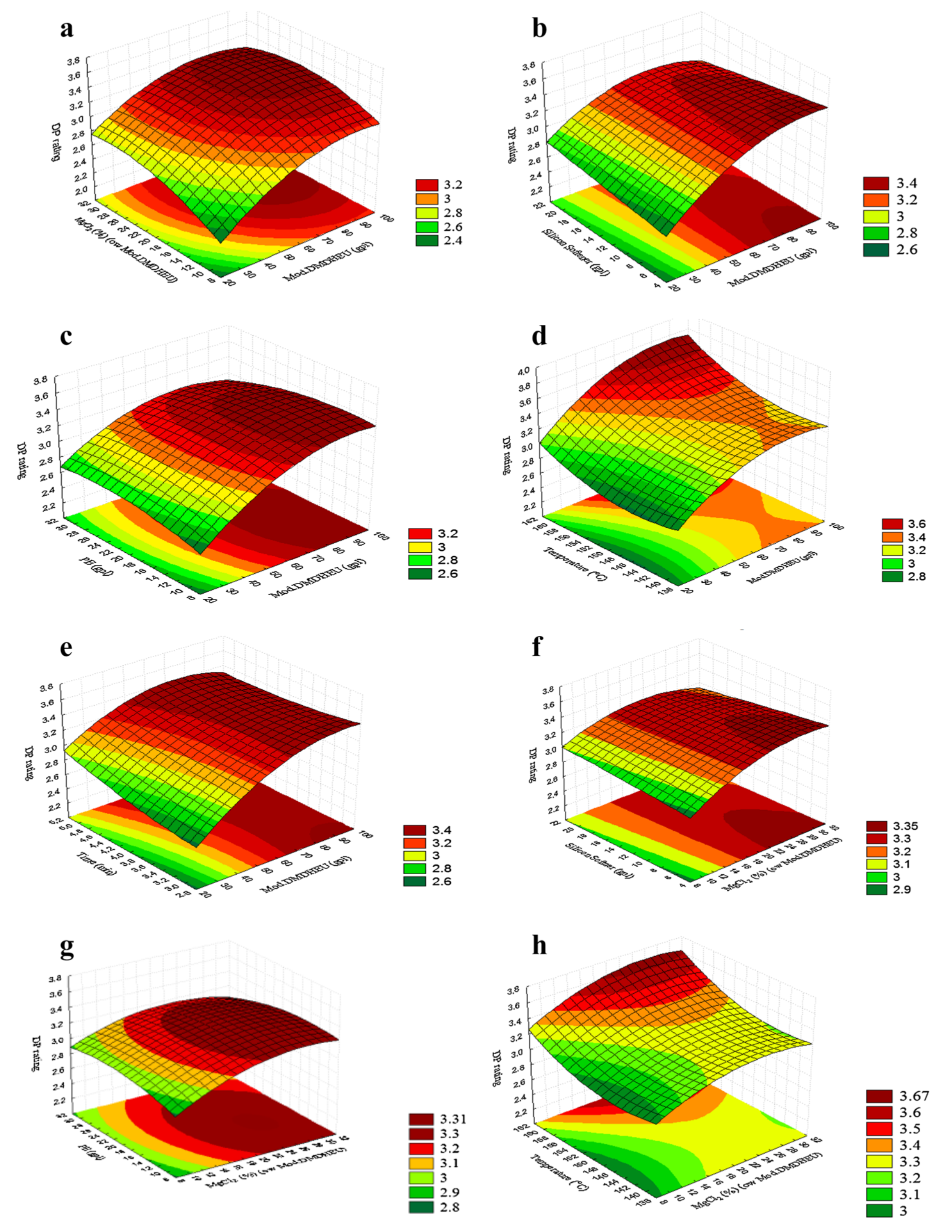

Fig. 1 Response surface plots of the DP rating data with combined effects of **a** modified DMDHEU and $MgCl_2$, **b** modified DMDHEU and softener, **c** modified DMDHEU and PE, **d** modified DMDHEU and temperature, **e** modified DMDHEU and time, **f** $MgCl_2$ and softener, **g** $MgCl_2$ and PE, **h** $MgCl_2$ and temperature at centre level point of rest of the factors (not mentioned in figure)

lack of fit F value of 3.430 shows the validity of the predictive model. In this case, X1, X2, X5, $(X1)^2$, $(X2)^2$ and $(X5)^2$ were found as significant model terms.

Further in order to obtain more precise sets of conditions, it was decided to run 3^3 Box Behnken design with three significant factors obtained from previous runs by narrowing level ranges based on obtained results. Significant factors, viz. concentrations of modified DMDHEU, $MgCl_2$ and curing temperature were considered from statistical analysis result and level ranges from the response surface Figs. 1a–h, 2a–g and Table 2. It was

