



# Modified chitosan pretreatment of polyester fabric for printing by ink jet ink

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## ABSTRACT

The present research deals with the use of pretreatment solutions of chitosan (CH), N-[(4-dimethyl aminobenzyl)imino] chitosan (DBIC), N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTACC), glycine (Gly), and a mixture of CH and Gly, for padding polyester fabrics prior to printing with a set of seven-color pigmented water-based ink jet inks. After padding the fabrics with the above cationic pretreatments, they were printed with a piezo-electric drop-on-demand jet printer. CH, DBIC and HTACC were characterized by IR and NMR spectroscopy. The zeta potentials of the pretreatment solutions, the inks and the fabrics were measured. The *K/S* values, color gamut, tone reproduction, outline sharpness, and the surface appearance of the fabrics were characterized. Statistical evaluation of the significance of the results was performed. Among the pretreatments, the HTACC at 0.1% (w/v) yielded fabrics with the highest *K/S* values, widest color gamut and gamut volume, more color saturation with good tonal reproduction, and the sharpest and smoothest outline of printed character, and a smooth fabric surface with less stiffness. The proposed ionic interactions between the protonated amino groups of CH and the anionic portion of the encapsulated ink pigments, and van der Waals and hydrophobic interactions between the polyester and the pigments are likely reasons for these enhanced properties of the printed fabrics.

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## 1. Introduction

The pretreatment of fabrics with a suitable agent is a requirement in textile-ink jet printing because the deposited pretreatment chemical on the fabric surface limits excessive ink spreading and controls ink migration and penetration into the fabric fibers, and yet allows the ink to dry after the ink has been jetted (applied) onto the fabric surface. This interaction of the pretreatment agent and the jet ink results in an increase in color gamut, sharpness and other properties of the printed fabric (Hakeim, El-Gabry, & Abou-Okeil, 2008; Leelajariyakul, Noguchi, & Kiatkamjornwong, 2008; Phattananarudee, Chakvattanatham, & Kiatkamjornwong, 2009; Wang et al., 2007; Yuen, Ku, Kan, & Choi, 2007).

Polyester, one of the more popular textile fabrics, needs dyeing and printing to provide the color and pattern ranges required by customers and hence the higher add-on value. Although polyester fabric is hydrophobic, it has a negative zeta potential value (Espinosa-Jiménez, Padilla-Weigand, Ontiveros-Ortega,

Ramos-Tejada, & Perea-Carpio, 2003). Thus, a prospective pretreatment agent with positive charges should be adsorbed onto the polyester fabric due to the requirement of an ionic interaction in enhancing the color and other properties (Samu, Moulee, & Kumar, 1999). Some types of cationic pretreatment agents have been reported to be able to increase the printed polyester color strength (*K/S*) by as much as 36% with ink jet printing when compared with the untreated polyester fabric (Wang et al., 2007).

Chitosan (CH) is widely used as a pretreatment reagent for synthetic polymers due to its green environmental advantages, easy to use and relatively low cost yet abundant supply. Indeed, CH has been extensively used for the dyeing and finishing of various textile fabrics, where the pretreatment of fabrics with CH produced a high color yield, good shrink resistance and provided some degree of antimicrobial activity (Abou-Okeil & Hakeim, 2005; Hakeim, Abou-Okeil, Abdou, & Waly, 2005; Julia, Pascual, & Erra, 2000). In textile-ink jet printing, CH has generally been used as a pretreatment agent for silk fabrics to expand the color gamut and to improve the crock fastness of the printed fabric (Chakvattanatham, Phattananarudee, & Kiatkamjornwong, 2010; Phattananarudee et al., 2009; Yuen, Ku, & Kan, 2008), whilst CH modified with dimethyl aminobenzaldehyde (DBIC) affected the color gamut of the printed polyester (Hakeim et al., 2008). CH is dissolved in acetic acid where upon its amino groups are protonated to form quaternary ammo-

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nium ions, which interact with anionic dyes through electrostatic attraction (Jocic et al., 2005). CH-padded fabrics result in a higher level of pigment adsorption onto the pretreated fabric surface compared to that of uncoated fabrics, and also gave a high color quality on the surface (Chakvattanatham et al., 2010; Phattananurudee et al., 2009).

Unfortunately, the retained acetic acid (from the CH) of the pretreated cotton fabric yields reduced color gamut, compared with the untreated one, and the acrid odor is retained in the printed fabrics after the post-treatment (Yuen et al., 2007), whilst CH also increases the stiffness of the fabrics (Phattananurudee et al., 2009). To solve these problems, the water-soluble CH derivatives with highly positive charges, O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (NMA-HTACC) and N-[(2-hydroxy-3-trimethyl ammonium)propyl] chitosan chloride (HTACC), were synthesized (Kim, Lee, Lee, & Park, 2003; Lim & Hudson, 2004a, 2004b). Previously, the use of NMA-HTACC was reported to increase the color yield in the dyeing of cotton fabrics, whilst HTACC generated antimicrobial activity in the textile (Seong, Whang, & Ko, 2000).

The aim of this research was to modify CH to a cationic form with better solubility. To this end, CH with two different molecular weights and deacetylation degrees were modified to HTACC and DBIC, respectively, so as to improve the pretreatment properties of CH. Due to the solubility of CH in acid, the low average molecular weight CH was used for direct pretreatment and the synthesis of DBIC. The synthesized HTACC and DBIC were then used as pretreatment agents for polyester fabrics, color printed with an ink jet ink. The effects of fabric pretreatment with HTACC, DBIC, CH, Glycine (Gly) and a mixture of CH and Gly were investigated in depth for the color appearance yield in terms of color gamut and gamut volume, color strength and tone reproduction of the subsequently ink jet printed fabrics. In addition, the outline sharpness and evenness of density of the positive and negative characters of the printed polyester fabrics were also investigated along with the stiffness of the printed fabrics.

## 2. Experimental

### 2.1. Materials

A plain weave polyester fabric, constructed of 182 ends/in. (warp)  $\times$  87 picks/in. (weft) with a basic weight of 127 g m<sup>-2</sup>, was used. Triton X-100, a non-ionic surfactant, was supplied by Merck (Frankfurt, Germany). CH flakes of 57,000 g/mol of average molecular weight and 85% deacetylation degrees (DD) was used for the synthesis of N-[(4-dimethyl aminobenzyl)imino] chitosan (DBIC) due to its lower water solubility while CH flakes of 100,000 g/mol of average molecular weight and 95% DD was used to synthesize N-[(2-hydroxy-3-trimethylammonium)propyl] chi-

tosan chloride (HTACC) due to its higher water solubility. Both types of CH were purchased from Seafresh Industry Public Co., Ltd. (Bangkok, Thailand). Gly (98.5% pure) was purchased from Ajax Finechem (Seven Hills, NSW, Australia). N,N'-dimethyl aminobenzaldehyde was purchased from Asia Pacific Specialty Chemical Ltd. (Seven Hills, NSW, Australia). Glycidyl trimethylammonium chloride (GTMAC) was purchased from Sigma-Aldrich (St. Louis, MO). A commercial set of seven-color, pigmented water-based jet inks (Epson Ultrachrome™ Ink), supplied from Seiko Epson Corporation (Suwa, Nagano, Japan), was used for printing the fabrics. Based on the manufacturer's claims, the pigment dispersions were treated by polymeric dispersant and polymer encapsulation to give an average particle size of the encapsulated pigment of approximately 100 nm.

