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Improvement of Ink-Jet Printing Performances Using β-Cyclodextrin Forming Inclusion Complex on Cotton Fabric

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Abstract: Cotton fabric was modified with β-cyclodextrin (β-CD) forming inclusion complex to yield color strength, pattern sharpness, and color fastness for ink-jet printing. The modified cotton fabric was confirmed with the presence of new strong absorption peaks around 1713 cm^{-1} and 1243 cm^{-1} in FT-IR. β-CD had been covalently grafted on cotton fabric via the esterification reaction of citric acid (CTR) with cellulose and β-CD. The results indicated that printing performances of the ink-jet printed fabric were enhanced through β-CD modification. The *K/S* value was enhanced from 4.21 to 6.72, the width of printed line was decreased from 1.48 mm to 1.25 mm, and the color fastness was improved to 3-4 level. These improvements were due to the truncated cone structure of β-CD, which can form inclusions with water-based pigment. Meanwhile, the crease recovery performance was also improved with the aid of CTR. A comparison between the unmodified and modified cotton fabric suggested that the crease recovery angle of β-CD modified cotton fabric was increased by 25.0 % in the warp direction. Therefore, printing performance and crease recovery performance of β-CD modified and water-based pigment printed cotton fabric were enhanced remarkably.

Keywords: Ink-jet printing, Modification, β-Cyclodextrin, Color strength, Cotton fabric

Introduction

Digital ink-jet printing technology has been widely applied in textile for two decades and it has found an increasing tendency of applications. Traditional flat and rotary screen-printing technologies might be partly replaced by ink-jet printing in the near future, considering ink-jet printing offers significant benefits such as flexibility, creativity in patterns design and cleanliness, energy-savings and eco-friendliness in the producing process [1]. Besides, the ink-jet printing technique has shorter period than the traditional techniques.

Aqueous dye-based ink is often used in ink-jet printing due to its good characteristics, such as low cost, excellent water solubility, high tinting strength, distinct color and superb stability. However, aqueous dye-based ink shows poor light and oxidation-reduction fastness, bad water resistance, and easy fading, which limit its application. On the contrary, pigment-based ink presents excellent washing and light fastness, good water resistance, not easily faded and giving fuller shades without any pretreatment [2]. In addition, pigment-based inks can be applied to all types of textile fabric substrates [3]. Besides, the environment-friendly ink has become the trend of development. Therefore, it is crucial to develop water-based pigment inks.

Cotton fabrics are widely used as substrate in ink-jet printing for its excellent characteristics such as soft handle, good absorbency, and permeability. In general, cotton fabrics printed with reactive dye-based ink are treated with aqueous liquor containing alkali, urea, and thickening agent via a pad-dry process. Alkali is used to promote dye fixation on the fabric. The hydroxyl groups of cotton fabric react with the reactive groups of reactive dye to form covalent bonds. However, the conventional printing chemicals, such as alkali, urea, thickener, and adhesive, could not be incorporated into the ink-jet printing ink formulations and used in ink-jet printing process directly [4]. Besides, the alkali will cause corrosion of the printing nozzle [5].

Cyclodextrins (CDs) produced from enzymatic starch degradation are natural cyclic oligosaccharides with 6-12 anhydroglucose units in their ring structure. The cavity of CDs is suitable for hydrophobic molecules to lodge inside owing to its similarity and intermiscibility. However, CDs and their complexes are highly water-soluble because the exterior of the toroid. Due to its special structure, CDs can form the host-guest complexes with hydrophobic molecules, and thus they have been widely applied in textile, such as spinning [6], pretreatment [7,8], dyeing, printing [9], and finishing [10-12]. In general, α-, β-, γ-CDs with 6(α), 7(β), 8(γ) anhydroglucose units in the ring structure are used in experiment and industry. Of these CDs, β-CD is more suitable for small molecule dyes in the level dyeing process [13] due to its proper inside cavity size and lower cost for production. Owing to its special structure of β-CD, it can be applied to enhance the dope-dyed effect, color strength and color fastness. In the dope-dyed process, β-CD is used as a bridge to link the substrate with hydrogen bonds and dyes with inclusions via its special truncated cone structure [14]. Color strength and fastness of cotton fabrics are significantly improved via formation of inclusion complexes and host-guest interactions, which enhance the extent of interaction and fixation [15]. β-CD can be also employed as a retarding reagent for polyacrylonitrile (PAN) fibers dyed with cation

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*Corresponding author: wangchaoxia@sohu.com dyes to gain darker colors and better color levelness [16]. However, during ink-jet printing process, ink droplets sprayed onto fabrics are easily penetrated to the surroundings resulting in motion blur patterns and poor color strength [17]. Thus, pretreatment is needed to prevent bleeding and improve absorption property, pattern sharpness and aesthetic feeling of fabric [18,19]. The special structure of β-CD can form inclusion compounds with dyes, which can enhance the absorbency and light stability of dyes. For some aromatic ring cyanine dyes with big substituents, β-CD can be used to improve light stability significantly [20]. Ink-jet printed polyester fabric modified with β-CD exhibits higher sharpness and deeper color strength than the unmodified polyester fabric [21].