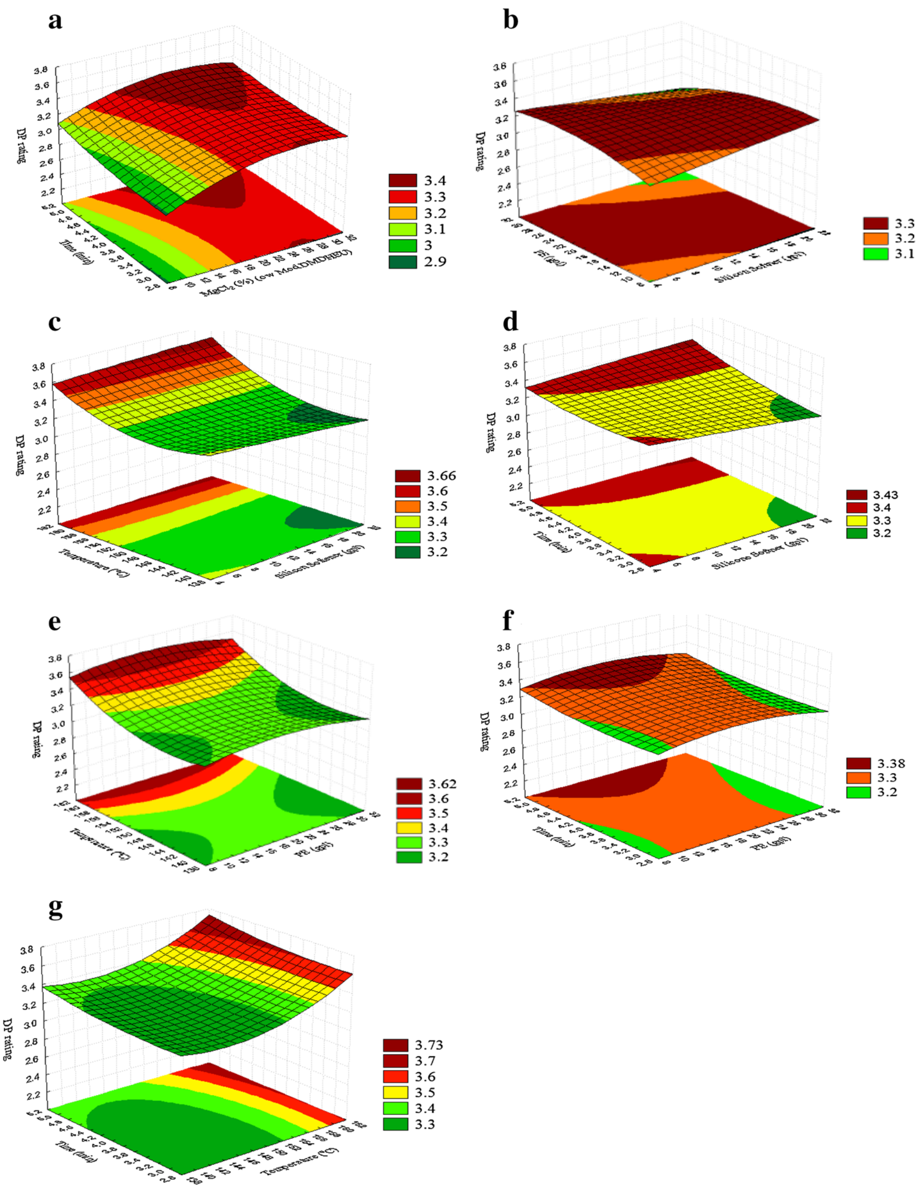

Fig. 2 Response surface plots of the DP rating data with combined effects of **a** $MgCl_2$ and time, **b** softener and PE, **c** softener and temperature, **d** softener and time, **e** PE temperature, **f** PE and time, **g** temperature and time, at centre level point of rest of the factors (not mentioned in figure)

Table 3 Regression equation for DP rating in terms of coded values for modified DMDHEU

Response (Y)	Regression equation with all factors	R	R^2	Adj. R^2	F value
DP rating	$Y = +3.267 + 0.233\,(X1) + 0.129\,(X2) - 0.012\,(X3) - 0.017\,(X4) + 0.146\,(X5) + 0.050\,(X6) - 0.146\,(X1)^2 - 0.125\,(X2)^2 - 0.004\,(X3)^2 - 0.071\,(X4)^2 + 0.125\,(X5)^2 + 0.033\,(X6)^2 - 0.050\,(X1{*}X2) - 0.063\,(X2{*}X3) - 0.050\,(X2{*}X4) + 0.019\,(X2{*}X5) - 0.025\,(X2{*}X6) - 0.075\,(X1{*}X3) - 0.075\,(X3{*}X4) + 0.038\,(X3{*}X5) + 0.050\,(X3{*}X6) - 0.063\,(X1{*}X4) + 0.050\,(X4{*}X5) - 0.050\,(X4{*}X6) + 0.025\,(X1{*}X5) + 0.050\,(X5{*}X6) - 0.075\,(X1{*}X6)$	0.933	0.87	0.735	6.45

X1 modified DMDHEU (gpl), *X2* $MgCl_2$ (% ow modified DMDHEU), *X3* SS (gpl), *X4* PE (gpl), *X5* curing temperature (°C), *X6* curing time (minute) decided to limit the further study with resin concentrations kept at 50, 60, 70 gpl, as it showed best results with 60 and 90 gpl, too excess of resin was not considered as it would lead to excessive strength loss of cotton. $MgCl_2$ was kept at 15, 20, 25%, as it showed best results at 20 and 30% for most of the runs. In most cases, curing temperature of 160 °C produced better crosslinking and therefore the new levels selected were 150, 160, 170 °C.

For most of the sets of runs (combinations) resulting best DP rating, SS and PE showed required results at 12.5 and 20 gpl respectively against curing time of 4 min, therefore, these were kept unchanged for next experiment design runs. All factors and levels studied further for design are shown in Table 4.

The effects of the independent factors (Table 4) and their interaction on the DP ratings were studied from the response surface Fig. 3a–c, showing the DP rating as a function of two factors, whilst the third factor was kept at its constant centre level. The DP ratings (dependent variable) obtained are shown in Table 5.

