Inkjet printing: effects of binder particle size and chitosan pretreatment on the qualities of silk fabric

W Kangwansupamonkon,[1] M Suknithipol,[2] S Phattanarudee[2] and S Kiatkamjornwong[2,3*]

[1]National Nanotechnology Centre, National Science and Technology Development Agency, 130 Thailand Science Park, Paholyothin Road, Klong 1, Klong Luang, Phathumthani 12120, Thailand

[2]Imaging Technology Research Unit, Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

[3]Division of Science, the Royal Institute of Thailand, Dusit District, Bangkok 10300, Thailand

Inkjet inks for fabric printing usually contain either a dye or a pigment as colourants. The most important requirement of pigmented inks is the pigment dispersion stability and performance over a wide range of conditions, temperatures and times.[1] The binder of an inkjet ink may contain one or more polymer types to control the viscosity of the ink system, to promote droplet formation, and to serve as a binder for the colourant, providing adhesion to the printing surface by the formation of a localised film.[2] The development of a truly effective binder that is suitable for inkjet inks still remains a great challenge due to the strict requirements of particle size, size distribution, surface tension, viscosity, stability, compatibility with other components of the inks, and the printing system. There also needs to be controlled drop formation, jetting and fabric wettability. In this light, nanoscale binders appear as likely candidates for pigment-based inkjet ink printing on fabrics. Indeed, inks containing nano-sized binders and commercial pigment dispersions have previously been demonstrated to give excellent printability, good colour fastness and softness of the printed fabrics.[1]

Silk is the strongest natural fibre, with a fine continuous monofilament of high lustre, strength, flexibility and high absorbency. The fabric is porous, soft and pliable, and so it needs to be pretreated to limit the excess spreading of inks during printing. The surface finishing binder that is deposited on the fabric helps smooth the fabric surface and give better opportunities for the creation of a uniform ink film. Moreover, the functional groups of the pre-treating compounds are expected to assist in providing better reception of the ink on the fabric. Pre-treating solutions contain one or more of many oligomeric or polymeric solutes/dispersions that contain functional groups which allow the substrate to accept the ink molecules on the fabric surface. In this way, the ink penetration speed becomes slower and greater colour strength characteristics can be achieved.

Chitosan is based on a natural polymer and forms one type of pre-treating biomaterial. Chitosan contains amino groups and has a pKa value of approximately 6.5. Therefore, chitosan is positively charged and soluble in acidic solutions/dispersions ,with a charge density that is dependent on the local pH, its average molecular weight, and its degree of deacetylation.

The inkjet inks that are of interest to the current study were prepared using two nanometer-sized binders and two different pigment-to-binder ratios. The inks were printed on untreated silk fabric and on chitosan-pretreated silk fabric. Comparisons of those binder sizes, pigment-to-binder ratios and chitosan pre-treatments that affect the printed colour quality and physical properties of the printed silk fabrics were established.

Methodology

Materials

The four pigment inks used for this purpose were standard in jet inks. The four pigment dispersions (cyan, magenta, yellow and black), provided from Modern Dyestuffs & Pigments Co Ltd (Bangkok, Thailand), were chemically confirmed by FT-IR spectroscopy. They were used as received and were as follows: cyan (MaxNano Jet SPC): CI Pigment Blue 15:3; magenta (MaxNano Jet SPM): CI Pigment Red 122; yellow (MaxNano Jet SPY): CI Pigment Yellow 138; and black (MaxNano Jet SPK): CI Pigment Black 7. The properties of the pigment dispersions are shown in Table 1.

The polymer binders Mowilith LDM 7668 (an acrylic acid ester-co-styrene copolymer plus surfactants to provide some penetrating power) and Printofix Binder 710 (a self-cross-linking acrylate-based copolymer dispersion based on butadiene) were obtained from Clariant Chemicals Ltd (Bangkok, Thailand). Their components were confirmed by FT-IR prior to use. The polymer binders differed in their molecular weight, particle size, pH, viscosity and T_g (see Table 1).

Other ingredients, namely diethylene glycol, glycerine and urea (all of analytical grade, supplied by Univar Ajax Finechem Corporation, Auckland, New Zealand), and sodium lauryl sulphate (Texapon N 70 LST, Cognis Thai Ltd, Bangkok, Thailand) were used as received. Chitosan (FL-80), having an average molar mass of 120 kDa, with an N-deacetylation degree of 88%, was used as the pre-treating biopolymer (Koyo Chemical Co Ltd, Tokyo, Japan).

Preparation of pigmented inks

The inks were prepared from binders, assembled on the basis of the two different particle sizes of styrene-co-acrylate binders that were used (Mowilith LDM 7668 and Printofix Binder 710), with their average particle size of 66 ± 25 and 195 ± 45nm, respectively. The other ingredients in the formulations were the nano-size pigments diethylene glycol, glycerol, urea and a surfactant (see Table 1). The

Table 1: Properties of pigment dispersions and binders

Pigment dispersions and binders	Solid content (%w/w)	Average diameter(nm)	ξ (mV)	pH	Viscosity* (mPa s)	T_g (°C)
Cyan						
(MaxNano Jet SPC)	3.7	59 ± 28	−30 ± 1	8.8	8.9	–
Magenta						
(MaxNano Jet SPM)	2.8	108 ± 44	−23 ± 1	8.6	8.5	–
Yellow						
(MaxNano Jet SPY)	12.1	102 ± 58	−38 ± 1	7.8	8.8	–
Black						
MaxNano Jet SPK)	3.4	104 ± 46	−26 ± 1	7.9	8.6	–
70-nm binder						
(Mowilith LDM 7668)	40	66 ± 25	−52 ± 1	8.5	47.7	9.7
180-nm binder						
(Printofix Binder 710)	40	195 ± 45	−37 ± 1	6.5	47.5	−15.5

ξ is zeta potential

*The viscosity was measured at a shear rate 310s^{-1} at 25°C by Brookfield Viscometer

Table 2: Ink recipes containing 1:1 and 1:2 pigment-to-binder ink formulations

Ingredients	1:1 pigment-to-binder ink (%w/w)				1:2 pigment-to-binder ink (%w/w)			
	Cyan	Magenta	Yellow	Black	Cyan	Magenta	Yellow	Black
Pigment dispersion	40.5	50.0	30.6	44.1	40.5	50.0	30.6	44.1
Binder	3.8	3.5	9.3	3.8	7.5	7.0	18.5	7.5
Diethylene glycol	10	10	10	10	10	10	10	10
Glycerol	10	10	10	10	10	10	10	10
Urea	5	5	5	5	5	5	5	5
Surfactant	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Water	30.65	21.45	35.15	27.05	26.95	17.95	25.85	23.35

formulations were prepared at 1:1 and 1:2 (w/w) pigment-to-binder ratios (see Table 2). Each component was added individually to avoid any unfavourable inhomogeneity in the solution/dispersion. After mixing, the inks were filtered using a cellulose acetate filter (pore size 0.45μm, Sartorius Stedim Biotech GmbH, Göettingen, Germany) to remove all coarse particles, thus removing the risk of any clogging the print head of the inkjet printer.

