

CHAPTER 4

RESULTS AND DISCUSSTION

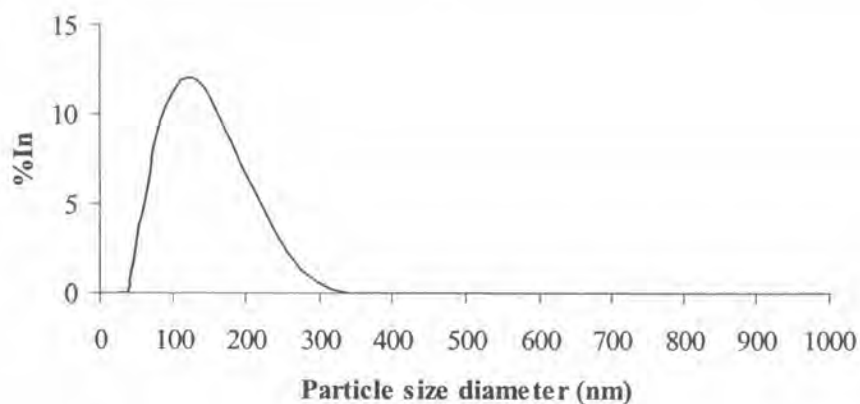
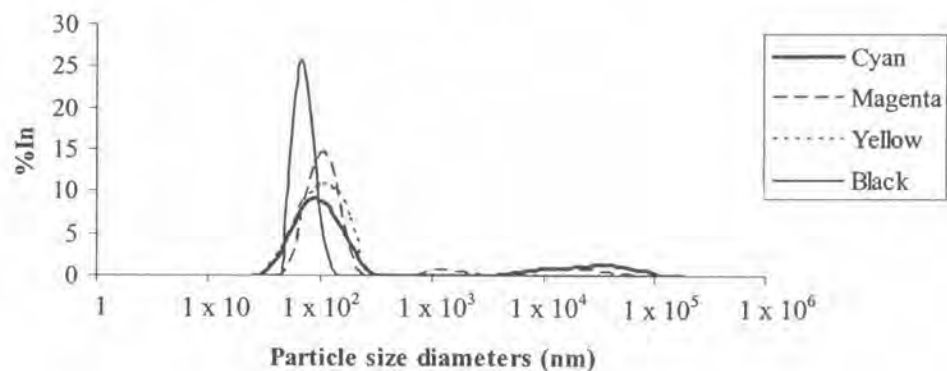
4.1 Properties and stability of the pigmented ink jet inks.

4.1.1 Particle size and stability

The particle sizes of the pigments and binder for the in-house ink jet inks based on the formulations in Table 3.3 (before filtration) are shown in Table 4.1. For the binder S-711 (Figure 4.1), the average particle size is found approximately of 120 nm. The black and yellow pigmented dispersions as shown in Figure 4.2 have narrower particle size distributions. The average particle sizes of these pigmented dispersions are of around 100 nm while the cyan and black inks are below 100 nm. The cyan and magenta pigmented dispersions have the largest particle sizes in the range of $30 - 1.2 \times 10^5$ and $50 - 6.9 \times 10^4$ nm, respectively. The zeta-potential indicates the strength of the repulsive force between colloids. The zeta-potential of the pigmented dispersions informed that the charge on the pigment surfaces is negative (Table 4.1). Therefore, the pigmented dispersions dispersed very well due to a high zeta-potential, originated from the sulfonate group on the pigment surface. The negative charges of pigment particle generated from the sulfonate group, according to Cabot Company [44].

Table 4.1: Particle sizes of the pigment dispersions before filtration

Pigmented dispersions	Average particle sizes (nm)	Zeta-potential (mV)
Cyan (C.I. Pigment Blue 15:4)	91	- 55
Magenta (C.I. Pigment Red 122)	105	- 57
Yellow (C.I. Pigment Yellow 74)	105	- 52
Black (C.I. Pigment Black 7)	69	- 64
Binder (S-711)	120	-38

**Figure 4.1:** Particle size distribution of S-711 binder**Figure 4.2:** Particle size distributions of the pigment dispersions

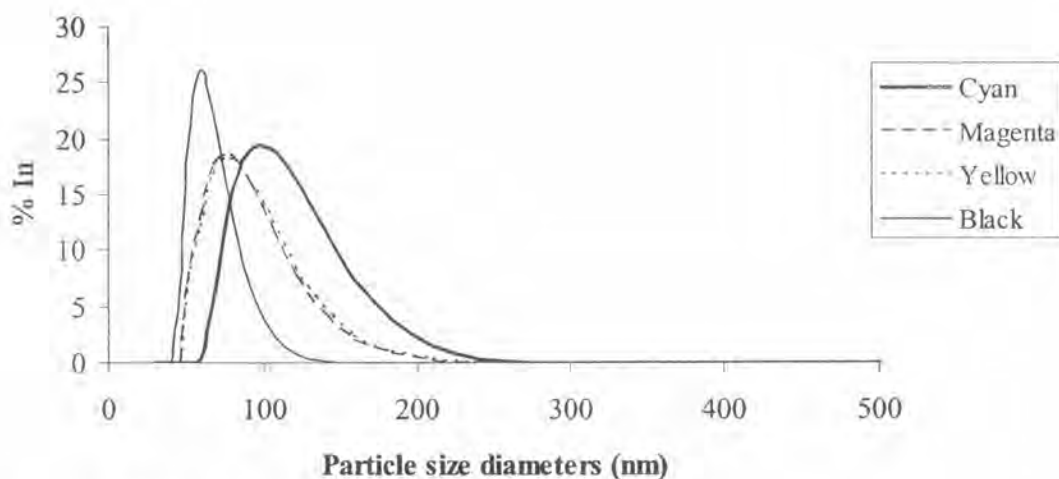
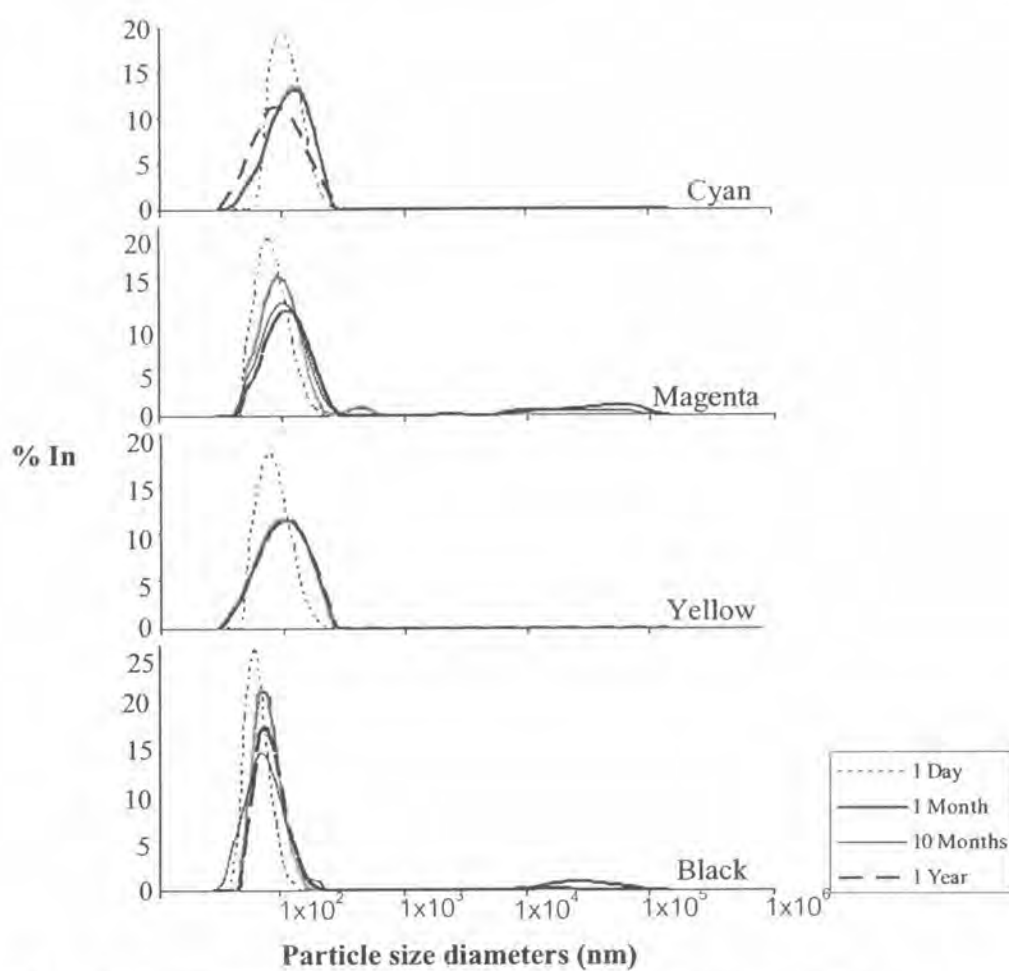


Figure 4.3: Particle size distributions of the four color inks

The prepared inks (Cyan, Magenta, Yellow, and Black) have pHs in the range of 8-9. The particle sizes of the inks must be measured after filtration to check for the oversize of ink particles in cartridges. The large sizes of ink particles may clog the orifice of the printer during printing so the inks must be filtered before printing. The four color inks have different average particle diameters depending on the types of pigment. The black ink jet ink has the smallest particle size of 60 nm whereas the cyan ink jet has the largest particle size of 105 nm. Both of the magenta and yellow inks have the similar particle size of 79 nm (Figure 4.3). As a whole, the four-color inks have the particle size distribution in a range of 46 – 240 nm at different frequencies.

Table 4.2: Particle sizes of the inks during storage

Inks	Average particle sizes (nm)			
	1 Day	1 Month	10 Months	12 Months
Cyan	105	120	120	91
Magenta	79	91	105	105
Yellow	79	105	105	105
Black	60	69	69	79

**Figure 4.4:** The particle size distributions of the inks after various storage times

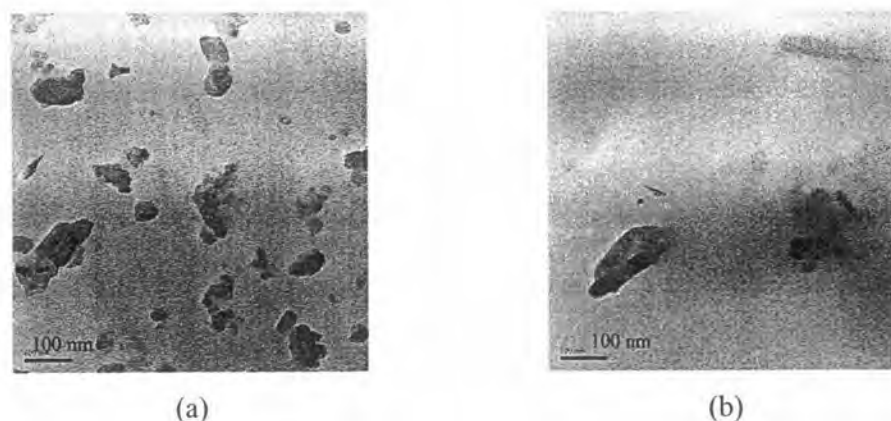


Figure 4.5: TEM of (a) the cyan ink and (b) the yellow ink for 1-year storage

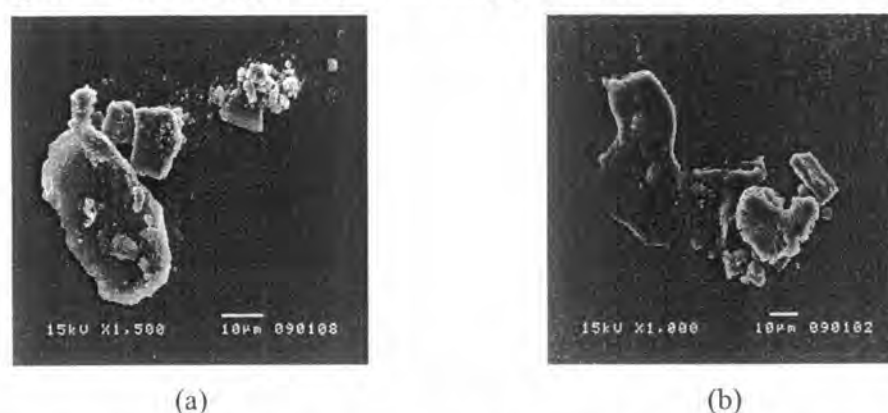


Figure 4.6: SEM of (a) the magenta ink and (b) the black ink for 1-year storage

These inks have much narrower particle size distributions. Figure 4.4 and Table 4.2 illustrate the stability of the inks by measuring the particle size distributions of the inks during storage. The results showed that the particle sizes of cyan and yellow inks maintained fairly constant within 1 year in which the particle sizes did not change. The large particle sizes of the magenta ink are in the range of $1.67 \times 10^3 - 1.2 \times 10^5$ nm and black ink are in the range of $8.7 \times 10^3 - 1.01 \times 10^5$ nm for 10-month and 1-year storages, respectively. The ink particle sizes confirmed by TEM and SEM are shown in Figures 4.5 and 4.6. Moreover, TEM of the pigment particles was investigated in the Appendix A (a – d). The particle sizes of cyan and yellow inks are less than 200 nm whereas the magenta and black inks contained the large particles at around $5 \times 10^3 - 1.2 \times 10^5$ nm. After filtering, all the pigmented inks are thus suitable

for the ink application because the particle sizes remain unchanged for 10 months. The ejections of these inks were smooth during printing and the head nozzle requires a few times of cleaning.

4.1.2 Viscosity

Typically, viscosity of ink jet ink is about 1 – 5 mPa s. Above this range, the ink is too viscous to flow through the nozzle or pass through the orifice, resulting in a clogging problem during the drop ejection [14]. All the ink viscosity of the prepared inks measured at room temperature (25°C) exhibit a typical Newtonian flow in which shear stress linearly depends on shear rate (Figure 4.7). The results in Figure 4.8 show that all inks have viscosities approximately of 2.5 mPa s. This low viscosity allows the inks to be printed by Epson inkjet printer using the piezo technology. The piezo print head uses high shear force in jetting the ink; thus, the inks should be durable to shear force.