In this paper, a facile modification method of cotton fabric with β-CD to improve the ink-jet printing performances is proposed. Cotton fabric was modified with β-CD and crosslinked with citric acid (CTR), which sodium hypophosphite (SHP) was applied as a catalytic agent. The β-CD modified cotton fabric exhibited better performances in terms of color strength, pattern sharpness and color fastness. Most importantly, both the β-CD modification and ink-jet printing process were all energy-saving and very efficient. The β-CD modification method of cotton fabric offers a promising way to improve the ink-jet printing performances.

Experimental

Materials

The poplin, 100 % singed, desized, scoured, and bleached cotton substrate (Density: 320×230, Fabric weight: 153 g/m^2), was supplied by Jiangsu Hongdou Industrial Co., Ltd. (China). β-cyclodextrin (β-CD) and citric acid (CTR) employed as a surface modifier and crosslinking agent were purchased from Sinopharm Shanghai Chemical Reagent Co., Ltd. (China). Sodium hypophosphite (SHP) which was used as a catalyst was purchased from Shanghai Lingfeng Chemistry Co., Ltd. (China). C.I. Magenta (PR.122, purity 99.9 %, as shown in Figure 1) was acquired from Jiangsu Multicolor Fine Chemical Industry Co., Ltd. (Wuxi, China). Water-based pigment ink-jet printing inks were prepared in the laboratory [22].

Preparation of β-CD Modified Cotton Fabric

β-CD/CTR and SHP were dissolved in water at 80 °C under continuous stirring until adequate dissolution. Cotton fabrics were twice dipped into the adequately stirred aqueous solution and the dipped cotton fabrics were padded three times with a 70 % wet pick-up. Then the fabrics were dried at 90 °C for 6 min, cured at 180 °C for 10 min, and washed with 50 °C water for three times to remove the residual β-CD and CTR. Cotton fabrics were modified with modified liquid containing 100 g/*l* β-CD, 100 g/*l* CTR, and 30 g/*l* SHP.

Ink-Jet Printing of Modified Cotton Fabrics

Aqueous pigment inks were prepared by adding ultra-fine pigment. Ink-jet printing was carried out by an Epson R-230 ink-jet printer under the condition of 25 °C and 65 % relative humidity (R.H.). Cotton fabric was printed with pigment-based inks and its default line width was 0.5 mm, 1.0 mm and 1.5 mm. The resolution of ink-jet printing was 1440 dpi on the fabric. Printed samples were dried in a preheated oven at 60 °C for 20 min and cured at 150 °C for 5 min. The chemical structures of β-CD, CTR, and C.I. Magenta and the modification, printing, and finishing processes of cotton fabric were shown in Figure 1.

Characterization

FT-IR spectra were recorded with a Bruker Vector 22 spectrometer using a DTGS detector. Prior to the preparation