Characterisation of pigmented inks

The pH of the ink was adjusted to be within the suitable range for printing, as measured at room temperature. A Brookfield viscometer (Brookfield viscometer DV III, programmable rheometer, Middleboro, Massachusetts, USA) was used to measure viscosity of the pigment dispersions and the formulated inks at 25°C and a shear rate 310s^{-1}. Dynamic light scattering (Zetasizer nano series, Malvern Instruments Ltd, Worcestshire, UK) was used for the analysis of the particle size of the ink formulations. The particle-size distributions of the ink formulations were measured after one day, one month, three months and six months to establish the storage stability of the inks. The charge of the pigment surface was evaluated at 25°C by dynamic light scattering. The surface tension of each ink was measured at room temperature by the Nouy Ring method using a surface tensiometer (K8, Kruss, Hamburg, Germany). Differential scanning calorimetry (DSC, 204 F1 Phoenix, NETZSCH-Gerätebau GmbH Selb/Bavaria, Germany) was used to measure the glass-transition temperature of both binders. The temperature range was scanned from -50 to 200°C, with a heating rate of 10°C min^{-1} under liquid nitrogen. A transmission electron microscope (TEM, JEOL, JEM-2100, Tokyo, Japan) was used to view the particle morphology and particle-size distribution of the pigment dispersions using an operating voltage of 15kV. The densities of the inks were measured using a 25ml pycnometer with an accuracy of ±1% (Aldrich Chemical Company Inc, Milwaukee, Wisconsin, USA) and calculated as standard.

Preparation of the silk fabrics

Plain weave silk fabric (The Thai Silk Co Ltd, Thailand), constructed at 88 × 99 lines inch^{-1}, with a basic weight of 0.08kg m^{-2}, was washed with a commercial detergent solution, then cleaned with de-ionised water and dried under ambient conditions. The fabric was cut into a 21cm x 29cm rectangular shape, and then ironed to a flat and smooth surface.

Chitosan solution pretreatment

The chitosan pre-treating solutions were prepared by dissolving the chitosan powder at 0.5, 1 and 1.5% (g/100cm^3 in a 1% (v v^{-1}) acetic acid solution, followed by heating at 60°C until homogeneous solutions were obtained. The silk fabrics were padded with 0.5, 1 or 1.5% (g/100g) pre-treatment chitosan solutions at a 75% pick-up ratio, using a padding machine (padding machine, HF-47993, Mathis, Switzerland), and then fixed at 80°C for five minutes and 110°C for two minutes in a stenter (Rapid Labortex Corporation, Taipei, Taiwan).

Printing process

The untreated and chitosan-treated silk fabrics were supported on a flat plastic sheet using a double-sided adhesive tape to give a stable dimension of the fabric for the inkjet printing. The fabric was printed with the in-house formulated inkjet inks using an Epson stylusTM C65 printer at a resolution of 5,760 x 1,440 optimised dpi. After printing, the printed ink on the silk was fixed at 150°C for five minutes.

Evaluation of printed quality

Colour gamut

A colour test chart of the printed fabric was evaluated for CIE L*a*b* (Commission International I'E clairage), which was measured using a spectrophotometer, X-Rite (SP62, d/8, X-rite Incorporated, Michigan, USA) with the D50 illuminant and the 2° observer and a 4mm measuring area. The equations for CIE 1976 L*a*b* (CIELAB) colour space are as reported elsewhere.[3]

Colour bleeding and outline sharpness

The fabrics were treated with a 1.5% (w/w) chitosan solution, dried and then printed with the word 'LEN', with a 1:2 w/w pigment-to-binder ratio. They were then viewed to give a visual assessment of the image quality.[4,5] The prints were then viewed by an image analyser in an optical microscope (DP70, BX51, Olympus Optical Co, Tokyo, Japan) at 5x/0.10.

Optical density

A solid tone pattern was printed on the untreated fabric and on the treated silk fabric. The optical density of the printed fabrics was measured using a densitometer (R730, IHARA Electronic Ind Co Ltd, Ichinomiya, Aichi, Japan) and the average was calculated from ten such measurements.

Ink penetration

The printed silk fabrics were cross-cut in the warp and weft directions to confirm the depth of the ink penetration. The cross-section of the print was viewed by an image analyser in the optical microscope.

The penetration of the ink fluids/pastes through the fabric, as determined using Equation 1, was assessed on the printed, dried and cured samples on the basis of the difference in reflectance between the face and back of the printed area, measured on the spectrophotometer, using the derived (K/S) vales for the front and the back of the fabric as reported.[6]

$$Penetration = \frac{100(K/S)_b}{0.5\left[(K/S)_f + (K/S)_b\right]}$$

Equation 1

The $(K/S)_f$ and $(K/S)_b$ values are for the front and back of the fabric, respectively. K is the absorption coefficient of the printed colour on the surface, and S is the scattering coefficient caused by the coloured substrate.

Applying a simple physical approach to the penetration of a liquid flowing under its own capillary pressure, the Lucas-Washburn equation (Equation 2) can be used to indicate the depth or speed of penetration in fabrics as reported.[5]

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

Equation 2

Where h is the penetration distance after time, t, and r is the pore radius. γ is the surface tension, η is the contact angle and is the liquid viscosity. This equation takes into consideration the surface tension, the viscosity and the contact angle. From the Lucas-Washburn equation, the square root of the surface tension-to-viscosity ratio, $(\gamma/\eta)^{1/2}$, indicates the depth or speed of penetration of the ink into a fabric, which affects the solid tone density, the colour gamut and the gamut volume because the low surface tension and low viscosity inks wet the fabric surface rapidly and penetrate deeper into the fibre, giving a lower optical density and limiting the extent of ink spreading. The optical density results are an inverse tendency predicted by $(\gamma/\eta)^{1/2}$, which was applied to the experimental values.[5]

Crock fastness

The crock fastness of the printed fabric was evaluated using an AATCC crockmeter (Atlas Electric Devices Corporation, Chicago, IL,USA) by AATCC Test Method 8–2001.[7] The amount of colour transferred from the printed surface to the receiving testing surface by rubbing was judged using a grey scale for staining or by using a chromatic transference scale. Grades from 1 to 5 were then judged and assigned, where 5 denotes the best performance and 1 denotes the worst performance.

