CHAPTER 4

RESULTS AND DISCUSSION

In this research, pigment dispersions by surfactant were used to prepare two sets of four-color ink jet inks. The ink binders in the chemical class of acrylate/styrene copolymer having two different sizes in nanoscale i.e. 70 nm and 180 nm were used in the ink formulations (Figure 4.1). The size effect of the polymeric binder on the ink properties was investigated. Two sets of ink jet inks based on the pigment-to-binder ratios of 1:1 and 1:2 were formulated while the other ink ingredients were fixed. These inks were then printed on the silk fabric, untreated and treated with chitosan. After the printing, comparisons of the fabric print quality in terms of color gamut, optical density, ink penetration, inter-bleeding, crock fastness, wash fastness, and air permeability were thoroughly analyzed.

4.1 Properties and stability of the pigmented ink jet inks

Ink jet inks should be formulated with precise viscosity, consistent surface tension, and a long shelf life without settling or mould growth [33]. Chemical stability of an ink or its pigment is an assurance certified that no agglomeration or particle size increase occurs. Physical stability can be accessed in a system that settling of ink ingredients was observed and detected [34].

4.1.1 Properties of raw materials

Pigmented ink jet inks used in this work consist of pigment dispersed by surfactant and binder, which are main composition of all inks. The inks were prepared from two different sizes of binder for comparing the size effect of the binder in an average particle size of 70 and 180 nm (Figure 4.1). The average particle sizes of these pigment dispersions are considered being in the range of 75 to 85 nm except for the cyan ink which is below 40 nm the smallest particle size in the four inks (Table 4.1 and Figure 4.2). The zeta potential of the pigment dispersions and the binders indicated that the charges on their surfaces are negative (Table 4.1).

Pigment dispersions and binders	Average particle size (nm)	Zeta potential (mV)
Cyan (MaxNano Jet SPC)	40 ± 1	-37
Magenta (MaxNano Jet SPM)	86 ± 3	-23
Yellow (MaxNano Jet SPY)	77 ± 2	-30
Black (MaxNano Jet SPK)	83 ± 1	-26
70-nm binder (Mowilith LDM 7668)	70 ± 1	-47
180-nm binder (Printofix Binder 710)	180 ± 4	-40

 Table 4.1: Particle size and change of the pigment dispersions and the binders

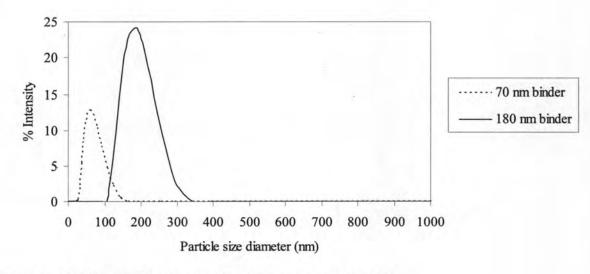


Figure 4.1: The particle size distributions of the two binders.

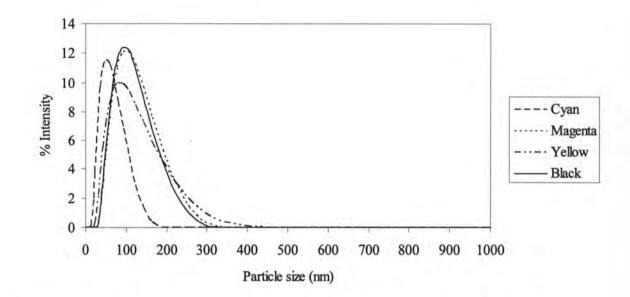


Figure 4.2: The particle size distributions of the pigment dispersions after filtration.

The chemical structures of the pigments are shown in Figures 2.5 to 2.8. Phthalocyanine pigments are the standard bright greenish blue shades. Transparency, brightness, tinting strength, color purity, and high degree of permanency are unique characteristics of the phthalocyanine pigment. Pigment blue 15:3 and 15:4 are the beta crystal form, just stronger, solvent and heat stable, greener, less bronzing tendency. Pigment red 122 is a bright bluish-red shade with high performance and high degree of intermolecular bonding. Pigment yellow 138 is greenish yellow shade. Pigment black 7 is the most important black pigment, which is composed of 90-99% carbon [35].

The chemical structures of the pigments are shown in Figures 2.5 to 2.8 were confirmed by FT-IR Spectroscopic method, suggesting the complicated spectra in Figure 4.3. The peak of the cyan pigment (Figure 4.3(a)) is mainly attributed to C=C stretching of aromatic, the peak at 1721 cm⁻¹ is due to C=N stretching, and the peak at 1106 cm⁻¹ is sulfonate salt.

The IR spectrum of the magenta pigment in Figure 4.3(b) shows the peak at 1117 cm^{-1} due to sulfonate salt, the peak at 3429 cm⁻¹ attributed to N-H stretching, and the C=O of the ketone group found at 1580 cm⁻¹.

The IR spectrum of the yellow pigment (Figure 4.3(c)) shows the peak at 1107 cm⁻¹ attributed to sulfonate salt, and the peak at 1602 cm⁻¹ corresponded the C=O of the amide group. Also, the C=O of the ketone group is found at 1724 cm⁻¹.

The IR peaks of black pigment in Figure 4.3(d) at 2889 cm⁻¹, 1550 cm⁻¹, 1059 cm⁻¹ and 684 cm⁻¹ are due to the C-H stretching, C-C stretching, sulfonate salt and C-H bending, respectively. Table 4.2 lists all the peak assignments according to the chemical structures of the pigments.

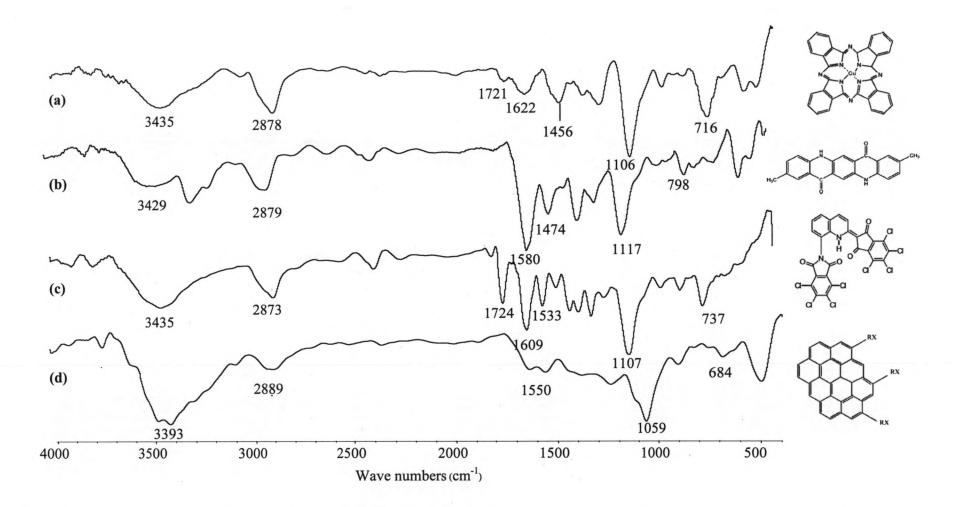


Figure 4.3: Infrared spectra of pigment dispersions containing (a) the cyan pigment, C.I. pigment blue 15:3; (b) the magenta pigment, C.I. pigment red 122; (c) the yellow pigment, C.I. pigment yellow 138, and (d) the black pigment, C.I. pigment black 7.

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Cyan p	pigment	Magenta	pigment	Yellow	pigment	Black pigment		
Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	
N-H stretching	3435	N-H stretching	3429	N-H stretching	3435	-C-H stretching	2889	
-C-H stretching	2878	Sulfonate salt	1117	-C-H stretching	2873	C-C stretching	1550	
C=N stretching	1721	-C-H stretching	2879	C=O (amide)	1609	Sulfonate salt	1059	
C = C	1622	C=O	1580	C=O	1724	C-H bending	684	
stretching (aromatic)		(ketone)		(ketone)			,	
Sulfonate salt	1106	C-C stretching	1474	C-C stretching	1533			
C-C stretching	1456	C-H bending	798	Sulfonate salt	1107			
C-H bending	716			C-Cl	737			

Table 4.2: Assignments for the FTIR spectra of the cyan, magenta, yellow, and black pigment dispersions in Figure 4.3

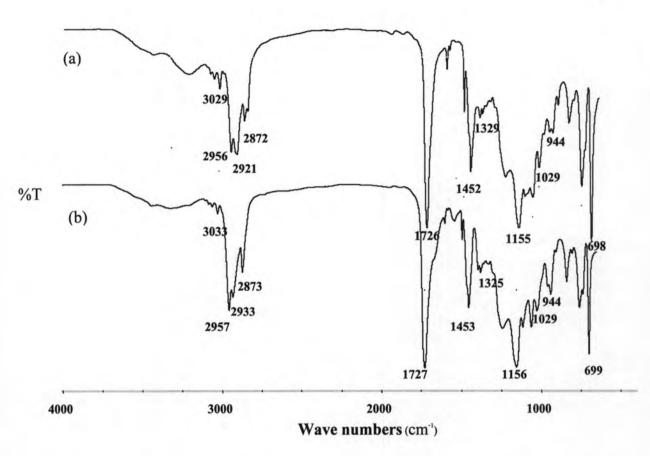


Figure 4.4: Infrared spectra of (a) the 70-nm binder, Mowilith LDM 7668 and (b) the 180-nm binder, Printofix Binder 710.

The molecular structures of both binders in ink jet inks are confirmed in Figure 4.4 and Table 4.3. The Figure 4.4(a) illustrates the IR spectra of the 70-nm binder in which the peak at 3080–3010 cm⁻¹ is the =C-H stretching of aromatic, the peak at 2960–2850 cm⁻¹ is the C-H stretching of aliphatic, the peak at 1726 cm⁻¹ is for the C=O stretching of the ester moiety; the peak at 1452 cm⁻¹ is due to the deformation of CH₂ and CH₃, the peaks at 1329 cm⁻¹ were caused by the CH₃ bending, the peaks at 1199 and 1155 cm⁻¹ are the C–O stretching of ester functional group, the peaks at 1029 and 944 cm⁻¹ are for the C–H out of plane deformation, and 770–730 cm⁻¹ indicated the monosubstituted aromatics ring. Another binder used in the ink jet inks has spectra characteristic closed to 70-nm binder (Figure 4.4(b)). Thus, it is speculated that 180-nm binder might contain similar structure to the 70-nm binder (Table 4.3).