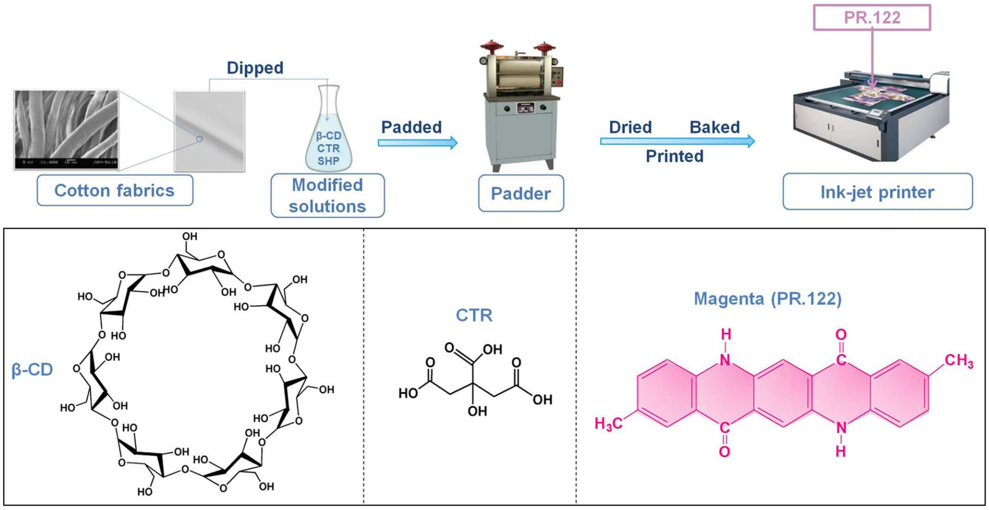

Figure 1. β-CD modified and water-based pigment inks printed cotton fabric processes.

of the KBr pellets the cotton samples were cut into small pieces and ground with a ZM-1 (Retsch, Haan, Germany) rotor mill. The spectra were scanned for 200 times and the spectral resolution was 4 cm^{-1}. Chemical structures of cotton fabrics were investigated by FT-IR spectroscopy. The cotton fabrics were dipped into adequately stirred aqueous solution for three times with a bath ratio of 1:50 before they were padded. The unmodified and modified fabrics were scanned by the Fourier-Raman spectrometer in the region between 400 and 4000 cm^{-1} in order to investigate the β-CD modification of cotton fabrics.

Crease Recovery Measurement of β-CD/CTR Modified Cotton Fabrics

Crease recovery properties were determined according to the standard AATCC Test Method 66-2008 using a crease recovery tester model YG(B)541D supplied by Wenzhou Darong Textile Instrument Co., Ltd. The test was carried out at 21 °C and 65 % R.H. for 24 h using a load of 10 N for 5 min. The samples were typically cut into a standard rectangular shape for crease recovery measurements. The fast elasticity was recorded when the pressure was immediately relieved and the delayed elasticity was recorded when the pressure was relieved 5 min later. Crease recovery angle can render the evaluation of cross-linking reaction between a crease-resistant finishing agent and the cellulosic material.

Breaking Strength Measurement of β-CD/CTR Modified Fabrics

Breaking strength was measured in accordance with ASTM D5034-09 (2013) “Standard Test Method for Breaking Strength and Elongation of Textile Fabrics (Grab Test)”. The samples were kept at 21 °C and 65 % R.H. for 12 h. Measurements were made in the warp and weft directions, respectively.

Measurement of Shear Properties

Shear stiffness was measured in accordance with ASTM-D5379 (2013) “Standard Test Method for Shear Properties of Composite Materials by the V-Notched Beam Method”.

Measurement of Color Strengths

Color strength was tested by an X-Rite 8400 spectrophotometer obtained from American X-Rite Co. Ltd.. *K/S* value of ink-jet printed cotton fabric was measured by the system of CIE Lab, D65 lamp-house, and the 10° visual angle. Color strength denoted by *K/S* value was determined with the Kubelka-Munk equation,

$$\frac{K}{S}=\frac{(1-R)^2}{2R}$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the fractional reflectance (value from 0 to 1) of the colored fabric at the wavelength of maximum reflectance. Five different regions of the ink-jet printed cotton fabric were measured to ensure the accurate results.

Video Microscope Image Measuremrnt of Ink-Jet Printing Design

The printed pattern lines were photographed into images and magnified 75 times with a magnification (Pinnacle Studio Version 8.0). The width of the printed line on front side and back side of printed fabric was measured by the line width measurement software (Image-Pro Express), and then the actual width of the line was averaged.

Color Fastness Test

Washing fastness of printed cotton fabric was tested according to ISO 105-C06:2010 “Textiles-Tests for color fastness-Part C06: Color fastness to domestic and commercial laundering” with 12-A washing fastness tester supplied by China Wenzhou Darong Textile Machine Factory. Fading percentage of ink-jet printed cotton fabric was calculated according to the equation as follows,

$$D=\frac{r_A-r_B}{100-r_B}\times 100\%$$

where D is fading percentage, r_A is the reflectance after washing fastness test and r_B refers to the reflectance before washing fastness test.

Crocking fastness was measured in accordance with ISO 105-X12:2005 “Colorfastness to Crocking: AATCC Crockmeter Method-Partly Equivalent” using Y5711 dyeing rubbing color fastness device obtained from Laizhou Electronic Apparatus Co. Ltd. The color change and staining were evaluated by the greyscale.