Wash fastness testing

Wash fastness testing was carried out using a Gyrowash (Gyrowash 815, James, H Heal & Co Ltd, Halifax, England) using ISO 105-C06 (1994).[8] A specimen of 10 × 4cm size, in contact with the specified adjacent fabric, was washed, rinsed and dried. Each printed fabric, sewed with a multifibre strip, was washed at 40°C for 30 minutes in a liquor containing 4g of AATCC standard reference detergent WOB (without an optical brightener) per litre of water at a liquor volume of 150ml. The multifibre adjacent fabric (DW) contained wool fibres, acrylic fibres, polyester fibres, polyamide fibres, bleached fibres, cotton fibres and diacetate fibres. A change in colour of the staining on the adjacent fabric was compared using a grey scale for staining, in accordance with ISO 105–A03. The colour difference in the printed fabrics obtained before washing and after washing was also recorded in terms of the colour strength (K/S), and the relative colour strength is given in Equations 3 and 4. The ratio of K

to S is calculated from the Kubelka-Munk equation:

$$Colour\,strength,\ K/S = \frac{(1-R)^2}{2R}$$

Equation 3

$$\mathrm{Re}\,lative\,colour\,strength = \frac{(K/S)_{after\,washing}}{(K/S)_{before\,washing}}$$

Equation 4

where R is a decimal fraction of the reflectance of the printed silk fabric at the highest absorption of each printing ink colour. The fabrics were printed as a solid pattern in cyan, magenta and yellow colours plus black. The printed fabrics, before and after washing, were evaluated spectrophotometrically (X-Rite, SP62, d/8, diffuse sphere, X-Rite – Asia Pacific Headquarters, Hong Kong, China) in a UV-excluded mode. The spectral reflectance from each sample was measured five times and the average K/S values calculated.

Stiffness testing

Stiffness is generally regarded as an ability of a material to resist deformation (elongation) and is measured in terms of the bending length. JISL 1096:1999 Stiffness (45° cantilever method) was used to determine the stiffness of 2cm x 15cm pieces of fabric (1999).[9] The average bending length in the warp and weft directions, obtained from five measurements, was used to determine the average stiffness. The flexural rigidity or stiffness is correlated with the bending length, and was evaluated and expressed as the fabric flexibility (G) in mg.cm, as shown in Equation 5:

$$G = W \times C^3$$

Equation 5

where G = flexural rigidity in mg cm; W = fabric mass per unit area, mg cm^{-2}; and C = bending length, cm.

Air permeability

The ASTM D 737–96 for assessing the air permeability of a textile fabric was used to study the effect of the padding and printing of the fabrics.[10] The air permeability of the fabric is indicated by the rate of air flow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of a

material. The measurement is generally expressed in SI units as $cm^3 \ s^{-1} \ cm^2$.

Results and discussion

Ink property

Inkjet inks should be formulated to the appropriate viscosity with consistent surface tension characteristics, and be able to offer a long shelf life without pigment settling or the occurrence of mould growth.[11] The chemical stability of the ink as a composite system or of each of the components (pigment, solvents for the binder, additives) can give some assurance against agglomeration or increase in the particle size. Physical stability needs to be monitored so that no settling of the ink's ingredients is observed, as detected by light scattering-based analytical methods.[12] The pigmented inkjet inks that were used in the work that underpins this paper were based on formulations containing one of each of four pigments that were dispersed in the medium that also contained a surfactant and a binder, the major components of inks. The purposes of adding the surfactant were to enhance binder penetration through webs in the fabric and to improve the affinity between the binder and fibres. In a comparison of the size effect of the binder particles on the printing ink qualities, the majority of the inks were prepared from binders with average particle sizes in their dispersions within the range of 102 ± 58 to 108 ± 44nm. An exception was the cyan ink, in which the particle size was in the range of 59 ± 28nm (see Table 1 and Figure 1). The zeta potential of the pigment dispersions and the binders indicated that the charges on their surfaces were negative (see Table 3). The inks were thus stable.

The four coloured inks had a pH that was in the range of 7.8 to 8.8, a surface tension in the range of 35 to 45mN m^{-1} and a density of about 1g cm^{-3} (see Table 3). The inks were characterised as Newtonian fluids due to their relatively constant viscosity at various shear rates. It should be noted that the inks were filtered prior to measurement of the particle sizes, and thus agglomerates would have been excluded. Filtration of the inks is required to avoid large sized ink particles causing clogging of the print head of the printer during printing. Thus, the data on ink particle size distributions represent a realistic portrayal of the inks

Figure 1: The particle-size distributions of (a) the 70 and 180nm binders, and (b) the pigment dispersions after filtration
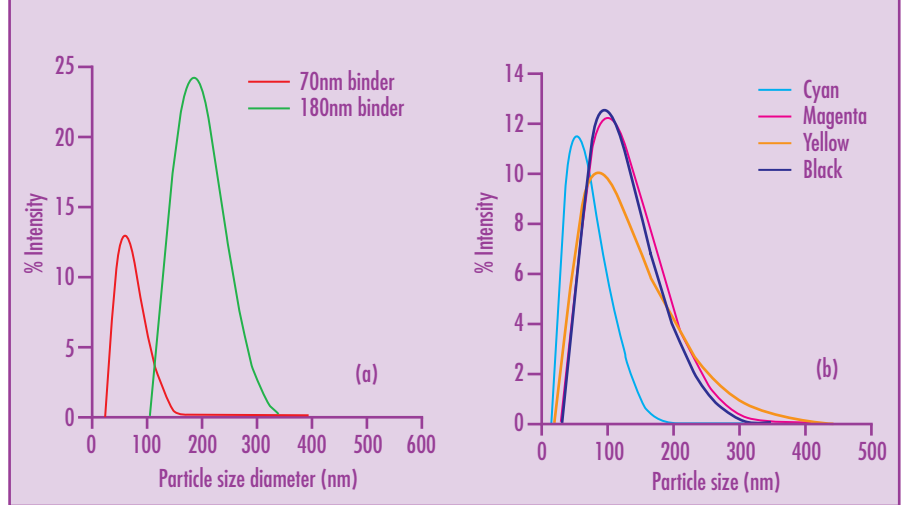
Table 3: The average particle size of the 1:1 and 1:2 pigment-to-binder ratio inks

| Ink colour | 1:1 pigment-to-binder ratio | | | | 1:2 pigment-to-binder ratio | | | |
| | Inks with 70nm binder | | Inks with 180nm binder | | Inks with 70nm binder | | Inks with 180nm binder | |
	D (nm)	ξ (mV)	D (nm)	ξ (mV)	D (nm)	ξ (mV)	D (nm)	ξ (mV)
Cyan	71 ± 38	−40 ± 2	141 ± 82	−41 ± 1	73 ± 37	−45 ± 2	225 ± 112	−44 ± 1
Magenta	131 ± 77	−37 ± 1	221 ± 131	−35 ± 1	97 ± 37	−39 ± 1	200 ± 77	−39 ± 1
Yellow	79 ± 31	−41 ± 1	213 ± 77	−41 ± 1	94 ± 56	−38 ± 7	216 ± 73	−43 ± 1
Black	99 ± 47	−40 ± 1	142 ± 74	−41 ± 1	97 ± 42	−35 ± 1	164 ± 87	−35 ± 1

that were used for printing. The four colour inks had different average particle diameters depending on the types of pigment that were used. The 1:1 (w/w) pigment-to-binder ratio gave particle sizes in the range of 71 to 131nm and 141 to 221nm for the 70 and 180nm binders, respectively. The zeta potential values of both inks that were formulated on the basis of a 1:1 (w/w) pigment-to-binder ratio varied from −37 to −41mV. Moreover, the average particle sizes of the inks formulated from a 1:2 (w/w) pigment-to-binder ratio were 73 to 97 and 164 to 225nm for the 70 and 180nm binders, respectively, with zeta potential values in the range of -35 to -45mV. The ink stability, as determined by measuring the particle-size distributions of the inks during storage, was excellent for at least six months.