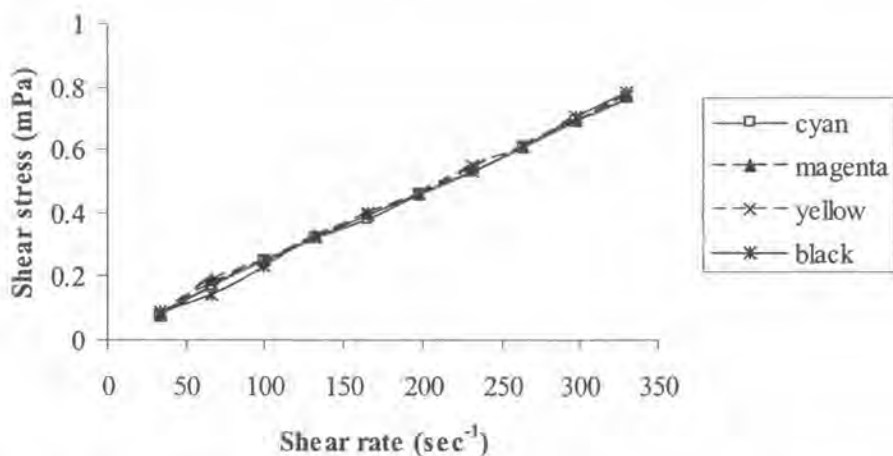


Figure 4.7: Shear stress – shear rate relationship of the four-color inks

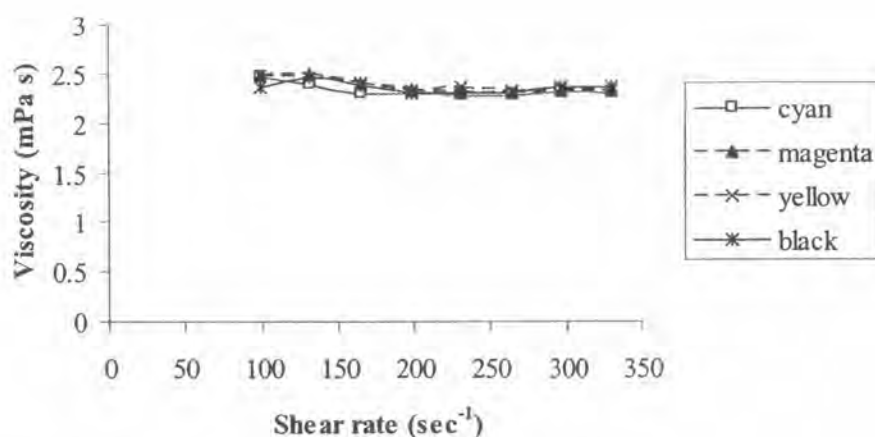


Figure 4.8: Viscosity of the four-color inks measured at 25°C

Inks were prepared by adding the pigments with stirring to a mixture of deionized water, urea, binder, DEG and glycerol. The ink properties showed an acceptable behavior for the inkjet textile printing system. The density of the inks was about 1 g cm^{-3} and zeta-potential of the inks informed that the pigment particles in the inks dispersed very well (-42 to -51 mV) as shown in Table 4.3.

Table 4.3: Ink properties

Inks	Viscosity (mPa s)	Surface tension (mN m ⁻¹)	Density (g cm ⁻³)	Zeta-potential (mV)	Solid Content (%)
Cyan	2.40	44.1 ± 1.6	1.04	-47.86	28.30
Magenta	2.45	44.1 ± 1.0	1.05	-42.52	27.85
Yellow	2.45	44.7 ± 0.5	1.05	-42.46	28.16
Black	2.52	43.3 ± 0.3	1.05	-50.86	28.63

The DSC analysis was measured, showed that T_g of the binder is -3.1°C , suggesting that the binder was elastic and would exhibit viscous deformation at room temperature. The inks made from the surface-modified pigment had a low viscosity and a high surface tension because of a low content of dispersant addition which is a major component in the ink dispersion. Surface modification of pigments generally yields the high surface tension. Since water has a high surface tension at 72 mN m^{-1} , the surface tension of the ink was reduced to 44 mN m^{-1} (Table 4.3) by the other components in the inks [7]. A dispersant on the pigment surface can migrate from the surface during the ink preparation, resulting in a zeta-potential decrease.

Table 4.4: The relation of viscosity, surface tension of the ink jet inks, and optical density of the printed fabrics

Inks	Viscosity (mPa s) (η)	Surface tension (mN m^{-1}) (γ)	$\sqrt{\frac{\gamma}{\eta}}$	Optical density
Cyan	2.40	44.8	4.32	0.31 ± 0.03
Magenta	2.45	44.0	4.24	0.32 ± 0.04
Yellow	2.45	44.6	4.27	0.46 ± 0.04
black	2.52	43.2	4.14	0.61 ± 0.03

The optical density of the printed fabrics is evaluated from Equation 4.1, indicating the ink density. The higher optical density promotes the higher ink density.

$$D = \log_{10} O \quad (4.1)$$

Here D = optical density, O = intensity of incident light / intensity of transmitted light [45]

From Table 4.4, when the surface tension of the inks is decreased, the penetration distance is also decreased, the optical density of the prints increase. This phenomenon has been expressed by the Lucas – Washburn equation (Eq. 4.1) as follows [43]:

$$h = \left(\frac{r\gamma \cos\theta}{2\eta} \right)^{1/2} t^{1/2} \quad (4.1)$$

Where h = penetration distance after time t ; r = pore radius; γ = surface tension; θ = contact angle; η = viscosity.

The optical density of printed fabric is high when the square root of surface tension divided by viscosity ($\sqrt{\frac{\gamma}{\eta}}$) is decreased. The remaining parameters (r , θ , and t) are approximately similar in all inks. The higher optical density resulted from a higher deposition of the ink film on the printing surface.

4.2 Characterization of the pretreated and printed silk fabrics

4.2.1 Wicking test on the pretreated fabrics

All results of wicking test were reported at the highest concentrations of pre-treating solutions. The P/F ratio was evaluated from the ratio of the absorbing length in the warp and weft directions. Theoretically, the P/F ratio (warp/weft) closes to 1 denotes a uniform wicking behavior of the fabric in the warp and the weft directions. From Table 4.5, the P/F ratio indicates that the weft yarns have more hydrophilicity than the warp yarns because the P/F ratio of the weft in water is higher than that in 2 octanol. This could be explained according to the observation that the weft yarns have a slightly yellower color than that of the warp yarns, implying that the weft yarns of the fabric contain more sericin (silk glue) which tends to absorb moisture.

Table 4.5: Water (W) and 2-Octanol (O) wicking rate of the pretreated fabrics

Pretreatments	Fluid	Warp (P) (cm)	Weft (F) (cm)	P/F	W/O
Non-treated	W	3.7 ± 0.4	5.7 ± 0.1	0.7	0.6
	O	4.4 ± 0.2	4.2 ± 0.4	1.1	
10% Serine	W	5.8 ± 0.3	5.8 ± 0.4	1.0	1.0
	O	4.9 ± 0.2	4.6 ± 0.2	1.1	
5% Aspartic acid	W	5.4 ± 0.5	5.4 ± 0.1	1.0	0.7
	O	4.7 ± 0.2	3.5 ± 0.0	1.4	
20% Glycine	W	5.7 ± 0.1	4.6 ± 0.0	1.3	1.1
	O	4.6 ± 0.2	3.9 ± 0.1	1.2	
15% Sericin	W	3.6 ± 0.3	4.0 ± 0.2	0.9	0.8
	O	3.9 ± 0.1	3.5 ± 0.1	1.1	
2% FL-80	W	1.8 ± 0.3	2.0 ± 0.3	0.9	0.8
	O	3.1 ± 0.2	3.0 ± 0.2	1.0	
2% FM-80	W	0.2 ± 0.2	0.5 ± 0.1	0.3	0.3
	O	2.6 ± 0.2	2.4 ± 0.1	1.1	
1% FM-40	W	0.5 ± 0.1	0.7 ± 0.1	0.7	0.7
	O	2.8 ± 0.1	3.0 ± 0.3	1.0	
10% Sanfix 555	W	5.6 ± 0.3	4.6 ± 0.2	1.2	1.0
	O	4.5 ± 0.2	3.8 ± 0.1	1.2	

The W/O (the average value of the warp and weft wicking rates in water and in 2-octanol) is an index describing the relation of the fabric to wick hydrophobic versus hydrophilic fluids. W/O is more than 1, indicating the hydrophilicity whereas hydrophobicity is implied when W/O is less than 1.

When the silk fabrics were treated with some pre-treating solutions, the hydrophilicity of the fabric is improved. The pretreatments can improve the ink absorption because the medium of the ink jet ink is also water. The pre-treating materials with low MW yield more hydrophilicity because they can easily dissolve and can diffuse faster than those of high MW substances. The amino acid pretreatments provided a higher W/O ratio because they are of low molecular weight. The W/O value of aspartic acid pretreatment was smaller than those of serine and glycine since the concentration prepared (at 5% w/v) could be in an excess amount, resulting in a thicker coating on the fabric surface in which the yarns took a longer time to wick water. Chitosan solutions coated on the fabrics had decreased the hydrophilicity of the fabrics. The W/O ratio of the chitosan coated fabric was the lowest. The reason for such a result is that the high MW chitosan cannot dissolve easily in water; thus, the wicking of the silk fabrics coated with chitosan was the worst. This result was confirmed by the water contact angle of 120.5° as shown in Figure 4.9 (a). The water contact angles on other pretreated fabrics cannot be measured because the water drop disappears in a second (Figure 4.9 (b)). All pre-treating agents except chitosan improved the silk fabric hydrophilicity. Nevertheless, the chitosan coated silk fabrics received a higher amount of ink jet inks on their surfaces as seen in next section.

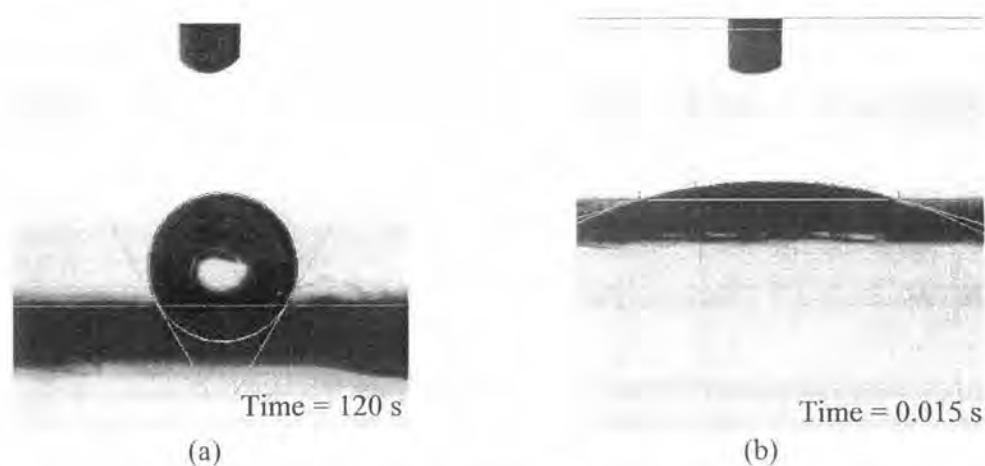
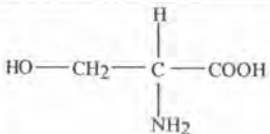
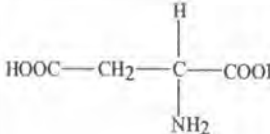
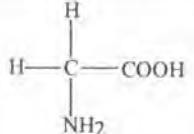
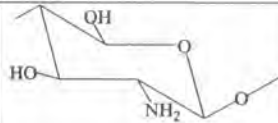
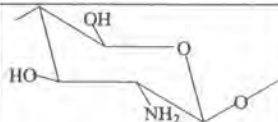
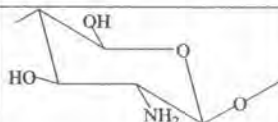


Figure 4.9: Contact angles of water on (a) 2% w/v chitosan (FM-80, MW = 3.7×10^5 Dalton) coated silk, (b) 20% glycine coated silk

4.2.2 Properties of the pre-treating solutions

The color saturation of the ink jet ink depended greatly on the prior occurrence of capillary flow into the fiber. Therefore, the viscosity and surface tension of the pre-treating solutions are the two important factors governing the color strength on the fabric surfaces. The Lucas – Washburn equation (Eq. 4.1) is then valid to determine the penetration depth of the ink which is a direct proportional to the square root of the surface tension to viscosity ratio of the fluid. Based on Table 4.6, we calculated this value for each pre-treating agent, and found that 10% w/v of serine, 20% w/v of glycine, and 10 w/v of Sanfix 555 produce a higher square root of surface tension to viscosity ratio ($\sqrt{\frac{\gamma}{\eta}}$), giving a deeper ink penetration, while the chitosan and sericin pretreatments yield a lower number of such parameter, indicating a short distance of ink penetration. These results are supported by the cross-section of the treated silk fibers shown in Figures 4.10 – 4.11.

Table 4.6: Properties of the pretreatments

Pretreatments (Molar)*	Molecular structure	MW (Dalton)	Viscosity** (mPa s)	Surface tension (mN m ⁻¹)	$\sqrt{\frac{\gamma}{\eta}}$
10% Serine (0.95 M)		105	1.33	71.1 ± 1.3	7.31
5% Aspartic Acid (0.38 M)		133	Not available		
20% Glycine (2.66 M)		75	1.45	72.4 ± 0.2	7.07
15% Sericin (3.80 × 10 ⁻⁴ M)	Figure 3.2	4 × 10 ⁵	92.30	48.3 ± 0.1	0.39
2% Chitosan (FL-80) (1.67 × 10 ⁻⁴ M)		1.2 × 10 ⁵	35.40	64.1 ± 2.1	1.35
2% Chitosan (FM-80) (5.41 × 10 ⁻⁵ M)		3.7 × 10 ⁵	234	66.8 ± 1.3	0.56
1% Chitosan (FM-40) (1.18 × 10 ⁻⁵ M)		8.5 × 10 ⁵	60.10	61.2 ± 1.4	1.01
10% Sanfix 555 (3.80 × 10 ⁻⁴ M)	Figure 3.3	4 × 10 ⁵	1.39	53.8 ± 3.0	6.22

*The concentration of each pre-treating chemical was limited by its solubility in water.

**The viscosity was measured at a shear rate of 25 rpm at 25°C by Brookfield Viscometer.

4.2.3 Cross - section of the silk fabric

The fabrics printed with the four-color inks were cut in the cross section direction and observed by the Image analyzer. It is noticed that the pretreatments reduce ink spreading significantly. After the pretreatment, the depth of ink penetration in the pretreated fabric becomes less than that of the untreated one as shown in Figure 4.10, yielding an increase in the deposition ink.