### 2.2. Synthesis of the modified chitosans

#### 2.2.1. N-[(4-dimethyl aminobenzyl)imino] chitosan (DBIC)

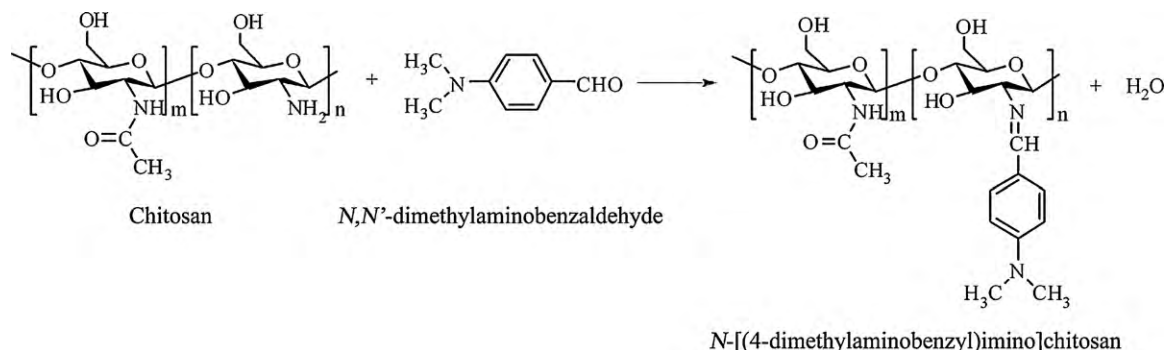
DBIC was prepared based on the method of Hakeim et al. (2008). CH (5 g, average molecular weight = 57,000 g/mol and 85% DD) and dimethyl aminobenzaldehyde (9.3 g) were mixed in 150 mL methanol for 10 h. The product was filtered through a 100-mesh aluminum screen sieve, washed with 300 ml of a 1:1 (v/v) ratio of mixed methanol-acetone solution and then dried overnight at room temperature. The intense yellowish dried product obtained was then characterized by IR spectroscopy (Spectrum One, PerkinElmer Life and Analytical Sciences Inc, MA). The synthetic route is shown in Scheme 1.

#### 2.2.2. N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTACC)

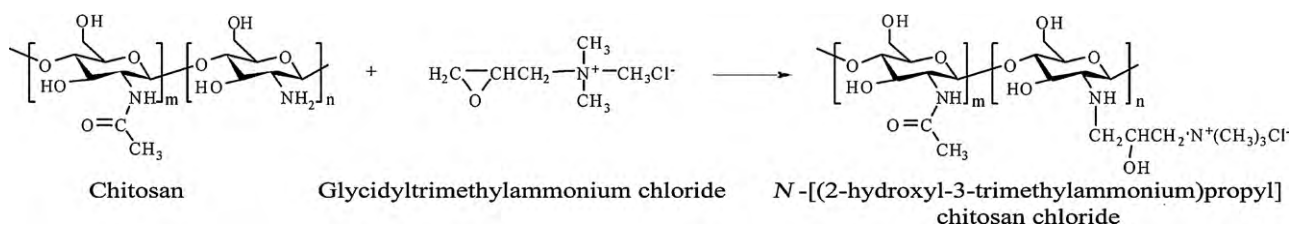
The synthesis of HTACC was modified from that of Seong et al. (2000). In brief, 0.50 g of CH (average molecular weight = 100,000 g/mol with DD = 95%) was dissolved in 25 cm<sup>3</sup> of 1% (v/v) aqueous acetic acid. Then 0.9 g of GTMAC was slowly added into the CH solution whilst maintaining the reaction temperature at 70 °C during the mixing and over the subsequent 24 h. The solution was then poured in a dialysis tubing cellulose membrane (average flat width of 76 mm, Sigma, St. Louis, MO) for dialysis for 5 days against 1000 cm<sup>3</sup> of deionized water, changed every day. The white colored product obtained was freeze dried in a freeze drier (Labconco, MO), and aliquots were then characterized by IR spectroscopy (Spectrum GX, PerkinElmer Life and Analytical Sciences Inc, MA.) and NMR spectrometry (Advance 300 MHz NMR Spectrometer, Bruker, Switzerland). The reaction is shown in Scheme 2.

#### 2.2.3. Preparation of pretreatment solutions

The pretreatment agents of the unmodified CH, having 0.1, 1, 2, 3 and 4% (w/v), were prepared by stirring in 2% (v/v) of acetic acid until the CH (57,000 g/mol) was dissolved. Gly concentrations, from



**Scheme 1.** Synthesis route of N-[(4-dimethyl aminobenzyl)imino] chitosan from chitosan.



**Scheme 2.** Synthesis route of N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTACC) from chitosan.

5 to 15% (w/v) in deionized water (Elga Deionizer, LA1, Elga Labwater, UK), were prepared. Likewise, 15% (w/v) of Gly was mixed with 1% (w/v) of CH to give a mixed pretreatment solution. The solutions of the two modified CH (HTACC and DBIC) at a concentration of 0.1% (w/v) were prepared by dissolving 0.25 g HTACC in deionized water in a 250 cm<sup>3</sup> volumetric flask, whereas 0.25 g of DBIC was dissolved in 250 cm<sup>3</sup> of 2% (v/v) acetic acid.

#### 2.2.4. Purity of the polyester fabric

Purity of the polyester fabric was evaluated by testing the presence of starch and poly(vinyl alcohol) by iodine in potassium iodide solution by observing the development of purple color. Carboxyl methyl cellulose (CMC) was examined by mixed solution of ferric chloride and potassium thiosulfate which was followed by dropping solution of potassium ferrocyanide. The presence of CMC can develop a purple color on the fabric surface (Livengood, 1983). The optical brightener may interfere the color data therefore the fabric was viewed in an MEDA light color viewing booth under ultraviolet irradiation where the presence of visible fluorescent light shall be detected.

#### 2.2.5. Zeta potential measurement

The ink jet inks, pretreatment solutions, polyester fabric and the pretreated polyester fabrics were all measured for zeta potential using a Nano-ZS, Zeta potential Analyzer (Malvern Instruments Ltd., UK) in a disposable U-shaped cell with each wall accommodating one small piece of a Cu electrode. The zeta potential of the untreated polyester fabric and the pretreated polyester fabrics were measured by first preparing a fabric suspension by pulling out the fibers from the piece of fabric and then cutting the fibers into small pieces of approximately 0.05 cm long. They were then soaked in deionized water for 24 h. The suspension obtained was used for measuring the zeta potential of the pretreated fabrics.

#### 2.2.6. Fabric pretreatment

The polyester fabrics were cleaned with Triton X-100, rinsed in distilled water and dried at room temperature. The cleaned polyester fabrics (23 cm × 32 cm) were then padded with the above mentioned pretreatment solutions using a padding machine (PB-1, Copower Technology Co., Ltd., Taiwan) with a 70% wet pick up. The pretreated fabrics were then dried in an oven (M-3, Copower Technology Co., Ltd., Taiwan) at 80 °C for 5 min and cured at 110 °C for 2 min.

#### 2.2.7. Ink jet printing and post-treatment

The untreated and pretreated polyester fabrics were printed with a set of seven-color, pigmented ink jet inks (cyan, light cyan, magenta, light magenta, yellow, black and light black colors), using commercially available water-based inks on a piezo-electric drop-on-demand type ink jet printer (Epson Stylus Photo 2100, Seiko Epson Corporation, Nagano, Japan). A color test chart, composed of 294 color patches, several lines and characters, was used for investigating the quality of the printed polyester fabrics. Post-treatment of the printed fabric was performed by steaming at 100 °C for 5 min in a steamer (HTS-3, Copower Technology Co., Ltd., Taiwan).

#### 2.2.8. Color gamut evaluation

The color test chart of each printed fabric was measured in tristimulus values using an X-Rite spectrophotometer (SP62, X-Rite Inc., MI) with an illuminant D50, the CIE 1931 2° observer in a specular light excluded mode. The tristimulus values (X, Y, Z) were transformed to chromaticity coordinates (x, y, z) for creating a color gamut in a two-dimensional color space. The  $L^*$ ,  $a^*$  and  $b^*$  color values were used to calculate a gamut volume in a three-dimensional space by SHIPP program (Fair, 1997; Putthimai, 2003). In the same manner, the  $L^*$  vs.  $C^*$  space was also created by measuring the sample lightness and chroma in the CIE  $L^*C^*H^*$  spaces.

#### 2.2.9. Color strength (K/S) measurement

The color strength of inks was determined based on the Kubelka–Munk equation, and expressed as a K/S value, fluctuating from the maximum absorption wavelength of each color within the visible spectrum. The percentage of reflectance was measured by the same spectrophotometer with a specular light excluded condition. The K/S value was calculated according to Eq. (1) (James, 1997):

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

where  $K$  is the absorption coefficient of the printed color on the surface,  $S$  is the scattering coefficient caused by the colored substrate, and  $R_\infty$  is reflectance of the colored sample at an infinite opacity. Evaluation of the significance level of K/S values of the pretreated fabrics compared with the untreated fabric was performed by one-way analysis of variance (ANOVA) with the least square difference (LSD) tests used for post hoc evaluations of differences between groups in Statistical Package for the Social Science (SPSS) version 14.0 software, at a confidence level of 95.0% ( $\alpha = 0.05$ ).