At this stage, it is possible to state that the two binders, even those possessing a low T_g as mentioned, did not clog the nozzles. The inks maintained their low viscosity and were able to give reliable jetting, achieving adequate stability (at

least six months). In addition, the inks gave long-time stability to sedimentation, coagulation and phase separation.

Effects of ink binder particle size, pigment-to-binder ratio and chitosan pretreatment on print performance

Ink penetration

As shown in previous studies,[5] SEM analyses revealed that the untreated silk fibres appeared to be smoother and less swollen than those that had been pretreated with chitosan. The chitosan pretreatment appeared to have decreased the inter-fibre spaces and increased the roughness and compactness of the yarn.

The colour strength, as K/S values, were measured at the front and at the back of the printed areas to give an impression of ink penetration in the printed fabrics,

revealing that the amount of the binder in the inks effectively decreased the ink penetration into the silk fabrics, although there was essentially no significant difference in *K/S* between prints that were based on the inks containing the 70 or the 180nm binder. Moreover, the chitosan pretreatment was able to tie the silk fibres, reducing the opening voids of the inter-fibre space. As a result, the ink could not penetrate further into the yarn and so resided on the surface for a longer time.[13] In this way, ink penetration into the chitosan-pretreated fabrics was further reduced. This reduction was greater when increasing amounts of chitosan were used in the pretreatment.

Analysis of the colour strength, as *K/S* values, of the printed silk suggested that the greater the chitosan loading, the larger was the amount of the ink that was held on the printed surface. At both of the 1:1 and 1:2 ratios, the black ink increased in *K/S* values on increasing the amount of chitosan, whilst the yellow did not. Little change was observed with the cyan inks and the magenta inks. The strength of the ink colour (*K/S*) on the back side (non-printed area) of the printed areas seemed to be constant regardless of the size of the binder and the pigment-to-binder ratio used. Indeed, one can see that:

- with the untreated fabric, the ink penetration was the greatest (ie the lowest *K/S* value);
- increasing the amount of chitosan used in the chitosan pretreatment on the fabric decreased the amount of ink penetration;
- the effect of the binder particle size at both pigment-to-binder ratios was a key parameter with respect to ink penetration.

For the untreated fabrics, the 70nm binder gave deeper ink penetration in comparison with the 180nm binder, as shown in Figure 2a *versus* Figure 2b. Even in the chitosan pretreated fabric, as shown in Figures 2c and 2d, the ink containing the 70nm binder penetrated deeper than that containing the 180nm binder, respectively. This is because the 70nm binder (Mowlith LDM 7668) is designed as a penetrating primer. Therefore, its ink penetration is deeper than that of the 180nm binder (Printofix 710), especially on and into porous materials. In addition, in the ink containing the 180nm binder particles, each particle has a larger surface

Figure 2: Cross-sectional views of ink penetration into the printed fabric by 1:2 (w w⁻¹) pigment-to-binder ratio ink containing the 70nm binder (a and c) and 180nm binder (b and d) binder, and printed onto (a and b) the untreated fabric or (c and d) 1.5% (w w⁻¹) chitosan treated fabrics.
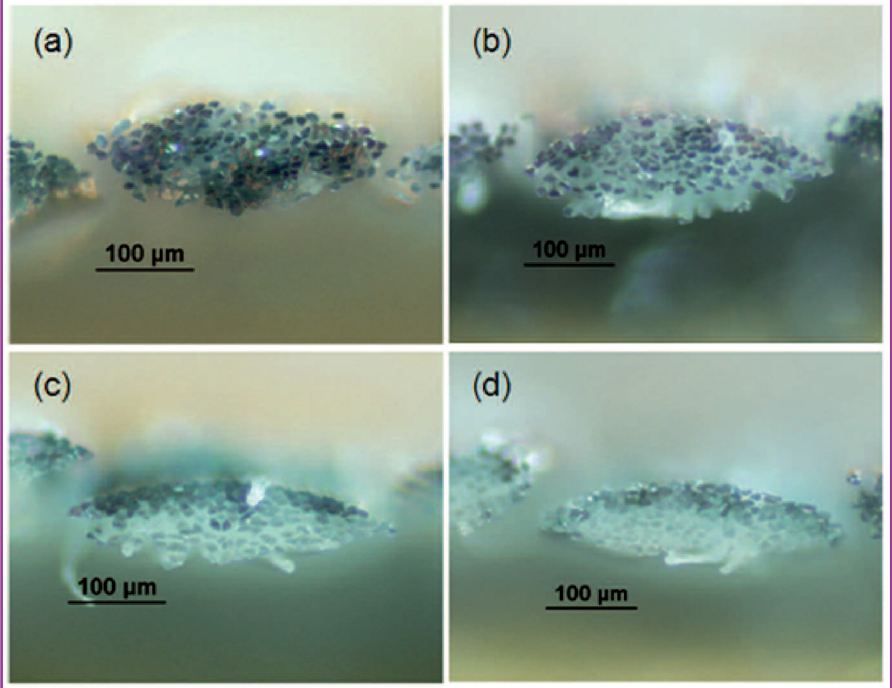
area that is available to interact with more chitosan molecules on the fabric surface. This position is somewhat compromised by the fact that the total surface area per unit mass of the particles that are available for interaction increases as the particle size decreases, a point that has rheological significance with respect to physical stability. Hence some form of compromise is required.

Considering the Lucas-Washburn equation relating to penetration depth (see Equation 2), the parameter of $(\gamma / \eta)^{1/2}$ can be used to correlate the theoretical view point with the experimental results. The greater the $(\gamma / \eta)^{1/2}$ values, the deeper would be the ink penetration. The penetration depth of ink into the silk yarn, based on the *K/S* values of the printed silk was thus evaluated and the data are summarised in Table 4. There was not a perfect correlation between $(\gamma / \eta)^{1/2}$ and the penetration depth from the experimental data (see Table 4). The penetration depth of the four coloured inks used, as determined from the derived *K/S* measurements, were all in a broad range of 42% to 82%, depending on the extent of the chitosan pretreatment. As expected, the 1:2 (w/w) pigment-to-binder ratio produced a lesser ink penetration depth into the silk fabric because the

greater amount of ink binder and the greater ink viscosity can retard ink penetration. The combined effects of the binder particle size, its amount and the chitosan pretreatment on ink penetration depth is caused by the pigment being absorbed into the interstitial voids of the binder itself. Also, the other additives contribute to there being denser particle packing in the ink film during ink drying.

