CHITOSAN AND IMPROVED PIGMENT INK JET PRINTING ON TEXTILES

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Doctor of Philosophy

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DECLARATION

I, Nasar Harun Momin certify that:

a. except where due acknowledgement has been made, the work is that of the candidate alone;
b. the work has not been submitted previously, in whole or in part, to qualify for any other academic award;
c. the content of the thesis is the result of work which has been carried out in the school of Fashion and Textiles, RMIT University between April 2004 and 2008.
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Nasar Harun Momin

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DEDICATION

This work is dedicated to my grandparents, parents and family members.

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LIST OF ABBREVIATIONS

CIJ	Continuous Ink Jet
CMYK	Cyan, Magenta, Yellow, Black
CH	Chitosan
CH82	Medium molecular weight chitosan with DD of 82%
CH90	Chitosan with DD of 90% and molecular weight less than 5000
CH95	Low molecular weight (~150,000) chitosan with DD of 95%
CH98	Medium molecular weight (>375,000) chitosan with DD of 98%
Conc.	Concentration
cps	Centipoise
DC	Degree of Carboxymethylation
DD	Degree of Deacetylation
DOD	Drop on Demand
dpi	Dots Per Inch
DQ	Degree of Quaternization
DS	Degree of Substitution
FTIR-ATR	Fourier Transform Infra Red-Attenuated Total Reflectance
$g.L^{-1}$	Grams Per Litre
HLB	Hydrophilic/Lipophilic Balance
IJP	Ink Jet Printing/Printer
MFDA	Multifunctional Dispersing Agent
MW	Molecular Weight
M_v	Viscosity Average Molecular Weight
NCMCH82	N-Carboxymethyl Chitosan with DD of 82%
nm	Nanometre
SEM	Scanning Electron Microscopy
SMCB	Surface Modified Carbon Black
Tg	Glass Transition Temperature
WI	Whiteness Index
WPU	Wet Pick Up

ABSTRACT

The purpose of this research was to explore the application of chitosan, a biopolymer, for ink jet printing of textiles. Two ways of using chitosan for ink jet printing of textiles were explored. One was to apply chitosan as a post-treatment on the fabric ink jet printed with pigment based inks for the fixation of pigments on the fabric. The second approach was to incorporate chitosan as a binder in pigment based ink jet ink formulations. The incorporation of chitosan to formulate ink jet inks was carried out in two ways. One way was direct addition of chitosan into the ink formulations containing surface modified pigments. The second way was to prepare chitosan encapsulated pigment nanoparticles using complex coacervation technique and using these nanoparticles for the formulation of ink jet ink.

The degree of deacetylation (DD) influences the physicochemical properties, biological properties, antibacterial activity and more importantly, the applications of chitosan. Therefore it is important to accurately determine the degree of deacetylation of chitosan sample before utilising and investigating it for a particular application. The DD was determined using FTIR spectroscopy. Various protocols proposed by researchers were used to determine the degree of deacetylation of chitosan samples and the water-soluble derivative of chitosan (N-carboxymethyl chitosan) used in the present study. The protocol proposed by Raut was found to be fairly accurate in determining the degree of deacetylation of chitosan samples. The molecular weight of chitosan was estimated using dilute solution viscometry method. The characterisation of the film forming ability of chitosan was evaluated using scanning electron microscopy (SEM). The colour strength (K/S), colour difference, colour characteristics and colour fastness to laundering and rubbing of ink jet printed fabrics post treated with chitosan were evaluated using standard methods.

Post-treatment (pad-dry-cure method) of cotton fabric ink jet printed with pigment based inks revealed that chitosan (CH82) could effectively fix the pigments on cotton compared to the commercial textile binders and the water-soluble derivative of chitosan (NCMCH82). This indicated the potential use of chitosan as a surface finish for fixation of pigment based ink jet inks printed on cotton fabric.

Further studies were focused on evaluating the effect of molecular weight, application methods, concentration, pH and depolymerisation of chitosan on degree of fixation of pigment based inks on cotton fabric. The effect of plasticizer and textile softeners on the degree of fixation and colour fastness properties were also studied. The laundering durability and performance properties such as tensile strength and stiffness of ink jet printed cotton fabrics post treated with chitosan were discussed.

The chemical interaction between chitosan and cotton fabric was illustrated by FTIR-ATR analysis and through determination of carboxyl group content. It was found that the cross-linking reaction between cellulose and chitosan during film formation arises by Schiff base formation between carbonyl groups of cellulose and primary amino groups of chitosan. Increase in carboxyl group content did not enhance the fixation of pigments.

Post-treatment with chitosan (MW 156,000) of different textile fabrics such as 50/50% Polyester/cotton blend, wool, silk and viscose showed around 79%, 85%, 99% and 90% of pigment fixation, respectively. The degree of fixation of ink jet printed 100% polyester fabric post treated with chitosan was found to be around 28% due to the inert nature of polyester and lack of bonding with chitosan. The ink jet printed cotton fabric post treated with 3 $g.L^{-1}$ chitosan (MW 156,000) maintained almost 86% of bacterial reduction against *Klebsiella Pneumoniae* even after 50 launderings.

Inks containing chitosan were formulated for ink jet printing of cotton fabric and were characterised for ink stability. The inks containing chitosan were found to be stable in terms of mean particle size and viscosity over a period of one month and for 4 freeze/thaw cycles. A magenta ink formulation containing chitosan was selected for ink jet printing of cotton fabric. It was found that the degree of fixation was around 97% for magenta ink containing chitosan compared to around 53% fixation for magenta ink without chitosan on cotton fabric.

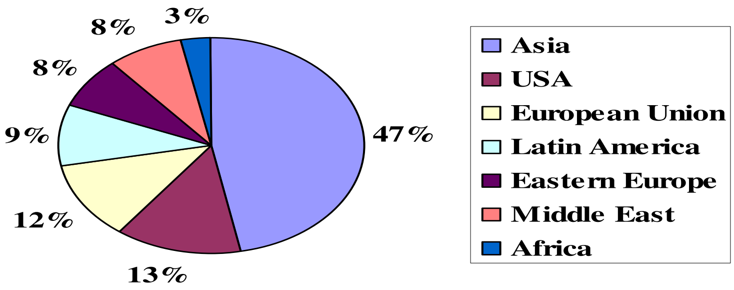
Surface modified carbon black pigment with carboxylated (COO^-) surface functionality was selected to prepare chitosan encapsulated pigment nanoparticles by complex coacervation technique. Chitosan encapsulated pigment nanoparticles with mean particle size diameter of 880 nm and 740 nm were formed when 5 ml of 0.1% w/v pigment was mixed with 2 ml and 3 ml of 0.1% w/v chitosan, respectively. However, no correlation was found between the particle size of the nanoparticles formed and the concentration of chitosan. Ink containing chitosan encapsulated pigment nanoparticles was formulated and ink jet printed on cotton fabric. The degree of fixation with ink containing chitosan encapsulated pigment nanoparticles was found to be around 98% while the blank ink with only surface modified carbon black pigment showed 44% fixation.

CHAPTER I INTRODUCTION

1.1 The Global Market for Textile Printing

Textile printing is the process of application of colour in the form of a design or a pattern onto a textile substrate. The current worldwide production of printed textile fabrics is over 34 billion square metres per year and is dominated by rotary screen printing [1]. It is estimated that around 11-13% of textile products are printed each year worldwide with an annual growth rate of 2% [2]. The worldwide market for digitally printed textiles is expected to reach 6 billion US dollars within the next five years [1]. The geographical distribution of printing production is shown in Figure 1-1.