#### 2.2.10. Tone reproduction measurement

The tone reproduction was evaluated by plotting the optical density versus the percentage of the dot area. The optical density was measured by a densitometer (R730, IHARA Electronic Ind. Co., Ltd., Nagoya, Japan).

#### 2.2.11. Outline sharpness and contrast assessment

The printed outline sharpness on the fabrics was measured by optical microscopy (PM10-AD, Olympus Corporation, Tokyo, Japan) with a 4× magnification of 10-point printed positive and negative “E” characters. The black and white line strips printed on the fabrics at the applied spatial frequencies of 0.5, 1 and 2 lines mm<sup>−1</sup> in the two directions (weft and warp) of the polyester fabric of the bar target were measured by a microdensitometer (Konica, PDM-7, Tokyo, Japan). The scanning aperture was set at a width of 20 μm and a reflection mode of 500 μm, and data were then acquired at 20 data points per second to give a total scanning of 400 data points. The densities in each sample were measured and normalized to the untreated fabrics. The contrast at each frequency was calculated from Eq. (2):

$$\text{Contrast}(\omega) = D_{\max}(\omega) - D_{\min}(\omega) \quad (2)$$



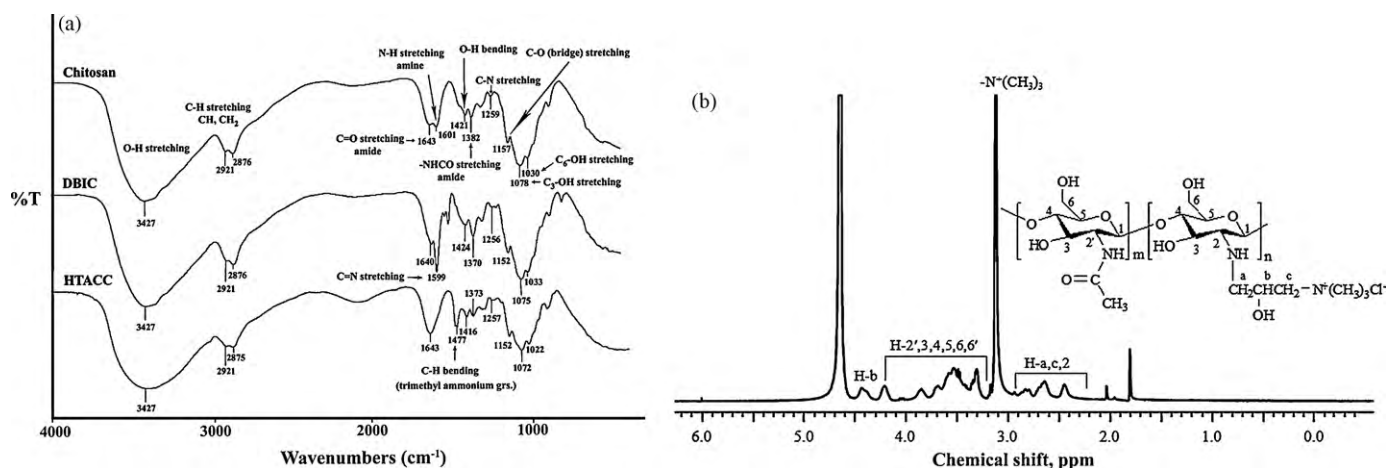


Fig. 1. Confirmation of modified chitosans: (a) IR spectra of chitosan, DBIC and HTACC; (b) <sup>1</sup>H NMR spectra of HTACC (solvent: D<sub>2</sub>O, 25 °C).

where  $D_{\max}$  and  $D_{\min}$  are average maximum and minimum densities, respectively, and  $\omega$  is the spatial frequency. Plots of the densities against the measured frequencies in both the weft and warp fabric directions were constructed. However, calculation of the contrast in the warp direction could not be measured because of the problems in measuring both the densities.

#### 2.2.12. Surface appearance of the pretreated polyester fabrics

The surface of the pretreated polyester fabrics was examined by scanning electron microscopy on a Spectrum One (PerkinElmer Life and Analytical Sciences, Inc., MA) at a magnification of 2000 $\times$ .

#### 2.2.13. Stiffness of the treated fabrics

The stiffness of the fibers was measured in terms of the bending length by following the JISI 1096:1999 stiffness 145° cantilever method (Stiffness Method A, 1999). Pieces of each fabric, sized 2 cm  $\times$  15 cm, were measured and the average bending length in the warp and weft directions, obtained from five measurements, were expressed as the average stiffness. The bending length of the fabrics treated with the selected loadings of the pretreatments were then compared with that for the untreated fabrics, within the same pretreatment agent at various levels, and at the same selected loadings of the five pretreatment agents. The significance of the test was performed by one-way analysis of variance (ANOVA) with the least square difference (LSD) tests being used for post hoc evaluations of differences between groups in Statistical Package for the Social Science (SPSS) version 14.0 software, at a confidence level of 95.0% ( $\alpha = 0.05$ ).

#### 2.2.14. Color fastness to washing and rubbing

The effects of the pretreatment agents on color fastness to washing and to rubbing of the fabrics were investigated based on ISO 105-C10:2006 (E), and AATCC TM 8, respectively.

### 3. Results and discussion

#### 3.1. Characterization of the fabric and the modified chitosans

Under the test conditions mentioned above, it showed that the polyester fabrics were free from starch, poly(vinyl alcohol), and CMC, because the mixed solution of iodine and potassium iodide for starch and poly(vinyl alcohol) did not give the purple color, and a mixed solution of ferric chloride and potassium thiosulfate for CMC did not produce the purple color on the fabric surface either. It was also found that the polyester fabric was free from optical brightener, because the visible fluorescent light

was not observed on the exposed surface under ultraviolet irradiation.

The IR spectra of the unmodified CH and the two modified CHs (DBIC and HTACC) are given in Fig. 1(a). That for CH shows the overlapped peaks of N-H stretching and O-H stretching at 3427 cm<sup>-1</sup> and O-H bending at 1421 cm<sup>-1</sup> which indicates the presence of hydroxyl groups (Sun, Zhou, Xie, & Mao, 2007). The weak absorption peaks at 2921 and 2876 cm<sup>-1</sup> are assigned to the C-H stretching (Huacai, Wan, & Dengke, 2006). The strong characteristic peaks of CH at 1643, 1601, 1382 and 1259 cm<sup>-1</sup> are assigned to the C=O stretching, N-H bending and -NHCO stretching of the amide (Zhang, Wang, & Wang, 2007), and C-N stretching (Singh, Sharma, Tripathi, & Sanghib, 2009), respectively. In addition, the weak characteristic peaks at 1157, 1078 and 1030 cm<sup>-1</sup> are ascribed to the stretching of the C-O bridge (Huacai et al., 2006; Mun et al., 2008) and the C<sub>3</sub>-OH and C<sub>6</sub>-OH groups (Zhang et al., 2007), respectively.

The CH amine N-H bending at 1601 cm<sup>-1</sup> in the IR spectrum of DBIC is absent, but rather the spectrum displays a strong absorption peak at 1599 cm<sup>-1</sup> corresponding to the C=N stretching of DBIC (Hakeim et al., 2008). This confirms that DBIC was synthesized by the reaction between the amino groups of CH and the aldehyde groups of dimethyl aminobenzaldehyde to become the imino groups (C=N) in DBIC.

The IR spectrum of HTACC reveals that the characteristic amine N-H bending peak at 1601 cm<sup>-1</sup> is absent, but rather reveals the presence of the peak at 1477 cm<sup>-1</sup> assigned for the C-H bending of the trimethylammonium groups (Lim & Hudson, 2004a). In addition, the N-H bending of primary amine groups is absent due to changes to the secondary amine. The peak at 3400 cm<sup>-1</sup> was somewhat broadened, caused by the overlapping of the O-H group with the N-H stretching. A weak and broad band at 2200–2000 cm<sup>-1</sup> was observed, potentially assigned to a combination of the asymmetrical N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> bending vibration and to the torsional oscillation of the N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> group.