Optical density

The pretreated fabrics printed with the inks containing the 70nm binder particles gave a greater optical density than those printed with the inks containing the 180nm binder particles. Although the 70nm binder particles in the relevant ink penetrated deeper into the fabric than did the larger-sized binder particles and less ink was deposited on the fabric (see Figure 2), the 1:2 (w/w) pigment-to-binder ratio from the ink containing the smaller-sized binder particles yields a greater optical density for the yellow ink than did the 1:1 (w/w) pigment-to-binder ratio of the larger-sized binder particles because of the closer packing of the smaller binder particle size. However, the difference was not significantly great with the other three inks. The chitosan pretreatment enhanced

Table 4(a): Comparison of the penetration depth of a silk yarn and the measured K/S of printed fabric at 1:1 w/w pigment-to-binder ratio

| Pigment colours | Penetration of 70nm binder | | | Penetration of 180nm binder | | |
| | Treatment with chitosan (% w/w) | | | Treatment with chitosan (% w/w) | | |
	$(\gamma/\eta)^{1/2}$ of the inks	0	1.5	$(\gamma/\eta)^{1/2}$ of the inks	0	1.5
Cyan	4.5	62.7	46.3	4.3	67.4	48.7
Magenta	4.4	66.8	51.4	4.3	74.9	48.6
Yellow	4.0	62.4	52.6	3.9	60.9	49.5
Black	4.6	79.5	47.8	4.5	82.1	49.5

Table 4(b): Comparison of the penetration depth of a silk yarn and the measured K/S of printed fabric at 1:2 w/w pigment-to-binder ratio

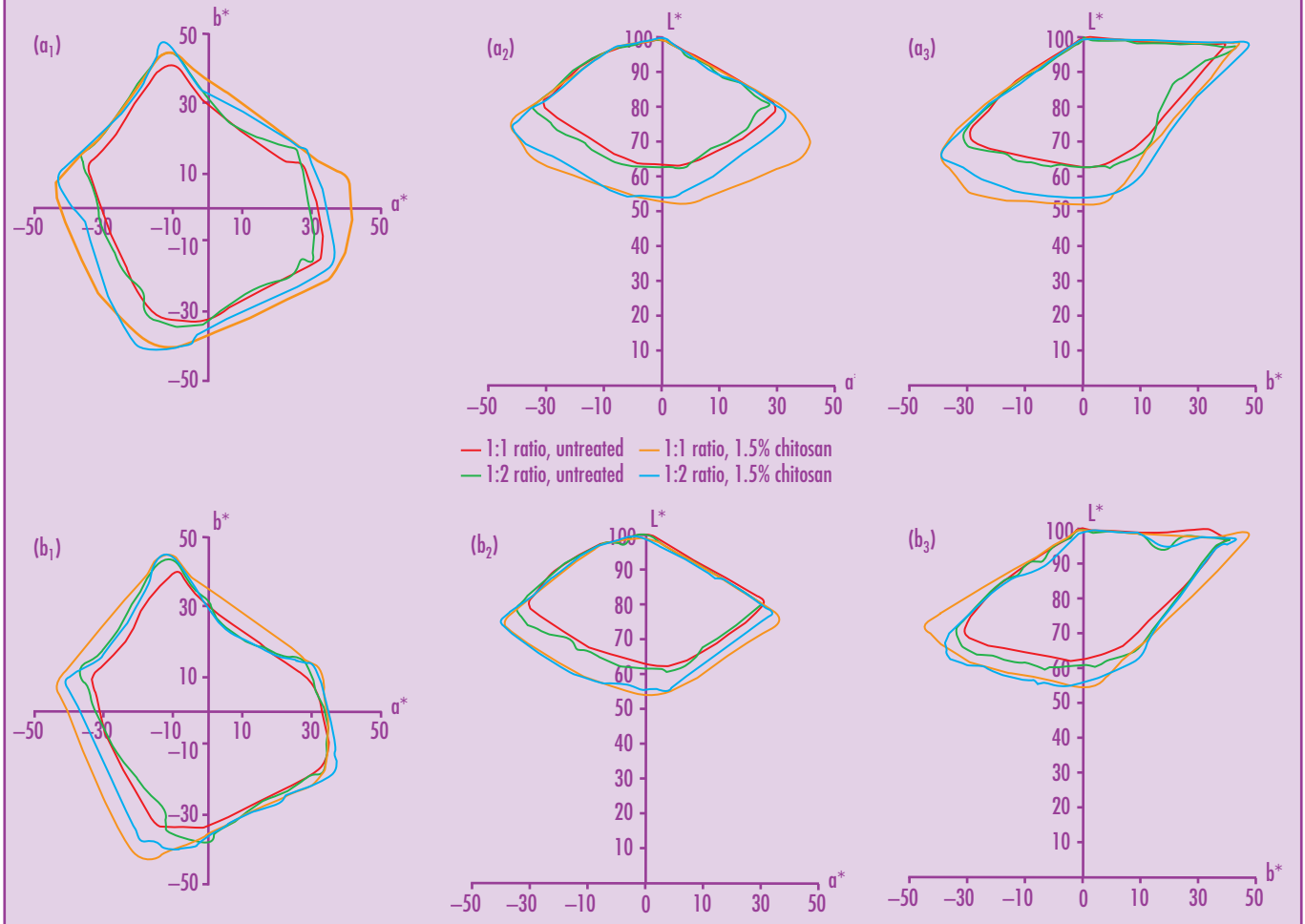| Pigment colours | Penetration of 70nm binder | | | Penetration of 180nm binder | | |
| | Treatment with chitosan (%w/w) | | | Treatment with chitosan (%w/w) | | |
	$(\gamma/\eta)^{1/2}$ of the inks	0	1.5	$(\gamma/\eta)^{1/2}$ of the inks	0	1.5
Cyan	4.3	62.1	42.4	4.2	51.7	42.0
Magenta	4.2	69.8	52.9	4.3	60.2	48.7
Yellow	3.8	53.9	49.8	3.2	61.1	49.6
Black	4.0	72.6	49.7	4.3	74.4	49.2

the optical density only slightly because the amount of free amino groups from the chitosan on the fabric surface was insufficient and did not provide significant ink-chitosan interaction. The colour appearance provided by the four ink types was similar to those of the same inks that were printed on paper. The lesser optical densities of the inks on the fabrics may be caused by (i) the ink films being relatively transparent, and (ii) the geometrical configuration of the device that was used to measure the optical density of the fabric not being fully suitable for the evaluation of a diffuse and porous surface.