Results and Discussion

FT-IR Spectroscopy

Figure 2 showed FTIR spectra of the β-CD modified and unmodified cotton fabric. The new strong absorption peaks

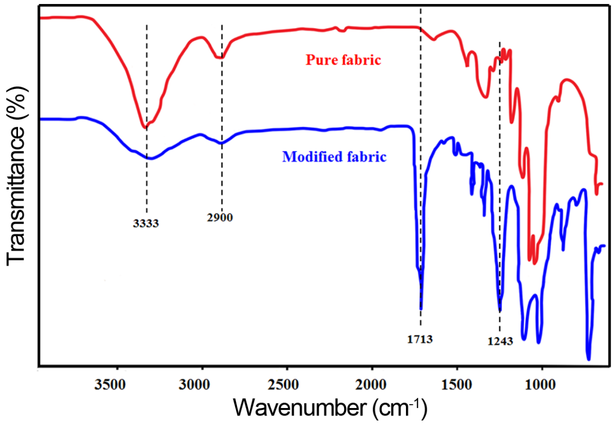

Figure 2. FT-IR spectra of cotton fabrics.

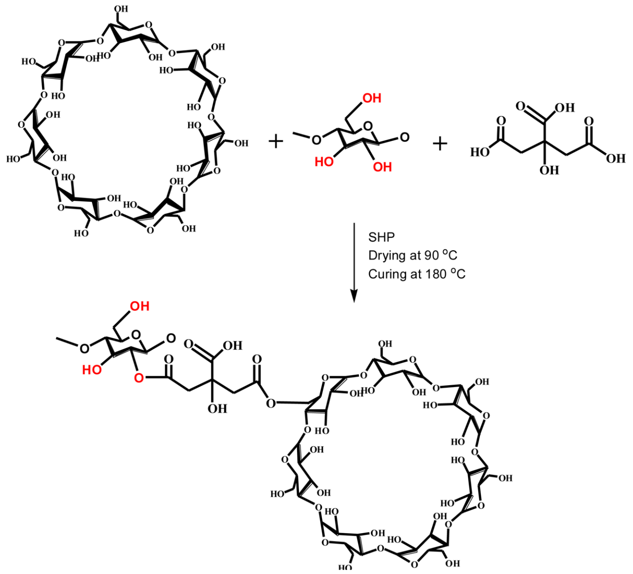

Figure 3. Mechanism of β-CD modified cotton fabric.

appearing around 1713 cm^{-1} and 1243 cm^{-1} of the modified cotton fabric were attributed to -C-O stretching vibration, which was in accordance with the theory of cotton fabrics modified by β-CD/CTR. Ester bond (-COO-) was generated between hydroxyl groups of both β-CD and cotton fabric reacted with the carboxyl groups of CTR. FTIR analysis showed that the existence of a covalent link and indicated that cotton fabric was modified by β-CD/CTR.

Figure 3 illustrated that carboxylic groups (-COOH) of CTR are able to form ester linkages (-COO-) with hydroxyl groups (-OH) of both cotton fabric and β-CD via esterification reaction. Cotton fabric is treated by modified liquid, padded to a wet pick up of 70 %, dried at 90 °C for 6 min, and cured at 180 °C for 10 min. The carboxyl groups of CTR may not react with the hydroxyl groups of cotton fabric and β-CD under drying condition. Upon curing condition, CTR reacts with both cotton fabric and β-CD via esterification reaction, resulting in β-CD modified cotton fabric through the ester linkage [23].

Fabric Crease Resistance

CTR is usually used as a finishing agent in the wrinkle recovery or free easy-care finishing process of cotton fabric. In this paper, CTR was used as a crosslinking agent and it also played a role in improving the crease recovery performance of cotton fabric. Table 1 indicated that the crease recovery performance of the modified cotton fabric was improved. The fast and delayed elasticity of the modified and unmodified cotton fabric were compared in warp and weft directions, respectively. The fast elasticity of the unmodified cotton fabric was 41.1 °, while the modified cotton fabric was 51.6 ° in the warp direction, which increased by approximately 25.0 %. The fast and delayed elasticity were improved by approximately 33.1 % in the weft direction. As known, higher recovery angle represents better crease resistance property. The obvious improvement of crease recovery performance was attributed to the covalent crosslinks formed between cellulose molecular chain and CTR. The covalent crosslinks enable the β-CD modified cotton fabric to remain its original shape when it was deformed by external force.