The <sup>1</sup>H NMR spectrum of HTACC in Fig. 1(b) shows the integrations of the trimethyl ammonium group equals to 1, and the integration of the Hs at the positions 2', 3, 4, 5, 6 and 6' equal to 0.8. The degree of substitution (DS) of GTMAC in HTACC was calculated from Eq. (3):

$$\%DS = \left\{ \frac{\text{integral of the } N^+(CH_3)_3/9}{(\text{integral of the H-2', 3, 4, 5, 6, 6'}/6) \times (95/100)} \right\} \times 100 \quad (3)$$

where %DD is the degree of deacetylation (95/100). From the results, it confirms that HTACC contained 87.7% DS. The calculated

**Table 1**  
Zeta potentials of the materials used.

Type of material	Zeta potential, $\zeta$ (mV)
Ink jet inks	
Cyan	−43.1
Magenta	−56.5
Yellow	−34.7
Black	−36.7
Pre-treating solutions	
1% (w/v) CH	+83.4
15% (w/v) Gly	+24.7
1% (w/v) CH + 15% (w/v) Gly	+65.1
0.1% (w/v) DIBC	+73.2
0.1% (w/v) HTACC	+36.6
Fabrics	
Untreated fabric	−22.6
Treated fabric with 1% (w/v) CH	−21.6
Treated fabric with 15% (w/v) Gly	−26.4
Treated fabric with 1% (w/v) CH + 15% (w/v) Gly	−28.8
Treated fabric with 0.1% (w/v) DIBC	−24.6
Treated fabric with 0.1% (w/v) HTACC	−23.1

average molecular weight of HTACC based on the above mentioned data is 165,000 g/mol with an aqueous solution pH of 6.8.

### 3.2. Zeta potential measurement

The zeta potentials of all four base ink colors were found to be negatively charged, with the magenta color having the highest negative value and the yellow color the lowest, but still relatively high (Table 1). To the best of our knowledge, the pigments of Epson inks are encapsulated by a type of crosslinked polymer to prevent coagulation. It implies that the encapsulated pigmented inks had anionic functional groups (generated negative charges), consistent with their good dispersion stability. Similarly, the polyester fabric also had a negative zeta potential, although of a lower magnitude but still sufficient to likely prevent agglomeration of the particles. For the pretreatment solutions, all of them had positive zeta potentials with CH having the highest value, some 2.3-fold higher than HTACC, whilst Gly had the lowest zeta potential. However, all can be considered to highly likely be stable in an aqueous state. Nevertheless, when the fabrics had been padded with the pretreatment solutions, all the zeta potentials of the treated fabrics became negative at around 22–29 mV, which can be considered to be less stable in terms of agglomeration and aggregation. It is clear that the fabric has a dominant effect because the analyzer measured the entire bulk solution of the substrate with thus only a relatively small (by mass) influence from the deposited thin film from the pretreatment agent. One may assume that at least a minute amount of the pre-

treatment solution and thus agent could be absorbed on the surface and a larger amount penetrated into the polyester fabric, leaving a very thin layer on the fabric surface.

### 3.3. Effects of the pretreatment agents

#### 3.3.1. Color strength

The ink jet inks are transparent due to the inherent nature of the pigments used. The CH solutions in acetic acid (CH having average molecular weight of 57,000 g/mol) were slightly yellow to yellowish brown and so made the background yellowish. The CH having average molecular weight of 100,000 g/mol can dissolve slightly in acetic acid, therefore, CH with average molecular weight of 57,000 g/mol was used as a representative for the fabric treatment. The background color of the fabric interfered with the printed ink color, resulting in inappropriate color assessments. The color value so measured is basically the combined data of both the background color and the ink color. The background color of the fabric was, therefore, used as a reference for all the measured color values so as to obtain the real color yield of the ink and the resultant effect of the pretreatment agent and the ink.

The color strength ( $K/S$ ) of the fabrics subjected to the various pretreatment solutions is summarized in Table 2. Theoretically, all of the pretreated fabrics gave generally the higher  $K/S$  values than the untreated fabrics. For the CH-treated fabrics, lower  $K/S$  values were obtained for cyan, magenta and yellow inks at all CH loadings compared to the untreated fabric. Only the black ink showed a numerically, but not statistically significantly, increased  $K/S$  level at three out of the five CH loadings, that is not for those at 2 and 4% (w/v) CH which had lower  $K/S$  values. In contrast to CH, compared to the untreated fabric, the  $K/S$  values were higher for cyan, yellow and black inks for all Gly loadings tested, whereas for magenta the  $K/S$  values were higher than the untreated fabric at 5% (w/v) Gly, but decreased with increasing Gly loadings to equal to and lower than the untreated fabric at 10 and 15% (w/v) Gly, respectively. However, when the mixed pretreatment of 1% (w/v) of CH with 15% (w/v) of Gly was used, the  $K/S$  values were all lower than that for the untreated fabric and were not as high as those of the pure Gly or CH at the same respective loading levels, except for the yellow ink which was higher than that for 1% (w/v) CH alone. However, none of these numerical differences in the  $K/S$  values relative to the untreated fabric were statistically significant except for those at 1% (w/v) CH for cyan color, 15% (w/v) Gly and the 15% (w/v) Gly mixed with 1% (w/v) CH for cyan, black and magenta colors.

Pretreatment of the fabric with DIBC also gave lower  $K/S$  values than the untreated fabric for all four inks. In contrast, pretreatment of the fabric with HTACC gave a remarkable and the highest improvement in the  $K/S$  values with the concentration of HTACC

**Table 2**  
The color strength ( $K/S$ ) and gamut volume of untreated and pretreated polyester fabrics.

Polyester fabrics		$K/S$ at $\lambda_{\max}$				
Pretreatment	Concentration (% w/v)	Cyan 620 nm	Magenta 540 nm	Yellow 400 nm	Black 400 nm	Gamut volume
Untreated	–	2.53	4.79	5.38	3.61	6859
CH-treated	0.1	2.61	3.54	5.11	4.25	6967
	1	1.77	3.25	2.78	4.40	7535
	2	1.54	2.56	3.05	2.93	6820
	3	2.12	3.21	3.37	5.74	6961
	4	1.57	2.47	5.20	2.40	7205
Gly treated	5	3.57	5.07	6.77	3.77	7557
	10	3.04	4.80	7.00	8.50	7703
	15	2.90	4.19	6.26	7.57	7846
CH + Gly treated	1 + 15	1.67	3.10	4.56	2.61	6277
DBIC treated	0.1	2.28	4.48	4.2	3.02	7219
HTACC treated	0.1	8.74	14.15	29.14	30.40	12950