Figure 1-1 Geographical distribution of textile printing production



The major production markets for textile printing are Asia (47%), the USA (13%) and the European Union (12%) [3]. Table 1-1 shows a breakdown of textile printing in terms of the major fibres and the predominant colourants and printing techniques employed [4-6].

Table 1-1 Principal textile printing technologies

Type of fibre	%	Colorant class	%	Printing technique	%
Cotton	35	Pigment	48	Rotary screen	58
Polyester	25	Reactive dyes	24	Flat bed	28
Viscose	19	Disperse dyes	18	Transfer	5
Polyester-Cotton blends	16	Vat dyes	4	Intaglio/ engraved roller	3
Polyacrylonitrile	4	Acid dyes	3	Hand screen	6
Wool/ Silk	1	Others	3	------	----

The above table shows that 95% of the fabrics printed worldwide comprised cotton, polyester, and cellulosic fibres in both blend and 100% fabrics. Wool, silk, nylon, polyacrylamide made only small contributions to the printed fabric market. 83% of the printing market is dominated by woven fabrics [7], although knit and nonwoven fabrics have shown significant increase in the market share in the past 7 years.

90% of the textile printing is performed using three colorant classes namely pigments (48%), Reactive dyes (24%) and Disperse Dyes (18%). Printing with reactive and disperse dyes involves costly post processing steps such as steaming for their fixation. Subsequent to printing, washing is necessary to remove unfixed dye particles from the fabrics. In 1937, pigment printing was first introduced in the textile market [5]. In pigment printing, a simple heat treatment, known as curing, is the only post processing step required. Hence, pigment printing dominates the market due to the ease of application and elimination of costly post processing for printed fabrics.

The oldest printing technique is "block" printing and is still used in some countries on a limited scale. In this technique, a pattern to be printed is carved on the surface of wooden blocks. These blocks are dipped in a dye solution and pressed onto the fabric to produce an image. Today, conventional printing includes roller printing, table screen, flatbed screen, rotary screen and transfer printing [8]. Except for transfer and roller printing, all of these techniques require a screen for colour application to the fabrics. The drawback of roller printing is that it cannot print fabrics wider than 120 cm. Table screen printing is now limited for preparing printed fabric samples, art works and end products like printed silk ties [7]. Flat bed printing operates at speeds 30-50m/min and the screen can be up to 9 metres wide [9].

Rotary screen printing, with 58% market share, is still the dominant printing method. It was developed by converting flatbed screens into cylindrical screens. The intermittent printing operation due to flatbed screens was changed to continuous one due to rotating cylinder screens. This led to the highest print production speeds of 80-100 m/min that can be achieved for printing textiles. The preparation of screens involves coating of screens with a polymeric material and engraving a design or pattern to be printed. Laser engraving technology is now employed as it allows use of computer aided drawing systems, digital storage of patterns and flexibility to manipulate designs. Many fabrics with up to 150-160 cm or greater width are now printed using rotary screen printing.

Transfer printing is a process in which a design printed previously on a substrate, normally paper, is transferred onto a textile material by applying heat. The transfer of the design from paper to fabric takes place either by sublimation, film-release, semi-wet or melt transfer techniques. This technology has been limited to 100% polyester fabrics. Transfer printing with a global market of about 500 million m^2/ year became popular in 1970s. However, a fashion shift towards cellulosic fibres favoured other conventional printing methods [9]. Currently, transfer printing is integrated with digital printing where a design is printed on transfer paper by an ink jet printer and the ink is transferred on textile substrate by a heat press.

1.2 Changes in the Global Textile Printing Market

Textile printing markets are changing rapidly due to demands imposed by globalisation, mass customisation, DAMA (demand activated manufacturing architecture), quick response, cost effectiveness and ecology. These factors have significantly influenced the global textile printing scenario leading to the evolution of digital printing and are discussed below:

1.2.1 Geographical Changes

Textile printing production has largely shifted to the low-wage countries especially those in Asia. Printers in the European Union and USA have been forced to focus on niche markets. There is a need for the printing companies in these countries to develop competitive strategies in order to survive in the textile printing market [9].

1.2.2 Mass Customisation

The textile printing market is a seasonal, cyclical and highly fashion dependent [3]. Changes in fashion seasons up to 5 or 6 times a year can now be expected [10]. Exclusive and original designs are the ongoing demands of the fashion trade. Expression of individuality, flexibility of choice and wide variety of styles, colours and designs are the increasing demands of today’s textile consumers. This trend is known as mass customisation. The conventional printing techniques are unable to meet these demands due to high volume production requirements, labour costs and longer lead times for new designs [11].

1.2.3 Change in the Business Model

The traditional textile business model involves creating profit through mass production and then discounting the surplus production at each level in the distribution chain. In the end this requires the retailers to stockpile the inventory and sell the products in staged discounts. Though this process has lowered costs, it has also lowered the profit and has limited customer choice [12]. Moreover now, due to increasing stock holding costs, the retailers wish to retain only minimum stocks and re-order more frequently to replenish their depleted stocks [9].

1.2.4 Quick Response and Just in Time Delivery

Before placing the order, customers need to view new print designs and colour combinations on the selected fabric. All the traditional screen and roller based printing techniques require long lead times to create a new design or pattern, prepare the screens and print several square metres of sample fabric. Printing a new design on fabric usually involves creating the design with CAD systems, breaking the design into individual colours, production of screens for each colour, formulating each colour and printing the sample fabric. This sample fabric may also be converted into a sample garment for display. Production of screens itself is a complex, costly and time consuming process. It involves preparation, storage and replacement in case of damage, cleaning and drying of screens after every production run. All this consumes over half the total production time [10]. As noted above, today's textile market demands 'quick response' manufacturing strategies and just in time delivery of mass customised products.

1.2.5 Economic Factors in Textile Printing

The economic models of the conventional printing industry are based upon the volume of fabrics that can be printed each year. Conventional screen printing technologies were developed in an industrial age where the economies demanded a mass production business model. These developments aimed at economic productions of long run lengths of printed fabrics. The conventional printing technologies, with the long lead and production times and high costs of screen development, demanded and still demand large production run lengths to be economical. It is thus obvious that fabric length is the factor with greatest effect on cost of printing. In 1997, the average run lengths were 5300 metres in USA, 3200 metres in Asia and 750 metres in Europe [3]. The average run lengths have decreased almost 50% in last 8 years [13]. Within Europe, the average production run is now only 500 metres [9]. This decrease in run length has made it difficult for conventional printing technologies to meet the demands of today's markets cost effectively.

Productivity is also an important cost factor. Today the average speed of a conventional textile printing machine is 30m/minute. The machine is out of operation for 50% of the production time due to current run lengths, changeover times, setting up and repair work and also for clarification of quality matters. In 1997, a study conducted by Kurt Salmon Associates reported that the textile industry loses 45 billion US Dollars each year due to long manufacturing time cycles leading to high costs of inventory, overruns and stock-outs [13].

One of the biggest cost factors is sampling. Sampling usually takes 4-6 weeks and costs from US$ 5000 to US$ 10,000 for each printed fabric sample. One screen for each colour costs between US$ 250 to US$ 350 [11]. From every five printed samples, only one sampled design goes into actual bulk production. The cost of sampling significantly limits the number of designs introduced into the market. Hence, textile companies need new quick response, mass customised manufacturing technologies for sampling as well as for short to medium production runs.