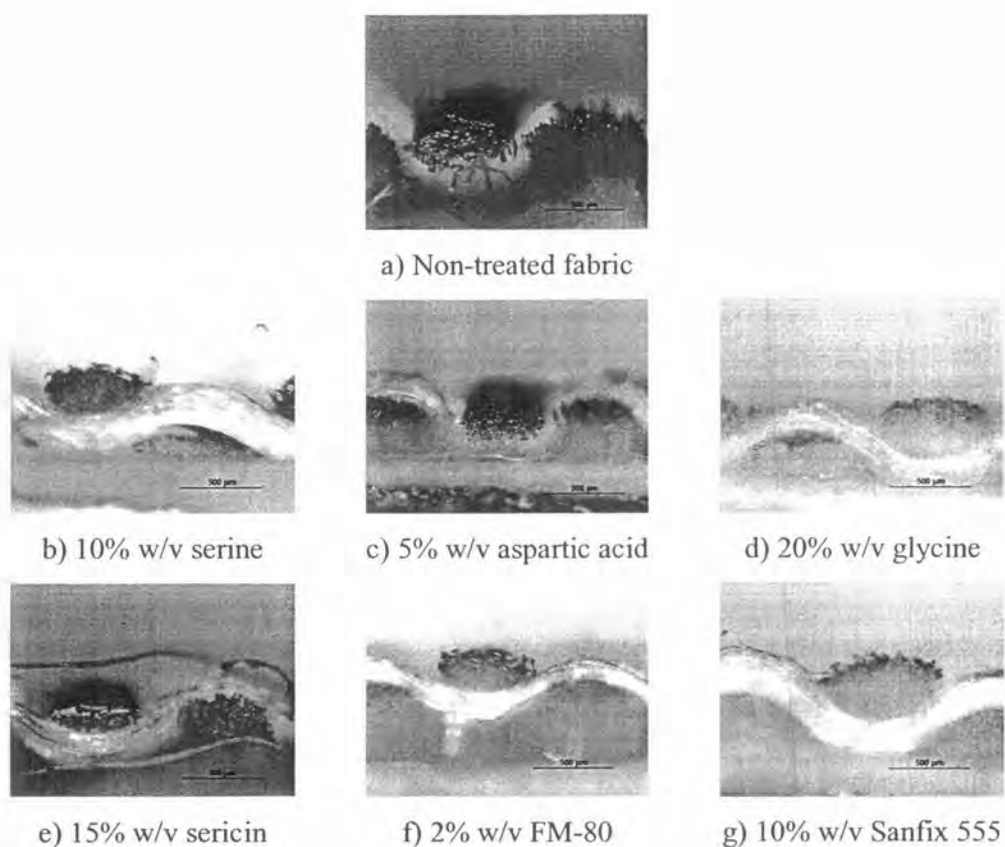


Figure 4.10: Image analyzed cross-section of the non-treated and treated silk fiber in the weft direction after printing with black color ink

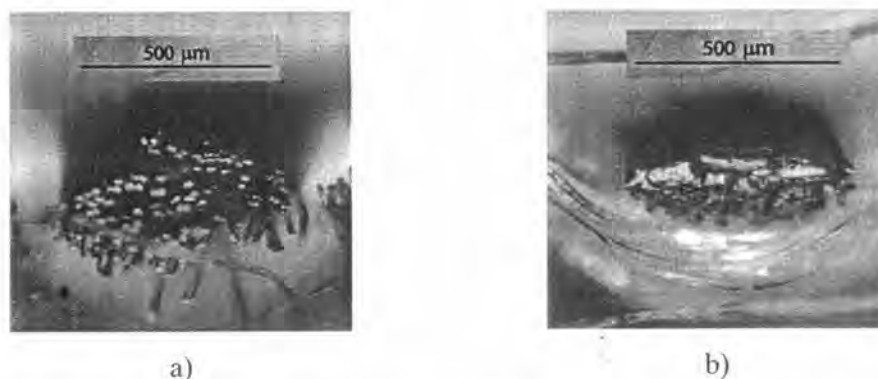


Figure 4.11: The enlargement of image cross-section of (a) the non-treated and (b) 15% w/v of sericin treated fabric in the weft direction after printing with black color ink

As shown in Figure 4.11 with enlarged cross-section image, the cross-section of the sericin pretreated fabric in Figure 4.11 (b) is shorter than the non-treated fabric in Figure 4.11 (a) because the viscosity and surface tension of the sericin pretreatments affect the ink penetration distance. This is because the space of inter-fiber of the pretreated fabric was decreased. The ink penetration in sericin and chitosan coated layers is much shorter than those of the amino acid pretreatments. Since both sericin and chitosan are viscous solution, which could block inter-fiber spaces; thus, the inks were mostly deposited on the yarn surfaces (Figure 4.12 (e-h)). As a result, the sericin and chitosan provide a larger color gamut (Figures 4.15 – 4.17). Besides, these pretreatments contain many functional groups to fix the inks on the fabric surfaces, and give higher color strength. Likewise, ink penetration in the warp direction is similar to that of the weft direction as shown in the Appendix C. The relationship between the ink penetration distances (h) calculated from the Lucas – Washburn equation (Eq. 4.1) had been further confirmed by cross-sectioned pictures of the printed fabrics. The pretreatments with chitosan and sericin yielded a low value of the square root of surface tension to viscosity ratio (Table 4.6), resulting in a low

ink penetration depth in which the penetration distance directly relates to $\sqrt{\frac{\gamma}{\eta}}$. The result indicates that the ink pigments are deposited on the pretreatment layer of the fabrics during printing, while the water and solvent have been penetrated further into the fabric [43].

4.2.4 Surface appearance of the pretreated silk fabrics

From the cross-sectioned surfaces (Figure 4.12 (a)), the non-treated fibers in the yarn are distributed loosely. The amino acid and Sanfix 555 pretreatments also provided similar fiber arrangement (Figure 4.12 (b-d, i)). The silk yarns were more compacted when the fabric was coated with chitosan and sericin as shown in Figure 4.12 (e-h). This is because these two materials are viscous and able to pack the yarns together, reducing the opening areas of the inter-fiber spaces. As a result, the ink cannot further penetrate into the yarn because decreased inter-fiber spaces cannot accommodate a large amount of inks, and more inks were resided on the surface as shown in Figures 4.11. The SEM micrographs in Figure 4.13 (a-d, i) show that the serine treated surface appeared to be as smooth as the untreated surface while the aspartic acid, glycine, and sanfix 555 increased roughness of the silk fibers. The sericin was obviously found on the silk surface in a speck form (Figure 4.13 (e)). All chitosan treated surfaces appeared to be as smooth as the untreated surface as well. The chitosan pretreatment decreased debris fibers and increased smoothness of the yarn surface (Figure 4.13 (f-h)).

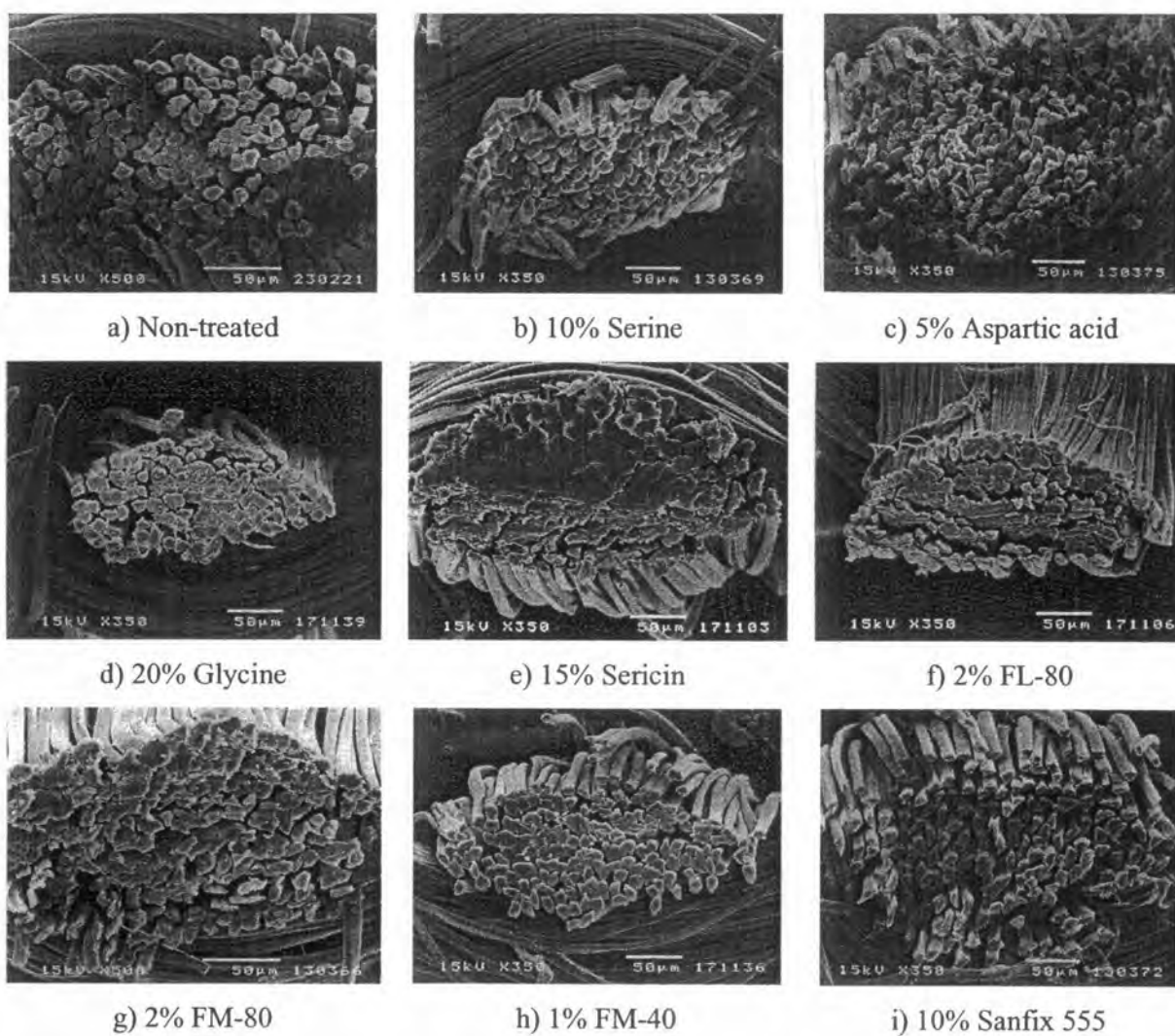


Figure 4.12: Cross-section of the non-treated and the treated silk fiber

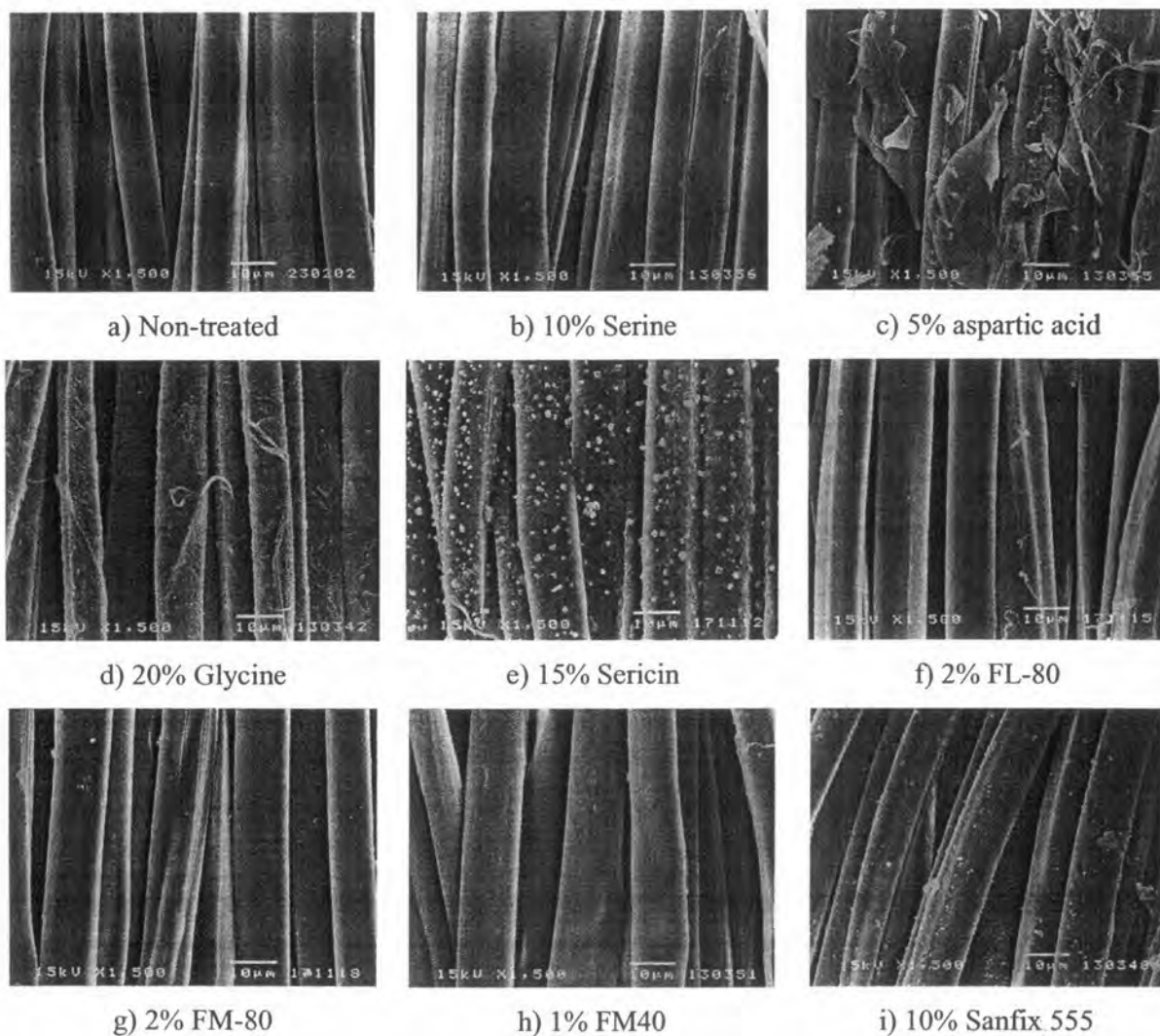


Figure 4.13: SEM Micrographs of the non-treated and the treated silk fiber surfaces

The amino acids with low MW penetrated deeper into the fibers, so the inks promoted the penetrating depth (Figures 4.10) resulting in good crock fastness. When the concentrations of glycine and sericin were increased on the fabrics, the roughness of silk surface was also enhanced (Figure 4.14 (a –f)); moreover, the silk yarns were well packed (Figure 4.14 (k –m)). The surface of chitosan remains the same when the concentration of the pretreatment was increased (Figure 4.14 (g-j)).