Table 4 Factors and levels in Box–Behnken design with significant factors using modified DMDHEU

Coded factors	Independent factors	Levels		
		−1 (low)	0 (centre)	1 (high)
X1	Modified DMDHEU (gpl)	50	60	70
	$MgCl_2$ (%) owf resin	15	20	25
X3	Curing temperature (°C)	150	160	170

At fixed silicone softener of 12.5 gpl, polyethylene emulsion of 20 gpl and curing time of 4 min

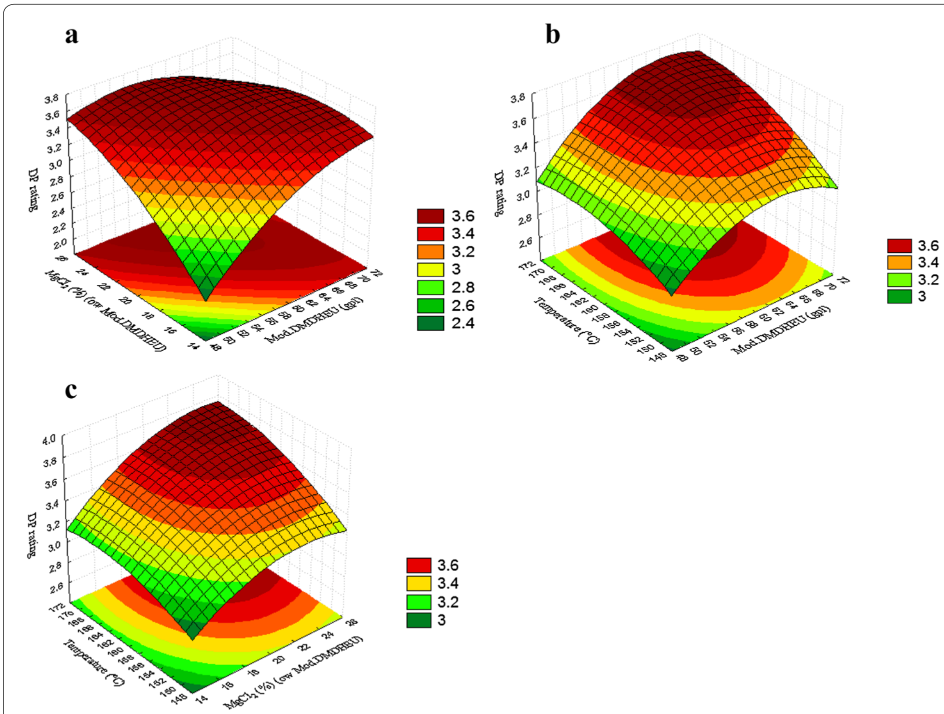

Fig. 3 Response surface plots of the DP rating data with combined effects of **a** modified DMDHEU and $MgCl_2$, **b** modified DMDHEU and temperature and **c** $MgCl_2$ and temperature at centre level point of third factor (not mentioned in figure)

Table 5 Box–Behnken design layout and their response using modified DMDHEU

Run no.	Independent variables			Dependent variables
	X1: modified DMDHEU (gpl)	X2: $MgCl_2$ (%)[a]	X3: curing temperature (°C)	DP rating
1	50	15	160	2.5
2	70	15	160	3.5
3	50	25	160	3.5
4	70	25	160	3.5
5	50	20	150	3.1
6	70	20	150	3.2
7	50	20	170	3.3
8	70	20	170	3.6
9	60	15	150	3.1
10	60	25	150	3.3
11	60	15	170	3.3
12	60	25	170	3.7
13	60	20	160	3.6
14	60	20	160	3.5
15	60	20	160	3.6

[a] $MgCl_2$ (% ow modified DMDHEU)

DP ratings showed best results when modified DMDHEU concentration was maintained at ≥60 gpl (Fig. 3a–c), probably because of formation of inadequate cross-links with cotton at lower concentration. Increase in the concentration of catalyst ≥20% didn't produce any major change in DP rating. At higher concentration of modified DMDHEU (60–70 gpl) and curing temperature (160–170 °C) both, DP ratings were ≥3.5 due to adequate cross-link formation. At lower curing temperature and higher concentration of modified DMDHEU showed slight increase in DP rating (≤3.5); but vice versa didn't produce better DP results. It could be concluded that both temperature and modified DMDHEU were playing concurrent role in DP rating. With increase in both concentration of $MgCl_2$ and curing temperature there was increase in the DP rating to beyond 3.5. From response Fig. 3a–c and Table 5, modified DMDHEU (60 gpl), $MgCl_2$ (20%) and curing temperature (above 160 °C) developed required DP rating of 3.5.

From statistical analysis it was found that all these three factors played significant role on DP rating. Regression equation for DP rating is mentioned in Table 6. The regression model obtained was significant with F value of 9.346 which is remarkably more than table value of 4.77, implying that the model is significant. The model showed statistically insignificant lack of fit, as is evident from the P value of 0.136. The lack of fit F value of 6.500 shows the validity of the predictive model. In this case, X1, X2, X3, $(X1)^2$ and (X1*X2) were found as the significant model terms. The optimized conditions

Table 6 Regression equation for DP rating in terms of coded values for modified DMDHEU

Response (Y)	Regression equation with all factors	R	R^2	Adj. R^2	F value
DP rating	$Y = 3.567 + 0.175\,(X1) + 0.2\,(X2) + 0.15\,(X3) - 0.183\,(X1)^2 - 0.133\,(X2)^2 - 0.083\,(X3)^2 - 0.250\,(X1{*}X2) + 0.050\,(X2{*}X3) + 0.050\,(X1{*}X3)$	0.972	0.944	0.843	9.346

X1 modified DMDHEU (gpl), *X2* $MgCl_2$ (% ow modified DMDHEU), *X3* curing temperature (°C) obtained from software were modified DMDHEU (60 gpl), $MgCl_2$ (25%) and temperature (170 °C). The experimental result obtained was same as predicted response for optimized conditions.