1.2.6 Ecology

Textile printers are under significant pressure due to social pressure and legislative demands to minimize waste disposal and to reduce environmental discharges. The traditional printing technologies, to varying degrees depending upon the technology being used, results in the need to dispose of excess pastes and colourants and requires high levels of water and energy use.

1.3 Why Digital Ink Jet Printing of Textiles?

Existing printing technologies are not sufficiently cost-effective and competitive to meet the new requirements of global markets. For conventional printing techniques, sample production time scale is 2 to 8 weeks and the bulk production time scale is 3-12 weeks. Moreover, they are labour intensive. For short runs, conventional printing techniques are uneconomical due to high downtime, high engraving and labour costs, lengthy set-up times for production like colour matching, print paste preparation, sampling, design and registration. Particularly design sampling and screen production are very lengthy and costly processes [2].

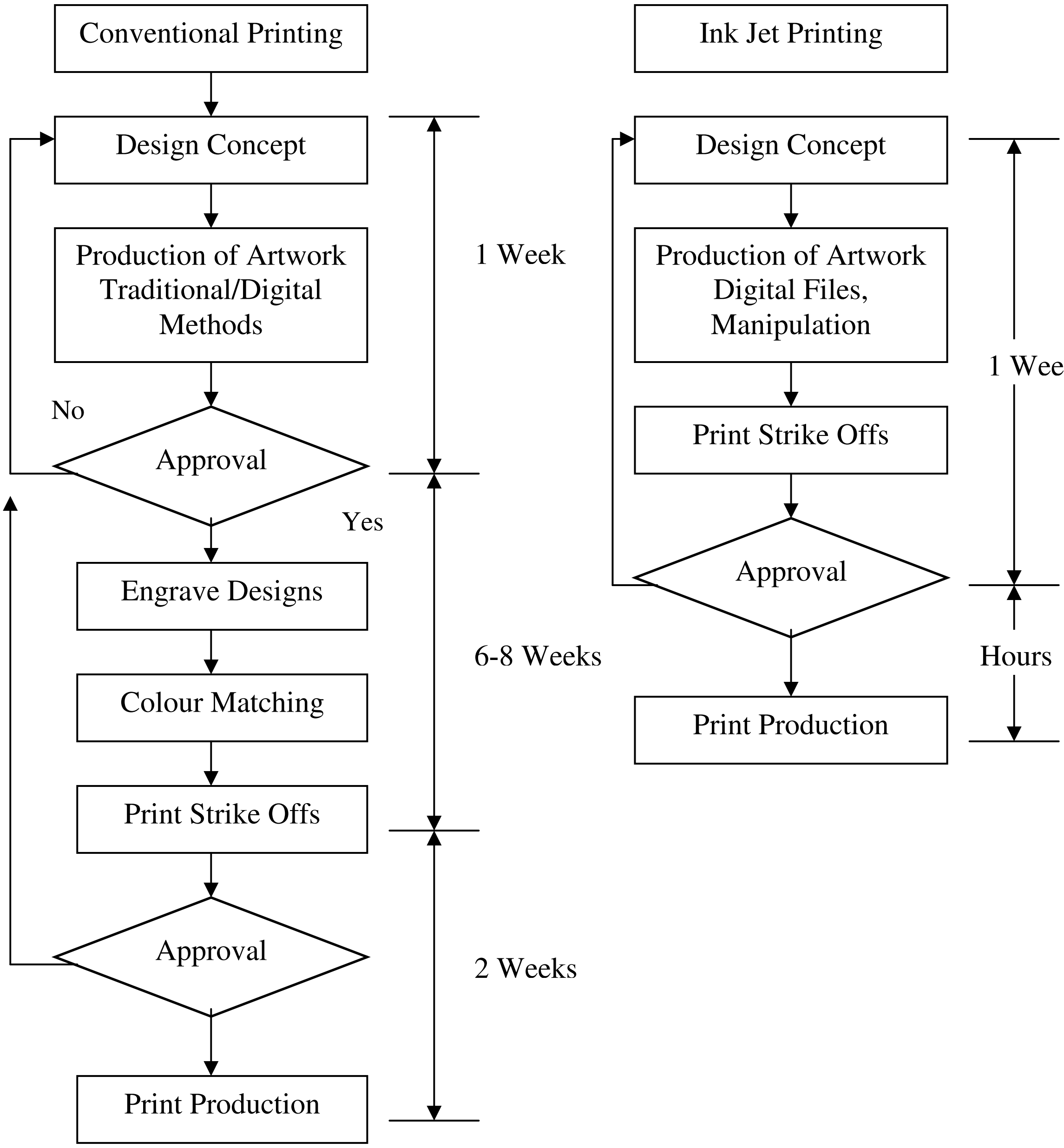
New printing technologies like digital ink jet printing and electrophotography (xerographic printing) have the potential to meet the new market requirements. Furthermore they have the capability to produce printed fabrics with significantly reduced effluent outputs and with lower water and energy usage. These technologies are currently being explored and developed for commercial textile printing. Although ink jet printing has begun to make the leap into the mainstream, xerographic printing is still in its development stage. Xerographic printing on paper is known and research is now focused on utilising this technology for textile printing [14-15].

Digital ink jet printing is a non-contact printing technology where droplets of ink are produced and deposited on various substrates such as paper or textile materials in response to an electronic signal. It has full potential to meet the market demands such as quick response and mass customisation. It also offers unlimited design possibilities with respect to repeat size and colour range. Digital printing of textiles offers number of potential benefits over conventional screen printing methods. It eliminates the set up cost associated with screen preparation and can potentially enable cost effective short run production. It allows visual effects such as tonal gradients and infinite pattern repeat size which cannot be practically achieved by a screen printing technique. It is recognised as the best available technique and is simple and environmentally clean technology. It provides an opportunity to western countries to offset the threat from lower wage-cost countries. Other benefits include flexibility, reproducibility, creativity and competitiveness. Comparison of conventional printing and digital ink jet printing and their production routes are shown in Table 1-2 and illustrated in Figure 1-2 [10].

Table 1-2 Comparison between ink jet printing and rotary screen printing [10]

Features	Rotary Screen	Ink Jet
Inks	Aqueous colour pastes in large batches	Pre-formulated inks in small containers supplied by the machine manufacturer
Print speed	Up to 30-70 metres/minute	Up to 1-4 metres/minute
Pre-treatment	Nil	Required
Resolution	Usually 100 dpi with maximum of 255-300 dpi	Up to 1440 is possible
Screens	Screen cost for engraving, washing and storage	No screens- no washing, no storage
Effluent	More	Much less
Screen contact	There is screen contact with the fabric	No contact with the fabric
Half tones	Difficult	Not a problem
Repeat distance	Restrictions	No restrictions
Registration	Usually designs misregister at set-up	Instant registration
Strike-offs	Strike-offs on proof may differ from bulk	Strike-offs on bulk machine

Figure 1-2: Comparison of production routes of conventional and digital textile printing



1.3.1 The Current Status and Future of Digital Printing of Textiles

Currently, digital printing is a small global market, estimated to print 200-300 million square metres of fabric per year by around 400 firms, each with up to six ink jet printing machines [6]. The current digital printing cost of \$5-10 (ink + substrate) for less than 500 linear metres per design makes it profitable [1]. It is estimated that by the end of this decade or shortly thereafter, 10 % of all the printed textiles will be achieved by digital printing [16]. Still, this technology suffers from two major limitations viz., low printing speeds and limited availability of suitable (in terms of cost and performance) inks.