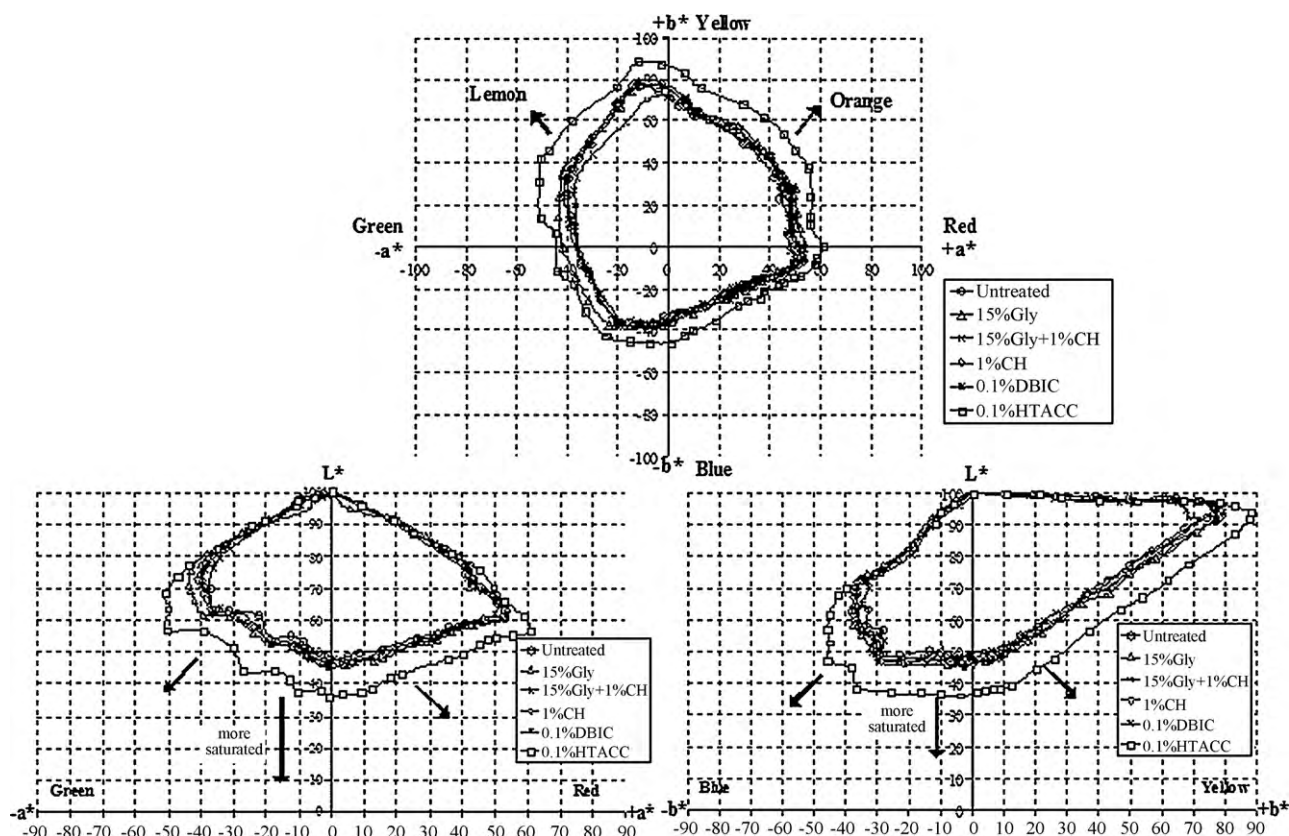


Fig. 2. Color gamuts of the printed fabrics after various pretreatments expressed as  $a^*b^*$  for the red–green color vs. yellow–blue color;  $L^*a^*$  for lightness vs. red–green color;  $L^*b^*$  for lightness vs. yellow–blue color. Data are the mean values, derived from 3 independent repeats.

as low as 0.1% (w/v). Indeed, HTACC pretreatment increased the  $K/S$  values of the cyan, magenta, yellow and black inks by some 5-, 4-, 9- and 11-fold, respectively, above that of the untreated fabric. These numerical increases in  $K/S$  values were statistically significant ( $p < 0.05$ ).

### 3.3.2. Color gamut and gamut volume

A more meaningful presentation of color is the color gamut in the CIE  $L^*a^*b^*$  and  $L^*C^*H^*$  system because a more complete color information can be obtained. The color gamut produced by the pretreatment solutions is given in Fig. 2, in which the CIE  $a^*b^*$ ,  $L^*a^*$  and  $L^*b^*$  gamuts are shown separately. In all the three gamuts, the 0.1% (w/v) HTACC pretreatment clearly gave the widest gamut followed by 15% (w/v) Gly, while the rest of the pretreatment solutions were only slightly different from each other and the untreated reference fabric. The HTACC treatment produced a far more saturated lemon and orange color, as shown in the CIE  $a^*b^*$  gamut, a saturated green and red color, as shown in the  $L^*a^*$  gamut, and saturated blue and yellow colors, as seen in the  $L^*b^*$  gamut. Moreover, the calculated gamut volumes of the untreated and treated fabrics are summarized in Table 2. One can see that increasing the pretreatment solution increased the gamut volume of the printed colors whereas only 0.1% (w/v) of HTACC padded fabric produced the highest gamut volume. Interestingly, the  $K/S$  values and the size of gamut volume were not really related in every case, as seen in the case of 0.1 and 1% (w/v) treatment by CH (Table 2). This is due to the fact that the  $K/S$  was calculated from colors of the cyan, magenta, yellow and black inks, whereas the gamut volume was calculated from all colors produced in the color sphere. Thus, the gamut volume is a better tool for comparison of the effect of pretreatment of the fabric on the color yield from subsequent printing because it represents the colors that are actually seen.

### 3.3.3. Tone reproduction

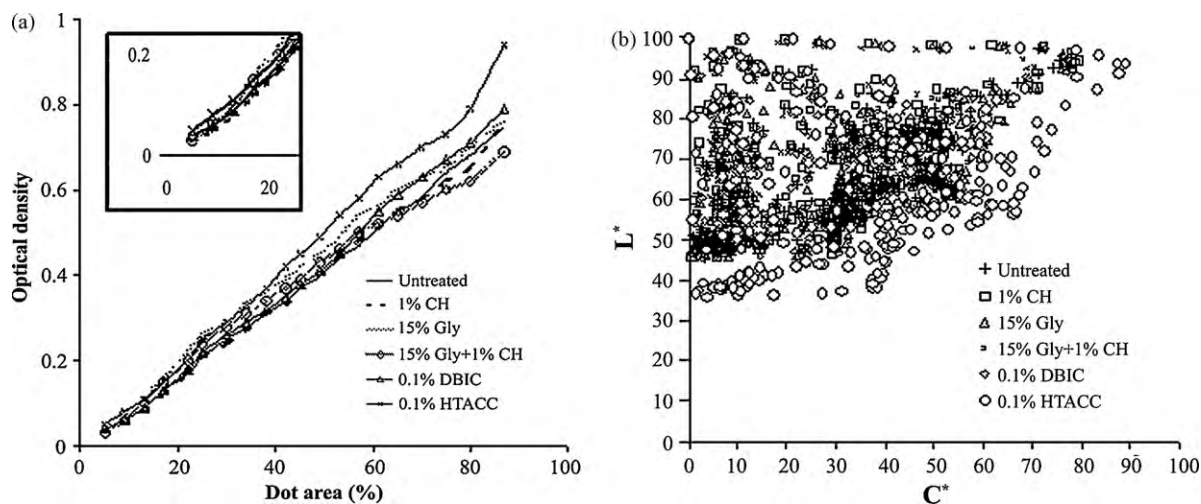
Tone reproduction represents the reproduced optical density with respect to the dot area in a continuous range. The higher the density, the more saturated the printed fabric becomes. Fig. 3(a) shows the tone reproduction of the pretreated fabrics, revealing that different sloped tone reproduction plots were observed for each of the different pretreated fabrics. The tonal densities of the fabrics pretreated with CH, Gly, the CH–Gly mixture and DBIC were all relatively close at the lower dot areas but they gave relatively higher tone densities at the higher dot areas. Very interestingly, the HTACC pretreated fabrics revealed a steadily increasing tonal density for the whole range of dot areas, with a much higher optical density when the dot areas were higher than 40%.

### 3.3.4. Chroma or color saturation

The components of color appearance are represented by  $L^*$  (lightness),  $C^*$  (chroma) and  $H^*$  (hue angle), and so an  $L^*C^*$  plot is another method to observe the extent of color saturation after printing on fabrics pretreated with the different solutions. In this representation, the higher the  $C^*$  value is, the greater the color saturation becomes. Most of the pretreated fabrics gave higher color saturations at all lightness, even at the low lightness areas (Fig. 3(b)). Pretreatment brings out a higher color saturation, as indicated by the scattering of the points in the  $L^*C^*$  plot. Basically, an ideal color production is judged by the evenly and widely scattering of the points at all lightness and chroma values, i.e., from the low to high values of both axes. With a wide scattering of the points on the  $L^*$  and  $C^*$  plot, a better tone reproduction with more details can be obtained.

When considering the CH pretreated fabrics, the color saturation was slightly increased as the CH concentrations increased. In the Gly pretreated fabrics, the color saturation increased gradu-





**Fig. 3.** Color yield: (a) The  $L^*C^*$  boundary of the printed fabrics with various pretreatments; (b) tone reproduction (shown as a plot of dot area against optical density) of the printed fabrics with various pretreatments. Data are the mean values, derived from 3 independent repeats.

ally with increasing Gly concentrations up to a maximum at 15% (w/v) Gly. However, when a 1% (w/v) CH and 15% (w/v) Gly mixture was used, the color saturation obtained was lower, being at the same level as that observed with the 1% (w/v) CH pretreated fabric samples. In contrast, when the HTACC was used, higher color saturation was found in the HTACC pretreatment compared to that found with DBIC pretreatment at the same concentration. Indeed, the 0.1% (w/v) DBIC treatment resulted in similar color saturation as that of fabrics pretreated with 1% (w/v) CH.