Further it was decided to study the best level for non-significant factor's as well. The non-significant factors (concentration of SS, PE and curing time) from first design run which were kept unchanged during second design run, were varied keeping significant factors unchanged. The levels selected were similar to the previous best, i.e. softener at 12.5 gpl, PE at 20 gpl and time for 4 min; although these factors were not showing statistically significant influence on DP ratings, but have had influence on change in physical properties of fabric. SS was added because resin finish produces stiff hand due to cross-linking, and PE helps in tear strength retention imparting elasticity. Curing time had direct effect on the strength properties of the finished fabric, as high temperature with longer curing time would cause strength loss with increased chances of fabric degradation.

In order to obtain more optimized conditions for non-significant factors, a further Box Behnken design was run for levels range, viz. for SS (10, 12.5, 15) gpl, PE (15, 20, 25) gpl and curing time as (3, 4, 5) min, keeping concentration of modified DMDHEU at 60 gpl, $MgCl_2$ at 20% and curing temperature at 160 °C fixed. These runs were planned to obtain more combinations with better as well as acceptable DP rating. It was found that concentrations of SS and PE both played no significant role on DP ratings, but high curing times of 4–5 min showed better results. Also, it was observed that for most of the runs, DP rating was close to 3.5. The best results were achieved when softener and emulsion concentrations were at 12.5 and 20 gpl respectively with curing time of 4 min.

Citric acid

Concentration of citric acid and catalyst (SHP) played crucial role as these form five membered anhydride rings on heating at higher curing temperatures. As none of the previous run conditions showed results with better DP rating or comparable with that in modified DMDHEU finished fabrics rating, it was decided to further select those factors and levels based on the results in Table 7 showing all runs with better performance to achieve the best set of runs (combinations) for adequate DP ratings. The modified combinations are shown in Table 8; concentrations of chemicals were kept unchanged with

Table 7 Selective sets of runs developing maximum DP rating using citric acid

Run no.	X1: CA (gpl)	X2: SHP (% ow CA)	X3: SS (gpl)	X4: PE (gpl)	X5: curing temperature (°C)	X6: curing time (min)
2	80	50	10	0	160	4
7	40	80	10	10	160	4
23	60	65	0	10	160	6
26	80	65	10	0	150	4
28	80	65	10	10	150	4
29	40	65	10	0	170	4
32	80	65	10	10	170	4
36	60	80	10	5	170	2
40	60	80	10	5	170	6
49	60	65	10	5	160	4

exception to increase the curing temperature to 180 °C and curing time for 2 min (not beyond these prescribed limits to avoid fabric degradation and yellowing both).

CA (40 gpl) with even high SHP concentration (65, 80%) could not produce the desired DP rating though increase in concentration of CA (60 and 80 gpl) with same SHP concentrations produced DP rating of 3.5 or too close of it in presence of same amount of SS and PE (Table 8). Increase in concentration of CA with simultaneous reduction in concentration of SHP or vice versa resulted in the desired DP rating of ≥3.5 with SS concentration unchanged (10 gpl) but variation in concentration of PE. However, a PE concentration was found to be adequate at 5 gpl. In all these cases, too high curing temperature (180 °C) developed yellowness in finished fabric due to formation of unsaturated acids, viz. itaconic, aconitic acid etc. through dehydration of citric acid; the yellowness disappeared completely on moistening (washing) of finished fabric for 30 s for reconversion of these unsaturated acids to saturated citric acid (Table 8). The factors with respective levels considered for next runs are mentioned in Table 9. Citric acid levels were raised to 50, 60, 70 gpl as the concentrations of 40 and 80 gpl developed DP rating of 3 and substantial strength loss due to partial degradation of fabric with appearance of yellowness respectively. SHP concentration (%) was kept at 60, 70 and 80, as lower concentration (50%) didn't develop the desired DP rating while curing time levels were kept at 60, 90 and 120 s. From Tables 7 and 8, it was decided to maintain SS and PE concentration at 10 and 5 gpl respectively with curing temperature at 180 °C. The runs with factors from Table 9 are mentioned in Table 10 with their respective DP rating as response.