Colour gamut, inter-colour bleeding and outline sharpness of prints

The chitosan pretreatment increased the size of colour gamut significantly compared with that of the untreated fabric. However, fabrics that were treated with solutions containing 0.5, 1 and 1.5g of chitosan per 100g of medium did not produce a marked increase in colour gamut. The diagrams of a*b*, L*a*, and L*b* (see Figure 3) of the printed silk fabrics indicate the effects of the binder size, the pigment:binder ratio and the use of the 1.5g of chitosan per 100g of medium pretreatment on the colour gamut. Figures 3a and 3b show that

the colour gamut of the treated fabrics was relatively wider for prints that were based on the ink containing the 70nm binder than that containing the 180nm binder. In this, the greatest difference was found with the cyan colour (the blue-green region) and the lemon colour (the yellow-green region). For the untreated fabrics, the pigment-to-binder ratios did not influence the colour gamut because both gamut sizes were almost overlapped. The colour gamut of the untreated fabric, printed with inks containing the 180nm binder was slightly larger than that of the inks containing the 70nm sized binder in a*-b*, L*-a*, and L*-b* gamut because in these the size effect of binder predominated. This result indicates that the binder in the ink gave some control over the colour strength that was achieved. In contrast, the three gamut sizes from the inks containing the 70nm binder were relatively greater than those containing the 180nm binder on the chitosan-treated fabrics. Similarly, at both pigment-to-binder ratios and regardless of the chitosan pretreatment content, the colour gamut provided by the inks containing the 70nm binder was larger than the colour gamut provided by the inks containing the 180nm binder. Even though the smaller-sized binder would be expected to penetrate deeper into the porous fabric,

it is presumed that the 70nm binder can form a better quality of film and bring out more colour saturation to the treated surface. A combination of the chitosan pretreatment and the ink binder synergistically increased the colour gamut of the printed fabrics in both chroma and colour saturation. This is because the primary amino groups ($-NH_2$) were prorogated (NH_3^+) under the acidic conditions, allowing enhanced electrostatic adherence of the negative charges of the pigment. Hakeem et al[14] has shown that the increase in K/S values was more than three times greater in the presence of the binder (styrene-acrylate based copolymer dispersion) when modified chitosan derivatives were used as a surface treatment (ie the nitrogen content at the surface was greater). The entrapment of chitosan molecules onto the fabric surface, and thus the greater density of charged amino groups that were available to interact with the anionic dyes/pigments in the inks to increase the chroma value, was influenced by the binder. This effect was predominantly enhanced following the chitosan pretreatment of the fabrics, which reduced ink penetration.

The word 'LEN' printed on the untreated fabric that was printed with inks containing the 70nm binder (see Figure 4a) was more spread out and blurred than that shown in Figure 4b, representing the fabric that had been coated with the chitosan solution (1.5g/100cm^3 of medium). The chitosan pretreated fabrics printed with inks containing the 180nm binder (see Figures 4c – non-chitosan treated, and 4d – chitosan treated) were sharper and less spread than were the prints on the untreated fabrics. The individual letter images printed with the ink containing the180nm binder were sharper, clearer and more evenly printed, to give the outline with less ragged edges and lines than those provided by the ink containing the 70nm binder. This is because the greater mass of the 180nm binder limited excessive ink spreading prior to ink penetration and solidification on the fabric surface. It should also be noted that increasing the chitosan content yielded increasingly less colour bleeding and better outline sharpness on the fabric.

Figure 3: a*b*$_1$, L*a*$_2$ and L*b*$_3$ diagrams of the inks printed on the untreated fabric and 1.5% (w v^{-1}) chitosan treated fabric by the ink containing 1:1 and 1:2 (w w^{-1}) pigment-to-binder ratios of (a) the 70nm and (b) the 180nm binder

— 1:1 ratio, untreated   — 1:1 ratio, 1.5% chitosan
— 1:2 ratio, untreated   — 1:2 ratio, 1.5% chitosan

Effects of binder size and binder-to-pigment ratio on the properties of the printed fabrics

Crock fastness

DSC analyses revealed that the glass-transition temperatures (T_g) of the 70nm binder were greater than that of the 180nm binder, being 9.7°C versus –15.5°C. This is because the former contained a greater styrene content in the acrylic acid-co-styrene copolymer content. Thus, the 180nm binder films would be expected to be soft and flexible at ambient temperatures because of this low T_g value (–15.5°C), and to undergo a significant change at this T_g value. Films based on the 70nm binder hardly changed after the heat treatment.[1] The 180nm binder gave another transition peak at 145°C which could indicate the presence of some decomposition.

Figure 4: Effect of the binder size and fabric surface treatment printed with the inks containing 1:2 (w w^{-1}) pigment-to-binder ratio on colour bleeding and outline sharpness of the characters of LEN with 70nm binder on (a) the untreated fabric and (b) 1.5% (w w^{-1}) chitosan treated fabric, and with the 180nm binder on (c) the untreated fabric and (d) 1.5% (w w^{-1}) chitosan treated fabric
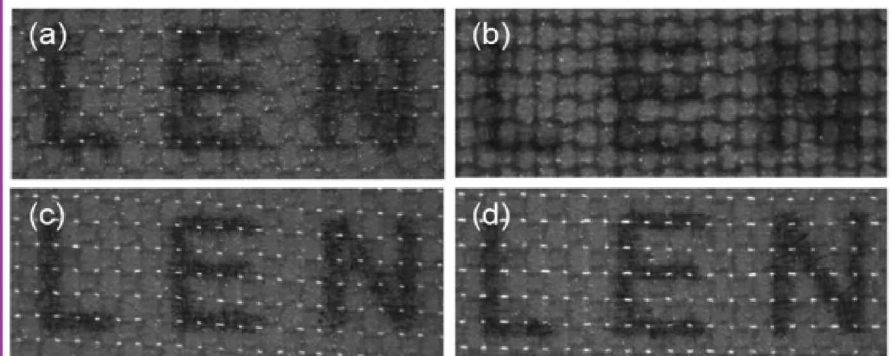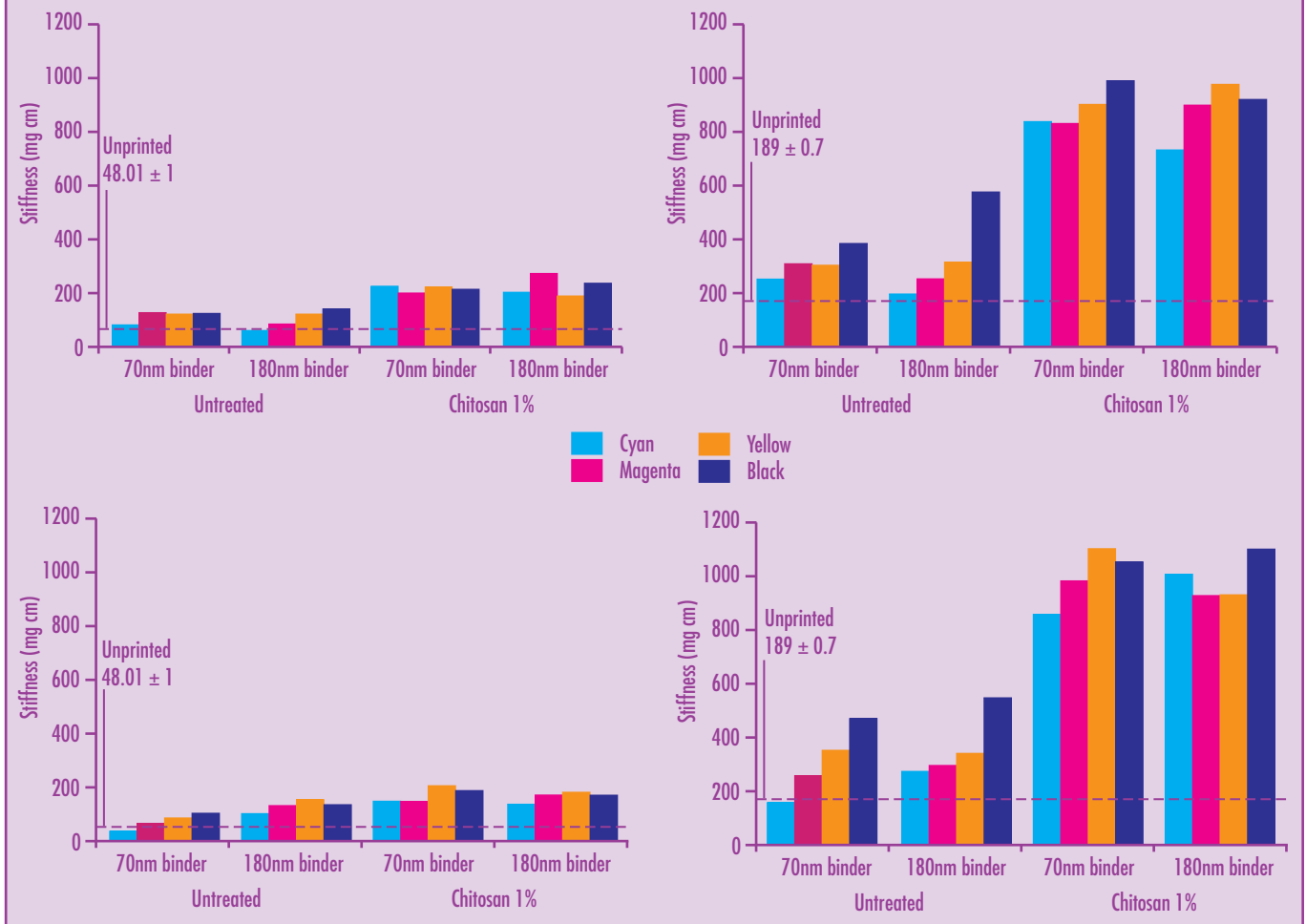
Figure 5: Effect of the untreated and 1% (w v⁻¹) chitosan treatment and binder size on stiffness of the fabrics at 1:1 (w w⁻¹) pigment-to-binder ratio in (a) the warp direction and (b) the weft direction; and at a 1:2 (w w⁻¹) pigment-to-binder ratio in (c) the warp direction, and (d) the weft direction