Mowilit	h LDM 7668	Printofix Binder 710				
Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)			
=C-H stretching	3080 - 3010	=C-H stretching	3080 - 3010			
(aromatic)		(aromatic)				
C-H stretching	2960 - 2850	C-H stretching	2960 - 2850			
CH ₃ and CH ₂		CH ₃ and CH ₂				
(aliphatic)		(aliphatic)				
C=O stretching	1726	C=O stretching	1727			
(ester)		(ester)				
deformation of	1452	deformation of	1453			
CH ₂ and CH ₃		CH ₂ and CH ₃				
CH ₃ bending	1329	CH ₃ bending	1324			
C-O stretching	1155	C–O stretching	1156			
(ester)		(ester)				
C-H out of	1029, 944	C–H out of	1029, 944			
plane		plane				
deformation		deformation				
monosubstituted	770 – 730	monosubstituted	770 – 730			
aromatics ring		aromatics ring				

Table 4.3 FTIR of the 70-nm binder, Mowilith LDM 7668 and the 180-nm binder,Printofix Binder 710

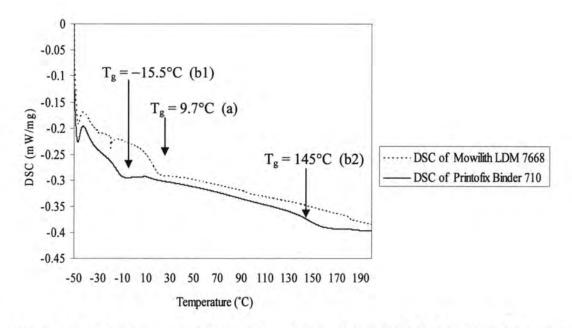


Figure 4.5: DSC diagrams of (a) the 70-nm binder, Mowilith LDM 7668 and (b1) and (b2) the 180-nm binder, Printofix Binder 710.

The DSC diagrams (Thermograms) in Figure 4.5 show that the glass transition temperature (T_g) of the Mowilith LDM 7668 (70-nm binder) and Printofix binder 710 (180-nm binder) are 9.7°C and -15.5°C, respectively. In this research, acrylate/styrene-based binders were used. The DSC diagrams show the different T_{gs} of both binders. The T_g of polystyrene and poly(butyl acrylate) were 99.8°C and -20°C, respectively. Thus, the Mowilith LDM 7668 which had a higher T_g was expected and it could be possible to summarize that the styrene part in the Mowilith LDM 7668 was less flexible than that of Printofix binder 710. The film from the Mowilith LDM 7668 was less flexible than that of Printofix binder 710. It will be seen later that, the ink jet inks prepared with the Mowilith LDM 7668 provided better dry/wet crock fastness than those inks from Printofix binder 710 (T_g of 9.7°C) because the inks contain the self-crosslinking acrylate binder, i.e., at least two double bonds at the acrylate sites can promote a film with ability to withstand rubbing. The low T_g (lower than -8°C) accounted for the reason for the softness of the fabrics which could hardly

change after the heat treatment [1]. Therefore, Printofix binder 710 with T_g at -15.5°C gives silk fabric a film with more flexibility and softness than does another binder Mowilith LDM 7668. Moreover, in case of Printofix binder 710, the T_g at about 145°C might be due to the self-crosslink part of the binder.

4.1.2 Properties of the inks

As mentioned above, the ink formulations in this research have two pigmentto-binder ratios (1:1 and 1:2). Furthermore, the pigmented ink jet inks were prepared from two sizes of the binders (70 nm and 180 nm). The four color ink jet inks had pHs in the range of 7.5-8.7 with surface tension of the inks in the range of 41-45 mN m⁻¹, and density of about 1 g cm⁻³ as given in Table 4.4.

Ratio Pigment to Binder	Type of Binder	Color of Inks	Viscosity (mPa s)	Surface tension (mN m ⁻²)	Solid content (%)	Density (g cm ⁻³)	pН
		Cyan	2.1	41.9 ± 0.1	14	1.1	8.50
1:1	70	Magenta	2.2	42.6 ± 0.3	15	1.1	8.62
	70 nm	Yellow	2.6	42.1 ± 0.2	19	1.1	8.24
		Black	2.0	43.4 ± 0.3	16	1.1	8.33
	1.000	Cyan	2.3	42.8 ± 0.2	17	1.1	8.24
	180	Magenta	2.4	44.3 ± 0.5	18	1.1	8.06
	nm	Yellow	2.9	44.8 ± 0.2	19	1.1	7.70
		Black	2.2	44.3 ± 0.1	18	1.1	7.96
		Cyan	2.2	41.5 ± 0.5	12	1.1	8.37
	70	Magenta	2.5	42.6 ± 0.4	17	1.1	8.29
	70 nm	Yellow	2.9	43.1 ± 0.3	23	1.1	8.20
		Black	2.6	42.6 ± 0.4	16	1.1	8.25
1:2		Cyan	2.4	42.9 ± 0.4	20	1.1	8.03
	180	Magenta	2.4	42.9 ± 0.1	19	1.1	8.20
	nm	Yellow	4.4	45.0 ± 0.6	21	1.1	7.64
		Black	2.3	43.0 ±0.2	19	1.1	7.84

Table 4.4: Properties of the ink jet inks

The ink jet inks are characterized as Newtonian fluid due to its relatively constant viscosity at various shear rates, which can be observed from the flow curves of viscosity shown in Figures 4.6 and 4.7. Viscosity of the other ink jet inks in the same trend is shown Appendix A. Comparing all the properties of ink jet inks prepared with those of standard ink jet inks, they are in the practical range for ink jet ink printing.

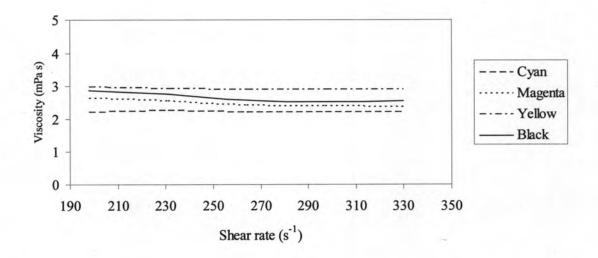


Figure 4.6: Viscosity of the four-color inks with 70-nm binder at 1:2 pigment-tobinder ratio (at 25°C).

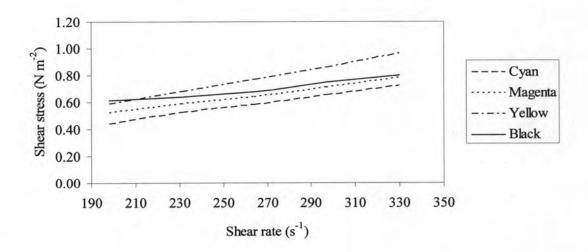


Figure 4.7: Shear stress-shear rate relationship of the four color inks with 70-nm binder at 1:2 pigment-to-binder ratio.

4.1.2.1 The particle size of ink jet inks

The particle sizes of the inks must be measured after a filtration to check for the oversize of ink particles in a cartridge. The large sizes of ink particles may clog the orifice of the printer during a printing so the inks were filtered before printing. The four color inks have different average particle diameters depending on the types of pigment (Figures 4.8–4.9). The 1:1 pigment-to-binder ratio gave the average particle sizes of the resulting inks in range of 50–90 nm and 110–180 nm for 70-nm binder and 180-nm binder, respectively. The zeta potential values of both inks formulated by 1:1 pigment-to-binder ratio are in range of (-32) to (-45) mV as shown in Table 4.5.

	Inks having	70-nm binder	Inks having 180-nm binder			
Ink Colors	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)		
Cyan	49 ± 2	-32	178 ± 1	-43		
Magenta	81 ± 1	-36	146 ± 1	-37		
Yellow	66 ± 1	-45	181 ± 1	-42		
Black	91 ± 1	-37	111 ± 1	-37		

 Table 4.5: Particle size of the 1:1 pigment-to-binder ratio

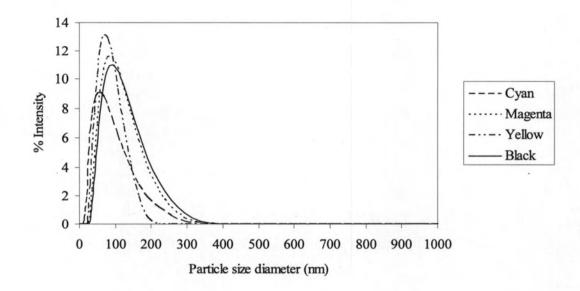


Figure 4.8: The particle size distributions of the 1:1 pigment-to-binder ratio of 70-nm binder.

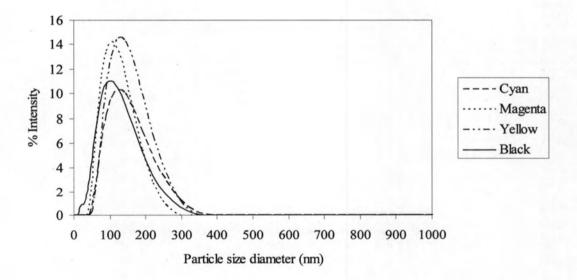


Figure 4.9: The particle size distributions of the 1:1 pigment-to-binder ratio of 180nm binder.