Table 8 Trial runs based on box behnken design results for DP rating with citric acid

Trial no.	CA (gpl)	SHP (%)	SS (gpl)	PE (gpl)	DP rating	WI (BW)	WI (AW)
1	60	80	10	10	3.5	69.31	77.82
2	60	65	10	5	3.4	69.63	79.20
3	60	80	10	5	3.5	71.04	79.12
4	80	65	10	10	3.5	69.13	78.75
5	80	50	10	5	3.5	67.66	77.31
6	40	80	10	10	3	71.86	79.11
7	40	65	10	5	2.9	73.08	78.88

SHP (% ow CA), *BW* before wash, *AW* after wash

Table 9 Factors and levels in Box Behnken design with citric acid

Coded factors	Independent factors	Factor levels		
		−1 (low)	0 (centre)	1 (high)
X1	Citric acid conc. (gpl)	50	60	70
X2	SHP (%) ow CA	60	70	80
X3	Curing time (s)	60	90	120

At fixed silicone softener of 10 gpl, polyethylene emulsion of 5 gpl and curing temperature of 180 °C

Table 10 Box–Behnken experimental design layout and their response using citric acid

Run no.	Independent variables			Dependent variable
	X1: CA (gpl)	X2: SHP (% ow CA)	X3: curing time (s)	DP rating
1	50	60	90	3.1
2	70	60	90	3.3
3	50	80	90	3.3
4	70	80	90	3.5
5	50	70	60	3.2
6	70	70	60	3.5
7	50	70	120	3.5
8	70	70	120	3.7
9	60	60	60	3.1
10	60	80	60	3.5
11	60	60	120	3.6
12	60	80	120	3.6
13	60	70	90	3.6
14	60	70	90	3.7
15	60	70	90	3.6

Influence of finishing parameters on DP rating and its statistical analysis

The effects of the independent factors (Table 9) and their interaction on the DP ratings were studied from the response surface Fig. 4a–c, showing the DP rating as a function of two factors, whilst the third factor was kept at its constant centre level. The DP ratings (dependent variable) are shown in Table 10. On curing in presence of SHP, citric acid reacts with hydroxyl groups of cellulose to form ester-type crosslinks. At low concentration of chemicals i.e. CA and SHP, DP rating was less; the latter increased with increase in concentration of CA at low concentration of catalyst (SHP) or visa-versa, (Fig. 4a). Increase in concentration of either or both CA and SHP with low curing time, or visa-versa resulted in desired DP rating of ≥3.5 due to formation of adequate ester-links with cotton (Fig. 4b, c). But when longer curing time was used along with increase in concentration of both chemicals it produced better DP ratings. Curing time longer than 90 s and CA concentration ≥60 gpl showed marked increase in DP rating. SHP at 60 and 70% concentration for longer curing time (120 s) caused improvement in ratings with no further change on increase in concentration of the same confirming formation of maximum cross-links with cellulose at given concentration of citric acid. Interestingly, at low concentration of CA (50 gpl) finished fabric appearance (DP rating) was not remarkably improved except for longer curing time (120 s) and higher catalyst concentration (70 gpl).

This confirmed that best DP rating could be obtained with CA (60 gpl), SHP (65% ow CA), curing time (120 s) and curing temperature (180 °C).

From the statistical analysis for durable press rating it was found that all the three independent factors, viz. concentration of citric acid, SHP and curing time were playing significant role on the DP rating. Regression equation for DP rating is mentioned in Table 11. The regression model obtained was significant with F value of 34.434 implying that the model is significant. The model showed statistically insignificant lack of fit, as

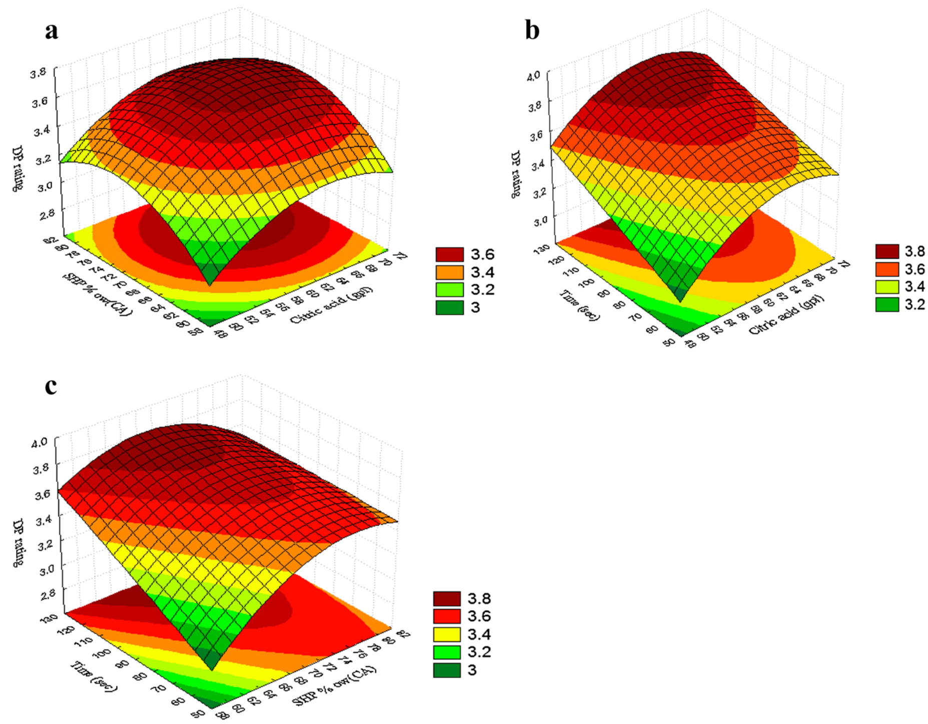

Fig. 4 Response surface plots of the DP rating data with combined effects of **a** citric acid and SHP, **b** citric acid and time and **c** SHP and time at centre level point of third factor (not mentioned in figure)

Table 11 Regression equation for DP rating in terms of coded values using citric acid

Response (Y)	Regression equation with all factors	R	R^2	Adj. R^2	F value
DP rating	$Y = 3.633 + 0.112\ (X1) + 0.1\ (X2) + 0.138\ (X3) - 0.154\ (X1)^2 - 0.179\ (X2)^2 - 0.004\ (X3)^2 - 0.100\ (X2{*}X3) - 0.025\ (X1{*}X3)$	0.992	0.984	0.956	34.434

X1 citric acid (gpl), *X2* SHP (% ow CA), *X3* curing time (seconds)

is evident from the P value of 0.858. The lack of fit F value of 0.250 shows the validity of the predictive model. X1, X2, X3, $(X1)^2$, $(X2)^2$ and (X2*X3) were found to be the significant model terms. The optimized conditions from the software are citric acid ≈60 gpl, SHP ≈ 70% (ow CA) and curing time ≈ 117 s, which are similar to the conditions optimized by study.

