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Crease Resistant Finishing of Cotton Fabric with a Complex of Fibroin and Citric Acid

Abstract
A complex of fibroin and citric acid was prepared and used for the crease resistant finishing of cotton fabrics, which increased the crease resistance of cotton and avoided fabric yellowing caused by citric acid as a finishing agent for cotton. An orthogonal experiment design and variance analysis were adopted to investigate optimum processing parameters for the multiple quality characteristics of treated cotton fabrics. According to range and variance analyses from the orthogonal experiments, fibroin was the most sensitive factor influencing the whiteness index of the fabrics, and citric acid had a more marked effect on crease recovery. The optimum combination of the processing parameters was 4% fibroin, 20 g/dm^3 of citric acid, 5% sodium dihydrogen phosphate, a pH 6 finishing bath and a curing temperature of 130 °C.

Key words: *fibroin, citric acid, crease resistance, orthogonal experiments, cotton fabrics.*

Introduction

A severe limitation of fabrics made of all or mostly cellulosic fibres is their tendency to wrinkle. Crease resistance is imparted to cellulosic fibres by restricting the slippage of molecular chains through crosslinking. Effective chemical finishing methods that can improve the resiliency of cellulosic fibres include graft-copolymerisation, reaction with epoxides, and dibasic acid anhydrides [1, 2]. Amino formaldehyde resins such as dimethyloldihydroxylethyleneurea (DMDHEU) have long been used for the crease resistant finishing of cotton, but they have one major disadvantage: formaldehyde release, which has an impact on human health and the environment [3 - 5]. These days, research on crease resistant finishing has focused on using such multifunctional carboxylic acids as nonfomaldehyde to replace traditional DMDHEU [6 - 8]. However, finishing based on multifunctional carboxylic acids causes yellowing in cotton fabrics [9]. Silk fibroin, which is a natural protein mostly composed of glycine, alanine, serine and tyrosine and contains large amounts of hydroxyl, has been studied in the field of biomaterials due to its specific functionality [10]. Due to the large amount of hydroxyl contained in silk fibroin, it is expected that silk fibroin may be used as an adhesive protein by itself or with other materials abundant in functional groups such as carboxyl. Although crease resistant finishings of silk fibroin (SF) with other finishing agents such as water-soluble polyurethane, glyoxal, etc, have been reported [11], there has been no study concerning multifunctional carboxylic acids used in crease resistant finishing with silk fibroin.

Experimental

Materials

Cotton fabrics (scoured and bleached plain weave, 120 g/m^2) were obtained from Chongqing No. 4 Weaving Factory. Fibroin was prepared from raw cocoons from the Institute of Sericulture and Systems Biology, Southwest University. All the chemicals used, such as citric acid, sodium dihydrogen phosphate, calcium chloride, ethyl alcohol, hydrochloric acid were analytical grade and purchased from Chongqing Chemical Reagent Factory (Chongqing, China).

Preparation of silk fibroin solution

The raw cocoon was degummed using aqueous sodium carbonate solution (0.3% o.w.f.) for 60 min with marseilles soap (0.5% o.w.f.) at boiling point to remove sericin and other impurities and then rinsed thoroughly in warm distilled water. The degummed silk fibroin was dissolved in a ternary solvent system of calcium chloride, water and ethyl alcohol ($CaCl_2$: water : eythyl alcohol = 1 : 8 : 2, molar ratio) at 85 °C for 30min under reflux and then dialysed in a semi-permeable cellulose tube (molecular cutoff = 12,000 - 14,000) for 3 days at room temperature to remove neutral salts. The aqueous silk fibroin solution was hydrolysed in hydrochloric acid (3 mol/dm^3) at 70 °C for 150 min and then neutralised with sodium hydroxide[12, 13]. The concentration of aqueous silk fibroin solution was about 10% and might be diluted according to experiment requirements.

Pad-dry-cure process

Test fabrics were impregnated by padding them through a finishing bath containing fibroin solution, citric acid, the complex of fibroin and citric acid, respectively, to give an approximately 100% pick up. The padded fabrics were dried at 80 °C for 5 min then cured for 3 min. The cured fabrics were washed with water and dried at room temperature. The experimental condition for the finishing process with a fibroin finishing agent is a concentration of silk fibroin of 5%, and a concentration of sodium dihydrogen phosphate of 0.3 g/dm^3. Crease resistant finishing with citric acid was carried out at a concentration of citric acid of 60 g/dm^3, and concentration of sodium dihydrogen phosphate of 60 g/dm^3. The experimental conditions of the treatment with the complex of fibroin and citric acid was a concentration of silk fibroin of 5%, a concentration of citric acid of 30 g/dm^3, a concentration of sodium dihydrogen phosphate of 1.5 g/dm^3. Results of the three experiments mentioned above are presented in ***Table 3***.