	Inks with	70-nm binder	Inks with 180-nm binder			
Ink Colors	Average particle size (nm)	Zeta potential (mV)	Average particle size (nm)	Zeta potential (mV)		
Cyan	57 ± 2	-45	159 ± 3	-44		
Magenta	80 ± 1	-39	165 ± 3	-39		
Yellow	77 ± 1	-38	196 ± 2	-37		
Black	81 ± 1	-35	126 ± 1	-35		

Table 4.6: Particle size of the 1:2 pigment-to-binder ratio

Table 4.6 shows average particle size and zeta potential of the inks formulated from the pigment-to-binder ratio of 1:2 (by weight). Particle sizes of the inks were found in range of 50–80 nm for 70-nm binder and 125–200 nm for 180-nm binder. (Figures 4.10–4.11) The zeta potential values of the inks indicated that the pigment particles in the inks had the negative charge in the range of -35 to -45 mV.

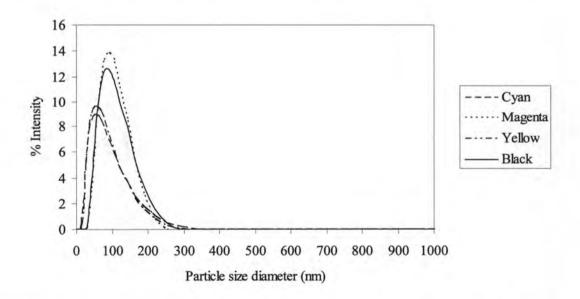


Figure 4.10: The particle size distributions of the 1:2 pigment-to-binder ratio from 70-nm binder.

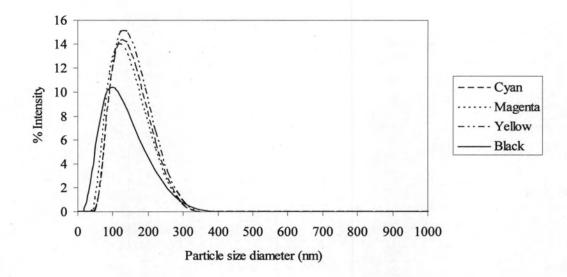


Figure 4.11: The particle size distributions of the 1:2 pigment-to-binder ratio from 180-nm binder.

4.1.2.2 The stability of ink jet inks

Tables 4.7 and 4.8 show the stability of the inks by measuring the particle size distributions of the inks during storage. The results show that the inks are stable for at least 6 months.

	Average particle size for storage time (month)										
Inks color		70-nm	binder		180-nm binder						
COTOR	0*	1	3	6	0*	1	3	6			
Cyan	49 ± 2	46 ± 1	48 ± 1	49 ± 1	178 ± 1	123 ± 3	124 ± 1	120 ± 2			
Magenta	81 ± 1	85 ± 1	77 ± 1	99 ± 1	146 ± 1	144 ± 1	146 ± 1	157 ± 1			
Yellow	66 ± 1	67 ± 1	67 ± 1	67 ± 0	181 ± 1	174 ± 1	176 ± 3	177 ± 1			
Black	91 ± 1	82 ± 1	78 ± 1	81 ± 1	111 ± 1	110 ± 1	105 ± 2	106 ± 2			

Table 4.7: The average particle size of the inks after various storage times of the 1:1 pigment-to-binder ratio

* The zero month for storage time means the immediate on-site measurement.

Table 4.8: The average particle size of the inks after various storage times of the 1:2 pigment-to-bin	inder ratio
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Inks color		Average particle size for storage time (month)										
		70-nm 1	binder		180-nm binder							
	0*	1	3	6	0*	1	3	6				
Cyan	57 ± 2	52 ± 1	52 ± 1	56±1	159 ± 3	186 ± 3	158 ± 1	163 ± 0				
Magenta	80 ± 1	80 ± 0	83 ± 0	80±1	165 ± 3	174 ± 2	185 ± 1	188 ± 3				
Yellow	77 ± 1	75 ± 1	69 ± 1	69±1	191 ± 1	196 ± 2	195 ± 1	192 ± 1				
Black	81 ± 1	82 ± 1	76 ± 1	86±1	126 ± 1	118 ± 1	123 ± 2	121 ± 1				

* The zero month for storage time means the immediate on-site measurement.

4.2 Characterization of pretreated and printed silk fabrics

4.2.1 Surface appearance of the pretreated silk fabrics

The SEM micrographs in Figure 4.12(a) and (b) show that the chitosan treated surface appeared to be as smooth as the untreated surface as well. From the cross section views, the chitosan pretreatment decreased spaces of the fiber and increases smoothness of the yarn surface. The silk yarns are more compacted when the fabric was treated with chitosan. Moreover, the inks cannot rapidly penetrate further into the yarn because inter-fiber spaces were decreased, so more inks resided on the fabric surface.

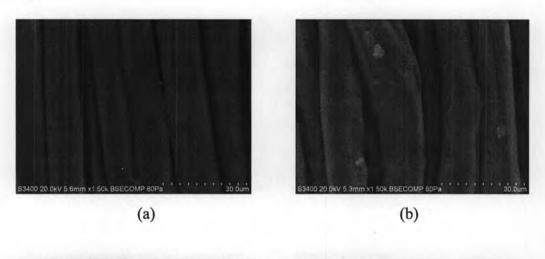




Figure 4.12: SEM of (a) untreated silk fiber, (b) 1.5% w/v chitosan treated silk fiber, (c) cross section of untreated silk fiber, and (d) cross section of 1.5% w/v chitosan treated silk fiber.

4.2.2 Penetration of ink fluid in the silk fabrics

Table 4.10 shows the trend of ink penetration in the printed fabrics that was calculated from K/S values are for the front and back of the printed area. Quantity of binder in the inks effectively decreases the ink penetration in the silk fabrics. In the Figures 4.13 and 4.16, the penetration of small-sized binder inks in the silk fabrics is lower than that of the large sized binder ink. Moreover, the chitosan are able to pack the fibers reducing the opening areas of the inter-fiber space. As a result, the ink can not further penetrate into the yarn, and then the inks were resided on the surface. To conclude, the penetration of ink in chitosan pretreated fabrics is reduced when chitosan pretreatment is increased.

Table 4.9 shows the effect of chitosan pretreatment on ink penetration of the printing areas. The K/S values of the printed silk measured and calculated by equation 3.3 show that the higher the chitosan treatment expressed as the higher percentage of chitosan concentration, the larger the amount of ink jet ink is held on the printed surface. The amount of ink K/S on the back of the printed areas seemed to be constant regardless of the sizes of the binder and the pigment-to-binder ratios. It is very interesting that the effects of binder particle size and pigment-to-binder ratio on K/S both the printed area and its back (non-printed areas) are very insignificant.

Based on the data in Table 4.9, the percentages of ink penetration at the printed areas calculated by Equation 3.3 are given in Table 4.10. One can see that.

- At the untreated fabric (no-chitosan), the %penetration of ink is the highest.
- Increasing the percentage of chitosan treatment on the fabric decreased the amount of ink penetration significantly.

- The effect of binder particle size at 1:1 pigment-to-binder ratio creates very important penetration data. For the untreated fabric the smaller the binder particle size, the higher the extent of ink penetration. On the other hand, the chitosan treated fabric gave the opposite data. The larger the binder particle size, the higher the extent of ink penetration. This is caused by the particle packing effect. The larger particle size binder tends to give more bound ink at the interstitial voids of the particles. On the other hand, at the 1:2 pigment-to-binder ratio, the ink penetration at all levels of chitosan pretreatment and untreatment is lower than those of 1:1 pigmentto-binder ratio. The more binder containing ink can form a better and smoother film to deposit on the chitosan pretreated surface.
- Figures 4.13 to 4.16 conclude the results of ink penetration dependence on chitosan for C, M, Y, K inks.

Size	Pigment-		K/S of printed silk fabrics							
of	to-binder	Ink colors	Untr	reated	0.:	5%	1	1% 1.5%		5%
binder ratio		Front*	Back**	Front*	Back**	Front*	Back**	Front*	Back**	
		Cyan	0.5	0.2	0.6	0.2	0.7	0.2	0.6	0.2
1:1	Magenta	0.9	0.4	1.1	0.5	1.2	0.4	1.1	0.4	
	Yellow	0.6	0.3	0.8	0.3	0.9	0.3	0.7	0.3	
70		Black	0.9	0.6	1.3	0.5	1.5	0.5	1.4	0.4
70 nm 1 : 2		Cyan	0.6	0.2	0.6	0.2	0.6	0.2	0.7	0.2
	1.2	Magenta	0.8	0.4	1.0	0.4	1.0	0.4	1.0	0.4
	1:2	Yellow	0.9	0.3	0.9	0.3	0.9	0.3	1.0	0.3
		Black	0.9	0.5	1.4	0.5	1.4	0.5	1.4	0.5
		Cyan	0.5	0.3	0.6	0.2	0.6	0.2	0.6	0.2
	1.1	Magenta	0.9	0.5	1.1	0.5	1.2	0.5	1.0	0.3
	1:1	Yellow	0.8	0.4	0.9	0.4	1.1	0.4	0.9	0.3
190		Black	0.9	0.6	1.3	0.6	1.2	0.5	1.3	0.4
180 nm		Cyan	0.6	0.2	0.7	0.2	0.7	0.2	0.7	0.2
	1.2	Magenta	1.0	0.4	0.9	0.4	1.0	0.3	1.1	0.4
	1:2	Yellow	1.0	0.5	0.8	0.3	0.9	0.3	0.9	0.3
		Black	0.9	0.5	1.3	0.5	1.2	0.5	1.3	0.4

Table 4.9: K/S of the printed silk fabrics measured at both sides of the fabric areas

* Front is the printed area.