The extent of the interaction depends on the pretreatment agent concentration, the molecular weight, degree of deacetylation, the location of remaining acetyl units and the local environment, as influenced by the pH, the molecular size of the colorant (Jocic et al., 2005; Leelajariyakul et al., 2008; Phattananurdee et al., 2009), and physical phenomena of surface properties. The major contributor towards the higher  $K/S$  values and wider color gamut can be obtained by the adsorption onto the modified CHs, or onto Gly, of the polymer treated pigment molecules under the environmental conditions. It is now realized that chemisorption, such as ion-exchange, electrostatic attractions and so forth, is the most prevalent mechanism, with the pH being the main factor affecting adsorption (Crini & Badot, 2008; Jocic et al., 2005; Pillai, Paul, & Sharma, 2009). Under acidic conditions, the amino groups of CH are protonated to positively charged amine ions ( $-\text{NH}_3^+$ ) that can electrostatically interact with the negative charge of the polymer encapsulated pigmented inks. It has been experimentally confirmed that the printed fabric color is enhanced under such acidic conditions. Furthermore, Jocic et al. (2005) elucidated the possible ionic states and interactions between wool, CH, CH-treated wool and dye, in an aqueous solution at either pH 4.2 or pH 6.5. This led to the postulation about the possible interactions between the polyester and the negative charge of the polymer encapsulated pigmented ink in the present case. Only one terminal end of the hydroxyl group per polyester molecule can be hydrogen bonded with the oxygen atom of the acetyl group of the adsorbed CH or the modified CH, or through van der Waals and hydrophobic interactions (Polyester/CH). Similar van der Waals and hydrophobic interactions between the polyester and the pigmented ink dispersion are also possible (Jocic et al., 2005).

Gly, a small amino acid molecule, has an isoelectric point (PI) at 5.97, the point or pH at which Gly will be centered between the  $\text{pK}_a$  of the two ionizable groups, the amino group and the carboxylic acid group. Therefore, electrostatic interactions between the protonated amino groups ( $-\text{NH}_3^+$ ) with the negative charge of polymer

encapsulated pigmented ink are also possible at a pH of less than 5.97.

When Gly was mixed with CH in an acidic condition (pH < PI), the additional protonation of  $\text{H}^+$  to the amino group of Gly was, at first, expected because the solution pH was lower than the isoelectric point and thus Gly should be in the protonated form. Unfortunately, the opposite result was obtained in that for the mixed Gly and CH pretreatment, a lower pH yielded fabric prints with lower  $K/S$  values and a narrower color gamut. This could be caused by the fact that the acid ( $\text{H}^+$ ) used for dissolving CH might protonate the carboxyl group of Gly instead.

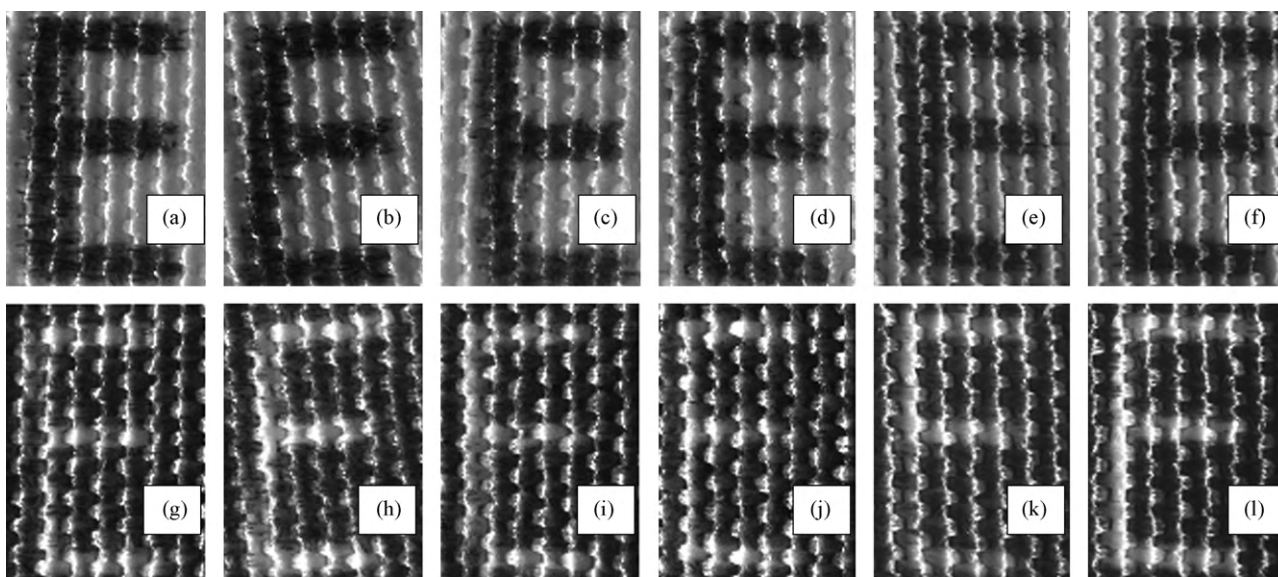
For the DBIC pretreatment solution, there are two nitrogen atoms per glucosamine unit, and so the  $K/S$  values and color gamut were thus larger than those of the untreated fabric and the CH-treated fabrics.

Introducing a quaternary ammonium group has long been known to enhance the solubility of CH. The conjugation of glycidyltrimethylammonium chloride (GTMAC) to CH produces a CH derivative, HTACC, a water-soluble polymer at all pH values. Therefore, having two nitrogen atoms, one secondary amino group and one quaternary ammonium group, the HTACC pretreatment can synergistically produce higher  $K/S$  values of each color, a higher gamut volume and a better color saturation when compared with the low effectiveness of the primary amino group of CH alone in neutral or dilute acid solutions.

The stable positive charges may interact with the negative charge of the polymer encapsulated pigmented ink via amidation or electrostatic interaction. The much higher  $K/S$  values and the larger color gamut boundary and volume induced by the HTACC pretreatment can be further caused by the ease of site accessibility due to the longer side chain. It is anticipated that this long side chain can allow both chemisorption and physical surface adsorption of the pigmented inks to take place. The protonated CH and HTACC can provide a rapid surface adsorption followed by diffusion and chemisorption of the modified pigment molecules in the CH network via electrostatic interactions (Bahmani, East, & Holme, 2000). Furthermore, HTACC has been reported to generate antibacterial activity to cellulosic fibers (Seong et al., 2000), which is another advantage to use HTACC in textiles.

### 3.3.5. Outline sharpness and contrast assessment

The outline sharpness of the printed character "E" visualized and then as measured by the optical microscopy, is illustrated for the positive characters in Fig. 4(a)–(f) and negative characters in



**Fig. 4.** Outline sharpness and printed character quality of the “E” on fabrics with various pretreatments: Positive character: (a) the untreated fabric, and the fabrics pretreated with (b) 1% (w/v) CH, (c) 15% (w/v) glycine, (d) mixture of 1% (w/v) CH and 15% (w/v) glycine, (e) 0.1% (w/v) DBIC and (f) 0.1% (w/v) HTACC; negative character: (g) the untreated fabric, and the fabrics pretreated with (h) 1% (w/v) CH, (i) 15% (w/v) glycine, (j) mixture of 1% (w/v) CH and 15% (w/v) glycine, (k) 0.1% (w/v) DBIC and (l) 0.1% (w/v) HTACC.

Fig. 4(g)–(l), printed on polyester fabrics after various pretreatments. In principle, the good printed qualities of characters are sharpness, even ink deposition and legibility. The sizes of the positive characters (Fig. 4(a)–(f)) are larger and shaper than those of the negative characters (Fig. 4(g)–(l)). Ink spreading in both vertical and horizontal directions was observed in the untreated fabric (Fig. 4(a) and (g)) and all the CH-treated fabrics (Fig. 4(b) and (h)). The edges of the positive characters were not so ragged but the negative characters were more ragged and unevenly printed. The printed positive characters and negative characters on 0.1% (w/v) DBIC pretreated fabrics in Fig. 4(e) and (k) or 0.1% (w/v) HTACC pretreated fabric in Fig. 4(f) and (l) gave a much better legibility with sharper edges, more evenly printed color densities and a higher contrast between the letter and the background than those of the untreated fabric. One obvious point was also seen in the blurred “E” characters (Fig. 4(c) and (i)) on the Gly pretreated fabrics, due to the lower viscosity resulting from the small molecular size of Gly. This observation is even more obvious in the negative characters (Fig. 4(i)).