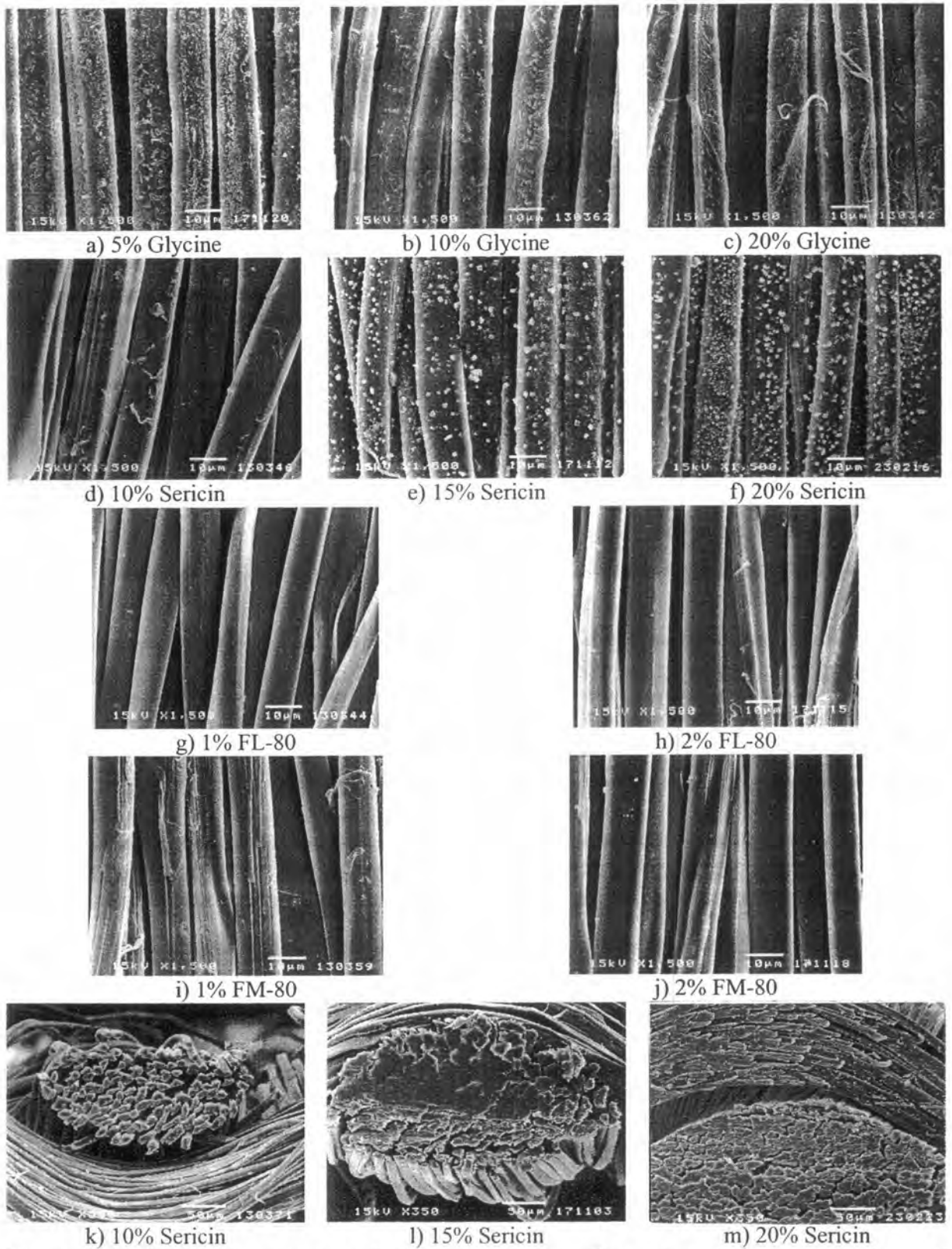


Figure 4.14: SEM Micrographs of the treated silk fiber at various concentrations of pretreatments.

4.2.5 Effect of pretreatment on color gamut of the treated fabrics.

The diagrams of $a^* b^*$, $L^* a^*$, and $L^* b^*$ (Figures 4.15 – 4.17) of the printed silk fabrics indicate that the color gamut of the pretreated fabrics gain a wider color area than the printed color on the non-treated fabrics. At the highest concentration of the pretreatments, the results indicate that sericin, chitosan and Sanfix 555 pretreatments highly improved the chroma while the color strength of the fabrics with chitosan and Sanfix 555 pretreatments were the highest. Especially, the chroma of the cyan colors was significantly improved. The color gamut of the amino acid pretreatments, however, was less increased than those of the treated ones each by sericin, chitosan, and Sanfix 555. The chitosan pretreatment could improve the color gamut of the printing inks because the chitosan molecule contains amino groups ($-NH_2$) which can be protonated to NH_3^+ groups in acidic solution, and react with sulfonate acid groups on the dye ions in low concentrated chitosan solutions [37]. While the sericin, a polar molecule, contains hydroxyl, carboxyl, and amino groups; thus, it can improve moisture absorbency. Similarly, the sericin, chitosan, and Sanfix 555 (cationic acrylate polymer) have a large amount of cations in the molecular structures, so the interaction between the cations from the pretreatment reagents and the anions from the pigment dispersion was enhanced. Furthermore, these cationic charges of all the pretreatments increased the active sites on the silk fabric surface and held the pigments on the fabric surface. The pre-treating solutions thus provide additional functional groups to fix more ink on the surface. In addition, the large amount of the ink was on the pretreated fabric surface because the inter-fiber spaces were decreased as shown in Figure 4.12 (e, f, i). The pretreatment exhibited a higher color gamut because it had been accepted on the fabric surfaces before excessive spreading of the ink jet inks and swelling capacity took place [46].

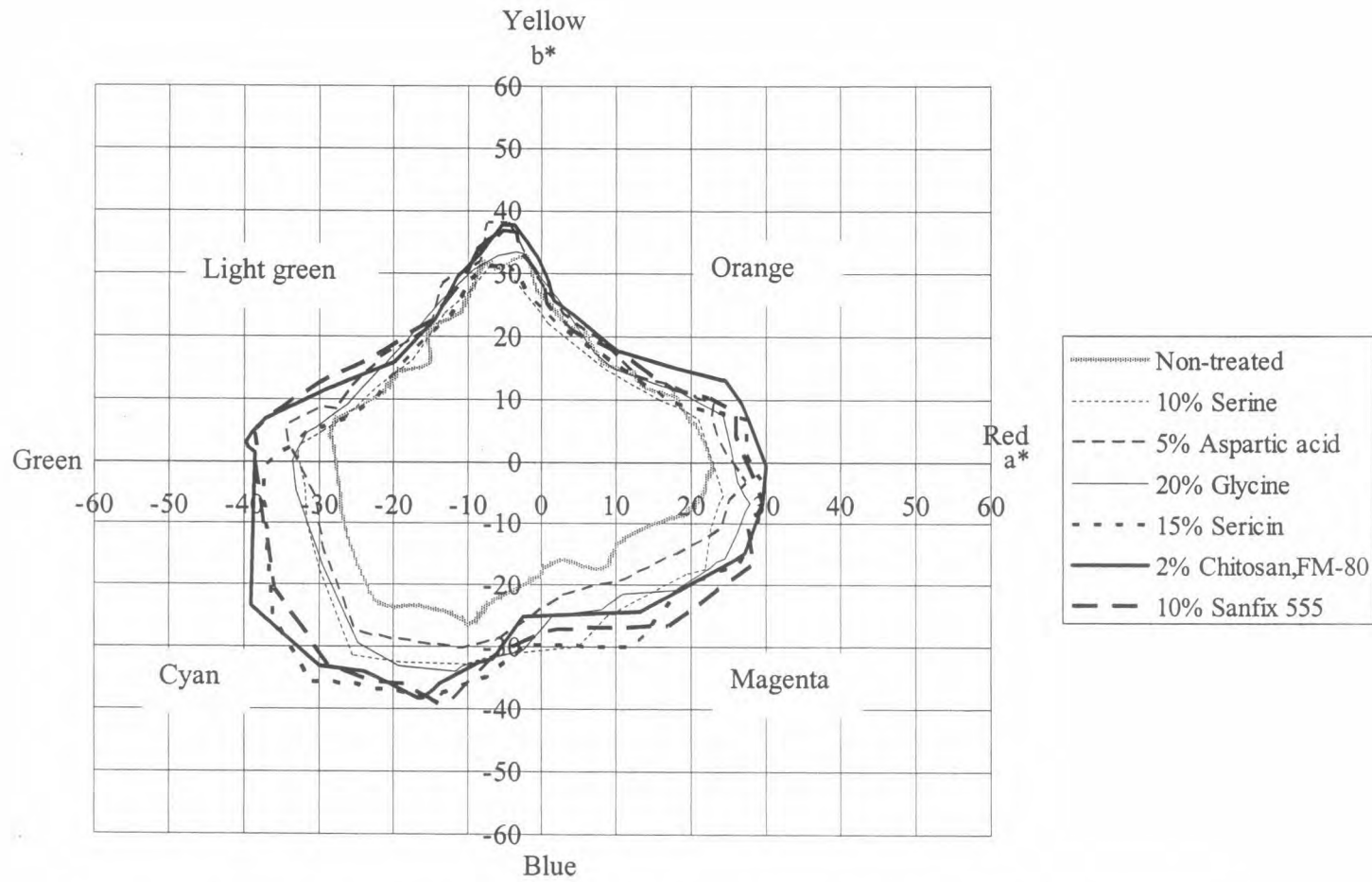


Figure 4.15: $a^* b^*$ diagram of the non-treated and the treated silks with various pretreatments.

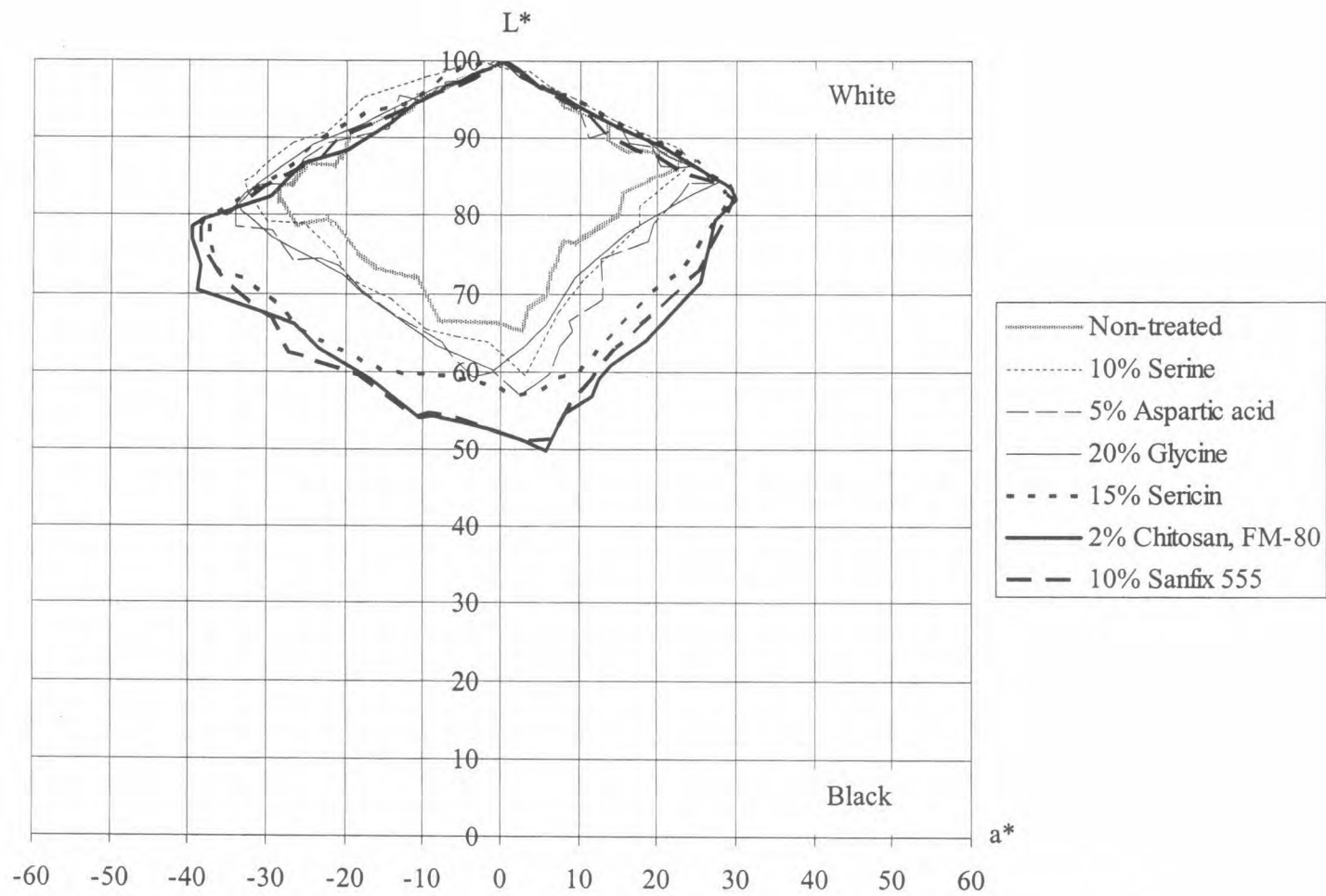


Figure 4.16: L* a* diagram of the non-treated and the treated silks with various pretreatments.

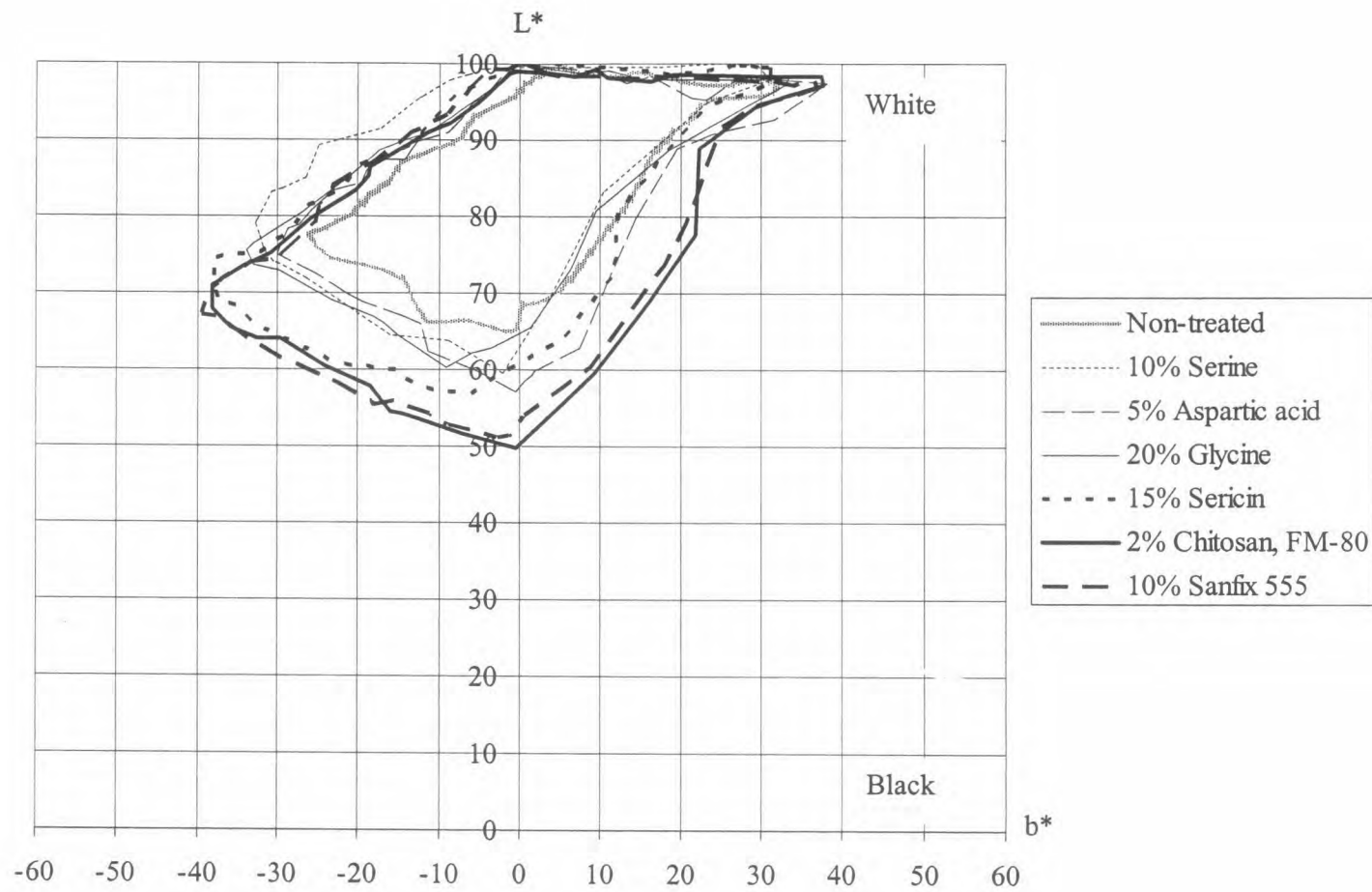


Figure 4.17: L* b* diagram of the non-treated silk and the treated silks with various pretreatments

Table 4.7: Zeta-potential of the pre-treating solutions

Pre-treating solutions	Zeta Potential (mV)	pH of concentration prepared
Serine	-14.03	5.65 – 5.75
Aspartic acid	+ 3.48	2.53
Glycine	- 0.07	6.07 – 6.27
Sericin	+ 7.26	9.25 – 9.43
Chitosan	+ 10.25	3.56 – 3.96
Sanfix 555	+ 8.29	9.66

The sericin, chitosan, and Sanfix 555 pretreatments greatly improved the color gamut because the positive charges on these pre-treating molecules as shown in Table 4.7 interacted with the negative charge on the pigment surface of the ink jet inks (see Table 4.1), enhancing the color gamut. The aspartic acid pretreated fabric has higher color strength than those of glycine and serine (Figures 4.16 – 4.17) since the amount of the positive charge of aspartic acid was higher. The serine and glycine pretreatments provided the negative charges on the fabric surface, so the color gamut of the pretreated fabrics was smaller.