** Back is the non-printed area (the back of the printed area)

Size	Pigment-			% Pene	tration	
of binder	to-binder ratio	Ink color	Untreated	0.5% chitosan	1% chitosan	1.5% chitosan
		Cyan	62.7	50.9	47.6	46.3
	1:1	Magenta	66.8	60.8	54.1	51.4
		Yellow	62.4	58.7	54.1	52.6
70 nm -		Black	79.5	58.0	50.7	47.8
		Cyan	62.1	47.9	47.4	42.4
	1:2	Magenta	69.8	53.9	53.4	52.9
	1.2	Yellow	53.9	53.5	51.5	49.8
		Black	72.6	50.7	50.5	49.7
		Cyan	67.4	52.1	50.6	48.7
	1:1	Magenta	74.9	62.2	60.4	48.6
	1.1	Yellow	60.9	58.3	54.8	49.5
180 nm		Black	82.1	63.5	62.4	49.5
100 1111		Cyan	51.7	48.5	46.0	42.0
	1:2	Magenta	60.2	56.4	49.3	48.7
	1.2	Yellow	61.1	58.4	50.0	49.6
		Black	74.4	58.6	54.0	49.2

 Table 4.10: % Penetration of the printed silk fabrics

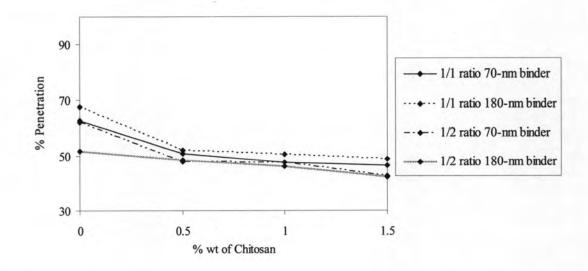


Figure 4.13: Penetration depth of cyan ink in the untreated and treated fabrics.

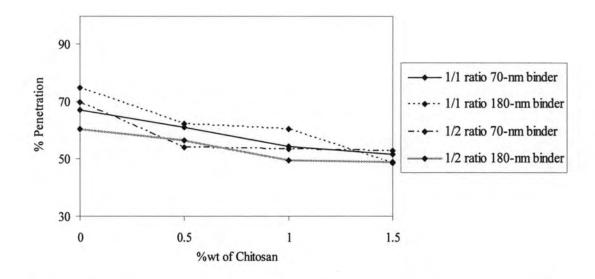


Figure 4.14: Penetration depth of magenta ink in the untreated and treated fabrics.

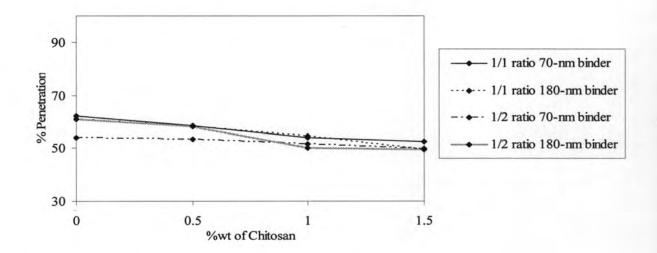


Figure 4.15: Penetration depth of yellow ink in the untreated and treated fabrics.

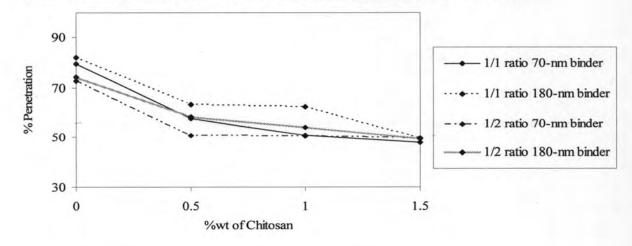
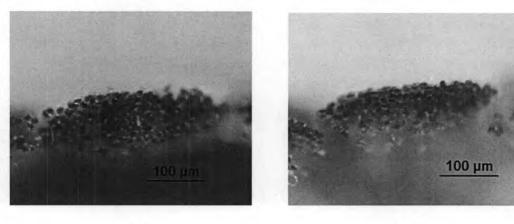


Figure 4.16: Penetration depth of black ink in the untreated and treated fabrics.

The cross sections of the silk fabric are viewed in Figures 4.17–4.18 to compare and confirm the ink penetration in the untreated and treated silk fabrics. All silk fabrics tested show the same result in which the ink jet inks penetrate in the untreated fabrics more than the treated silk fabrics. The treated fabric at 1.5%wt chitosan with 70-nm binder seems to less penetrate than the larger size binder (180 nm). Furthermore, the ink jet inks with 70-nm binder tend to deposit more in the pretreating layer than those obtained with another binder.



(a)

(b)

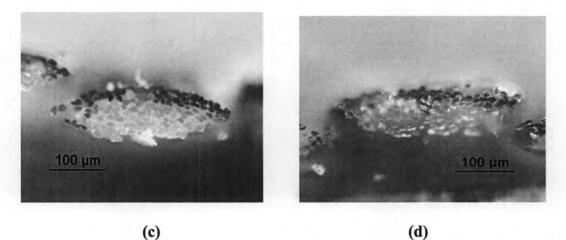
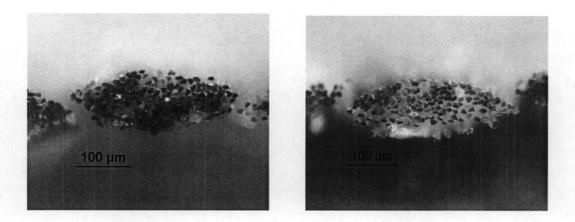


Figure 4.17: Cross sectional views of the black color printed silk by 1:1 pigment-tobinder ratio from (a) 70-nm binder printed on the untreated fabric, (b) 180-nm binder printed on the untreated fabric, (c) 70-nm binder printed on the 1.5% chitosan treated fabric, and (d) 180-nm binder printed on the 1.5% chitosan treated fabric.



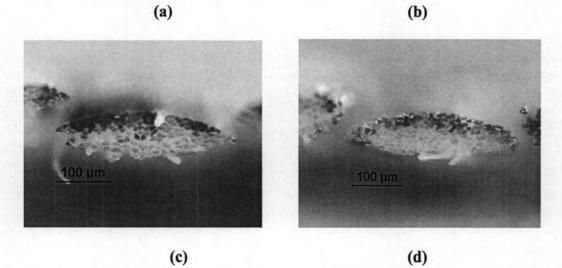


Figure 4.18: Cross sectional views the of black color printed silk by 1:2 pigment-tobinder ratio from (a) 70-nm binder printed on the untreated fabrics, (b) 180-nm binder printed on the untreated fabrics, (c) 70-nm binder printed on the 1.5% chitosan treated fabrics, and (d) 180-nm binder printed on the 1.5% chitosan treated fabrics.

Tables 4.11 to 4.12 summarize the comparison of the ink penetration depth of a silk yarn as shown in Figures 4.13 to 4.16 and the measured and calculated K/S are shown in Table 4.9. One can consider the Lucas-Washburn equation of penetration depth as follows. The parameter of $(\gamma/\eta)^{1/2}$ where γ is the ink surface tension and η is the ink viscosity, may be used to correlate the theoretical view point with experimental results. The higher the $(\gamma/\eta)^{1/2}$ values, the deeper the ink penetration. Based on Tables 4.11 to 4.12, there are not a perfect correlation between the $(\gamma/\eta)^{1/2}$ and the penetration depth. The penetration depth of the single yarn is always higher than that of corresponding color sample by Equation 3.3. The difference could be clause by the different technique of measurement. For color by Equation 3.3, the K/S values obtained depend on the measuring device.

However, the penetration depth of the four-color ink by K/S measurement is in the range of 42 to 82% depending on the amount of chitosan pretreatment. In the graphical measurement, the ink penetration depth is in the range of 25 to 88% depending on the amount of chitosan treatment. In a similar manner, at the 1:1 and 1:2 pigment-to-binder ratios, the 70-nm binder seems to give the less penetration depth than the 180-nm binder. At a fixed binder particle size, the 1:2 pigment-to-binder ratio produces the less penetration depth. The combined effect of binder particles size and its amount in the ink on ink penetration depth is caused by the ink absorbed in the interstitial voids and denser particle packing in the ink film during ink drying. The smaller binder particles absorbed less ink in the interstitial (interparticle) void and the less ink penetration depth could be achieved as well as the higher optical density of the printed fabrics.

		Penetrat	ion of 70-n	m binder		Penetration of 180-nm binder					
Pigment $(\gamma/\eta)^{1/2}$ colors of the inks	$(n)^{1/2}$ Treatment with chitosan (%)					Treatment with chitosan (%)					
	0		1.5		$(\gamma/\eta)^{1/2}$ of	(0		1.5		
	the inks	Measure	Graphic	Measure	Graphic	the inks	Measure	Graphic	Measure	Graphic	
Cyan	4.49	62.7	82.0	46.3	28.0	4.3	67.4	85.0	48.7	40.0	
Magenta	4.43	66.8	80.0	51.4	34.0	4.3	74.9	75.0	48.6	40.0	
Yellow	4.02	62.4	88.0	52.6	40.0	3.9	60.9	70.0	49.5	35.0	
Black	4.61	79.5	85.0	47.8	22.2	4.5	82.1	85.0	49.5	30.0	

Table 4.11: Comparison of the penetration depth of a silk yarn and the measured K/S of printed silk fabric at 1:1 pigment-to-binder ratio

Table 4.12: Comparison of the penetration depth of a silk yarn and the measured K/S of printed silk fabric at 1:2 pigment-to-binder ratio

Pigment colors	Penetration of 70-nm binder					Penetration of 180-nm binder					
	$(\gamma/\eta)^{1/2}$ of the inks	Treatment with chitosan (%)				$(\gamma/\eta)^{1/2}$	Treatment with chitosan (%)				
		0		1.5		of	0		1.5		
		Measure	Graphic	Measure	Graphic	the inks	Measure	Graphic	Measure	Graphic	
Cyan	4.33	62.1	70.0	42.4	25.0	4.2	51.7	60.0	42.0	33.3	
Magenta	4.15	69.8	70.0	52.9	48.0	4.3	60.2	65.0	48.7	40.0	
Yellow	3.84	53.9	70.0	49.8	40.0	3.2	61.1	70.0	49.6	35.0	
Black	4.03	72.6	95.0	49.7	37.5	4.3	74.4	95.0	49.2	37.5	

4.2.3 Optical density of the printed fabrics

The optical density of the printed silk fabric is shown in Table 4.13. Optical density of the printed fabrics with 70-nm binder ink jet inks is higher than that of the fabric with 180-nm binder ink jet inks. As described earlier, the large-sized binder ink penetrates deeper into the fabric silk than the small-sized binder as seen in Figures 4.17 and 4.18. For the different pigment-to-binder ratios, the 1:2 ratio can increase optical density in yellow ink but not significantly in other inks. Moreover, the chitosan pretreatment did affect significantly the optical density in which the chitosan can enhance the optical density. This could be that the amount of NH₂ group of chitosan on the fabric surface might be too low for holding the ink on the fabric. Another possibility could be that most of the chitosan pretreatment were lost during the padding process. As a whole, the optical densities of the present inks produced on silk fabrics are still low. Many causes attributed to this result shall be investigated.