In 1991, digital printing speeds were of the order of 6 m^2/ hour. The commercial ink jet printers today are mostly operated at 20-30 m^2/ hour. At the International Textile Machinery Association (ITMA) Exhibition 2003, the Italian print machinery manufacturer (Reggiani) demonstrated printing speed of 150 m^2/ hour with its Dream Digital printing machine. This showed that digital printing is potentially the most suitable technology for short to medium production runs. The current focus of the industry is now on economical printing of long production runs using this technology. Hence, most of the research activities on ink jet printing are focused on improving the machine speed and on developing new ink formulations which provide a wide colour range.

1.3.2 Inks and Processes for Digital Printing of Textiles

Ink jet printers used for printing on paper have been successfully adopted for printing onto textiles. This is not the case with the inks. Textile printing is different from paper printing. A conventional textile printer requires 8-12 basic colorants and up to 25 supplementary colorants to meet the wider colour space and fastness requirements. For decades, paper printing has been based on four process colours (C cyan, M magenta, Y yellow and K black). Commercial inks for fabric ink jet printing are now available with up to 8 to 12 colourants to achieve the required colour gamut. Printed textiles require aesthetic properties such as handle and feel. This is not the case with paper printing. In addition, an important difference is the high fastness to wash, rubbing and light required by the textile substrates. The number of inks available commercially, which can be used for digital textile printing is limited. There is a lack of suitable processes for the fixation of pigmented inks onto textile substrates. Hence, improved ink formulations with required rheology and fixation properties and processes for their fixation are needed to be developed for textile applications.

Significant research activities have been seen over past decade in the development of inks for textile ink jet printing. The inks must meet stringent physical and chemical requirements and must therefore be carefully formulated. Depending upon the type of colourants used, inks for digital printing of textiles can be broadly classified as dye based inks and pigment based inks. For textile ink jet printing, the first developments took place with water soluble dyes such as reactive and acid dyes. This was due to the relative ease in their development and availability of dye purification and filtration equipments with colourant manufacturers [17]. However, reactive and acid dyes usually require post printing process steps to fix the dye on to the textile and to remove the unbound colour. Inks based on dispersion technologies such as pigment and disperse dye inks are recent developments [18]. Each 1% adoption from traditional textile printing to digital printing creates a potential for 3 million litres of pigment ink, 1.3 million litres of reactive dye ink, 800,000 litres of disperse dye ink and 500,000 litres of acid dye ink [1]. Such inks and the processes for their fixation onto textiles, the subject of this research, provide significant prospects to the textile printing industry.

1.3.3 Dye Based Inks

Dye based inks using reactive, disperse and acid dyes have been developed and are now available commercially. Despite high colour quality, dye based inks suffer from some serious disadvantages. They are substrate dependent, requiring different sets of inks for different textile fibres. This substrate dependence requires frequent changes in colour-ways and/or fabrics leading to costly machine downtime. Ink jet printing of blends (19% of total fabric market) is not yet possible with dye based inks. Dye based inks require costly pre-treatments and post-treatments such as steaming and washing for their fixation. This may also add to the effluent waste and may require further expensive effluent treatment. Due to specific issues of solubility and stability of dyes in the inks, calibration of colours is difficult.

Another aspect to be considered is the necessity for changing the colour or the ink set on the same printer. Some printers require cleaning of the whole ink transportation system while others need replacing of whole print-head cartridges and its supply lines with the new one. In case of chemical incompatibility, the system must be cleaned with a solvent and then refilled with new inks. Thus, a colour or ink change on printers is a costly and time consuming process [19]. Use of dye based inks may also require the companies to employ more than one textile ink jet printing machine and to maintain a complex inventory of colorants. This becomes expensive for the companies especially for the new business ventures.

1.3.4 Why Develop Pigment Based Inks?

Different textile substrates have different colourant requirements due to the difference in the mode of colour-substrate interaction. This is shown in Table 1-3.

Table 1-3 Selection of colourant for textile substrates and their mode of interaction with fibres [20]

Colourant	Fibre	Colour- Fibre Interaction
Pigment	All fibres	No interaction – complex surface polymer bonding mechanism
Reactive dye	Cotton, Silk and Wool	Covalent fibre bonding
Disperse dye	Polyester	Hydrophobic- Solid State Mechanism
Acid dye	Silk, Wool and Nylon	Electrostatic and Hydrogen bonding with fibre

A single set of inks which can be used to print most of the textile substrates, especially blend fabrics, will have benefits such as lower production costs, better productivity, improved colour prediction and reproducibility and low effluent. One approach that has been undertaken by researchers was to develop a universal set of dye based inks which can enable ink jet printing on chemically diverse textile materials [21]. Another approach has been to develop pigment based inks as pigments are substrate independent and can be applied on most textile materials. Pigments appear to be the most suitable candidates to achieve the above mentioned benefits. With increasing environmental pressure on dye based colourant systems and with improvements in pigment applications, it is expected that there will be a rapid growth in pigment based colourant systems. In 2002, out of 24 billion square metres of fabric printed world wide, 48% was done using pigment as the colour source. In USA, the figure was above 90% [20]. A recent study by BASF predicted that textile printing using pigments will increase from 11 billion square metres in 2002 to 15 billion square metres in 2012 [5]. Thus, developing pigment based inks and fixation processes will have advantages of conventional pigment printing such as ease of application, simple fixation via curing and elimination of costly washing and steaming processes. The efficiency and economy of ink jet printing of textiles can be greatly improved using pigment based inks and processes for their fixation.

1.4 Limitations and Approaches in Development of Pigment Based Inks

Developing pigment based inks still presents a range of limitations with respect to particle size requirement, dispersion stability and the requirement of a binder. The effect of pigment binder on fabric handle is a major issue compared with dye based inks. Moreover, inks based on pearlescent, metallic and white inorganic pigments are still not available [1].

1.4.1 Particle Size

The particle size of the pigments for ink jet printers should be well below one micron in order to prevent the clogging of the fine jet nozzles. Also, in order to be comparable to dyes in colour vividness, the mean particle size should be around 100 nm. Recent developments in nanotechnology have allowed successful preparations of various dispersed pigment nanoparticle systems through a milling process [22-37].

1.4.2 Dispersion Stability

Pigments are insoluble in water and therefore do not dissolve as individual molecules but take the particulate form. Due to this, they form aggregates over a period of time leading to crystal growth which is main cause of clogging of the nozzles. Hence, stabilisation of pigment dispersions is a critical issue. Generally, pigments are dispersed in suitable aqueous or non- aqueous solvents. Conventional dispersion technology involves use of various dispersants and surfactants to stabilize pigments. The emerging dispersion technologies are microencapsulation and surface modification. These are discussed in detail later in the literature review. The current work intends to make use of these technologies along with developments in nanotechnology cited in the literature above.

1.4.3 Textile Binders for Ink Jet Printing

1.4.3.1 Binder Requirements

Pigments have very little affinity for textile fibres. This necessitates the use of binders, normally vinyl or acrylic based polymers, for pigment fixation. It is believed that a film is formed by cross-linking of the polymer on the fibres surface thereby entrapping the pigments and hence fixing them onto the fibre surface to achieve acceptable colour fastness [38-40]. Textile binders are synthetic polymers based on non renewable petrochemical products. Therefore, there is an incentive to develop binder systems based on natural, renewable resources. Also, for ink jet ink formulations, there is a limit to the amount of binder that can be used due to the viscosity profiles of the print head technology. Possible approaches for developing pigment based inks for most popular print head technologies are shown in Table 1-4.