4.3 Physical properties of the printed silks

4.3.1 Stiffness and air permeability of the pretreated fabrics

Stiffness is defined as the ability of silk fabric to resist deformation. A high bending length implies a high stiffness of fabric. The stiffness is reported from the average of five measurements. The trend of the stiffness in the warp or machine direction was similar to that of the weft or cross direction after treating and printing with the inkjet inks (Figures 4.18 – 4.19). The stiffness of the non-treated fabric with and without printing is similar. The pre-treating solutions with the high molecular weight materials resulted in the high stiffness of the fabric. From Figures 4.18 and 4.19, the stiffness of the silk fabrics treated with chitosan was significantly higher than other pretreatments because the chitosan solution grouped the silk fibers together, increasing the strength of silk yarns as shown in Figure 4.12 (e, g). The pretreatments increased the stiffness of the fabric since the stiffness depends on the amount of treating chemicals that were deposited on the fabric area [43]. The higher viscosity of the pretreatments provided the higher stiffness than the lower viscosity ones. This is attributed to the fact that the individual yarn loses its flexibility after the pretreatment with high MW materials but simultaneously gains the stiffness from the effect of fiber grouping. Thus, the stiffness of the glycine and Sanfix 555 pretreated fabrics whose solutions were of low viscosities (Table 4.6) was quite low, comparing with those of sericin and chitosan. Moreover, the fibers treated with these two solutions still distributed loosely (Figure 4.12 (d, i)), maintaining the softness of the pretreated fabrics.

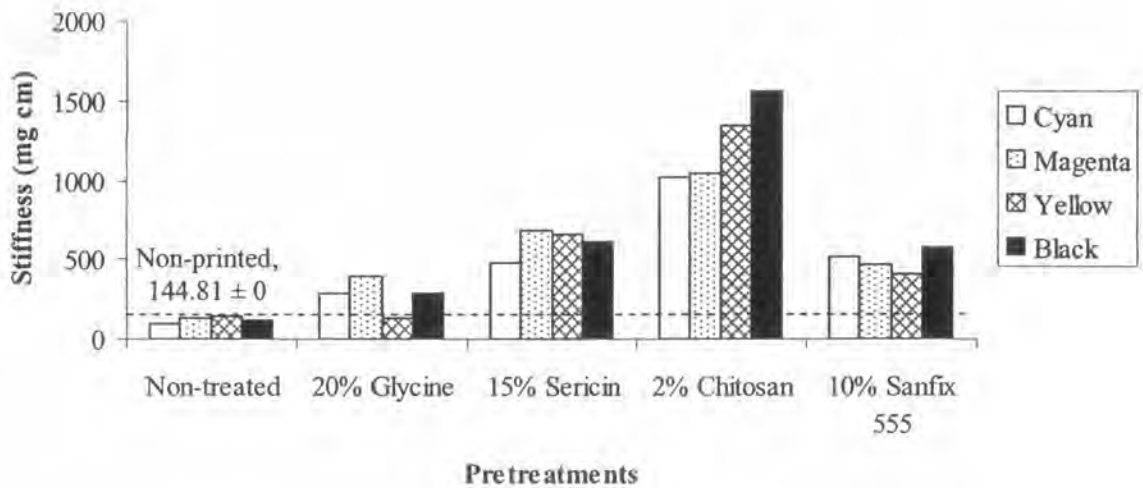


Figure 4.18: Stiffness of the non-treated and pretreated silk fabrics in the warp direction

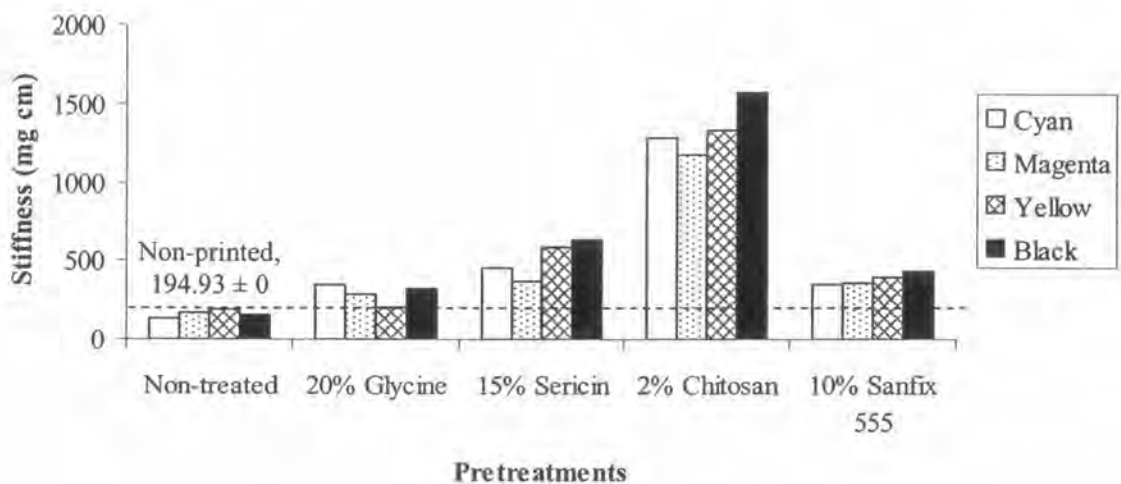


Figure 4.19: Stiffness of the non-treated and pretreated silk fabrics in the weft direction

The air permeability of the non-treated and the treated silk fabrics after printing is shown in the Figure 4.20. The air permeability depends upon the passage of the air in between the yarns (inter-yarn space), which is the major factor, and

inter-fiber spaces but not the inter-yarn spaces [43]. Therefore, the fabric that was treated with the high viscosity pre-treating solutions gave the better air permeability. The air permeability of the chitosan coated silk fabric was the highest because the chitosan was not only coated the yarns but also grouped the fiber to a bundle of fiber and became a packed yarn, introducing a wider inter-yarn space (Figure 4.12 (g)) while the air permeability of the sericin pretreatment was also better than that of non-treated silk fabric due to its high viscosity similar to the case of chitosan. The air permeability of the glycine and Sanfix 555 coated silk fabrics is close to that of the non-treated fabric because their viscosities were similar to the viscosity of water (1 mPa s). Besides, the glycine and Sanfix 555 solutions cannot group the fibers so the yarns distribute loosely (Figure 4.12 (d, i)), resulting in significantly less air to pass through a printed fabric. They did not cause any change in the structure of silk fiber.

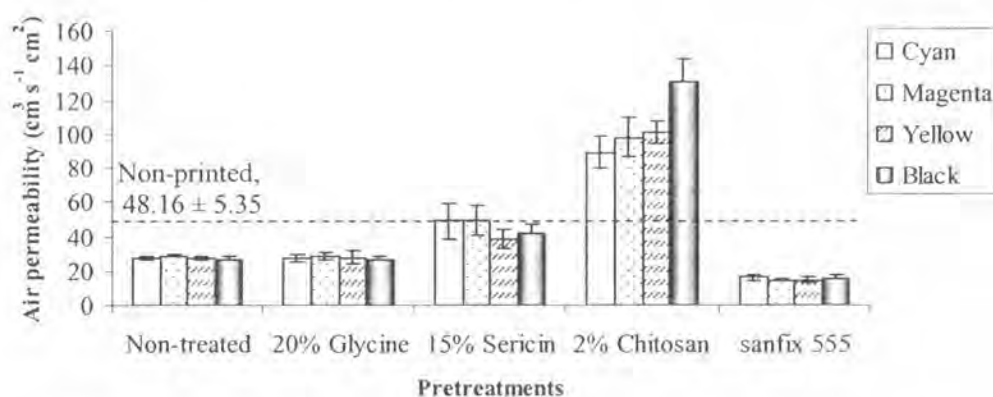


Figure 4.20: Air permeability of the pretreated silk fabrics

4.3.2 Effect of pretreatment on crock fastness of the printed fabrics

The non-treated silk fabric provided good dry/wet crock fastness (Table 4.8) because the inks contained the binder (S-711 acrylic) with a T_g of -3.1°C whose film was flexible and withstand the rubbing. The 15% w/v of the sericin pretreatment produced the highest dry crock fastness, while the serine and glycine pretreatments achieved the highest wet crock fastness. However, at 15% w/v of sericin pretreatment, the level of wet crock fastness was lower than its crock fastness in the dry state. The reason might be that the bonding between the sericin and the silk fiber is not a chemical bonding but perhaps a hydrogen bonding among the amide group and hydrogen atom of the chain. The coated sericin on the fabric (Figure 4.14 (e, f)) can be re-dissolved through the wet rubbing process. The concentration of serine and glycine pretreatments did not affect the dry crock fastness. They provided the best wet crock fastness because the pretty smooth films of these pre-treating solutions protected the threads of the fabric fibers from being rubbed as shown in Figure 4.13 (b,d). Aspartic acid did not enhance the rubbing resistance. At the maximum concentration, aspartic acid decreased the dry/wet crock fastness when it was compared with the non-treated fabrics because the prepared concentration could be in an excess amount, which resided on the fabric surface (Figure 4.13 (c)), and could be easily rubbed off.

The chitosan pretreatment slightly improved the fabric dry/wet crock fastness. In a dry condition, the concentrations did not affect the rubbing resistance, but the declining rubbing resistance was, of course, found more in a wet condition. After the pretreatment, some amount of trapped acetic acid remained in the fabric which could re-dissolve in a wet condition. Chitosan slightly improved the dry crock fastness while the wet crock fastness was enhanced at low concentrations of the pretreatment,

i.e. 0.25 and 0.5% w/v. The result of wet crock fastness was slightly decreased when the chitosan concentration was more than 0.5% w/v. For all chitosan pretreatments, the dry crock fastness results were better than those of the wet crock fastness because the chitosan could be re-dissolved through the wet rubbing process. The high molecular weight chitosan is hardly to re-dissolve than is the low molecular weight one; hence, the wet crock fastness of chitosan pretreatment was unchanged at the MW of 8.5×10^5 Dalton while the wet crock fastness by the chitosan pretreatment with MW of 1.2×10^5 and 3.7×10^5 Dalton. The high crock fastness of the silk printed with the ink jet inks was caused by the low ink pick-up on the surface of the fabric since the ink jet inks penetrated deeper into the fabric.

Table 4.8: Crock fastness of the pretreated silk fabrics

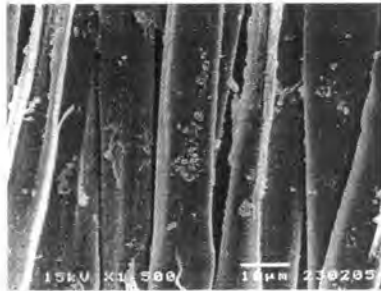
Pretreatments		Level of crock fastness							
		Dry stage				Wet stage			
		C	M	Y	K	C	M	Y	K
Non-treated		4	4	4/5	4	4	4	4	4
Serine (% w/v)	2.5	4	4/5	4/5	3/4	4/5	4/5	4/5	3/4
	5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5
	10	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Aspartic acid (% w/v)	1	4	4/5	4	4	4	4	4	4
	2	3	3	3	3/4	3	3	3	3/4
	5	3	3	3	3/4	3	3	3	3/4
Glycine (% w/v)	5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	10	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	15	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	20	4	4/5	4	4/5	4/5	4/5	4/5	4/5

Pretreatments		Level of crock fastness							
		Dry				Wet			
		C	M	Y	K	C	M	Y	K
Sericin (% w/v)	5	4	4	4/5	5	4	4	4	4
	10	4/5	5	5	5	4	4	4	4
	15	5	5	5	5	4	4	4	3/4
	20	5	5	4/5	5	4	4	3/4	3/4
Chitosan (FM-80) (% w/v)	0.25	4/5	4	5	4/5	4/5	4/5	4/5	4
	0.5	4/5	4/5	4	4/5	4/5	4/5	4/5	4
	1	4/5	4/5	4	4/5	4/5	4/5	4	3/4
	2	4/5	4/5	4	4/5	4	4/5	4	3/4
Chitosan (FM-40) (% w/v)	0.25	4/5	4/5	4	4/5	4/5	4/5	4/5	4
	0.5	4/5	4/5	4	4/5	4/5	4/5	4/5	4
	1	4/5	4/5	4	4/5	4/5	4	4/5	4
Sanfix 555 (% w/w)	10	4	4/5	4	3/4	4	4	4	3/4

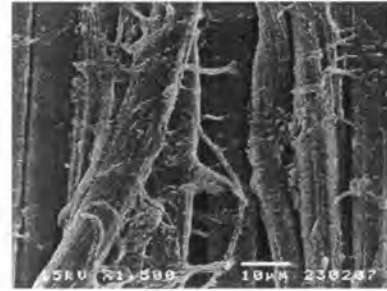
[5 stands for excellent crock fastness where no printed ink was removed (100% retention), 4 for good (80% retention), 3 for fair (60% retention), 2 for poor (40% retention), and 1 for very poor (20% retention)]

Figure 4.21 shows that the fibers of the sericin and aspartic acid pretreated fabrics after the rubbing in dry and wet condition. The result is that the dry crock fastness of the printed fabric was better than that of the wet crock fastness. Furthermore, the adhesion of the ink film to the fiber surface would be weakened by water so the wet film is also weakened and then damaged, thus the strength decreased [43]. The dry and wet crock fastness of 5% aspartic acid pretreated fabrics was in the

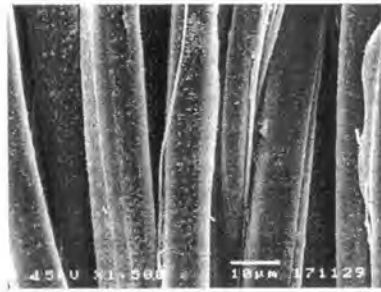
range of 3 – ¼ (a fair classification). This result indicates that 40% of the printed ink on the fabric was removed after the rubbing. Moreover, this damage arose not only in the ink film but also on the yarns themselves as deterioration of threads (Figure 4.21 (b, d, e, and f)).