Evaluation of physical properties of modified DMDHEU and citric acid finished cotton

Combinations (runs) showing desired durable rating (≥3.5) with their corresponding physical properties for both anti-crease chemicals are summarized in Tables 12, 13, 14. Increase in intermolecular crosslinking with cellulose resulted in restriction in the movement of cellulose chains and loss of mobility of cellulosic macromolecular network thus reducing the equalized stress distribution ultimately leading to loss in mechanical strength. Addition of polyethylene emulsion and softener provides lubrication and yarn slippage, and helps in retaining strength.

Table 12 Physical properties for sets of runs with maximum DP rating using modified DMDHEU

No.	Modified DMDHEU (gpl)	$MgCl_2$ (% ow resin)	SS (gpl)	PE (gpl)	Curing temperature (°C)	Curing time (min)	TCRA	Tensile strength (% retention)		Tear strength (% retention)		Bending length (cm)		WI	AP ($cm^3/cm^2/s$)
								Warp	Weft	Warp	Weft	Warp	Weft		
UN							155	100	100	100	100	2.3	1.52	78.80	17.96
1	50	25	12.5	20	160	4	228	73.74	67.2	85.29	81.99	1.95	1.58	79.42	14.77
2	60	20	10	20	160	3	222	71.33	69.2	86.19	84	2.1	1.6	80.49	14.32
3	60	20	10	20	160	5	240	73.03	63.71	86.71	84.15	2.04	1.58	79.95	15.42
4	60	20	10	15	160	4	253	74.36	69.46	80.16	82.32	2	1.49	79.2	14.82
5	60	20	12.5	15	160	5	257	70.96	61.27	83.92	80.74	2.13	1.56	79.87	14.92
6	60	20	12.5	20	160	4	245	74.18	66.88	87.5	82.36	2.07	1.6	79.48	14.46
7	60	20	15	20	160	3	239	73.79	69.4	86.99	83.1	2	1.56	78.97	14.82
8	60	20	15	20	160	5	251	75.19	70.16	85.49	83.8	2.05	1.53	79.97	15.51
9	60	20	12.5	25	160	3	242	71.95	63.27	89	84.14	2.05	1.54	81.46	15.45
10	60	20	12.5	25	160	5	248	72.46	66.94	88.12	84.87	2.0	1.59	80.36	15.63
11	60	20	15	25	160	4	263	77.03	62.78	87.89	83.69	1.9	1.48	80.19	15.21
12	60	25	12.5	20	170	4	239	68.13	59.88	78.79	80.02	2.1	1.55	79.9	15.77
13	70	15	12.5	20	160	4	243	70.61	63.16	88.03	78.07	2.1	1.53	79.78	14.02
14	70	25	12.5	20	160	4	256	67.29	60.18	81.31	79.98	2.1	1.53	80.57	14.99
15	70	20	12.5	20	170	4	248	65.2	57.37	77.63	76.09	2.13	1.6	80.05	14.43

UN unfinished cotton, *TCRA* total crease recovery angle, *WI* whiteness index, *AP* air permeability

Table 13 Physical properties and conditions with and without silicone softener and polyethylene emulsion using modified DMDHEU

Recipe no.	SS (gpl)	PE (gpl)	TCRA	Tensile strength (% retention)		Tear strength (% retention)		Bending length (cm)		WI	AP ($cm^3/cm^2/s$)
				Warp	Weft	Warp	Weft	Warp	Weft		
UN	–	–	155	100	100	100	100	2.3	1.52	78.80	17.96
1	0	0	199	52.47	50.22	60.62	62.46	2.5	1.6	77.57	14.89
2	0	10	203	57.96	58.03	75.89	73.3	2.1	1.58	77.66	14.1
3	0	20	211	60.47	57.79	76.64	72.25	2.2	1.55	77.43	13.65
4	10	0	218	63.62	61.08	65.9	64.04	2.3	1.55	78.57	13.52
5	20	0	236	66.61	68.24	66.75	67.98	2.1	1.53	79.26	14.43

Modified DMDHEU at 60 gpl; $MgCl_2$ at 20% (ow resin); Curing temperature at 160 °C and Curing time at 4 min were kept unchanged

UN unfinished cotton, *TCRA* total crease recovery angle, *WI* whiteness index, *AP* air permeability

In case of modified DMDHEU, high curing temperature of 170 °C had adverse effect on tensile strength as compared to that at 160 °C. Tensile strength for fill and warp directions were retained by at most 70.16 and 77.07% respectively, as compared to those of unfinished fabric. TCRA of the finished fabric was notably higher than that of unfinished fabric, showing substantial crosslinking. Increase in either curing time or resin concentration increased TCRA for most of the samples, while catalyst at higher concentration decreased tensile and tear strength retention of finished fabric. Increase in curing temperature synergized catalyst activity resulting in loss of tensile strength.