The optical densities of the four process colors by ink jet printing of the fabric are relatively low, although the color appearance of the four colors are similar to those of ink jet ink printed paper. These are caused by (1) ink films are transparent; (2) the spectrodensitometer include optical density of the fabric; (3) the geometrical configuration of the measuring device (spectrodensitometer) is not really suitable for porous surface.

Size of	Pigment -to- binder	Chitosan pretreatment	Optical density				
binder	ratio	(%wt)	Cyan	Magenta	Yellow	Black	
	1:1	Untreated	0.54	0.60	0.68	0.76	
		0.5	0.59	0.61	0.67	0.88	
		1	0.62	0.66	0.66	0.89	
70 nm		1.5	0.62	0.70	0.70	1.00	
/0 1111	1:2	Untreated	0.53	0.54	0.68	0.72	
		0.5	0.56	0.64	0.73	0.86	
		1	0.58	0.61	0.68	0.85	
		1.5	0.59	0.64	0.72	0.99	
		Untreated	0.50	0.52	0.54	0.68	
	1:1	0.5	0.59	0.62	0.59	0.88	
	1.1	1	0.60	0.61	0.55	0.86	
180 nm		1.5	0.60	0.64	0.64	0.93	
100 mm	1:2	Untreated	0.55	0.54	0.68	0.77	
		0.5	0.60	0.58	0.66	0.80	
		1	0.54	0.58	0.66	0.80	
		1.5	0.58	0.62	0.67	1.00	

 Table 4.13: Optical density of solid colors of printed silk fabrics

4.2.4 Color gamut of the printed fabrics

The diagrams of a^*b^* , L^*a^* , and L^*b^* (Figures 4.19 – 4.27) of the printed silk fabrics indicate the effects of binder size, pigment-to-binder ratio, and chitosan pretreatment on the color gamut. For the small-sized binder and chitosan pretreatment, the color gamut of the treated fabrics printed with the ink containing 70nm binder was somewhat wider than that of the ink containing 180-nm binder because the ink film obtained from the small-sized binder seems to be smoother than the larger sized one, as shown in the Appendix C. It is clear that chitosan effectively increases color gamut of the printed silk in both chroma and color strength. The chroma of colors were not improved significantly when they were printed with different pigment-to-binder ratios on the untreated fabric but the color gamut obtained from 1:1 pigment-to-binder ratio produced a larger color gamut compared to the 1:2 ratio printed on the treated silk fabrics. Such a result suggests that the smaller amount of the binder can form a thinner film which could bring out more colors onto the surface. The color gamut was slightly improved when concentrations of chitosan were increased.

The chitosan pretreatment can improve color gamut of printed silk fabric because the chitosan containing amino groups $(-NH_2)$ which was protonated to be the NH_3^+ . The NH_3^+ is the site for holding the pigment on the treated fabric surfaces. Cationic charges of the chitosan enhance the adherent of negative charges of the pigment in the styrene-acrylate binder. Hakeim et al. [35] found that the increase in color in terms of K/S are higher than three times in the presence of binder was obtained in the modified chitosan derivatives, i.e., the amount of nitrogen content was higher in the presence of self crosslinking acrylate-based copolymer dispersion. Trapping of chitosan molecules on the surface of fabrics was found to be imposed by the influence of the binder. As such a result, the number of fixed amino groups in chitosan which are the sites for acid dye increases. The increases in the amino groups and the dye sites in chitosan increase the color value [36]. As mentioned above, this effect is predominantly enhanced with the chitosan pretreatment since the treatment helps reducing ink absorbency into the fabric. Furthermore, the treatment is effectively enhanced the color gamut of the fabric printed with the small size binder suggesting that most of the ink particles can deposit on the fabric surface.

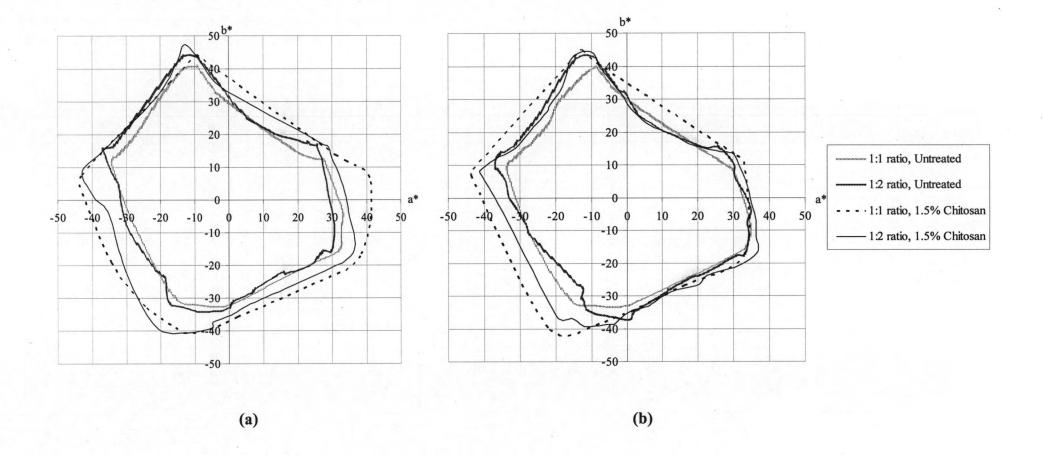


Figure 4.19: a*b* diagram of the inks printed on untreated and 1.5% W/V chitosan treated silk fabrics by the ink containing 1:1 and 1:2 pigment-to-binder ratios of (a) the 70-nm binder, and (b) the 180-nm binder.

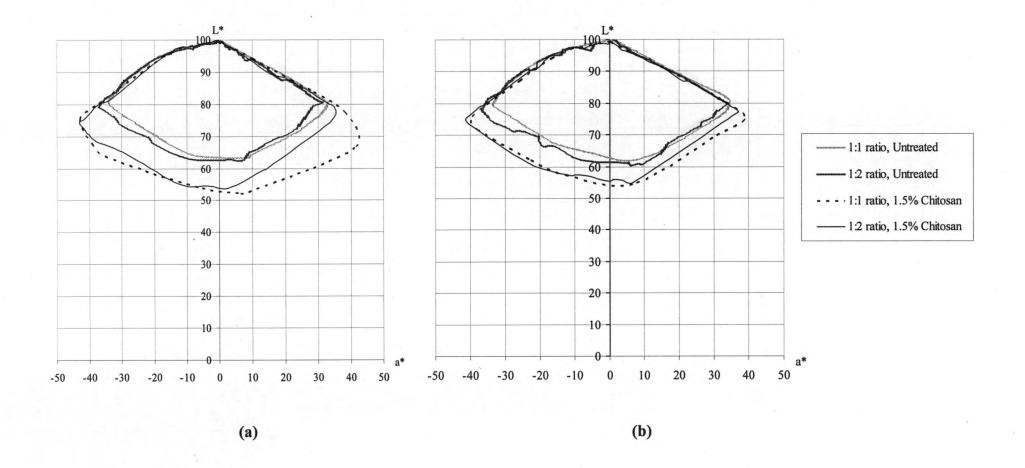


Figure 4.20: L*a* diagram of the inks printed on untreated and 1.5% W/V chitosan treated silk fabrics by the containing 1:1 and 1:2 pigment-tobinder ratios of (a) the 70-nm binder, and (b) the 180-nm binder.

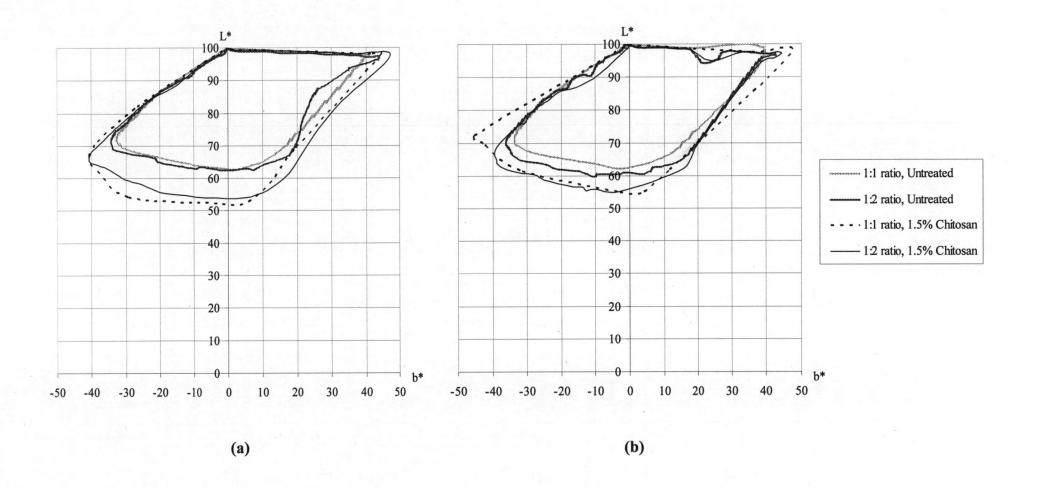


Figure 4.21: L*b* diagram of the inks printed on untreated and 1.5% W/V chitosan treated silk fabrics by the containing 1:1 and 1:2 pigment-to-binder ratios of (a) the 70-nm binder, and (b) the 180-nm binder.