Optimisation of crease resistant finishing with the complex of fibroin and citric acid

An orthogonal $L_{16}(4)^5$ test design for crease resistant finishing with the complex of fibroin and citric acid was used for optimisation of the treatment conditions. The process of the orthogonal experiments was same as the "Pad-dry-cure" process. In this study, sixteen treatments were carried out at curing temperatures of 130, 140, 150 and 160 °C, with a concentration of fibroin of 0, 2, 4, 6%, a concentration of citric acid of 10, 20, 30, 40 g/dm^3, a concentration of sodium dihydrogen phosphate of 5, 6, 7, 8%, and at pH 5, 6, 7, 8 on the basis of the single-factor test. ***Table 1*** shows the orthogonal experimental factors and their levels for crease resistant finishing with the complex of fibroin and citric acid. Then the control factors selected and their levels were placed into an $L_{16}(4)^5$ orthogonal

Table 1. Factors and levels for the orthogonal test.

Variable	Level			
	1	2	3	4
A, Fibroin, %	0	2	4	6
B, CA, g/dm3	10	20	30	40
C, NaH_2PO_4,%	5	6	7	8
D, pH	5	6	7	8
E, Cure temp., °C	130	140	150	160

Table 2. $L_{16}(4)^5$ orthogonal design.

No.	A	B	C	D	E
1	0	20	7	7	140
2	4	40	6	5	140
3	2	40	8	7	150
4	6	20	5	5	150
5	0	30	8	5	160
6	4	10	5	7	160
7	2	10	7	5	130
8	6	30	6	7	130
9	0	10	6	8	150
10	4	30	7	6	150
11	2	30	5	8	140
12	6	10	8	6	140
13	0	40	5	6	130
14	4	20	8	8	130
15	2	20	6	6	160
16	6	40	7	8	160

array according to the rules of the experiment, as indicated in ***Table 2***. A total of 16 experiments were conducted in accordance with the orthogonal array. The tearing strength, crease recovery angle (CRA) and whiteness index (WI) were tested for each group of the experiment, respectively.

Measurements

The tearing strength of the treated fabrics was tested according to ASTM Methods D 1424-96, and the retained strength ratio (TS) was calculated based on the difference between the tearing strength of the fabrics before treatment and that after treatment divided by that before treatment. The crease recovery angle (CRA) of the fabrics was measured on YG541D crease recovery apparatus, which is similar to that used in AATCC Standard Methods 66-1990. The fabric whiteness index (WI), namely R457 whiteness according to the ISO Standard, was determined on a WSB whiteness meter.

Results and discussion

We first studied the effects of the treatment on the tearing strength, the crease recovery angle (CRA) and whiteness index (WI) with three finishing agents, respectively. The results are presented in ***Table 3***.

It was evident that the crease resistant finishing increased the crease recovery of the fabric. The CRA for cotton without treatment was 122°. When the fabric was treated with fibroin, its CRA was enhanced to 161°, which was lower than that with citric acid. However, the crease resistant treatment of cotton caused a decrease in the tearing strength of the fabric.

We also studied changes in the whiteness index of the crease resistant finished fabrics. The fabric treated with citric acid appeared to have a lower whiteness index, which was 82, than without treatment, whereas the whiteness index for cotton treated with fibroin and the complex of fibroin and citric acid, respectively, was 88, 91. The improvement in the whiteness index was evidently caused by the etherification of citric acid and polyhydric-hydramine, such as threonine and serine, which is contained in silk fibroin in abundance. The yellowness-retarding effect of triethanolamine on crease resistant finishing with citric acid was reported in the literature[14, 15].

Table 4 shows the results of the orthogonal experiments. The following ***Tables 5 - 7***, were the weighting tables for each level of factors. According to the weighting tables, the optimum compounding among A, B, C, D and E could be found, which revealed the various trends for the different experimental factors and then guided further experiments with more optimum experimental compounding modes.

The range analysis could be calculated and the comparative importance of each factor distinguished, which was the maximum value minus the minimum value, denoted as R_j.