The data of the treatments disclose that the contrast transfer function (CTF) in the warp direction is higher than those in the weft direction. The trace lines of micro-density vs. distance in pixel, and their contrast calculated from the average micro-density in the weft direction are revealed in Table 3. The contrast in the warp direction cannot be calculated due to the configuration of the fiber and thus no data could be presented. One should bear in mind that the densities of the fabrics were bared. From these results, the 0.1% (w/v) HTACC pretreated fabric gave the highest contrast, followed by the 0.1% (w/v) DBIC pretreatment, whilst fabric pretreated with the mixed 15% (w/v) Gly and 1% (w/v) CH gave the lowest contrast. All the measured samples rendered a decreasing contrast with increasing spatial frequencies at each resolution. Therefore, among all the pretreatments, the fabrics treated with 0.1% (w/v) HTACC gave the highest smoother trace lines and resolution especially at the frequency of 2 lines per mm (data are not shown here). Two possible attributes to the above observations are the extent of ink absorption, spreading and fixation. The lower ink absorption produced a higher ink density and better contrast, while the better color fixation controls an adequate ink penetration and limited ink spreading to result in the fine and smooth edges of the characters.

### 3.3.6. Surface appearance and stiffness of the pretreated polyester fabrics

Fig. 5 shows the surface appearance of the untreated polyester fabrics and the various treated polyester fabrics. The untreated polyester fabric, as depicted in Fig. 5(a) is not smooth and has minute and shallow channels distributed widely on the fiber. When it was treated with 1% (w/v) of CH, the channels were reduced because the CH solution could fill up the channels. With higher CH concentrations, at 2, 3 and 4% (w/v), an uneven and rough layer of CH was deposited on the fiber surfaces which made the fibers become distorted (micrographs are not shown here). This behavior may induce stiffness to the fabrics. When an excessive amount of 15% (w/v) Gly was padded, small specks, agglomerates and layers of the pretreatment Gly were deposited widely on the fiber, as shown in Fig. 5(b). The fibers became smoother and less swollen when the mixed CH and Gly solution was padded (Fig. 5(c)). The stiffness of the fabric at this level of padding was hard to hand touch. The CH and Gly pretreated fabrics were not soft to hand touch because the fabric stiffness was increased appreciably. On the other hand, the fabrics padded with 0.1% (w/v) of DBIC or 0.1% (w/v) of HTACC (Fig. 5(e) and (f), respectively) had a smooth surface texture somewhat similar to that of the untreated fabric. For softness to hand touch, the 0.1% (w/v) DBIC or 0.1% (w/v) HTACC pretreatment gave a relatively similar stiffness as that for the untreated fabric regardless of the high molecular weight of HTACC. Based on Crutzen (1995) model of ditallowdimethyl ammonium chloride deposition on cotton, this model was adopted to explain the similar softening result of the high molecular weight HTACC. The long side chain of N-(2-hydroxyl-3-trimethylammonium)propyl chloride attached at the nitrogen atom of the amine occupied more spaces on the fabric. The combined effects of adsorption and the softening power of quaternaries enable the fabric to behave somewhat like the cationic softener treated fabric.

Fig. 6 shows the extent of the bending length of the printed fabrics in the warp and weft directions for the fabrics pretreated with the different solutions. The stiffness of the untreated warp direction was higher because it is naturally stronger than that of the weft direction, due to having more incorporated fibers (182 ends in.<sup>-1</sup> for the warp fiber vs. 87 picks in.<sup>-1</sup> for the weft). When 0.1% (w/v) CH, 0.1% (w/v) HTACC and 0.1% (w/v) DBIC were used to treat the



**Table 3**  
Print contrast in the weft direction of polyester fabrics printed by ink jet inks after pretreatment with the indicated solutions.

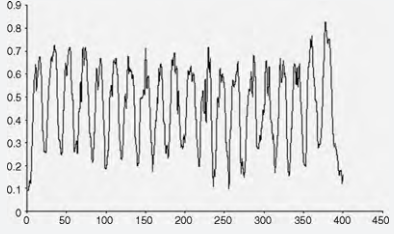
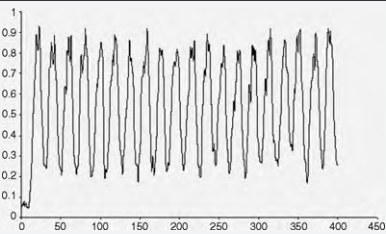
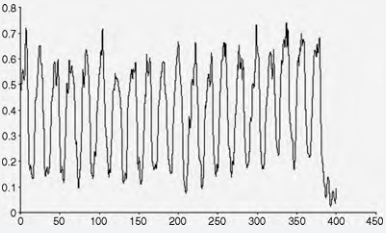
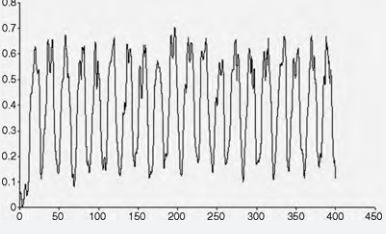
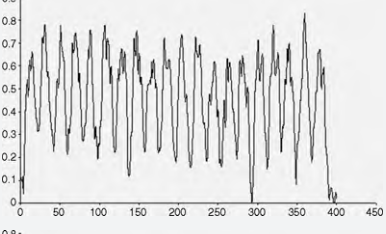
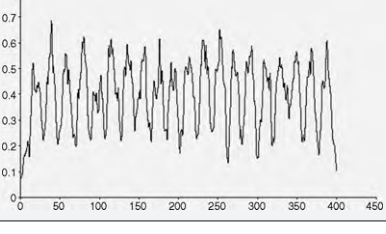
Type of fabrics	Traces of micro-density vs. distance (pixel)	Contrast of the printed fabrics at the applied spatial frequency (lines per mm)		
		0.5	1	2
Untreated		0.69	0.58	0.53
0.1% (w/v) CH		0.57	0.51	0.47
1% (w/v) CH		0.63	0.60	0.51
2% (w/v) CH		0.59	0.52	0.36
3% (w/v) CH		0.55	0.48	0.37
4% (w/v) CH		0.57	0.52	0.44
0.1% (w/v) DBIC		0.69	0.69	0.51

Table 3 (Continued)

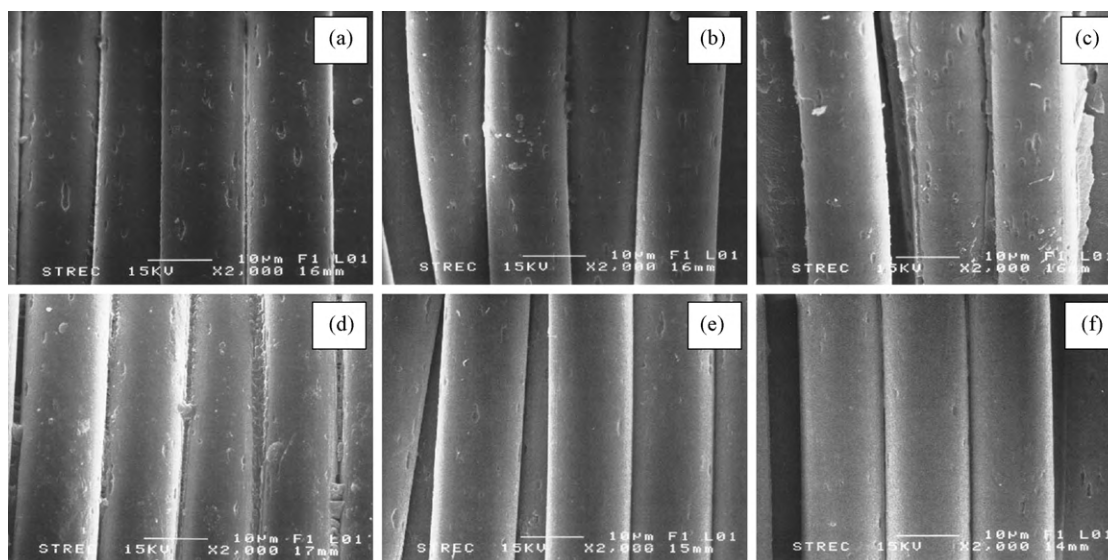
Type of fabrics	Traces of micro-density vs. distance (pixel)	Contrast of the printed fabrics at the applied spatial frequency (lines per mm)		
		0.5	1	2
0.1% (w/v) HTACC		0.85	0.80	0.62
5% (w/v) Gly		0.65	0.60	0.48
10% (w/v) Gly		0.60	0.53	0.48
15% (w/v) Gly		0.70	0.58	0.48
15% (w/v) Gly + 1% (w/v) CH		0.50	0.44	0.35