As crosslinking diminishes the fibre extensibility and restricts chain slippage it tends to produce decreased tear strength of finished fabric. Polyethylene emulsion improves slippage of yarns improving tear strength; the effect was prominent at a concentration of 20–25 gpl. Either of higher curing temperature and/or high catalyst concentration caused substantial fall in tear strength. Bending length (stiffness) of the sample was almost maintained in both the directions for all sets of finishing combinations. Whiteness index was almost same for finished and unfinished cotton. Air permeability of finished cotton had decreased.

The effect of concentration of PE and SS was further studied to ensure their influence on physical properties of finished fabric. Five combinations were selected along with their physical properties as mentioned in Table 13. PE concentration played important role on retention of tear strength (Table 13); recipe nos. 2 and 3 caused better retention as compared to those of finished with no PE in the recipe (recipe nos. 1, 3 and 5). Presence of SS (recipe nos. 4 and 5) resulted in better tensile strength compared to those of finished in its absence (recipe nos. 1, 2 and 3); even presence of softener caused better TCRA. Absence of softener and polyethylene emulsion increased stiffness due to obvious reasons. This indeed confirmed influence of both SS and PE on mechanical properties of finished cotton.

In case of citric acid (Table 14) tensile strength retention was at most 75 and 70% for warp and fill directions respectively. Higher concentration of citric acid and SHP caused noticeable loss in tensile and tear strength due to more acid degradation of fabric as compared to resin treatment (pH of citric acid bath was 2.7–3). High curing temperature

Table 14 Physical properties for sets of runs with maximum DP rating using citric acid

No.	CA (gpl)	SHP (% ow CA)	Curing time (s)	TCRA	Tensile strength (% retention)		Tear strength (% retention)		Bending length (cm)		WI	AP ($cm^3/cm^2/s$)
					Warp	Weft	Warp	Weft	Warp	Weft		
UN	–	–	–	155	100	100	100	100	2.3	1.52	78.8	17.96
1	50	70	120	195	64.99	62.95	79.1	76.01	1.6	1.31	76.16	15.1
2	60	60	120	215	74.92	67.28	78.99	82.25	1.65	1.21	75.9	16.35
3	60	70	90	210	73.45	63.31	76.75	75.89	1.7	1.24	76.94	15.75
4	60	80	60	210	74.88	70.24	80.9	78.55	1.68	1.18	76.69	16.38
5	60	80	120	206	66.84	62.59	77.31	80.66	1.64	1.23	75.08	15.36
6	70	70	60	213	71.14	65.83	75.59	82.25	1.6	1.25	77.17	15.68
7	70	70	120	223	67.3	63.42	72.99	72.78	1.64	1.26	75.83	16.01
8	70	80	90	213	65.07	61.56	78.42	76.99	1.65	1.23	76.12	16.13

UN unfinished cotton, *TCRA* total crease recovery angle, *WI* whiteness index, *AP* air permeability

(180 °C) too resulted fall in tensile strength. Softener and polyethylene emulsion at lower concentrations, viz. 5 and 10 gpl respectively, produced remarkably lower bending length (stiffness). TCRA was not comparable with that of resin finished cottons, although there was improvement in it. Whiteness index was found to be close to the unfinished cotton fabric after keeping it in open for 24 h so that unsaturated acids were converted back to saturated acids which caused some yellowness in samples after curing. Air permeability was better than that with resin finished cottons.

Comparison of performance of finishes modified DMDHEU and CA on cotton

Optimized finishing parameters and related physical properties of finished cotton with modified DMDHEU and citric acid are shown in Tables 12, 13 and 14 respectively. Modified DMDHEU and CA both produced good DP rating (≥3.5) at 60 gpl with respective concentration of catalyst at 20% ($MgCl_2$) and 65–70% (SHP) respectively; the latter resulted in more tendering of finished cotton. Citric acid itself developed a pH of around 2.7–3 in bath and further addition of SHP increased acidity causing severe tendering. The optimum curing temperature was 160 and 180 °C for modified DMDHEU and CA respectively to obtain DP rating of ≥3.5. Higher curing temperature caused high strength loss and yellowing of finished cotton. More concentration of SS and PE was required for modified DMDHEU because of stiffness developed compared to lesser concentrations of these two in CA based formulation. TCRA was better with modified DMDHEU while CA caused more loss in tensile and tear strength. Citric acid produced yellowing of fabric which was removed by conditioning it in open. Whiteness index were comparable with that of unfinished fabric. Air permeability was less in case of resin finished cotton.

Conclusions

Both modified DMDHEU and citric acid finished cotton resulted desired DP rating at various combinations. Relatively high curing temperature was required in citric acid finish; yellowness developed on fabric had faded away on subsequent conditioning in open air. High acidic conditions in citric acid finish caused substantial fall in tensile and tear strength compared to those with modified DMDHEU. Modified DMDHEU resulted stiffness and better TCRA both than those with citric acid due to long cross-linking chains. Air permeability of finished cotton was less with modified DMDHEU compared to that in citric acid finish. SS and PE showed no significant effect on DP rating but on physical properties of the finished fabric.

Authors' contributions

Both GD and JNC planned the work, GD carried out the work and drafted the manuscript. Both authors read and approved the final manuscript.

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Competing interests

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References

Andrews, B. A. (1990). Nonformaldehyde DP finishing of cotton with citric acid. *Textile Chemist and Colorist, 22*(9), 63–67.