According to the range analysis of the crease recovery angle (CRA), the important influencing factors were B, E, C, D, A in sequence. According to a similar analysis of the strength ratio retained (TS), E, A and B had the most sensitive effect on the tearing strength of cotton fabrics. For the whiteness index (WI), the concentration of fibroin finishing agent had a more sensitive effect on the whiteness index than the other factors - D, E, B, C.

Table 3. Performance of the finished cotton fabrics.

Treatment	CRA/°, (W+F)	TS/%	WI
Untreated	122	100	87
Fibroin	161	87	88
CA	179	72	82
Fibroin/CA	176	88	91

Table 4. Results of the $L_{16}(4)^5$ orthogonal experiment.

No.	CRA/°, (W+F)	TS/%	WI
1	185	77	84.8
2	169	52	86.6
3	173	50	86.3
4	207	22	85.7
5	164	95	84.7
6	182	90	90.2
7	175	94	90.3
8	164	94	90.5
9	192	97	83.6
10	172	68	91.0
11	172	74	92.7
12	169	97	92.3
13	174	117	88.0
14	190	101	89.4
15	178	72	89.7
16	178	49	89.1

Table 5. Range analysis of crease recovery (CRA).

Levels	A	B	C	D	E
I_j	715	718	735	715	703
II_j	698	760	703	693	695
III_j	713	672	710	704	744
IV_j	718	694	696	732	702
R_j	20	88	39	39	49

Table 6. Range analysis of strength ratio retained (TS).

Levels	A	B	C	D	E
I_j	386	378	303	263	406
II_j	290	272	315	354	300
III_j	311	331	288	311	237
IV_j	262	268	343	321	306
R_j	124	110	55	91	169

Table 7. Range analysis of WI.

Levels	A	B	C	D	E
I_j	341.1	356.4	356.6	347.3	358.2
II_j	359.0	349.6	350.4	361.0	356.4
III_j	357.2	358.9	355.2	351.8	346.6
IV_j	357.6	350.0	352.7	354.8	353.7
R_j	17.9	9.3	6.2	13.7	11.6

Table 8. *Distinctiveness showing the variance for each experimental factor.*

Indicators	A	B	C	D	E
CRA	19.83	355.0	72.17	69.17	124.2
TS	705.1	687.7	135.6	353.9	1220
WI	17.90	9.300	6.200	13.70	11.60

Further variance analysis managed to detect the distinctiveness of each experimental factor, which was achieved by way of calculating the variance for each factor among the different levels, $V_j = S_j/f_j$, where S_j is the sum of deviations squared for each factor and f_j - the freedom defined as the level number minus one.

According to the distinctiveness shown in ***Table 8***, the most sensitive factor influencing the crease recovery of cotton was the concentration of citric acid, which had little effect on the tearing strength and whiteness index of the fabrics; hence the optimum concentration of citric acid was 20 g/dm^3. The concentration of fibroin had a marked influence on the whiteness index and tearing strength. Compromising between the two indicators, the optimum concentration of fibroin was 4%. A significant factor for the strength ratio retained was the cure temperature, whose optimum was 130°C. Due to the pH and concentration of sodium dihydrogen phosphate, this had little marked influence on experimental results; the optimum condition was pH = 6 and $C_{NaH_2PO_4}$ = 5%, being a compromise between the three indicators.

Under optimum experimental conditions i.e. $C_{Fibroin}$ = 4%, C_{CA} = 20 g/dm^3, $C_{NaH_2PO_4}$ = 5%, pH = 6 and T_{cure} = 130 °C, the crease recovery angle, whiteness index and strength ratio retained increased to about 180°, 90 and 95%. It was evident that the performance of cotton fabrics treated with a complex of fibroin and citric acid was improved.

Conclusions

The complex of fibroin and citric acid can remarkably improve the crease resistance of cotton fabrics, such as the crease recovery angle and tearing strength, and can especially increase the whiteness index; hence it is an effective crease resistant finishing agent for cotton fabrics.

Traditional pad-dry-cure process technology can be used in the crease resistant finishing of cotton fabrics with the complex of fibroin and citric acid. In this study, the orthogonal method was used to establish optimum processing parameters for the multiple quality characteristics of treated cotton fabrics with few experiments. According to the range and variance analyses, optimum combinations of the processing parameters are shown below: 4% fibroin, 20 g/dm^3 of citric acid, 5% sodium dihydrogen phosphate, pH 6 finishing bath and a curing temperature of 130 °C .

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