Table 1-4 Matrix of textile pigment ink formulations and print head technologies [5]

Pigment ink	Low viscosity Piezo print-head	High viscosity Piezo print-head	Thermal print-head (Bubble-jet)
With no textile binder	Yes	Yes	Yes
with conventional textile binder	No	Yes	No
with special binder systems	Yes	Yes	No

Low viscosity inks are those inks with viscosity lower than or equal to 5 centipoise while those with viscosity ranging from 10 to 20 cps are high viscosity inks [5]. High viscosity inks have been formulated using conventional binders and are available commercially. However, pigment based low viscosity inks are still not available. Conventional textile binders tend to increase viscosity beyond the performance parameters of most of the ink jet printers.

1.4.3.2 Binder Application

In screen printing, binder is incorporated in the print paste, whereas for ink jet printing, possible approaches are:-

- Application of binder by a post-treatment after ink jet printing
- Incorporation of binder in the ink formulations
- Application of binder by a separate nozzle system [41]

The primary goal of this research was to develop a pigment ink jet printing system which used a natural biopolymer, chitosan, as the binding system. Two approaches to the application of the natural biopolymer were explored. One was to incorporate the biopolymer into pigment based ink jet ink. The second approach was to develop a two step process where the biopolymer was applied separately as a post-treatment after ink jet printing. Cotton was selected as the preferred substrate as this fibre dominates global printing production.

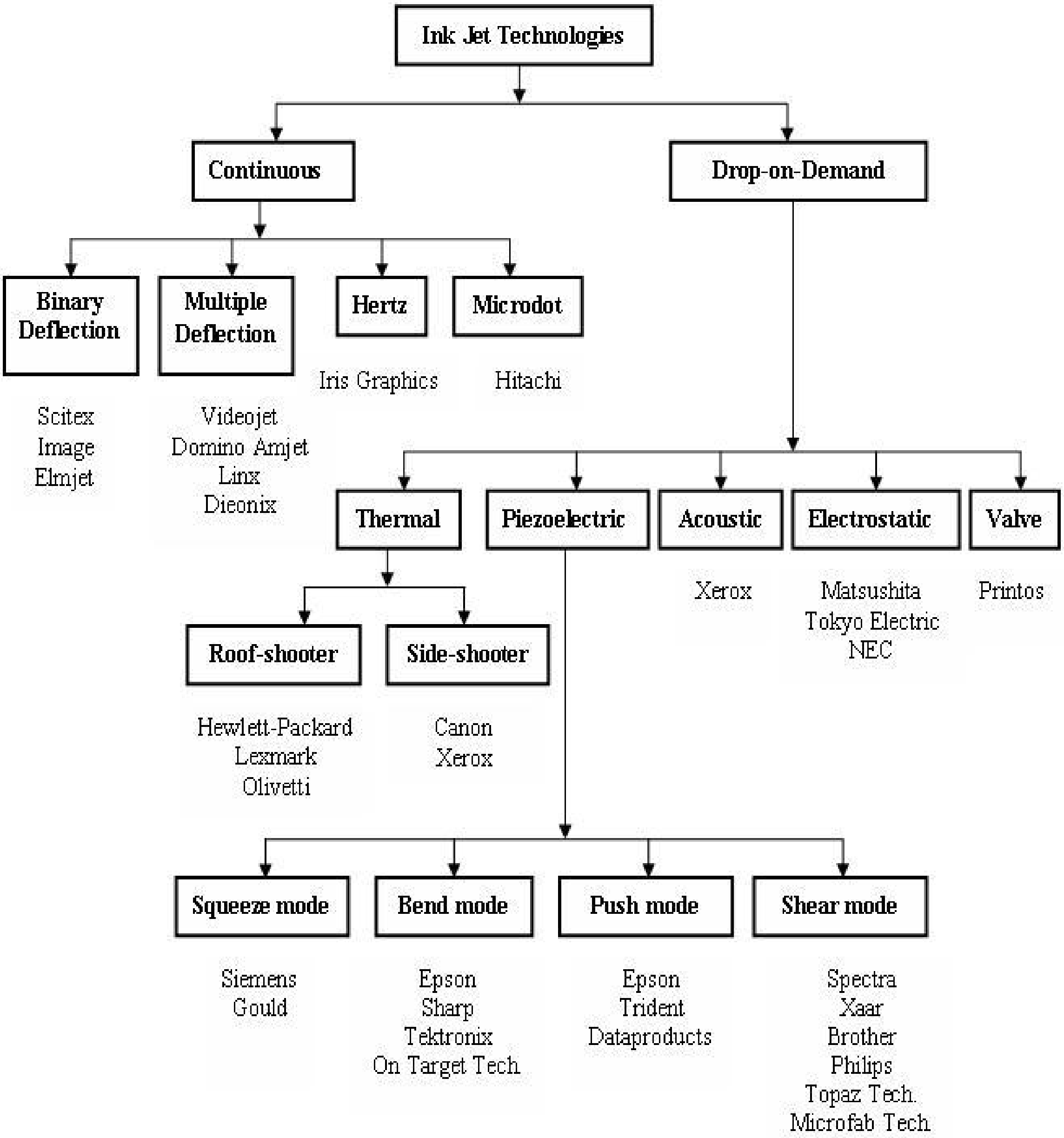
CHAPTER II LITERATURE REVIEW

2.1 Ink Jet Printing Technology

Ink jet printing is a non-contact printing technology in which fine ink droplets are formed and then deposited on a substrate in a specific order to form an image. The simple natural phenomenon of bubble formation when water is heated while making tea led to discovery of this revolutionary technology [42]. Though modern ink jet printers were developed in 1979, the first research on the ink jet was carried out by I'Abbe Nollet in France in 1749 [43]. In 1878, Rayleigh [44] explained the breaking up of liquid stream into droplets and in 1930 this mechanism was used as an ink jet for a recording device. In 1951, Siemens Elema introduced "Oscillomink" the first commercial ink jet recorder invented by Elmquist [45]. In 1960s, Sweet of Stanford University developed continuous ink jet technology and in 1967, Hertz from the Lund Institute in Sweden modified this technology which was licensed to Iris graphics and Stork [46-48]. In 1972, Zoltan, a pioneer of DOD (drop on demand) ink jet printing invented the principle of piezoelectric DOD ink jet printing [49]. Researchers at Canon discovered bubble jet technology in 1979 [50]. At nearly the same time, researchers at Hewlett Packard (HP) invented the same technology and named it as Thermal Ink Jet [51]. Comprehensive reviews of the development of ink-jet printing are available in the literature [52-55].

The various ink jet technologies used in the printers are shown in Figure 2-1. All the ink jet technologies differ in the method of drop generation and in the route to the substrate. They have unique characteristics and place different requirements on the inks that can be used. Basically, ink jet printing can be divided into two main technologies, continuous and drop on demand (DOD). In both the technologies, large numbers of nozzles (typically 10-100 microns in diameter) are used for each colour. Each system use basic process colours (4 or even up to 12) which are mixed on the substrate. The colour depth is controlled by the number of dots applied. Lighter shades are obtained by making the base fabric more visible at any given point in the design. Both technologies have their own advantages and disadvantages for textile printing.