Crease recovery performance of cotton fabric can also be reflected through shear stiffness after deformation. *G*, 2*HG*, and 2*HG*5 of shear stiffness represented the capacity of crease recovery resilience. Shear stiffness of cotton fabric before and after modification are shown in Table 2. As can be seen, the shear stiffness *G*, 2*HG*, and 2*HG*5 were decreased from 2.36, 3.55, and 10.18 N/cm of the unmodified cotton fabric to 2.07, 1.83, and 7.43 N/cm of the modified cotton fabric in the weft direction. Shear stiffness of the modified cotton fabric was lower than that of the unmodified cotton fabric in the warp and weft directions, which means crease recovery performance of the modified cotton fabric was better than that of the unmodified cotton fabric. All the test results above indicated that the improved crease recovery angle and the enhanced deformation response performance were due to mutual crosslinks generated between the

Table 1. Crease recovery performances of cotton fabrics

Fabrics	Acute elasticity (°)		Delayed elasticity (°)		Acute & Delayed elasticity (°)	
	Warp	Weft	Warp	Weft	Warp	Weft
Blank	41.1±5.6	47.8±4.4	47.1±3.0	53.8±2.5	88.2±4.9	101.6±3.2
Modified fabrics	51.6±3.3	55.9±6.1	65.8±4.4	67.1±3.9	117.4±3.9	122.9±4.3

Table 2. Shear properties of cotton fabrics

Fabrics	*G* (N/cm)		2*HG* (N/cm)		2*HG*5 (N/cm)	
	Warp	Weft	Warp	Weft	Warp	Weft
Blank	2.87	2.36	4.83	3.55	8.23	10.18
Modified fabrics	2.40	2.07	2.43	1.83	8.05	7.43

G: Shear stiffness; 2*HG*: Hysteretic ϕ=0.5 °; 2*HG*5: Hysteretic ϕ=5 °.

Table 3. Breaking strengths of cotton fabrics

Fabrics	Breaking strengths (N)	
	Warp	Weft
Blank	656±10	302±8
Modified fabrics	464±12	275±3

carboxyl groups of CTR and the hydroxyl groups of both cotton fabric and β-CD via esterification reaction.

Mechanical Properties

Cotton fabric is degraded easily under acidic condition and its strength tends to decline. Therefore, the strength of cotton fabric may decline when it is modified with the solution containing CTR. In order to investigate the strength changes before and after modification, the strength test was carried out and the results were shown in Table 3. As known, breaking strength of the modified cotton fabric was declined by 29 % in the warp direction and 9 % in the weft direction from that of the unmodified cotton fabric. The strength change of cotton fabric was affected by two main factors. Esterification reaction was developed between carboxyl groups of CTR and hydroxyl groups of β-CD and cotton fabric when CTR acted as crosslinking agent. The crosslinks enhanced breaking strength of the cotton fabric. However, the macromolecular chain of cotton fiber might degrade in CTR solution, resulting in the decreasing of breaking strength. As breaking strength of cotton fabric declined after the modification, it was proved that the latter factor effects more significantly.

Color Strength and Sharpness

Figure 4 showed that the maximum absorption wavelength (λ_{max}) of ink-jet printed modified cotton fabric presented the same λ_{max}(610 nm) with that of unmodified cotton fabric, which indicated that the hue of all printed cotton fabric was similar while the color strength, characterized by *K/S* value, was enhanced from 4.21 to 6.72. The front side *K/S* value of -CD modified cotton fabric was significantly increased by nearly 60 % as compared with that of unmodified cotton fabric. The back side *K/S* value of β-CD modified cotton fabric was 0.42, while the *K/S* value of unmodified cotton fabric was 0.73, decreased by 42.5 %. It illustrated that the degree of dye fixation in case of modified cotton fabric was higher than unmodified cotton fabric. The printed modified cotton fabric with water-based pigment ink had a higher *K/S* value and the ink was harder to penetrate to the back side of cotton fabric. The reason was that the pigment-based inks were blocked by β-CD/CTR.

In order to explore pattern sharpness of ink-jet printed cotton fabric, the actual widths of unmodified and modified cotton fabrics were measured in ink-jet printing system through design video microscope images. Figure 5 showed that the printed line width of modified cotton fabric was thinner than that of unmodified cotton fabric. The warp printed lines of unmodified and modified cotton fabric were wider than the weft direction. Due to its excellent hygroscopicity, the cotton fabrics presented good cohesive force to ink droplets. Therefore, it was easy for droplets spread to the internal fiber. Nevertheless, the β-CD modified cotton fabric was easier to generate more hydroxyls. So the ink droplets, which diffused into the surrounding or internal fiber, were blocked successfully by the intense cohesive force.