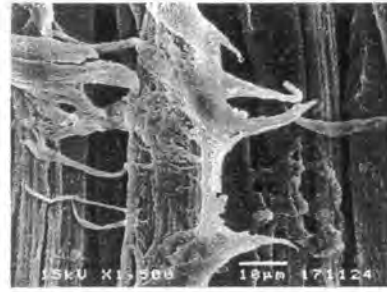
a) 20% Sericin after dry crock fastness



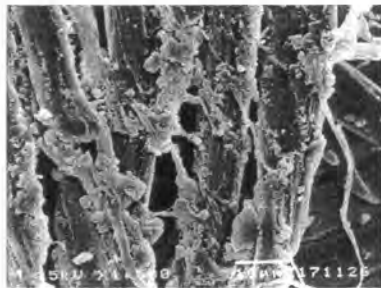
b) 20% Sericin after wet crock fastness



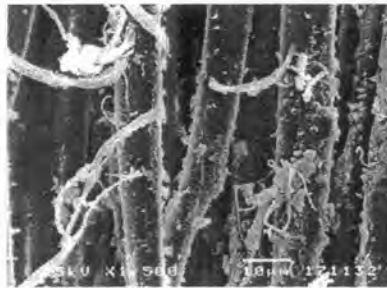
c) 1% Aspartic acid after dry crock fastness



d) 1% Aspartic acid after wet crock fastness



e) 5% Aspartic acid after dry crock fastness



f) 5% Aspartic acid after wet crock fastness

Figure 4.21: Appearance of the sericin and aspartic acid pretreated fabrics after the rubbing in the dry and wet conditions

4.3.3 Effect of pretreatment on wash fastness of the silk fabrics

The effect of pre-treating solutions on the wash fastness was determined by K/S of color on the fabric which was measured before and after the washings. The wash fastness of the printed fabrics ranged from good to excellent in all pretreatments as illustrated in Table 4.9 due to a negligible change of the K/S before and after the washings of all pretreatments. Furthermore, the pretreatments slightly improved the wash fastness as shown in Table 4.10. The relative color strength determined from the ratios of K/S of the printed fabric after the washing and before the washing, so the relatively high color strength indicates the good wash fastness. The relative color strength of the non-treated fabric is in the range of 0.8 – 0.9 while those of the pretreated fabrics are in the range of 0.8 – 1. The chitosan pretreated fabric can obviously enhance the wash fastness while other pretreatments slightly improve the wash fastness as explained in the previous section. The reason might be that the binder in the ink formulation improves the ink fixation on the silk surfaces. Moreover, these pretreated fabrics had been soaked in 5% wt of NaCl and steamed for 5 min to fix the inks as shown in the Appendix B.

Table 4.9: K/S of the printed silk fabrics before and after washing

Pretreated fabrics		K/S of the printed silk with the inks							
		Cyan		Magenta		Yellow		Black	
		Before	After	Before	After	Before	After	Before	After
		washing	washing	washing	washing	washing	washing	washing	washing
Non-treated		0.42 ± 0.00	0.35 ± 0.01	0.45 ± 0.03	0.41 ± 0.02	1.18 ± 0.05	0.96 ± 0.07	1.41 ± 0.01	1.16 ± 0.04
Serine (% w/v)	2.5	0.43 ± 0.01	0.38 ± 0.01	0.44 ± 0.02	0.41 ± 0.02	1.19 ± 0.00	1.09 ± 0.03	1.53 ± 0.04	1.33 ± 0.01
	5	0.60 ± 0.00	0.50 ± 0.00	0.69 ± 0.00	0.64 ± 0.00	1.51 ± 0.00	1.23 ± 0.00	1.73 ± 0.00	1.42 ± 0.00
	10	0.46 ± 0.08	0.42 ± 0.06	0.42 ± 0.01	0.39 ± 0.02	1.04 ± 0.02	0.84 ± 0.03	1.44 ± 0.09	1.12 ± 0.09
Aspartic acid (% w/v)	1	0.36 ± 0.01	0.39 ± 0.00	0.35 ± 0.02	0.36 ± 0.01	1.03 ± 0.06	0.99 ± 0.09	1.46 ± 0.03	1.33 ± 0.01
	5	0.29 ± 0.00	0.30 ± 0.01	0.32 ± 0.11	0.33 ± 0.01	0.96 ± 0.03	0.87 ± 0.04	1.92 ± 0.03	1.65 ± 0.10
Glycine (% w/v)	5	0.43 ± 0.01	0.39 ± 0.01	0.41 ± 0.03	0.40 ± 0.02	0.95 ± 0.03	0.83 ± 0.08	1.42 ± 0.00	0.94 ± 0.05
	15	0.41 ± 0.03	0.39 ± 0.03	0.40 ± 0.03	0.38 ± 0.03	0.92 ± 0.04	0.81 ± 0.06	1.22 ± 0.07	1.14 ± 0.02
	20	0.37 ± 0.01	0.33 ± 0.01	0.35 ± 0.00	0.34 ± 0.01	1.04 ± 0.03	0.86 ± 0.01	1.38 ± 0.12	1.19 ± 0.15

Pretreated fabrics		K/S of the printed silk with the inks							
		Cyan		Magenta		Yellow		Black	
		Before	After	Before	After	Before	After	Before	After
		washing	washing	washing	washing	washing	washing	washing	washing
Sericin (% w/v)	5	0.52 ± 0.07	0.48 ± 0.08	0.51 ± 0.05	0.46 ± 0.05	1.33 ± 0.12	1.16 ± 0.12	1.85 ± 0.19	1.73 ± 0.23
	15	0.56 ± 0.02	0.52 ± 0.05	0.53 ± 0.02	0.49 ± 0.01	1.07 ± 0.05	0.92 ± 0.05	1.53 ± 0.04	1.71 ± 0.13
Chitosan (FL-80) (% w/v)	0.25	0.38 ± 0.04	0.40 ± 0.06	0.39 ± 0.02	0.40 ± 0.02	1.10 ± 0.04	1.08 ± 0.08	1.43 ± 0.03	1.75 ± 0.03
	2	0.48 ± 0.04	0.47 ± 0.02	0.45 ± 0.03	0.45 ± 0.02	1.30 ± 0.01	1.28 ± 0.02	2.18 ± 0.04	2.24 ± 0.05
Chitosan (FM-80) (% w/v)	0.25	0.4 ± 0.02	0.41 ± 0.02	0.37 ± 0.01	0.38 ± 0.01	0.99 ± 0.04	0.96 ± 0.03	2.54 ± 0.19	1.72 ± 0.06
	1	0.45 ± 0.01	0.47 ± 0.03	0.47 ± 0.02	0.48 ± 0.01	1.29 ± 0.05	1.27 ± 0.06	2.20 ± 0.07	2.27 ± 0.02
	2	0.56 ± 0.06	0.55 ± 0.06	0.53 ± 0.01	0.51 ± 0.01	1.26 ± 0.09	1.23 ± 0.09	2.19 ± 0.14	2.15 ± 0.09
Chitosan (FM-40) (% w/v)	0.25	0.42 ± 0.02	0.44 ± 0.02	0.41 ± 0.01	0.44 ± 0.02	1.14 ± 0.01	1.14 ± 0.04	1.92 ± 0.03	1.93 ± 0.04
	1	0.45 ± 0.03	0.43 ± 0.02	0.45 ± 0.03	0.42 ± 0.03	1.34 ± 0.04	1.28 ± 0.05	2.54 ± 0.19	2.42 ± 0.24
Sanfix 555 (% w/w)	10	0.5 ± 0.01	0.46 ± 0.01	0.49 ± 0.02	0.44 ± 0.02	1.24 ± 0.06	1.06 ± 0.06	2.32 ± 0.01	1.70 ± 0.02

Table 4.10: Relative color strength of the printed silk fabrics after the washing

Pretreated fabrics		Average of relative color strength			
		Cyan	Magenta	Yellow	Black
Non-treated		0.82 ± 0.01	0.90 ± 0.00	0.81 ± 0.03	0.82 ± 0.02
Serine (% w/v)	2.5	0.88 ± 0.00	0.93 ± 0.00	0.92 ± 0.03	0.87 ± 0.02
	5	0.83 ± 0.00	0.93 ± 0.00	0.81 ± 0.00	0.82 ± 0.00
	10	0.92 ± 0.03	0.93 ± 0.05	0.81 ± 0.04	0.78 ± 0.02
Aspartic acid (% w/v)	1	1.10 ± 0.02	1.03 ± 0.03	0.95 ± 0.04	0.90 ± 0.01
	5	1.02 ± 0.02	1.03 ± 0.00	0.91 ± 0.02	0.86 ± 0.04
Glycine (% w/v)	5	0.92 ± 0.01	0.98 ± 0.02	0.87 ± 0.06	0.66 ± 0.04
	15	0.95 ± 0.00	0.95 ± 0.02	0.88 ± 0.02	0.94 ± 0.03
	20	0.89 ± 0.05	0.96 ± 0.01	0.83 ± 0.03	0.86 ± 0.03
Sericin (% w/v)	5	0.92 ± 0.01	0.9 ± 0.01	0.87 ± 0.01	0.93 ± 0.03
	15	0.93 ± 0.06	0.93 ± 0.02	0.85 ± 0.01	1.12 ± 0.11
Chitosan (FL-80) (% w/v)	0.25	1.04 ± 0.04	1.04 ± 0.01	0.98 ± 0.03	1.22 ± 0.00
	2	0.99 ± 0.03	1.00 ± 0.02	0.98 ± 0.02	1.03 ± 0.00
Chitosan (FM-80) (% w/v)	0.25	1.03 ± 0.03	1.03 ± 0.00	0.98 ± 0.01	0.68 ± 0.07
	1	1.03 ± 0.03	1.03 ± 0.01	0.98 ± 0.01	1.03 ± 0.02
	2	0.98 ± 0.00	0.96 ± 0.00	0.98 ± 0.01	0.98 ± 0.02
Chitosan (FM-40) (% w/v)	0.25	1.06 ± 0.01	1.06 ± 0.01	1.00 ± 0.02	1.01 ± 0.01
	1	0.95 ± 0.00	0.93 ± 0.00	0.96 ± 0.01	0.95 ± 0.03
Sanfix 555 (% w/w)	10	0.92 ± 0.02	0.91 ± 0.01	0.86 ± 0.01	0.73 ± 0.01

4.4 Chemical interaction between the pre-treating material of pretreatment and the ink on silk fabric

4.4.1 UV-Visible absorption of between the pre-treating agent and ink jet inks

The λ_{\max} of the cyan ink and the mixture of ink and pretreatments are separated into two peaks at 610 and 700 nm as shown in Figure 4.22 illustrated in UV absorption spectra of the pigment blue 15:4 of Cabot Company [44]. The λ_{\max} of the magenta ink and the mixture of this ink and pretreatments are approximately at 537 nm, the reflection of red and blue light (Figure 4.23). Figure 4.24 shows that λ_{\max} of the yellow ink and the pretreatments are at 420 nm, showing the green and blue light were reflected (Figure 4.24). These results indicate that no new chemical bonding between the ink and the pretreatments because λ_{\max} did not significantly shift when the inks were mixed in each pretreatment (Figures 4.22 – 4.24). The pre-treating solutions containing the amino groups interacted with the negative charges on the pigment surface by polar force since the surface-modified pigment contain the sulfonate group (SO_3^-) on its pigment surface, confirmed by FTIR spectrum in the sections 4.4.2 and 4.4.3.1, and agreed well with the information from the Cobot company [44].