Andrews, B. A. (1992). Safe, comfortable, durable press cottons: A natural progression for a natural fiber. *Textile Chemist and Colorist, 24*(11), 17–22.

Andrews, B. A., Blanchard, E. J., & Reinhardt, R. M. (1993). Fabric whiteness retention in durable press finishing with citric acid. *Textile Chemist and Colorist, 25*(3), 52–54.

Bhattacharyya, N., Doshi, B. A., & Sahasrabudhe, A. S. (1999). Cost effective catalyst for polycarboxylic acid finishing. *Textile Chemist and Colorist, 31*(6), 33–37.

Carr, C. M. (1995). *Chemistry of textiles industry* (1st ed.). Glasgow: Blackie Academic and Professional.

Choi, H. M. (1993). Nonionic and cationic curing additives which improve the whiteness of citric acid treated cotton. *Textile Chemist and Colorist, 25*(5), 19–24.

Cooke, T. F. (1983). Formaldehyde release from durable press fabrics. *Textile Chemist and Colorist, 15*(12), 19–24.

Cooke, T. F., & Weigmann, H. D. (1982). The chemistry of formaldehyde release from durable press fabrics. *Textile Chemist and Colorist, 14*(5), 25–31.

Harifi, T., & Montazer, M. (2012). Past, present and future prospects of cotton cross-linking: New insight into nano particles. *Carbohydrate Polymers, 88*(4), 1125–1140.

Heywood, D. (Ed.). (2003). *Textile finishing*. Bradford: Society of Dyers and Colourists.

Holme, I. (1993). New developments in the chemical finishing of textiles. *Journal of Textile Institute, 84*(4), 520–533.

Kittinaovarut, S. (2003). Acrylic and ctric acid in nonformaldehyde durable press finishing on cotton fabric. *AATCC Review, 3*(8), 62–64.

Murray, V. L. (1995). Investigation into the crosslinking of cotton cellulose with citric acid. Book of Papers, AATCC International Conference & Exhibition Atlanta, GA, *1*, 26–39.

Pastore, C. M., & Kiekens, P. (2001). *Surface characteristics of fibers and textiles: Surfactant science series* (Vol. 94). New York: Marcel Dekker Inc.

Patricia, A. A. (Ed.). (2012). *Understanding and improving the durability of textile* (Ist ed.). Cambridge: Woodhead publishing limited.

Ramachandran, T., Gobi, N., & Rajendran, V. (2009). Optimization of process parameters for crease resistant finishing of cotton fabric using citric acid. *Indian Journal of Fibre & Textile Research, 34*(4), 359–367.

Schindler, W. D., & Hauser, P. J. (2004). *Chemical finishing of textiles* (1st ed.). Cambridge: Woodhead Publishing Limited.

Schramm, C., & Rinderer, B. (1999). Optimizing citric acid durable press finishing to minimize fabric yellowing. *Textile Chemist and Colorist, 31*(2), 23–27.

Schramm, C., & Rinderer, B. (2000). Multifunctional carboxylic acids in DP finishing with BTCA and CA. *Textile Chemist And Colorist & American Dyestuff Reporter, 32*(4), 50–54.

Srivastava, M. L. (1987). Various approaches to produce DP cotton fabrics with low formaldehyde release. *Textile Dyer and Printer*, *20*(20), 17–20.

Srivastava, M. L., & Kumar, A. (1987). Mechanism of formaldehyde release from fabrics treated with N-methylol compounds and its toxicity. *Textile Dyer and printer, 20*(16), 19–23.

Technical Information. (2011). Fixapret® resin F-eco plus. *BASF The chemical company. TI/T Asia*.

Tomasino, C. (1992). *Chemistry & technology of fabric preparation & finishing*. Raleigh: North Carolina State University.

Voncina, B., Bezek, D., & le Marechal, M. A. (2002). Eco-friendly durable press finishing of textile interlinings. *Fibres & Textiles in Eastern Europe, 38*(3), 68–71.

Welch, C. M., & Peters, J. G. (1997). Mixed polycarboxylic acids and mixed catalyst in formaldehyde-free durable press finishing. *Textile Chemist and Colorist, 29*(3), 22–27.

Welch, C. M., & Peters, J. G. (1999). DP finishes using citric and tartaric acid with methyl hydrogen silicone. *Textile Chemist and Colorist & American Dyestuff Reporter, 1*(3), 55–60.

Welch, C. M., & Peters, J. G. (2000). Additives for improved whiteness and DP performance with citric acid finishing. *Textile Chemist and Colorist & American Dyestuff Reporter, 32*(10), 37–41.

Welch, C. M., & Peters, J. G. (2002). Effect of an epoxysilicone in durable press finishing with citric acid. *AATCC Review, 2*(1), 21–24.

Yang, C. Q., Mao, Z., & Lickfield, G. C. (2000). Ester crosslinking of cotton cellulose by polycarboxylic acids: pH-dependency. *Textile Chemist and Colorist & American Dyestuff Reporter, 32*(11), 43–46.

Yatagai, M., & Takahashi, Y. (2005). Effect of citric acid DP finishing on soiling with particulate soil of cotton fabric. *AATCC Review, 5*(1), 17–21.

Yatagai, M., & Takahashi, Y. (2006). Particulate soiling properties of cellulosic fabrics DP-finished with polycarboxylic acids. *AATCC Review, 6*(6), 44–48.