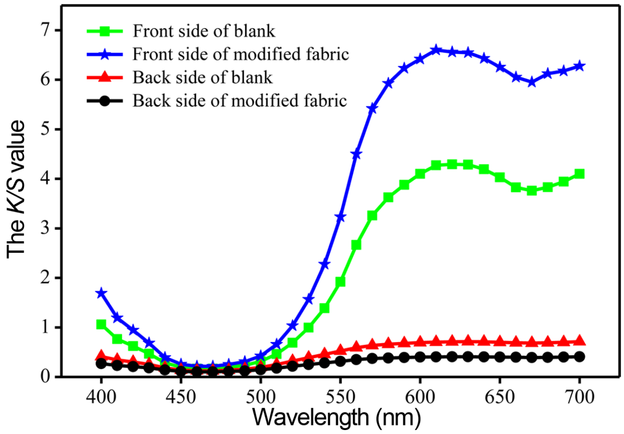

Figure 4. The *K/S* value of printed patterns on cotton fabrics.

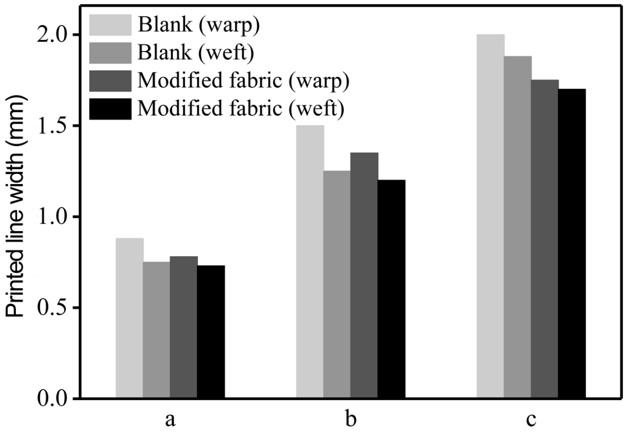

Figure 5. Printed line widths on cotton fabrics; (a) The width of the line is 0.5 mm, (b) the width of the line is 1.0 mm, and (c) the width of the line is 1.5 mm.

Table 4. Crocking and washing fastness of magenta water-based pigment ink-jet printing cotton fabrics

Cotton fabrics	Crocking fastness		Washing fastness	
	Dry	Wet	Color change	Staining
Blank	2	1-2	2	2-3
Modified fabrics	3-4	2-3	3	2-3

Color Fastness

Color fastness is one of the most important printing performances, which are determined by the stability of the ink-fiber system. The color fastness to washing and crocking of pigment ink-jet printed cotton fabrics were given in Table 4. As can be seen from Table 4, color fastness of β-CD modified cotton fabric was higher than that of unmodified cotton fabric by 1-2 grades. The dry crocking fastness of modified cotton fabric could reach 3-4 level. The improvement of color fastness indicated that the water-based pigment inks were fixed firmly on the β-CD modified cotton fabric for forming the inclusion complex between inks and β-CD.

Conclusion

β-Cyclodextrin (β-CD) was modified onto cotton fabric through crosslinkings with citric acid (CTR) in presence of sodium hypophosphite (SHP) as a catalyst. The printed modified cotton fabrics exhibit higher level of printing performances than the printed unmodified cotton fabric. Thus, the modification of cotton fabrics with β-CD might remove the pretreatment which is an environmental unfriendly process. The excellent performances obtained with the modified cotton fabric because that carboxyl groups of citric acid (CTR) reacted with hydroxyl groups of both β-CD and cotton fabric via esterification reaction at the curing temperature 180 °C and the β-CD formed inclusion complex to keep the water-based pigment ink inside the cavity for longer times. The color strength of the modified and unmodified cotton fabric was increased from 4.21 to 6.72 and the actual printing line width was declined from 0.88 mm to 0.74 mm in the warp direction when the ideal line of width was 0.5 mm after the modification. The washing and crocking fastness of the modified cotton fabric were enhanced by 1-2 grades in comparison with unmodified cotton fabric. The crease resistance of modified cotton fabric was also improved with the aid of CTR, and the crease recovery angle of the modified cotton fabric in the warp direction was increased by 25.0 % comparing with the unmodified cotton fabric at the same condition. A comparison between printed modified and unmodified cottons suggest that the method of β-CD modified cotton fabric has the potential application in ink-jet printing.

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