The dry and wet crock fastnesses of the untreated fabric and the treated fabrics were in the range of 5 and 4–5, respectively, and were obtained for prints that were based on the inks containing the 70nm binder in the 1:2 pigment-to-binder ratio, which was slightly superior to those of the prints from the 180nm binder. This is because the softer and weaker film cannot withstand severe rubbing. Increases in the pigment-to-binder ratios from 1:1 to 1:2 (w/w) improved the crock fastness because more binder molecules were able to hold more pigment particles strongly within the film and were thus held more firmly to the fabric surface. The chitosan pretreatment slightly decreased the crock fastness of the fabrics in a weakly dose-dependent manner. In the dry conditions, the pretreatment did not affect the rub resistance, but it slightly decreased the rub fastness in the wet conditions. After the chitosan pretreatment, the fabric retained some trapped acetic acid which might have been diluted under the wet conditions used in printing. The unwashed, treated fabrics usually retained some odour of acetic acid, an unpleasant aspect of the chitosan treatment, which was removed by the typical washing processes that are used for commercial printed fabrics. The high crock fastness of the printed silk was possibly caused by the low ink pick-up on the fabric surface, as shown by the fact that the ink penetrated deeper into the fabric yarn. The adhesion of the ink film to the fibre surface would be weakened by water-induced swelling, giving the wet film weaker adhesion to the surface, consequentially leading to a failure in adhesion.[15]

Wash fastness

The wash fastness of the printed fabrics ranged from good to excellent in all conditions. The colour data before and after washing did not indicate any significant changes based on a statistical evaluation. The relative colour strength ranged from 0.9 to 1.0, indicating good wash fastness, perhaps because the binder in the ink dispersion retained more pigment particles on the fabric surface. The binder was used as a fixing agent, incorporating the molecules of chitosan on the fabric surface, and subsequently increasing the colour durability after the washing of the printed fabrics. The 180nm binder can cause a self-association and interaction of the interactive functional groups of the acrylic acid-based copolymer to give insoluble and relatively hydrophobic polymer films on the fabric surfaces. Irrespective of the particle size of the binder, the pigment-to-binder ratio, and the chitosan pretreatment level, the average relative colour strength for all four tested colours was almost fully consistent.

Figure 6: Air permeability of (a) the untreated fabric, (b) printed by the ink having 1:1 (w w^{-1}) pigment-to-binder ratio on the fabrics, and (c) printed by the ink having a 1:2 (w w^{-1}) pigment-to-binder ratio
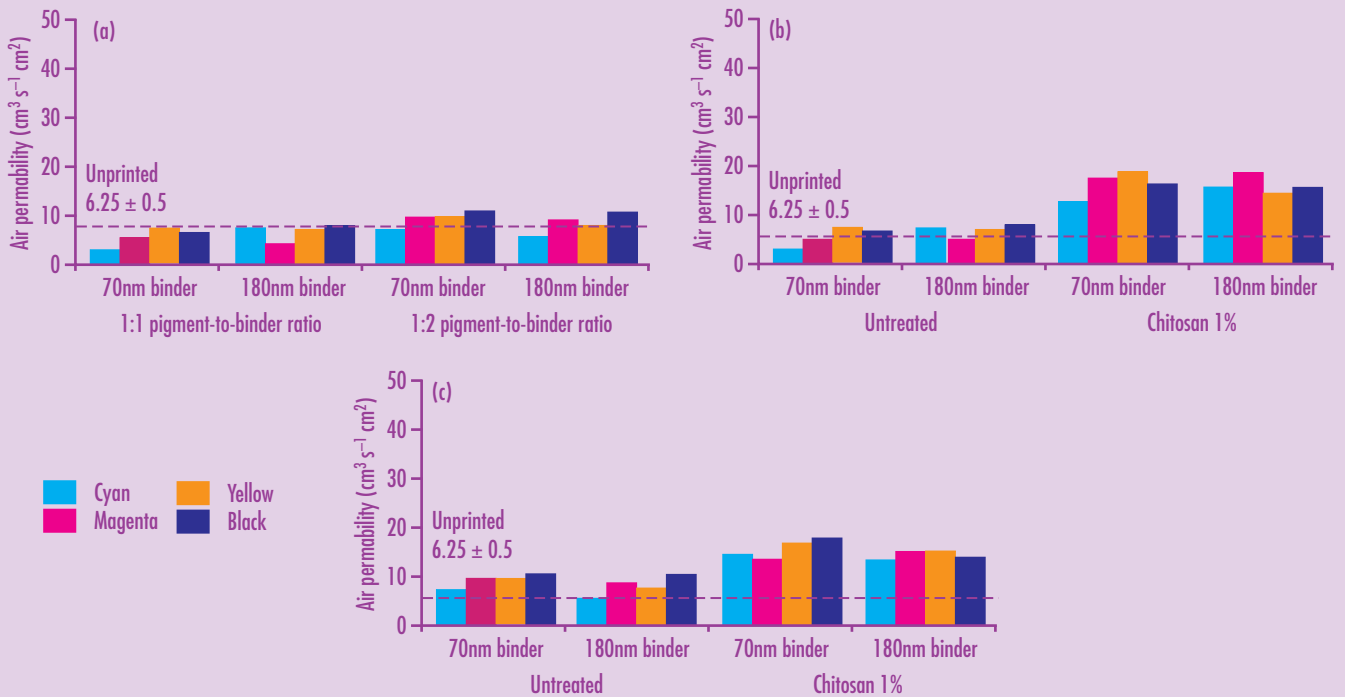
Ink binder selection is an important key parameter with respect to maintaining the permanence of an image with respect to the washing and rubbing of textile prints. The low T$_g$ binders are good for hand and feel sensations. Usually, the ink binder is soluble in its medium but water-soluble random or block copolymer, with multi-functionality, cross-linkable agents help in gaining increased rubbing and washing resistance when the prints are heat cured to give cross-linked networks on fabric.[16]