Figure 2-1 Ink jet printing technologies [48]



2.1.1 Continuous Ink Jet (CIJ)

I. Operating Principle

In this technology, a continuous stream of ink droplets is ejected from a nozzle at high pressure. This involves breaking the ink jet into droplets by vibrating the nozzle with a piezoelectric crystal which operates at up to 100,000 cycles per second and then generating a uniform continuous stream of drops. An electric charge is induced selectively on drops. The charged drops when passing through an electric field are deflected onto the substrate to form an image and the uncharged drops are collected in a gutter for recirculation or vice versa [46].

II. Advantages and Disadvantages

The fastest printing speeds to date are achieved with continuous ink jet technology. As inks are not heated, there is no limitation on ink formulations as is the case with thermal ink jet technology. Disadvantages are that these systems are relatively costly. Drop selection and recyling systems are required which makes it more expensive. The printing heads are complex with each nozzle having its own pump.

III. Types of Continuous Ink Jet (CIJ)

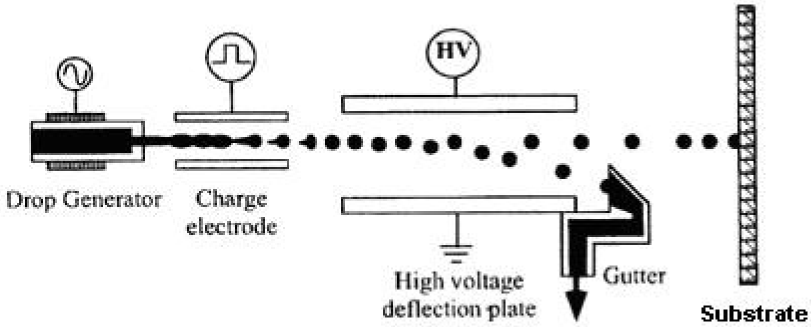
Depending upon the drop deflection method, CIJ can be classified as a binary or multiple deflection system.

A. Binary System

I. Operating Principle

In this system, the ink drops are either charged or uncharged. The uncharged drops form the image on the substrate while the charged drops are deflected into a gutter for recycling (Figure 2-2). With this system, only one dot position per nozzle is possible [56].

Figure 2-2 Principle of binary CIJ [54]



II. Advantages and Disadvantages

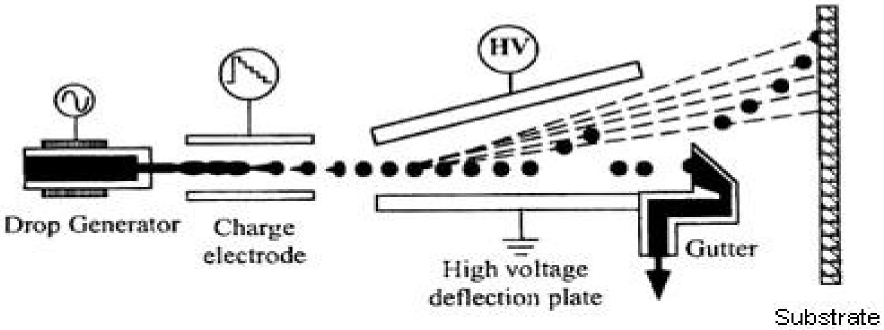
The system is relatively simple compared to other CIJ systems and reliable as clogging is minimized. However, this system is poorly adapted for process colours and offers low printing speeds. The manufacturing and maintenance of this technology is expensive.

B. Multiple Deflection System

I. Operating Principle

In this system, the charged drops are deflected on to the substrate at different levels and uncharged drops are collected into the gutter for recycling (Figure 2-3). This system allows a single nozzle to print at multiple positions (up to 30 different dot positions) on the substrate [42, 48,]. The drop diameter is approximately 1.9 times that of the nozzle for both binary and multiple deflection systems [42].

Figure 2-3 Principle of multiple deflection CIJ [48]



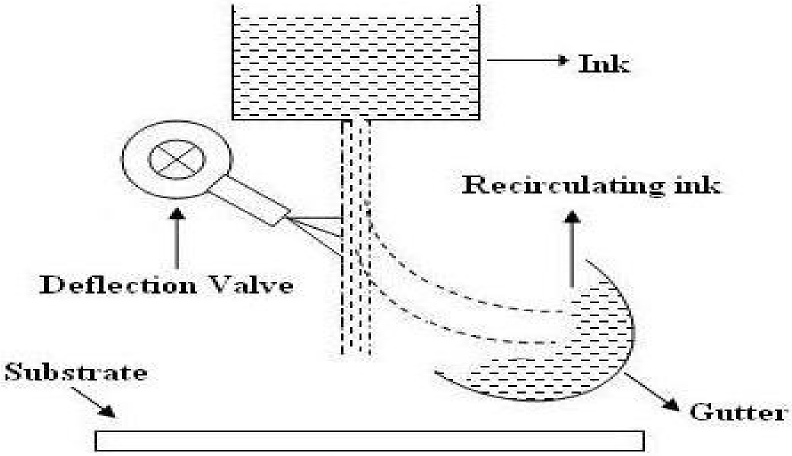
II. Advantages and Disadvantages

This system is suited for high speed printing because more droplets are created per second. Due to the continuous formation of ink droplets, there is less clogging of nozzles. Printing on textiles requires 5-6 times more ink than paper printing. This system should be beneficial for textile printing as larger droplets are created enabling more ink delivery per unit time. The disadvantages are that it is a complex technique, requires ink recycling systems and the large droplet size can reduce clarity in fine, highly detailed designs.

C. Other CIJ Systems

Hertz's and valve type fluid deflection can be classified as two separate CIJ methods. Hertz's technology is a modified binary ink jet system and is more suited to colour printing. In this method, gray-scale printing is obtained by controlling the amount of ink volume in each pixel by varying the number of drops laid down. This allows adjustment of the density in each colour to create the desired gray tone [47, 57]. In the valve type fluid deflection method, ink drops are deflected onto the substrate by opening the air valves (Figure 2-4). This system deposits large drop sizes and the resolution is about 20 drops per inch. Hence, the method is suitable for heavy substrates (e.g. carpets) where resolution is not an issue. The speed of this system can be up to 15 metres per minute and requires inks in the high viscosity range of 100-400 cps [58].

Figure 2-4 Valve type fluid deflection CIJ



2.1.2. Drop on Demand (DOD)

The drop on demand ink jet printer ejects the ink drop only when required for the image being printed on the substrate. This simple technology eliminates the complex drop charging and deflection hardware and the inherent ink recycling systems required for continuous ink jet technology. Today, the majority of activities in ink-jet printing are focused on the drop-on-demand technology. This technology can be divided into thermal, piezoelectric, valve, electrostatic, and acoustic ink-jet methods. Most of the modern ink jet printers use either the thermal or piezoelectric principle.