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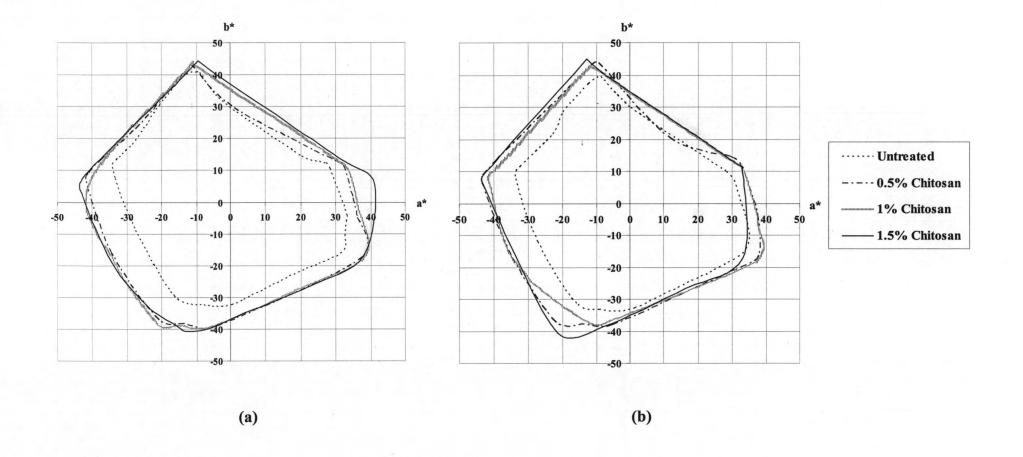


Figure 4.22: a*b* diagram of the inks from the ink containing the 1:1 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

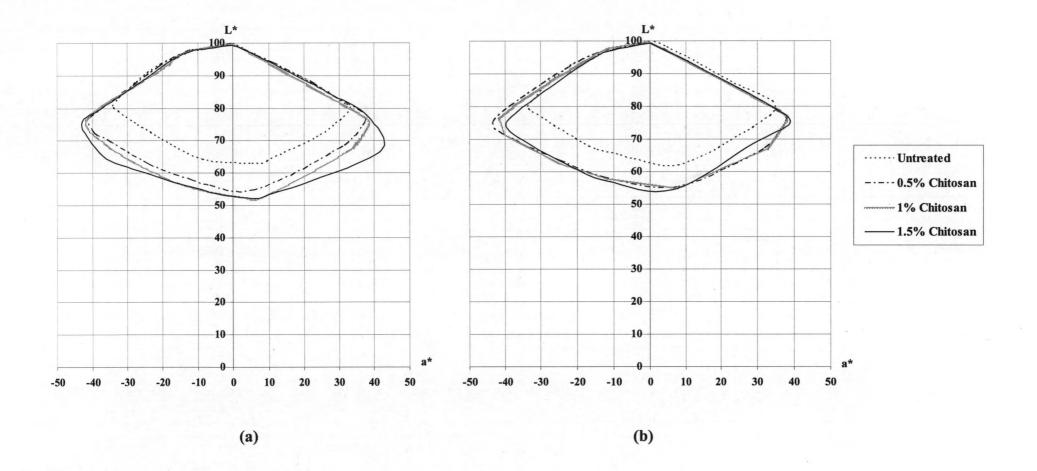


Figure 4.23: L*a* diagram of the inks from the ink containing the 1:1 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

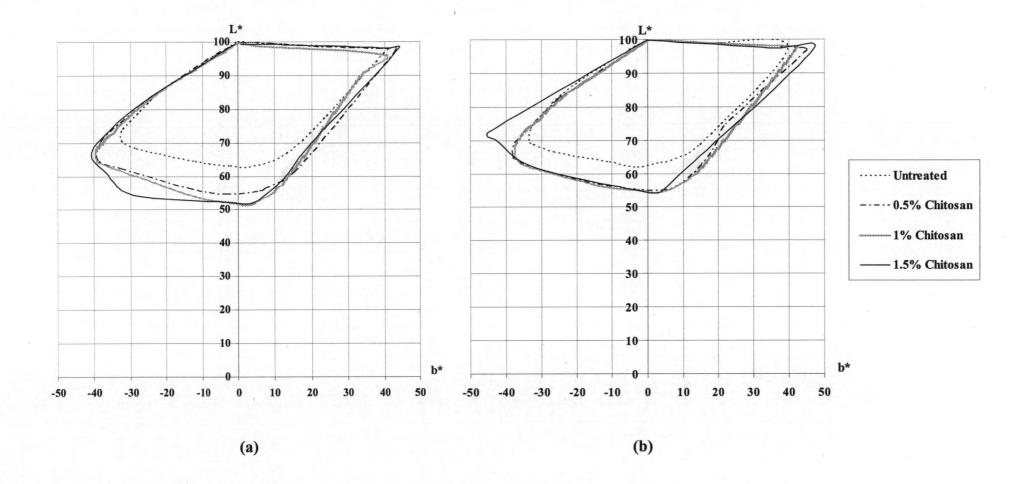


Figure 4.24: L*b* diagram of the inks from the ink containing the 1:2 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

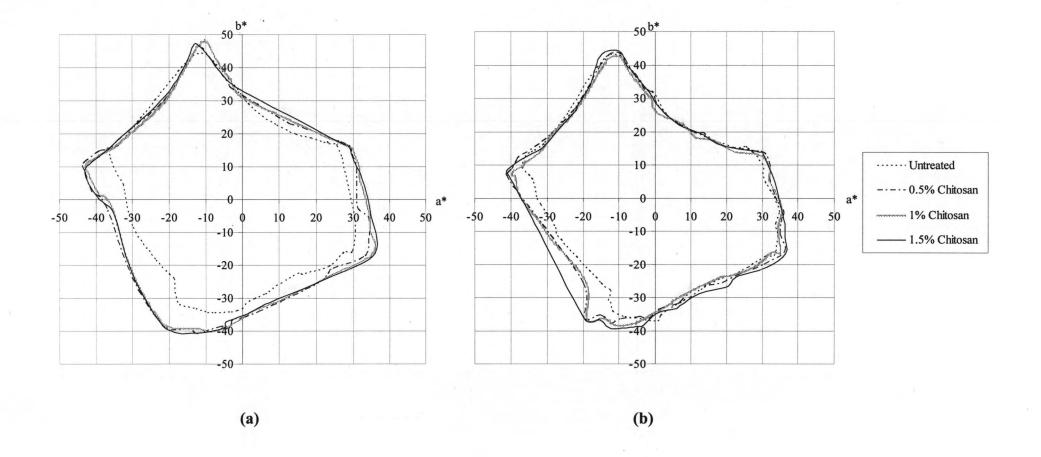


Figure 4.25: a*b* diagram of the inks from the ink containing the 1:2 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

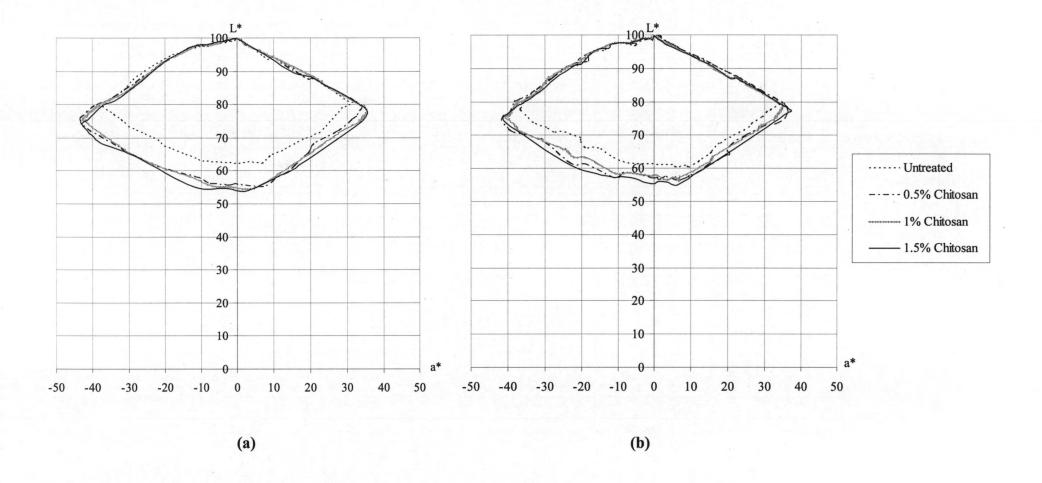


Figure 4.26: L*a* diagram of the inks from the ink containing the 1:2 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

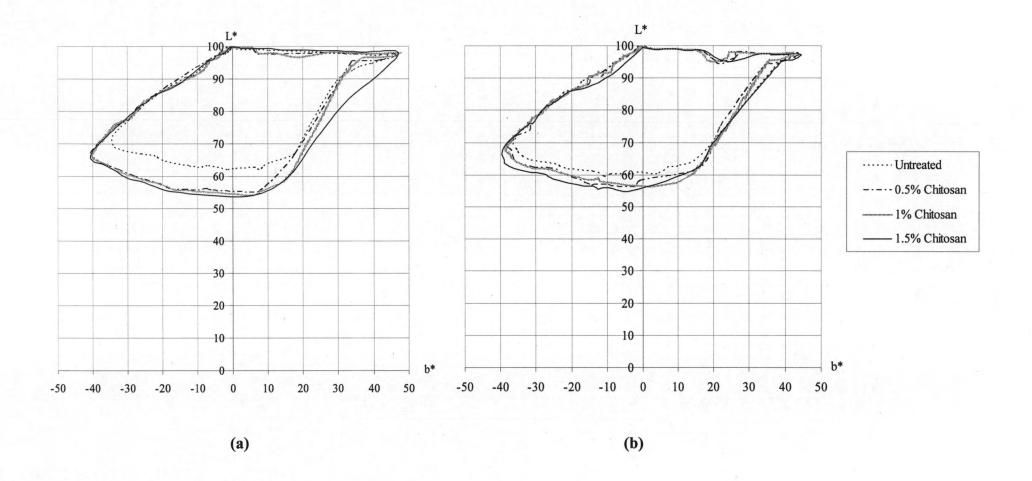
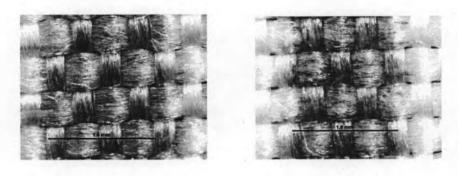


Figure 4.27: L*b* diagram of the inks from the ink containing the 1:2 pigment-to-binder ratio on untreated and chitosan treated silk fabrics by (a) the 70-nm binder and (b) the 180-nm binder.