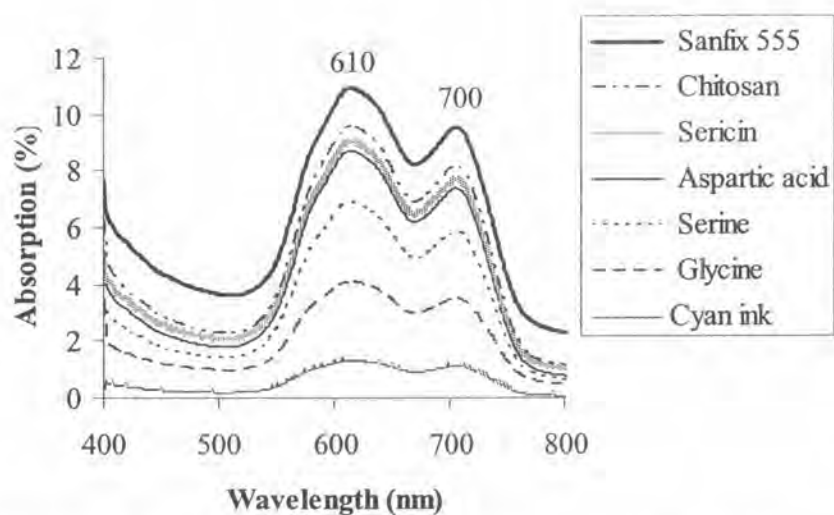


Figure 4.22: UV absorption of the cyan ink in the pre-treating solutions

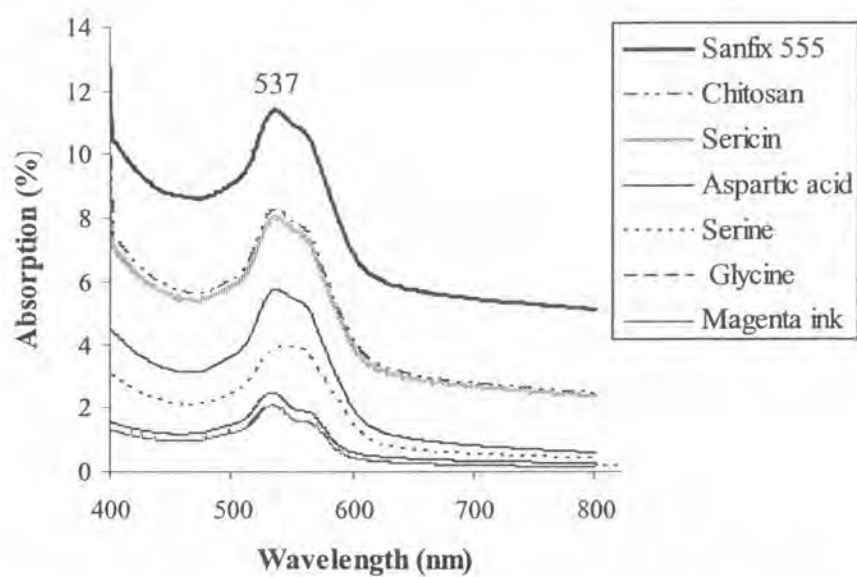


Figure 4.23: UV absorption of the magenta ink in the pre-treating solutions

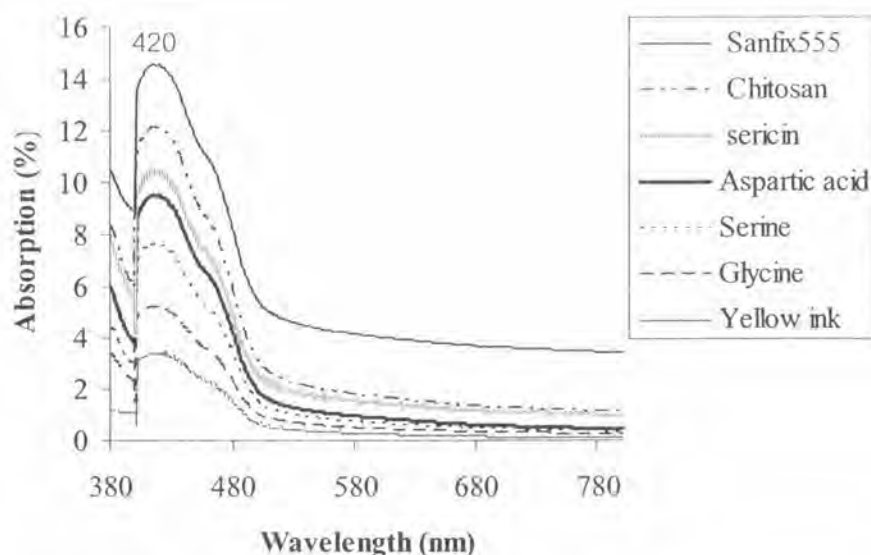


Figure 4.24: UV absorption of the yellow ink in the pre-treating solutions

4.4.2 FT-IR of the pigmented ink jet inks

The molecular structures of the pigmented ink jet inks shown in Figure 4.25 were confirmed by FT-IR Spectroscopic method, suggesting the complicated spectra (Figure 4.26). The band of the cyan pigment (Figure 4.26 (a)) at 1609 and 1507 cm^{-1} are attributed to $\text{C}=\text{C}$ stretching of aromatic, and band at 1507 cm^{-1} is due to $\text{C}=\text{N}$ stretching. The IR spectrum of the magenta pigment (Figure 4.26 (b)) shows the band at 1606 and 1504 cm^{-1} are attributed to the $\text{C}=\text{C}$ stretching of aromatic. Also, the $\text{N}-\text{H}$ stretching of the amino group is found at 3273 cm^{-1} . Figure 4.26 (c) is the IR spectrum of the yellow pigment in which the bands at 1594 and 1520 cm^{-1} are due to the $\text{C}=\text{C}$ stretching of aromatic and the band at 1554 cm^{-1} is the $\text{N}=\text{N}$ stretching. These spectra support the band of $\text{S}=\text{O}$ stretching of the $-\text{SO}_3^-$ group at around 1300 , 1100 cm^{-1} by the pigment manufacturer (Cabot Company) were modified with the sulfonate group before ink preparation. The absorption peaks of these pigments characterized are shown in Table 4.11.

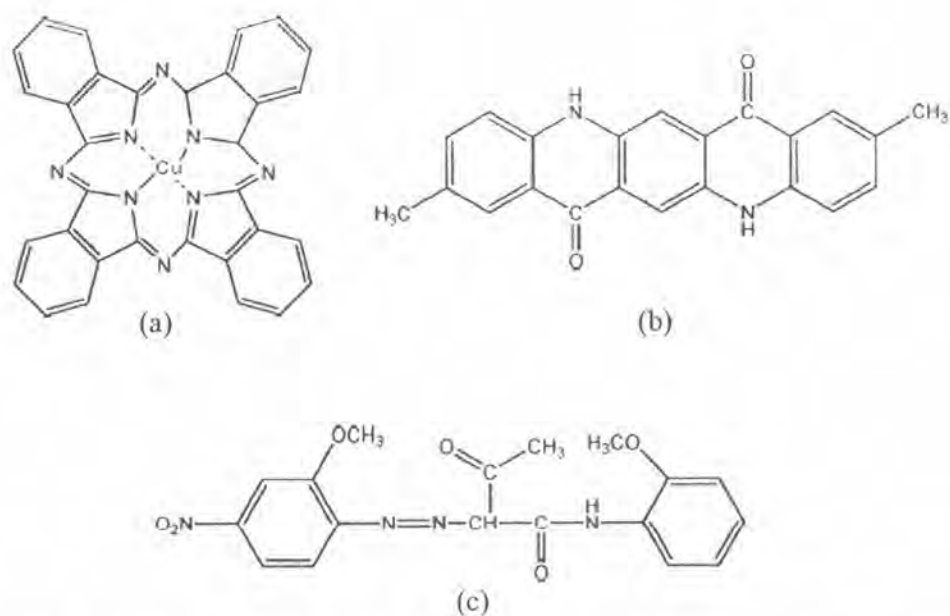


Figure 4.25: Chemical structures of (a) the cyan pigment, C.I. pigment blue 15:4; (b) the magenta pigment, C.I. pigment red 122; and (c) the yellow pigment, C.I. pigment yellow 74

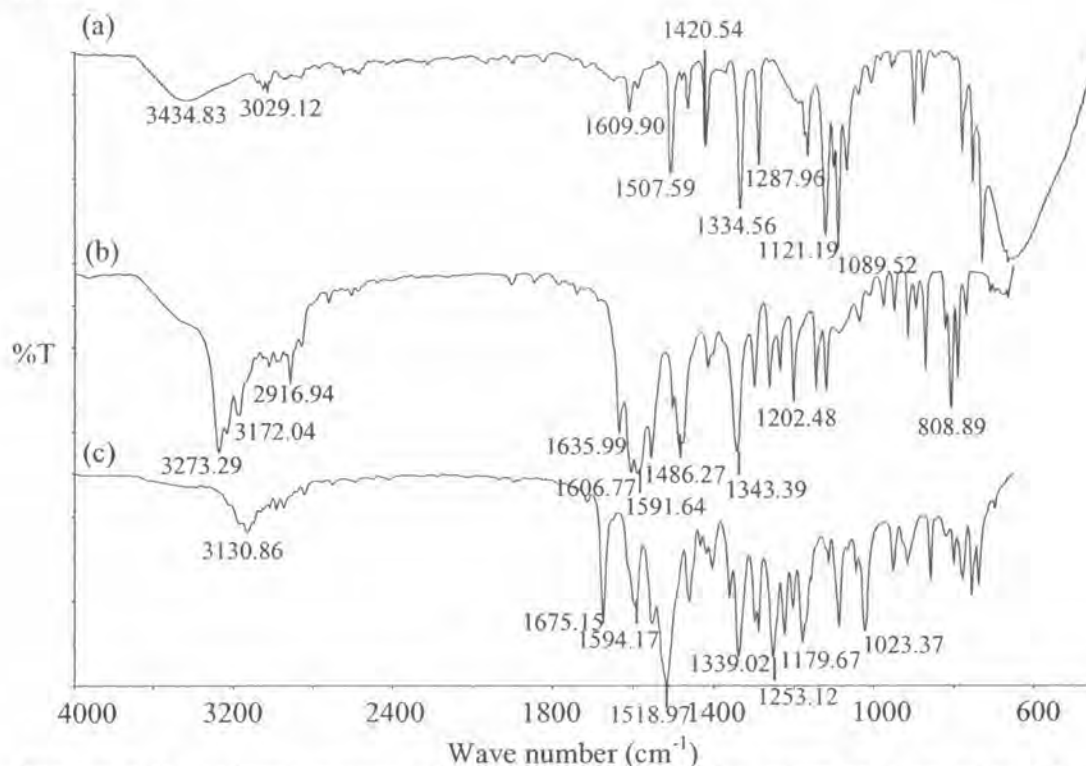


Figure 4.26: Infrared spectra of (a) cyan pigment, C.I. pigment blue 15:4; (b) magenta pigment, C.I. pigment red 122; and (c) yellow pigment, C.I. pigment yellow 74

Table 4.11: Infrared spectra of the cyan, magenta, and yellow pigment dispersions

Cyan pigment, C.I. pigment blue 15:4		Magenta pigment, C.I. pigment red 122		Yellow pigment, C.I. pigment yellow 74	
Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment
3434	N-H stretching	3273	N-H stretching	1675	N-H bending
1609	N-H bending	1635	N-H bending	2986	-C-H stretching
3029	=C-H stretching	2916	-C-H stretching	3130	=C-H stretching
1609 and 1507	C = C stretching (aromatic)	3172	=C-H stretching	1594 and 1520	C = C stretching (aromatic)
1089	C – N stretching	1606 and 1504	C = C stretching (aromatic)	1253	C – N stretching (2°)
1507	C = N stretching	1343	C – N stretching (2°)	1023	C-O-C stretching
1420	C-H bending for CH ₂ , CH ₃	1486	C-H bending for CH ₂ , CH ₃	1520 and 1339	N = O stretching
754	C-H bending (ortho)	1343, 1145	*S = O stretching of -SO ₃ ⁻	1554	N = N stretching
1334, 1165	*S = O stretching of -SO ₃ ⁻			1461	C-H bending for CH ₂ , CH ₃
				1339, 1179	*S = O stretching of -SO ₃ ⁻

* S = O stretching of -SO₃⁻ was designated for the sulfonate group present on the modified pigment surface.

4.4.3 The interactions between the pre-treating agent and pigment by spectroscopic methods

4.4.3.1 FT-IR technique

The spectrum of n- dodecyltrimethyl ammonium bromide (Figure 4.27 (a)) containing the N-H stretching of -NH_3^+ at 3426 cm^{-1} and the N-H bending at 1623 cm^{-1} (Table 4.12) was used as a standard to confirm the peak of N-H stretching of -NH_3^+ . IR spectra of the amino acid pretreatments are found at around 3300 cm^{-1} and $1600, 1500\text{ cm}^{-1}$, attributing to the N-H stretching of -NH_3^+ and N-H bending, respectively (Table 4.13). Moreover, the band of amino acid at around 1400 cm^{-1} is due to the carboxylate anion. From the IR spectra found that the each amino acid is dissociated to -COO^- and -NH_3^+ . The O-H stretching of sericin, chitosan and Sanfix 555, overlapped with the N-H stretching of -NH_3^+ (Table 4.14). The result indicates that the cationic charge of the amino group on the silk surface has reacted with the negative charges of the sulfonate group (-SO_3^-) present on the pigment surface which supports the higher ink adsorption on the printed silk as shown in Figures 4.15 – 4.17.

Table 4.12: FTIR of n-dodecyltrimethyl ammonium bromide

Wave number (cm^{-1})	Assignment
3426	N-H stretching of NH_3^+
1623	N-H bending
2909, 2842	-C-H stretching
3011	=C-H stretching
1480	C-H bending for CH_2, CH_3
1393	C-H bending for CH_3

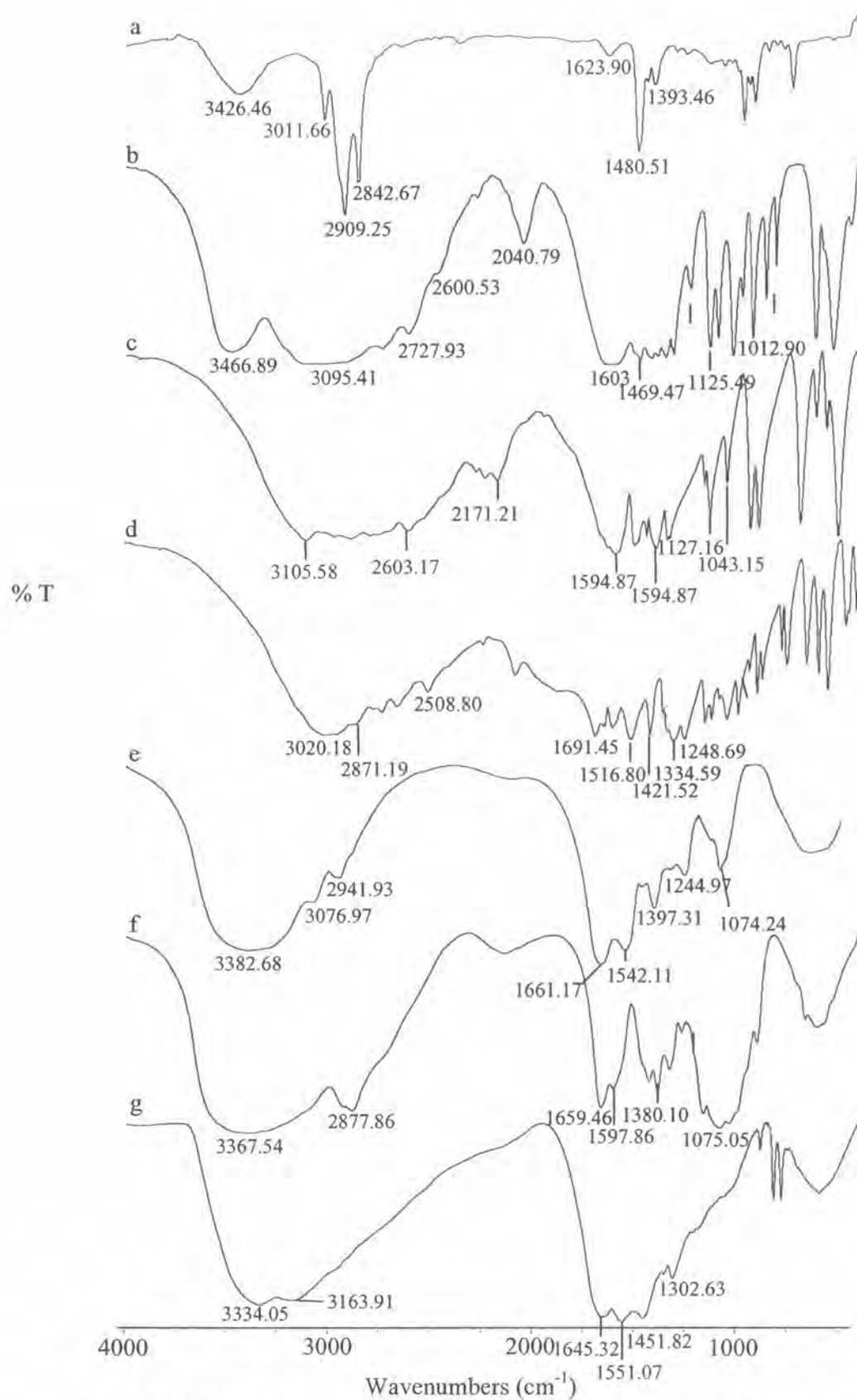


Figure 4.27: Infrared spectra of (a) n-dodecyltrimethyl ammonium bromide, (b) serine, (c) glycine, (d) aspartic acid, (e) sericin, (f) chitosan, (g) Sanfix 555