Fabric stiffness

Since a loading of 1.5% w/w chitosan gave very stiff fabrics to hand and feel, thus, a 1% w/w solution was used instead. The effects of the ink binder size, pigment-to-binder ratio, and the use of the 1% w/w chitosan pretreatment on the fabric stiffness or bending length are illustrated in Figure 5, where the greater bending length value indicates greater fabric stiffness. The stiffness in the weft direction was greater than that of the warp direction in all of the untreated fabrics. The stiffness did not significantly change, with differences in the particle size of the binder particles in the ink or with changes in the pigment-to-binder ratios. However, chitosan

pretreatment markedly increased the fabric stiffness as expected, because some of the chitosan pretreatment solution penetrated the fabric and gave some fusion of the assembled fibres to produce the greater fibre stiffness.[13] However, the number of lines assembled in a single yarn in the weft direction (99 lines/inch) was greater than that in the warp direction (88 lines/inch), which contributed to the greater stiffness in the weft direction. It should be noted that the fabric stiffness obtained from the inks containing the180nm binder gave similar behaviour to that obtained for fabrics that had been printed with inks containing the 70nm binder.

Air permeability

The air permeability of all the printed fabrics with 1% (w/w) chitosan pretreatment showed a similar trend to that seen in the study of the stiffness properties (see Figure 6), being only significantly enhanced by the chitosan pretreatment, presumably because the chitosan not only coated the yarns but also grouped the fibres within the yarn into bundles, forming a packed and rigid yarn matrix and introducing wider inter-yarn spaces,[13] whilst the untreated fabrics had

only the inter-fibre spaces but not the inter-yarn spaces. In contrast to the stiffness, the size of the ink binder particles had a slight effect on the air permeability, being less in the fabrics printed with the inks that contained the180nm binder than those fabrics that were printed with the inks that contained the 70nm binder because the latter can penetrate deeper to give more inter-yarn and inter-fibre spaces.

Conclusions

This research was focused on the effects of nanometre-sized binder/chitosan pretreatment-silk printing in terms of colour reproduction, print stability and appearance, and fabric performance.

Chitosan pretreatment helped to improve the ink deposition on the fabric surface and reduced deep ink penetration into the fabric. The pretreatment increased the colour gamut obtained using the inks containing the 70nm binder. Also, increasing the pretreatment agent (chitosan) loading in the surface treatment of the fabric gave less ink spreading and a shorter ink penetration depth.

The chitosan pretreatment increased the fabric stiffness with inks containing binders at both particle size and both pigment-to-binder ratios, especially in the weft direction.

Colour bleeding and outline sharpness were obtained from the combination of the use of the 180nm binder and the 1:2 pigment-to-binder ratio. The air permeability of the fabric was increased with chitosan pretreatment, regardless of binder sizes and pigment-to-binder ratios. The combination of using the binder in the ink and applying the chitosan pretreatment gave markedly enhanced colour appearance and significant improvements to the quality of the printed fabrics.

Acknowledgements

References

1. Xue C H, M M Shi, H Z Chen, G Wu and M Wang, 'Preparation and application of nanoscale microemulsion as binder for fabric inkjet printing', *Colloids and Surfaces,* **287**, 147–52, 2006

2. Leach R H, R J Pierce, E P Hickman, M J Mackenzie and H G Smith, *The Printing Ink Manual*, Blueprint, Cornwall, 1993

3. Berns R H, *Principles of Color Technology*, John Wiley & Sons, Canada, 2000

4. Koopipat C, A Janasak and S Kiatkamjornwong, 'Measurement and analysis of printed image on silk fabric by inkjet printer', International Congress of Imaging Science, Society of Imaging Science and Technology, ICIS'06, Springfield, VA, 2006

5. Leelajariyakul S, H Noguchi and S Kiatkamjornwong, 'Surface-modified and micro-encapsulated pigmented inks for inkjet printing on textile fabrics', *Progress in Organic Coatings,* **62**, (2), 145–61, 2008

6. Daplyn S and L Lin, 'Evaluation of pigmented ink formulations for jet printing onto textile fabrics', *Pigment and Resin Technology*, **32**, 307–18, 2003

7. 'Colour fastness to crocking: AATCC crockmeter method 8–2001', *American Association of Textile Chemists and Colourists Technical Manual*, 17–19, 2002

8. Textile-tests for colour fastness – Part 06: Colour fastness to domestic and commercial laundering, International Standard ISO 105–06 1–5, 1994

9. Bending stiffness method A JIS published standard, JIS L1096, 1999

10. Standard test method for air permeability of textile fabrics, ASTM International Designation: D737–96 202–206, 1996

11. Byrne C, 'Inkjet printing in the textile industry: Drawing up the battleline', *ATA Journal*, **5**, (12), 33–40, 2001

12. Sime K and P Bentley, 'Use of analytical techniques to characterise the stability of difficult inkjet pigment system', International Conference on Digital Printing Technologies, NIP17, Springfield, VA, 2001

13. Phattanarudee S, K Chakvattanatham and S Kiatkamjornwong, 'Pretreatment of silk fabric surface with amino compounds for inkjet printing', *Progress in Organic Coatings*, **64**, 405–18, 2009

14. Hakeim O A, L El-Gabry and A Abou-Okeil, 'Rendering synthetic fabrics acid printable using chitosan and binder', *Journal of Applied Polymer Science*, **108**, 2122–7, 2008

15. Kiatkamjornwong S, P Putthimai and H Noguchi, 'Comparison of textile print quality between inkjet and screen printings', *Surface Coating International Part B*, **88**, 1–82, 2005

16. Fu S, *Pigmented Ink Formulation*, CRC Press, Woodhead Publishing Limited, Cambridge, 2006