4.2.5 Inter-color bleeding of the printed fabrics

The result shown in Figure 4.28(a) and (c) suggests that bleeding occurs and spreads in the untreated fabric. After the pretreatment, the ink can be held more on the fabric surface in which the large-sized binder yields a slightly longer bleeding distance than the smaller one (Figure 4.28(b),(d)). It should be also noted that the increase in percentage of chitosan yields less bleeding on the fabric.



(a)



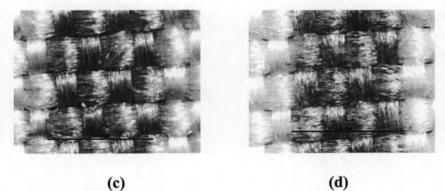


Figure 4.28: Effect of chitosan treatment and binder size of the inks containing 1:2 pigment-to-binder ratio on inter-color bleeding of the printed silk fabrics, (a) with 70-nm binder on the untreated fabrics, (b) with 70-nm binder on 1.5% chitosan treated fabrics, (c) with 180-nm binder on the untreated fabrics, and (d) with 180-nm binder on 1.5% chitosan treated fabrics.

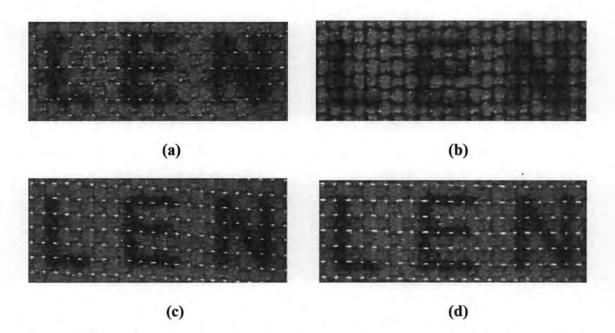


Figure 4.29: Effect of the binder size and surface treatment of the inks containing 1:2 pigment-to-binder ratio on color bleeding of the characters of LEN with (a) 70-nm binder on the untreated fabrics, (b) 180-nm binder on the untreated fabrics, (c) with 70-nm binder on 1.5% chitosan treated fabrics, and (d) with 180-nm binder on 1.5% chitosan treated fabrics.

The letter image "LEN" quality in Figure 4.29 was evaluated by naked eyes as having better quality after the treatment for the larger-sized binder. However, better techniques for evaluation of sharpness and bleeding shall be carried out [17, 37].

4.3 Physical properties of the printed silks

4.3.1 Effect on crock fastness on the printed fabrics

The dry and wet crock fastnesses of the untreated and treated fabrics obtained from the smaller-sized binder with a T_g of 9.7°C were better than those resulted from the larger one (with T_g of -15.5°C) because their films were far more flexible and withstand rubbing. As shown in Table 4.14, increase the pigment-to-binder ratio from 1:1 to 1:2 increases the crock fastness because more binder resin can hold more pigment and adhere stronger to the fabric surface. The chitosan pretreatment slightly decreases the crock fastness of the silk fabrics. When increasing the chitosan content, the dry/wet crock fastness decreases slightly. In the dry condition, the pretreatment does not affect the rub resistance, but its decreases the rub fastness in the wet condition. After the pretreatment, the silk fabric retained some amount of trapped acetic acid which might redissolve in wet condition. The treated fabrics usually retained the odor of acetic acid which can be one drawback of the chitosan treatment. The high crock fastness of the printed silk with the ink jet ink was caused by the low ink pick-up on the surface of fabric because the ink jet ink penetrated deeper into the yarn of fabric. The adhesion of the ink film to the fiber surface would be weakened by water so the wet film had lower adhesion to the silk surface and the strength was thus decreased [5].

Size	Pigment- to-binder	Chitosan pretreatment (%wt)	Level of crock fastness								
of binder			Dry condition				Wet condition				
	ratio		C	М	Y	K	C	М	Y	K	
70 nm	1:1	Untreated	4/5	4/5	5	5	4/5	4/5	4/5	5	
		0.5	4/5	4/5	5	4/5	4/5	4/5	4/5	5	
		1	4/5	4/5	5	4/5	4/5	4/5	4/5	5	
		1.5	4	4/5	4/5	4/5	4	4	4/5	4/5	
	1:2	Untreated	5	5	5	5	5	5	5	5	
		0.5	5	5	5	5	5	4/5	4/5	5	
		1	5	4/5	5	5	5	4/5	4/5	5	
		1.5	5	4/5	5	5	4/5	4/5	4/5	5	
180 nm	1:1	Untreated	4/5	4/5	5	5	4/5	4/5	4/5	5	
		0.5	4/5	4/5	4/5	4/5	4/5	4	4/5	4/5	
		1	4	4/5	4/5	4/5	4	4	4/5	4/5	
		1.5	4	4/5	4/5	4/5	4	4	4	4/5	
	1:2	Untreated	5	4/5	5	5	4/5	4/5	4/5	5	
		0.5	4/5	4/5	5	4/5	4/5	4/5	4/5	5	
		1	4	4/5	4/5	4/5	4	4	4/5	5	
		1.5	4	4/5	4/5	4/5	4	4	4/5	4/4	

Table 4.14: Crock fastness of the printed fabrics

4.3.2 Wash fastness on the printed fabrics

The wash fastness was determined by the K/S of the color on silk fabric which was measured before and after the washings. The wash fastness of the printed fabrics was ranged good to excellent in all conditions as illustrated in Table 4.15. The relative color strength was determined from the ratios of K/S of the printed fabrics after the washing and before the washing, so the relatively high color strength indicates the good wash fastness. The relative color strength is in the range 0.9-1.0 (Table 4.16). The reason might be that the binder in the ink formulation holds more ink on the fabric surface. Furthermore, the size of binder imposes an insignificant effect on K/S of the printed silk fabric. Likewise, differences of K/S before and after the washing are relatively insignificant which imply that the wash fastness is good for all colors. This is caused by the fact that the binders are self crosslinked acrylate-styrene based polymer to result in the insoluble polymer films on the fabric surfaces. Regardless of the binder particle size, the pigment-to-binder ratio and the level of chitosan pretreatment, the averages of relatively color strength of all colors are constant. This result indicates that ink color is waterfast because the ink films are crosslinked by the nature of self-crosslinking binder of the larger-sized binder. In addition, the cured ink films are hydrophobic which in resulting from the blend composition of the binder indicated by a high T_g value (Tg ~ 145°C).

Size of binder	Pigment-	Chitosan pretreatment (%wt)	K/S of the printed silk with the ink color								
	to- binder ratio		Cyan		Magenta		Yel	low	Black		
			Before washing	After washing	Before washing	After washing	Before washing	After washing	Before washing	After washing	
70 nm	1:1	Untreated	0.31 ± 0.01	0.30 ± 0.01	0.54 ± 0.02	0.52 ± 0.01	0.43 ± 0.03	0.42 ± 0.02	1.03 ± 0.00	1.03 ± 0.00	
		0.5	0.29 ± 0.01	0.28 ± 0.01	0.57 ± 0.03	0.57 ± 0.01	0.33 ± 0.05	0.30 ± 0.04	1.43 ± 0.06	1.41 ± 0.06	
		1	0.31 ± 0.00	0.30 ± 0.01	0.65 ± 0.01	0.64 ± 0.01	0.53 ± 0.02	0.51 ± 0.02	1.51 ± 0.00	1.49 ± 0.00	
		1.5	0.29 ± 0.00	0.28 ± 0.00	0.61 ± 0.02	0.59 ± 0.01	0.38 ± 0.00	0.37 ± 0.02	1.51 ± 0.01	1.48 ± 0.05	
	1:2	Untreated	0.34 ± 0.00	0.32 ± 0.00	0.54 ± 0.00	0.51 ± 0.01	1.07 ± 0.03	10.6 ± 0.01	1.10 ± 0.03	1.08 ± 0.00	
		0.5	0.30 ± 0.01	0.29 ± 0.01	0.57 ± 0.03	0.55 ± 0.03	1.05 ± 0.01	1.01 ± 0.02	1.44 ± 0.04	1.40 ± 0.00	
		1	0.31 ± 0.01	0.30 ± 0.01	0.62 ± 0.07	0.59 ± 0.06	1.11 ± 0.09	1.07 ± 0.07	1.60 ± 0.07	1.60 ±0.09	
		1.5	0.30 ± 0.01	0.29 ± 0.01	0.50 ± 0.01	0.48 ± 0.01	1.02 ± 0.01	0.96 ± 0.01	1.60 ± 0.07	1.51 ±0.05	
180 nm	1:1	Untreated	0.31 ± 0.00	0.31 ± 0.00	0.50 ± 0.07	0.49 ± 0.07	1.01 ± 0.02	0.95 ± 0.02	1.08 ± 0.13	1.04 ± 0.11	
		0.5	0.31 ± 0.02	0.30 ± 0.02	0.60 ± 0.00	0.59 ± 0.00	1.04 ± 0.00	1.03 ± 0.01	1.35 ± 0.02	1.34 ± 0.01	
		1	0.29 ± 0.00	0.28 ± 0.00	0.60 ± 0.01	0.59 ± 0.01	0.99 ± 0.00	0.99 ± 0.01	1.43 ± 0.00	1.40 ± 0.01	
		1.5	0.28 ± 0.00	0.28 ± 0.00	0.59 ± 0.00	0.57 ± 0.01	0.99 ± 0.01	0.97 ± 0.01	1.34 ± 0.03	1.32 ± 0.03	
	1:2	Untreated	0.34 ± 0.03	0.33 ± 0.03	0.54 ± 0.03	0.52 ± 0.01	0.99 ± 0.20	0.98 ± 0.21	1.01 ± 0.06	1.00 ± 0.05	
		0.5	0.31 ± 0.01	0.30 ± 0.01	0.57 ±0.00	0.55 ± 0.01	0.94 ± 0.01	0.93 ± 0.00	1.35 ± 0.08	1.30 ± 0.05	
		1	0.27 ± 0.00	0.27 ± 0.02	0.45 ± 0.01	0.44 ± 0.02	0.82 ± 0.02	0.78 ± 0.02	1.18 ± 0.05	1.12 ± 0.03	
		1.5	0.32 ± 0.00	0.31 ± 0.01	0.54 ± 0.03	0.52 ± 0.03	0.97 ± 0.04	0.90 ± 0.02	1.54 ± 0.01	1.45 ± 0.01	