Table 4.13: FTIR of serine, aspartic acid, and glycine

Serine		Aspartic acid		Glycine	
Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment
3466	O-H stretching of -OH group	3020	N-H stretching of -NH ₃ ⁺	3105	N-H stretching of -NH ₃ ⁺
3095	N-H stretching of -NH ₃ ⁺	1606, 1516	N-H bending	1594, 1497	N-H bending
1603, 1469	N-H bending	1248	C-N stretching	1043	C-N stretching
1217	C-N stretching	1421	Carboxylate anion	1127	C-O stretching
1125	C-O stretching	1691	Carbonyl group	1390	Carboxylate anion
1410	Carboxylate anion				

Table 4.14: FTIR of sericin, chitosan, and Sanfix 555

Sericin		Chitosan		Sanfix 555	
Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹)	Assignment
3382	O-H stretching, N-H stretching of -NH ₃ ⁺	3367	O-H stretching, N-H stretching of -NH ₃ ⁺	3334	O-H stretching, N-H stretching of -NH ₃ ⁺
1661, 1542	N-H bending	1659, 1597	N-H bending	1645, 1551	N-H bending
1244	C-N stretching	1262	C-N stretching	1400	C-N stretching
1397	Carboxylate anion	1075	C-O-C stretching	3095-3010	=C-H stretching
2941	-C-H stretching	2877	-C-H stretching	1645	C=N stretching
3076	=C-H stretching			1450	C-H bending for CH ₂ , CH ₃

4.4.3.2 FTIR - ATR technique

The FTIR-ATR spectra of the non-treated and pretreated fabrics are shown in Figure 4.28. The absorption band of the non-treated fabric is found at 3278 cm^{-1} , 1619 cm^{-1} , and 1512 cm^{-1} , attributing to the N-H stretching and N-H bending of the amino groups, respectively. The band at around 1225 cm^{-1} is due to the C-N stretching of the amino group (Figure 4.28 (a)). The band of serine pretreated fabric remains the same with the non-treated fabric (Figure 4.28 (b)). The spectra of other pretreated fabrics found at around $3300 - 2500\text{ cm}^{-1}$ (N-H stretching of $-\text{NH}_3^+$) and $1650 - 1590\text{ cm}^{-1}$, $1580 - 1500\text{ cm}^{-1}$ (N-H bending), are due to the protonated amino groups (Figure 4.28 (c - g)). The IR spectra of all pretreated fabrics represent the cationic amino interact with the negative charges (sulfonate group ($-\text{SO}_3^-$)) of the pigmented inks by a dipole-dipole interaction. These results support improvements of the color gamut by the pretreatments.

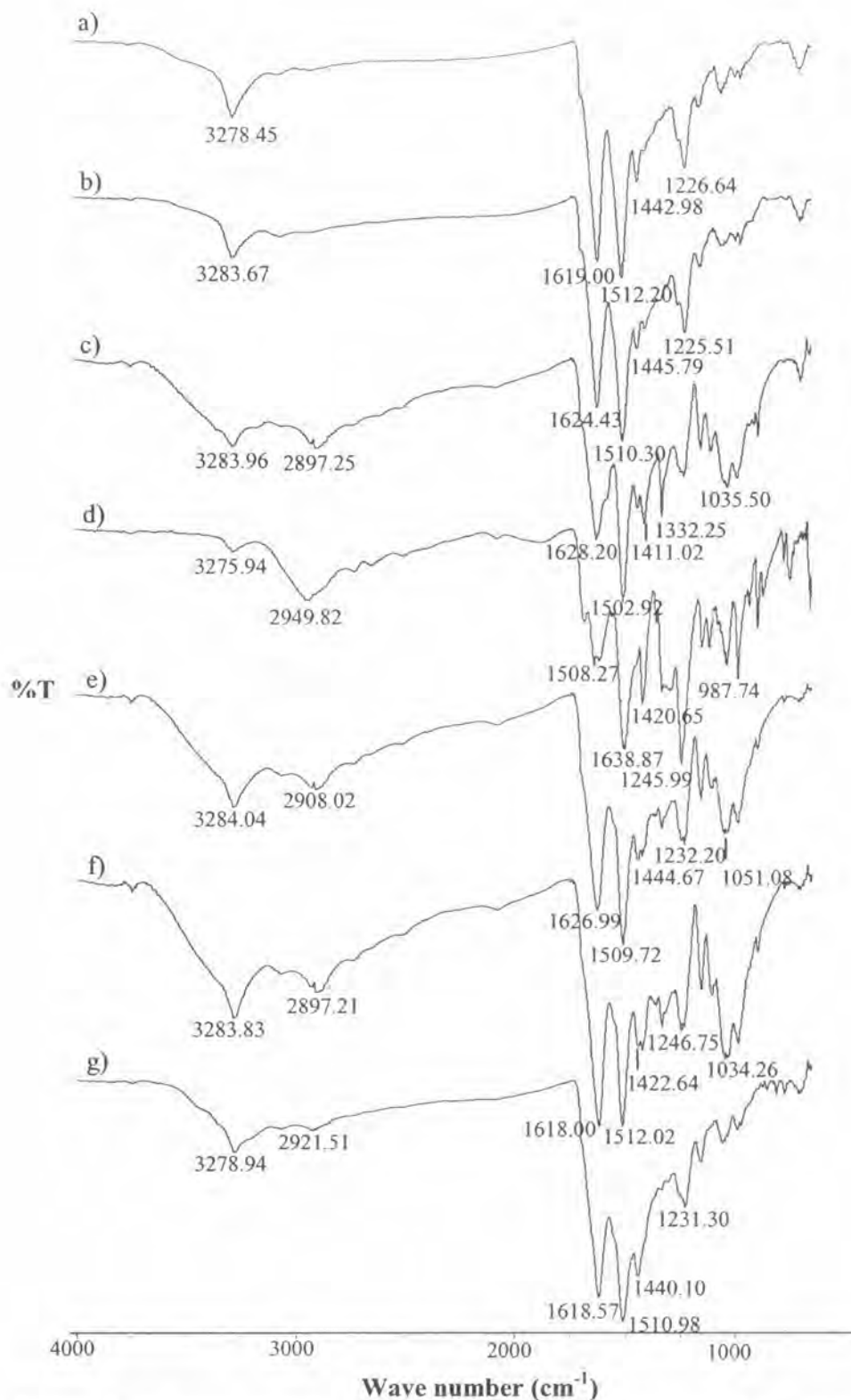


Figure 4.28: Fourier transform infrared spectrum-attenuated total reflectance of (a) silk before the treatment, silk treated with (b) serine, (c) glycine, (d) aspartic acid, (e) sericin, (f) chitosan, and (g) Sanfix 555

4.4.3.3 Raman spectroscopy of the pre-treating solutions and cyan pigmented ink

The Raman spectra of the cyan ink, serine pretreatment and the mixture of the cyan ink and serine also indicates that no new chemical bonding between the inks and the pretreatments because a new peak is not found in Figures 4.29 (c) and 4.30 (c).

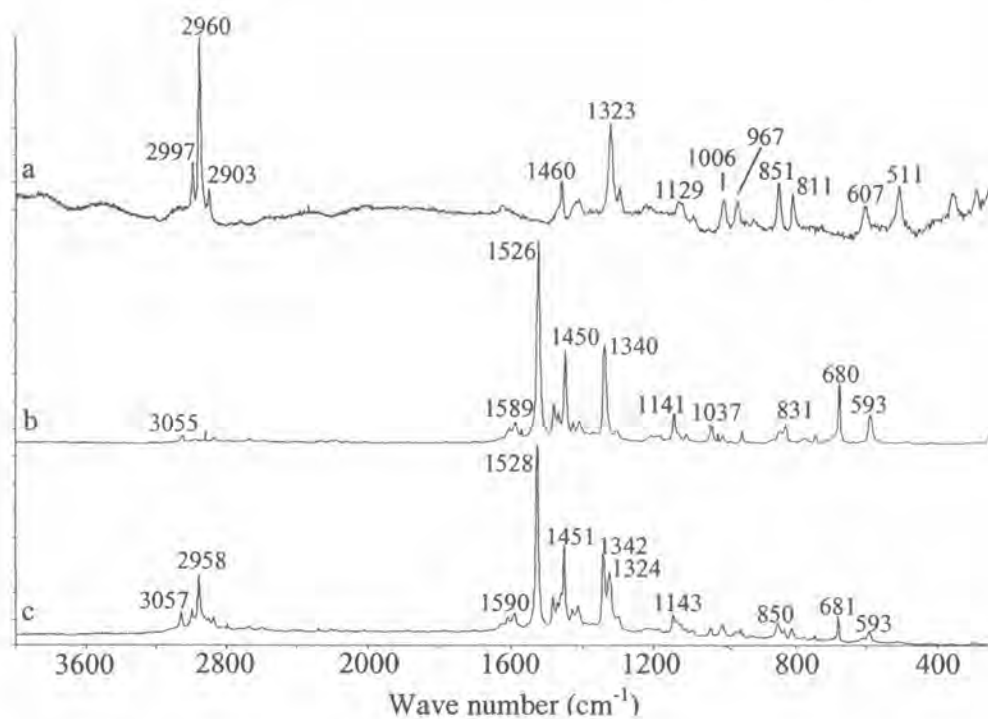


Figure 4.29: Raman spectra of (a) serine, (b) cyan ink and (c) the mixture of serine and cyan ink

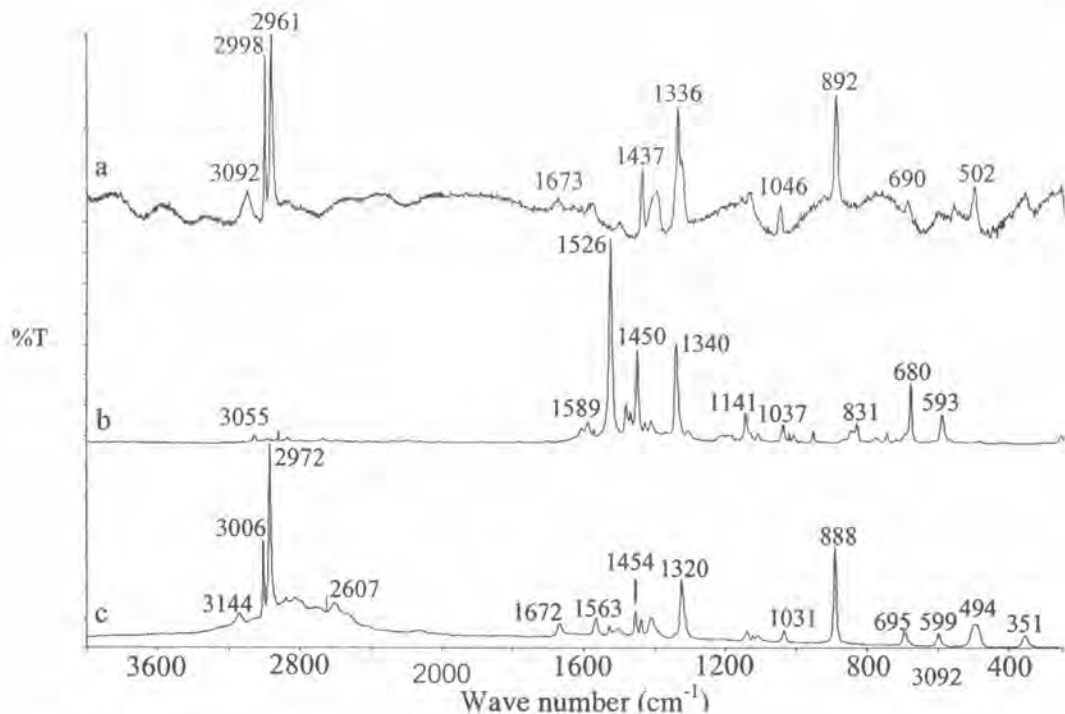


Figure 4.30: Raman spectra of (a) glycine, (b) cyan ink and (c) the mixture of glycine and cyan ink

4.5 Thermal properties of the sericin

Figure 4.31 shows that the pre-treating sericin has T_g at 81 °C and T_m at 167.5°C while the bleached sericin has T_m at 131°C. This indicates that the pre-treating agent of sericin comprises the amorphous region while only crystallinity is observed in the bleached sericin. Some of the natural sericin in the silk fabrics after the bleaching, which forms most of the crystalline structure was retained while the amorphous portion was removed. The same bleached fabric was later coated with the commercial sericin composing of both amorphous and crystalline, creating the most amorphous areas with a few crystalline structures. The amorphous region has more free volume than the crystalline region, allowing a higher ink deposition on the fabric surface, and leading to an increase in color gamut.

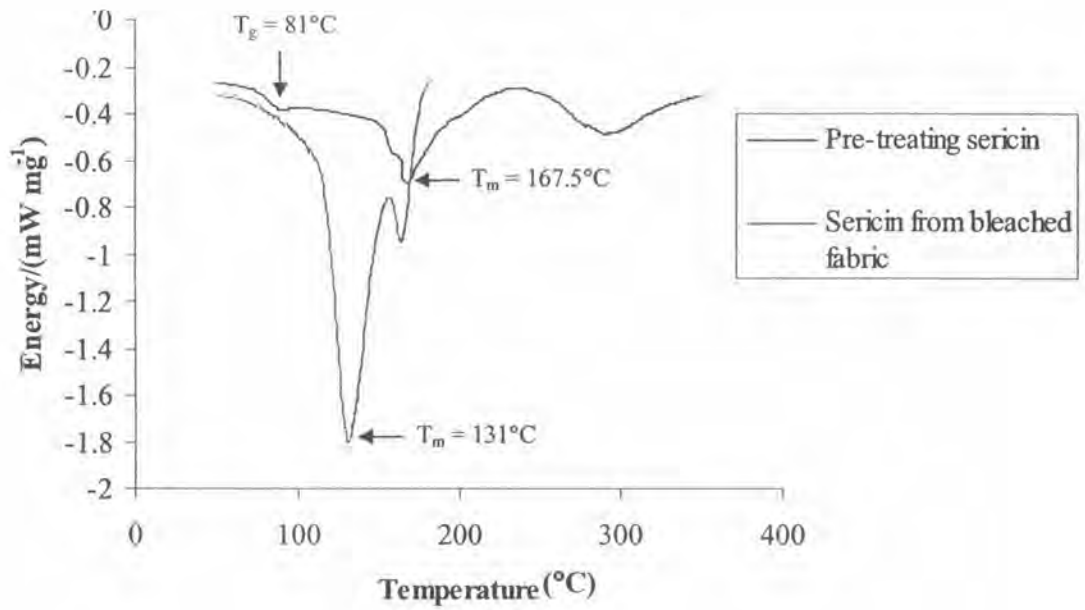


Figure 4.31: DSC diagrams of the pre-treating sericin and the sericin from the bleached fabric