fabrics prior to printing, the stiffness in the warp direction in each pretreated fabric increased, which was influenced by the strength of the warp fibers and the pretreatment solution ( $p \ll 0.05$ ). The HTACC pretreated fabric gave significantly lower fabric stiffness. The stiffness of the weft direction in the untreated and treated fabrics showed a similar trend as those seen for the warp direction. In contrast, when more concentrated pretreatment solutions were used, the stiffness in the weft direction increased rapidly. This is because the pretreatment solutions were absorbed easily by the fibers in the weak weft fibers due to the lower fiber density at 87 picks in.<sup>-1</sup> in this direction. Increasing the pretreatment of both chitosan solutions from 0.1 to 4% (w/v), and Gly solutions from 5 to 15% (w/v) significantly increased the stiffness in both the warp and the weft fiber directions, but with a greater increase in the weft fiber direction. When the fabrics were pretreated with the mixture of 1% (w/v) CH and 15% (w/v) Gly, the stiffness increased markedly and this was statistically significant ( $p \ll 0.05$ ). The greater the stiffness of the fabrics, the less comfortable they became. It is also

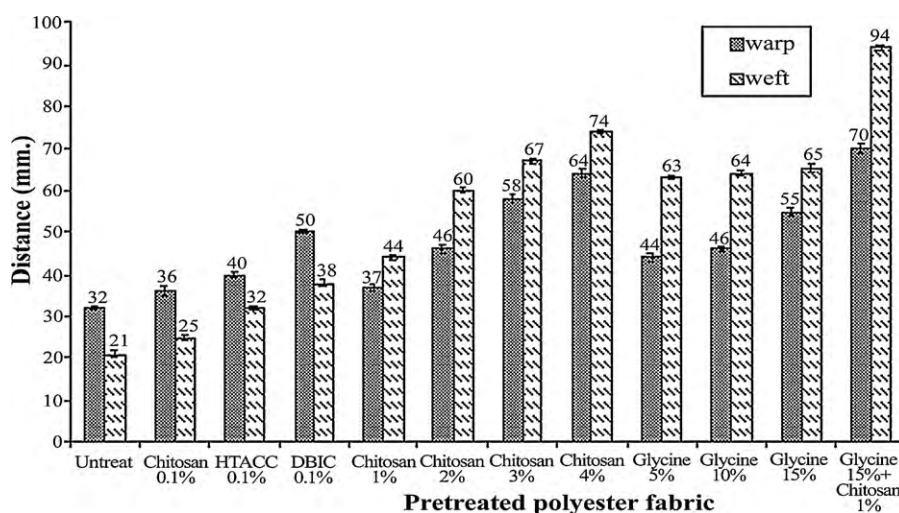
anticipated that the electrostatic interaction between the positive charges of the pretreatment agents and the negative charge of the polyester surface and the inks might be the major contribution to the increase in fabric stiffness. Therefore, there is a trade-off in the amount of pretreatment solution on the required printing property vs. the fabric performance properties. In the present case, HTACC is a good candidate as a pretreatment agent because only 0.1% (w/v) is required to obtain a satisfactory color strength, which does not yield too high a fabric stiffness and also has the advantage of potentially adding antibacterial activity, as reported elsewhere (Seong et al., 2000).

### 3.3.7. Effect of pretreatment agent on color fastness to washing and rubbing

Based on the ISO 105-C10:2006 (E) for evaluating color fastness to washing, and AATCC TM 8 for color fastness to rubbing, the results presented below are based on the five levels of evaluation that 5 stands for excellent, 4 for good, 3 for fair, 2 for poor, and 1



**Fig. 5.** Surface appearances of (a) the untreated fabric, and the fabrics pretreated with (b) 1% (w/v) CH, (c) 15% (w/v) glycine, (d) mixture of 1% (w/v) CH and 15% (w/v) glycine, (e) 0.1% (w/v) DBIC and (f) 0.1% (w/v) HTACC.



**Fig. 6.** Stiffness of the printed fibers of (a) untreated fabrics, weft direction, (b) untreated fabrics, warp direction, (c) treated with 0.1% (w/v) HTACC, weft direction and (d) treated with 0.1% (w/v) HTACC, warp direction. (Data are shown as the mean values  $\pm$  1 SD, derived from five independent repeats.)

for very poor:

Treatment	Color fastness level	Dry fastness level	Wet fastness level
Untreated	1	3–3.5	2.5
CH, Gly, DBIC	2	3–4	2.5–3, 2–3, 1.5–2.5
HTACC	3–4	3–4	2.5
Gly–CH mixture	3–4	3–4	2.5–3.5

The pretreated fabrics gave the higher color fastness to washing than the untreated one. The HTACC gave better color fastness to washing of the printed polyester fabric which might be contributed by HTACC as an interlayer between the ink and the fabric. Similar result was also observed for the Gly–CH mixture pretreated fabric. Color fastnesses to wet rubbing for all fabrics with all pretreatments are lower than those for dry rubbing. This could be caused by the weakness of the swollen film in the wet condition which can be easily rubbed off. One can also see that Gly–CH mixture pretreatment having the higher stiffness contributes somewhat the better color fastness to both dry and wet rubbings. It may be then said that the higher flexural modulus is also another contribution to rubbing.

Both HTACC and DBIC pretreatments gave the lower color fastness to wet rubbing because they are relatively hydrophilic in nature with low flexural modulus and the pretreated films are weak in water and under rubbing.

With a very smooth interface adhesion for the ink and substrate, the only forces holding the substrate and pretreatment agent together are the interfacial attractive forces. Internal stresses act to reduce adhesion and less external force is required to disrupt the adhesive bond. As film formation proceeds,  $T_g$  rises and free volume is reduced; the film becomes fixed in unstable conformations, and internal stress increases. Stresses also result from volume expansions, such as swelling of films by exposure to high humidity or water immersion. Thus delaminating of the printed ink film under rubbing can occur easily.

#### 4. Conclusions

The use of CH, Gly, and the two modified CHs (DBIC and HTACC) as the pretreatment reagents of polyester fabrics prior to ink jet printing indicated that these pretreated fabrics produced a much



better color quality than the untreated fabrics, but that the extent of this improvement largely depended on the type and concentration of the pretreatment solutions. Although polyester is a hydrophobic fabric, it had a negative zeta potential implying that it has negative charges on its surface. The important properties of the *K/S* value, color gamut and gamut volume, color saturation, tone reproduction, outline sharpness and surface appearance were evaluated. Overall, HTACC pretreatment gave overwhelming excellent properties over the rest of the pretreatments. Only 0.1% (w/v) of HTACC was required to provide a high color gamut and color saturation, good tone reproduction and outline sharpness, smooth surface and less fabric stiffness. Nevertheless, Gly could also be used as a pretreatment agent for good color reproduction, but it is not as good for outline sharpness because it produced rather poor outline sharpness and low contrast print, due to its high spreading caused by the low solution viscosity. Based on the numerical observation and statistical evaluation, the pretreatment agents gave better qualities than the untreated fabric and their efficiency can be ranked as follows for (i) color properties: HTACC  $\gg$  Gly  $>$  CH  $\approx$  DBIC  $>$  Gly–CH mixture (15% and 1% (w/v), respectively); (ii) for outline sharpness: HTACC  $>$  CH  $\approx$  DBIC  $\approx$  Gly–CH mixture (15% and 1% (w/v), respectively); and (iii) less stiffness: HTACC  $<$  DBIC  $<$  Gly  $<$  CH  $<$  Gly–CH mixture (15% and 1% (w/v), respectively); (iv) color fastness to washing: HTACC  $\approx$  Gly–CH mixture  $>$  CH  $>$  gly  $\approx$  DBIC; (v) color fastness to rubbing: Gly–CH mixture  $>$  gly  $\approx$  CH  $>$  HTACC  $>$  DBIC.

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