Table 4.15: K/S of the printed silk fabrics before and after washings

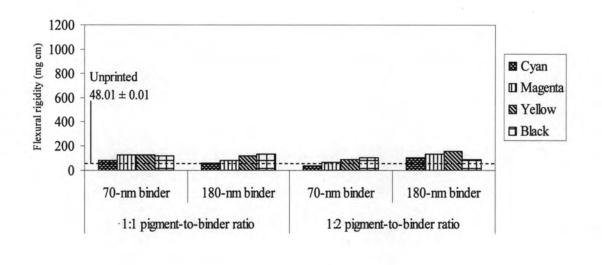
Size of binder	Pigment- to-binder	Chitosan pretreatment	Average of relative color strength						
	ratio	(%wt)	Cyan	Magenta	Yellow	Black			
70 nm	1:1	Untreated	0.97 ± 0.01	0.96 ± 0.01	0.97 ± 0.02	1.00 ± 0.00			
		0.5	0.98 ± 0.00	1.00 ± 0.03	0.92 ± 0.03	0.99 ± 0.00			
		- 1	0.98 ± 0.03	0.99 ± 0.03	0.96 ± 0.00	0.99 ± 0.00			
		1.5	0.98 ± 0.00	0.97 ± 0.02	0.96 ± 0.05	0.98 ± 0.04			
	1:2	Untreated	0.93 ± 0.01	0.93 ± 0.00	0.99 ± 0.02	0.98 ± 0.03			
		0.5	0.97 ± 0.00	0.96 ± 0.00	0.96 ± 0.01	0.97 ± 0.03			
		1	0.97 ± 0.01	0.94± 0.01	0.97 ± 0.02	0.97± 0.01			
		1.5	0.96 ± 0.00	0.97 ± 0.00	0.94 ± 0.00	0.94 ± 0.01			
180 nm	1:1	Untreated	0.97 ± 0.01	0.99 ± 0.01	0.99 ± 0.04	0.99 ± 0.02			
		0.5	0.98 ± 0.01	0.98 ± 0.01	0.99 ± 0.01	0.99 ± 0.00			
		1	0.97 ± 0.00	0.98 ± 0.01	0.97 ± 0.00	0.98 ± 0.01			
		1.5	0.98 ± 0.00	0.97 ± 0.01	0.98 ± 0.01	0.98 ± 0.00			
	1:2	Untreated	0.96 ± 0.00	0.97 ± 0.05	0.99 ± 0.02	0.99 ± 0.01			
		0.5	0.98 ± 0.01	0.96 ± 0.00	0.98 ± 0.00	0.96 ± 0.03			
		1	1.01 ± 0.05	0.97 ± 0.02	0.95 ± 0.01	0.96 ± 0.02			
		1.5	0.99 ± 0.02	0.96 ± 0.01	0.93 ± 0.01	0.94 ± 0.01			

Table 4.16: Relative color strength of the printed silk fabrics after the washing

4.3.3 Bending stiffness of the printed fabrics

The effects of binder size in inks, pigment-to-binder ratio, and pretreatment on fabric flexural rigidity (bending stiffness) properties of silk fabric are given in Figures 4.30 to 4.31, wherein the fabric bending length is measured. The higher bending length value means the higher bending stiffness of the fabric. The bending stiffness in the warp or machine direction was similar to that of the weft or cross-machine direction printing with the ink jet inks. In Figure 4.30, the bending stiffness by different binder sizes and different pigment-to-binder ratios are not different. The bending stiffness of the silk fabrics treated with chitosan was significantly increased than other factors because the chitosan solution grouped the silk fiber together (Figure 4.12). The pretreatments increased the bending stiffness of the fabric since the bending stiffness depends on the amount of treating chemicals that deposited on the fabric surface, the fibers being grouped possess less flexibility and tend to resist bending. In addition, the amount of fibrils assembles in a single yarn was found to be larger in the weft direction than those contained in the warp direction. This results in the addition of fabric bending stiffness. However, the fabric bending stiffness obtained from the larger-sized binder yields a comparable result with that of the small-sized binder.

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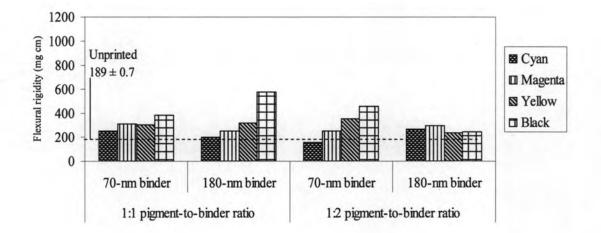
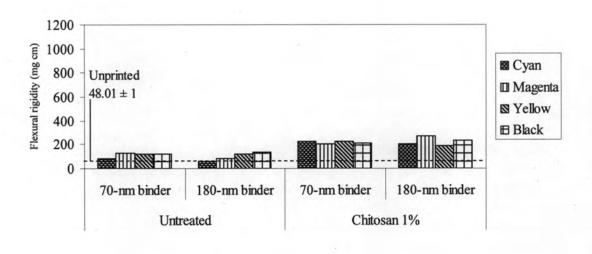
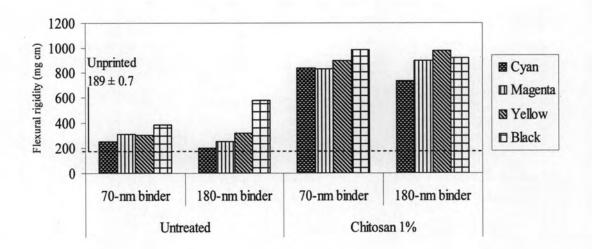




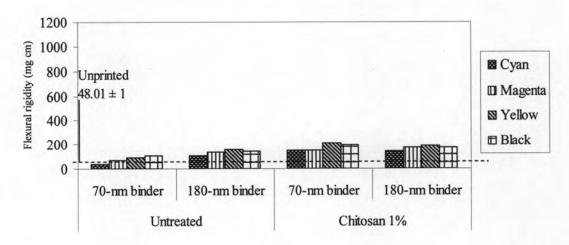
Figure 4.30: Effect of 1:1 and 1:2 pigment-to-binder ratio and binder size on bending stiffness of the untreated silk fabric (a) in the warp direction and (b) in the weft direction.



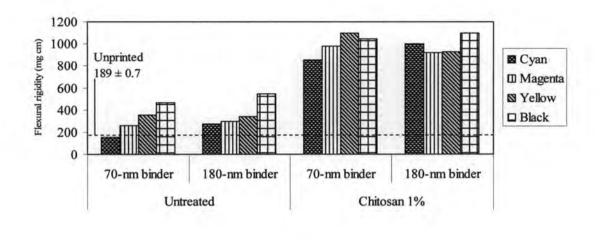




(b)



(c)



(d)

Figure 4.31: Effect of the untreated and 1% W/V chitosan treatment and binder size on bending stiffness of the silk fabrics: (a) at 1:1 pigment-to-binder ratio in the warp direction; (b) at 1:1 pigment-to-binder ratio in the weft direction; (c) at 1:2 pigmentto-binder ratio in the warp direction; (d) at 1:2 pigment-to-binder ratio in the weft direction.

4.3.4 Air permeability of the printed fabrics

The air permeability of all the printed fabrics is similar to the bending stiffness properties (Figures 4.32 to 4.34). Air permeability was significantly enhanced more than that of the untreated one in which increases in the chitosan concentration render a stronger, favorable effect. The air permeability of the pretreated silk fabric was the higher than that of the untreated one because the chitosan was not only coated the yarns but also grouped the fiber & within the yarn to bundles of fiber and became a packed and rigid yarn, introducing the wider inter-yarn spaces while the untreated fabric has inter-fiber spaces but not the inter-yarn spaces. Thus, air permeability of chitosan pretreatment fabric are higher than the untreated fabrics, Moreover, the size of binder particles in the inks had a slight effect on air permeability in comparison with the chitosan pretreated fabrics.

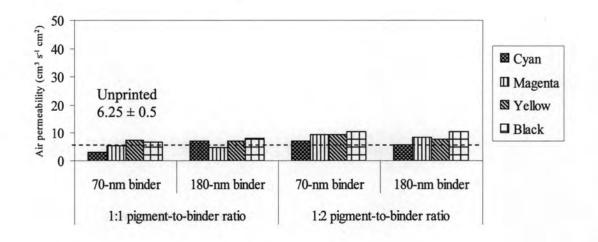


Figure 4.32: Air permeability of the untreated silk fabrics.

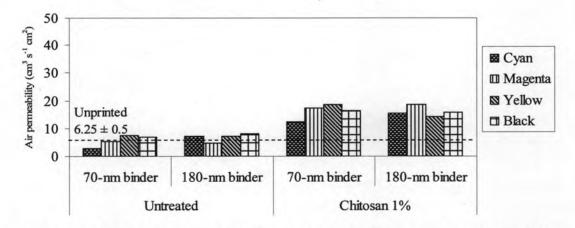


Figure 4.33: Air permeability of 1:1 pigment-to-binder ratio on silk fabrics printed with inks containing different binder contents