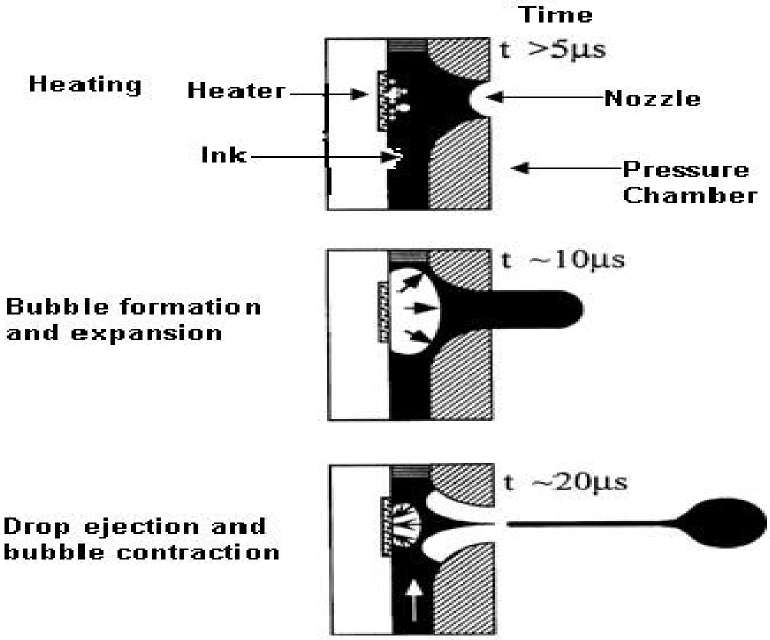
2.1.2.1 Thermal or Bubble Jet Technology

This technology is widely used in commercial Drop on Demand printers. Depending on its configuration, a thermal ink-jet can be a “roof-shooter” (Hewlett-Packard, Lexmark) with the nozzle located on top of the heater, or a “side-shooter” (Canon, Xerox) with the nozzle on a side located nearby the heater.

I. Operating Principle

In this technology, a computer signal raises the heater temperature (to 300-400^{0}C) to create a vapour bubble in a volatile component of the ink. The bubble instantaneously expands forcing an ink drop out of the nozzle on the substrate. This is followed by bubble collapse that creates a vacuum drawing new ink to replace the ejected ink droplet and the process is ready to start again (Figure 2-5). The bubble formation and collapse takes less than 10 microseconds and the ink refill time can be from 80 to 200 microseconds. The cycle time is limited to approximately 10,000 drops per second. The volume of ink per drop is around 150-200 picolitres which means the single thermal ink jet delivers approximately 0.1 ml of ink per minute [48].

Figure 2-5 Principle of thermal ink jet technology [48]



II Advantages and Disadvantages

The main advantage is the low cost of nozzle fabrication and the low cost of print heads. The major disadvantage is the high rate of nozzle and heater failure due to rapid thermal cycling. High temperature can cause nozzle burn out or decomposition of ink components leading to nozzle clogging. This can lead to poor quality production and makes this technology unreliable. As the drop size is large, the resolution of the prints is low. The thermal technology also restricts the inks to be used. Only thermally stable inks can be used. The components required for colour fixation have to be applied separately instead of incorporating them into the ink. The technology also limits the use of pigmented inks containing binder.

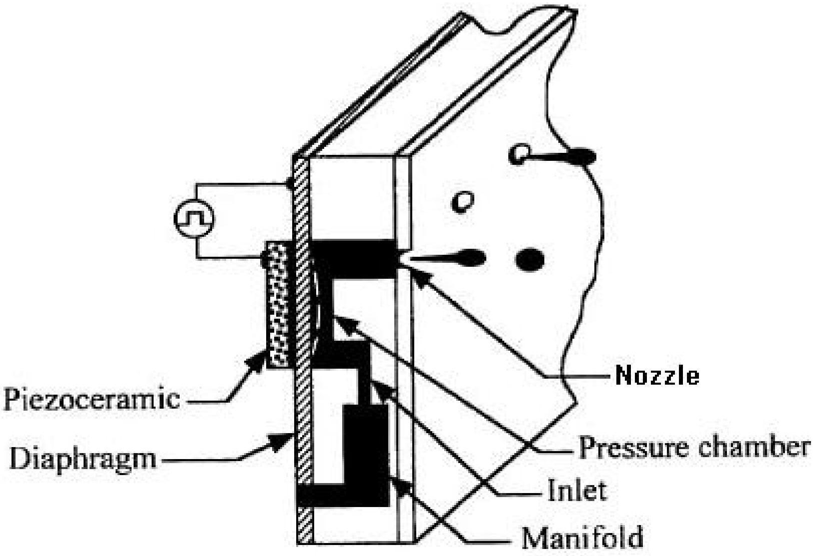
2.1.2.2 Piezoelectric Technology

This is another important ink jet technology and dominates textile ink jet printing.

I. Operating Principle

In this technology, an electrical potential causes deformation of the piezoelectric crystal producing a pressure wave in the ink. This causes the drop of ink to be ejected from the nozzle. On removal of the potential, the piezo crystal returns to its normal shape and the ink chamber is filled from the reservoir by capillary action (Figure 2-6). Depending on the piezoceramic crystal deformation, this technology can be classified as bend, push, shear and squeeze mode [48]. The cycle time is somewhat higher (14,000 cycles per second) than thermal ink jet printers and the drop volumes are small (150 picolitres) [59].

Figure 2-6 Principle of piezoelectric technology [48]



II. Advantages and Disadvantages

Piezoelectric print heads are reliable and have 100 times more print head life than thermal print heads. Due to the small droplet size, high resolution is achieved (1440 dots per inch is commercially available). The technology is capable of using a wide range of ink formulations such as water, solvent, UV based inks and pigment based inks containing binders. It is well suited for high volume printing. The speed is currently slow but is not the limit of this technology.

2.1.2.3 Other Drop on Demand Technologies

Other Drop on Demand technologies includes valve jet, electrostatic jet and acoustic ink jet. Valve jet printers used solenoid valves to control ink flow to the air stream that carries the drops to the substrate. The resolution is limited to 20 drops per inch. The ink drop diameter attainable by best performance solenoid valve printers is 500 micrometer compared to piezo and thermal ink jet printers (50 micrometer), which is unsuitable for apparel textile printing. The printers based on this technology have been used for printing bill boards, banners, draperies and carpets where the larger images are viewed from a distance and the relative lack of print definition is not an issue [60-61]. Color Wings and Zimmer Chromojet, printer manufacturers, used printing heads developed by Printos, manufacturer of print heads. The print heads are based on drop on demand valve technology instead of piezoelectric crystal. The advantages claimed over piezoelectric are the ability to apply high volumes of colour and the suitability for printing on thick and voluminous fabrics. The technology is most suited for low resolution printing at high speed. This technology does not depend upon specially formulated inks in terms of viscosity and particle size and does not need pixels or creation of a “raster”. Hence it is suitable for blotch printing. At ITMA 2003, Printos displayed three printing valves and heads; Printos P700 high flow valve for printing rugs and carpets which is used in Zimmer's chromojet, Printos E4 digital print engine that can produce four colour images at a speed of 50 sq. m/hour allowing control of jet variation for shading, grey scaling and bright spot colour printing, and Printos P16 print module consists of 16 jet drop on demand unit and can produce 4 colour images at 50 sq. m/hour [62].

In electrostatic ink jet technology, an electrically conductive ink is subjected to an electrical potential between the nozzle and the valving electrode. The potential pulls the ink drop from nozzle towards the electrode situated immediately behind the substrate being printed [63]. Both electrostatic and acoustic ink jet technologies are in the development stage with few commercial products available [64-68]. Further developments of these technologies especially electrostatic ink jet may find application in textile printing.

2.2 Textile Applications of Ink Jet Technologies

2.2.1 Early Developments

Carpet printing in 1970's was the first textile application of ink jet based on solenoid DOD valve technology. In 1975, Milliken introduced the Millitron continuous valve type ink jet printers for carpet and upholstery fabrics. These printers used 8 spot colours (largely, acid dyes) which required post steaming and washing. In the late 1970's, chromojet printers were introduced by Zimmer (Austria) followed by Titan MK IV by Godfrey Hirst (Australia), Colorburst from Gaston County and Technorama (Italy) [43,60]. Major developments in ink jet printing of textiles then occurred in the following 3 decades. A continuous ink jet printer with resolution of 100 dots per inch was developed by ICI. CSIRO (Australia) was developing a variable continuous ink jet printer. Burlington Corporation (USA) developed full scale 2 metre wide printer while Seiren (Japan) announced a full width continuous ink jet printer. In 1991, Canon, Kanebo and Toshin jointly announced the development of a textile ink jet printing system and prints from a prototype printer were displayed in Tokyo. Another joint venture, known as Eureka Project, between Stork, Swedish Match and Lund University (Sweden) developed a continuous ink jet printer based on the Hertz Binary method [42].

2.2.2 Continuous Ink Jet Technologies for Textiles

At the 1991 ITMA (International Textile Machinery Association) exhibition in Hanover, the earliest commercial ink jet printer (TruColor) for textiles was launched by Stork. The printer was based on the continuous binary method and used high purity reactive dyes based on Procion P dyes (Zeneca, now Dystar) [42]. Stork and Scitex proofing printers and a prototype continuous textile printing machine were exhibited at ITMA 95. Both the proofing and fabric roll printing machines were based on the binary continuous ink jet principle. The fabric roll printing machine could print 1.56 metre wide fabric at 4.2 linear metres per hour and could generate 25 million drops of dye per second. The machine used 8 colours made of purified reactive dyes.

Continuous ink jet printing using multi deflection technology was developed by Embleme for printing T-shirts. Stork exhibited its Amethyst printer at ITMA 1999 for production printing of textiles. The printer used 8 colours and was based on continuous ink jet multi deflection technology. The maximum production speed was 18 square metre/hour (sq m/hr) and designs with 250 dpi resolution can be printed [69]. Work of Toxot (France) showed that fastest textile printing can be achieved by continuous ink jet technology. However, the cost of CIJ print heads is considerably higher than DOD print heads.

2.2.3 Drop on Demand Technologies for Textiles

Canon's "Wonder Print" textile printing machine is based on thermal DOD technology. It can print 1.65 metre wide cellulosic, polyester and polyamide fabrics at a speed of approximately 1 metre/minute and a resolution of 360 dpi. Reliability problems have been reported for this machine. Various printers based on this technology were exhibited at ITMA 1999. Encad developed a 4-colour thermal DOD(from Lexmark) printer with 300 dpi resolution and speed of 7.5 sq m/hr. Colorspan used HP thermal technology and developed a printer to achieve 600 dpi resolution, 22.3 sq m/hr and a 12-colour capability [69].

Seiren is the largest fabric printing company in Japan and has used textile digital printers based on piezo drop on demand technology for many years. The approach taken by Seiren is to use number of small ink jet printers (0.1-0.5 yards/min) instead of using high output production machines. Their "Viscotecs" printers based on piezo technology have produced 10 million m^2 per year of ink jet printed fabrics with a value of approximately 105 million USD [42].

Most of the printers displayed at ITMA 1999 used Piezo DOD technology. Mimaki has developed a printer with an Epson Seiko Piezo head to achieve 720 dpi resolution and 7-colour capability. Perfecta Print used Xaar piezo technology and developed a printer with 4 colour capability and 200 dpi resolution. This printer can print at a speed of 100 sq m/hr but is limited to the use of solvent based dye systems. Stork has developed and displayed two machines viz., "Amber" and "Zircon", based on piezo technology [69].

2.2.4 ITMA 2003- Recent Developments in Textile Ink Jet Printing

A number of improvements to existing devices as well as new technologies and new approaches for textile ink jet printing were exhibited at the four yearly international textile machinery association (ITMA), 2003 in Birmingham, UK [62].

Reggiani, Scitex Vision Limited and Ciba Specialty Chemicals Inc. collaborated to develop the "DReAM" machine suitable for bulk industrial printing. The machine operates similar to a classical printing machine with the fabric being carried on endless adhesive printing blanket. A drying unit is attached immediately after the printing unit and the endless blanket is fitted with a continuous washing system. This machine requires industrial pre- and post-treatment facilities such as fabric preparation, steaming/fixation, washing and drying. The machine can print at speed of 150 sq m/hr with a printing width of 1.6 metres. Designs are produced using six colours (CMYK, Orange and blue). Scitex Vision's Aprion piezoelectric DOD technology is used in this machine that produces resolution up to 600 dpi. Each colour uses seven such print heads. The machine is controlled by Reggiani-Scitex Vision software and is suitable with most of the other graphic software. Ciba Specialty Chemicals Inc. has developed nine reactive dyes (Cibacron RAC inks) and nine acid dyes (Lanaset RAC inks) for the DReAM machine. It was claimed that the machine can print on all textile substrates and with all dye based inks while pigment and disperse dye based inks are being developed. The cost of the DReAM machine is of the order 750,000 Euros [62].

Robustelli and Seiko Epson Corporation jointly developed a novel production unit known as "Monna Lisa" machine suitable for bulk production as well as sample printing. The production speed can be between 26 to 78 sq m/hr with resolution of 360-720 dpi and printing width of 1.6 metres. The ink is delivered by piezoelectric DOD technology using 24 heads and eight colours. Seiko Epson Corporation developed the printing head and a range of reactive and acid dyes (supplied by Fortex S.R.L.) for this machine. The machine uses the LISACOLOR software and can be used with most graphic software. The machine is claimed to be suitable for all textile substrates but requires industrial pre- and post-treatment facilities. The cost of the machine is around 250,000 Euros [62].

The new "Artistri 2020" printer was the outcome of collaboration between Dupont and Ichinose (Japan). The machine is equipped with an in-line dryer for printed fabrics and a built in washing and drying unit for the adhesive endless printing blanket. Depending upon the print quality, the machine can print at 11 to 66 sq m/hr. Print resolution of 360 dpi to 720 dpi can be achieved and the printing width is up to 1.8 metres. The machine uses piezoelectric DOD technology with 16 print heads on two carriage rails. The print heads can be configured to apply 2x8 colours of one single dye type or 1x8 of two different dye types. Specially formulated aqueous “Artistri” inks-700 series are used for printing. A full range of inks are available for printing with this machine, viz. 13 acid dyes, 10 reactive dyes, 10 disperse dyes and 10 pigment dyes. Dupont “Artistri” software is used to control the machine. It is claimed that the machine can print on all textile substrates including stretch and knitted fabrics. For bulk production, the machine would require industrial pre- and post-treatment facilities. The cost of the machine is 250,000 Euros [62].

Spuhl AG, Switzerland and Leggett & Platt Digital Technologies jointly developed the VIRTU RS printer. The machine can print both in roll to roll for textiles and in flat mode for rigid materials and has an in-built ultra violet curing unit. The machine can print at speed between 35 to 125 sq m/hr with print resolution of up to 600 dpi. Machines with printing widths of 2.5 metres and 3.5 metres are available. Designs are produced using specially developed Virtul inks and HueV pigmented UV-curable inks. Piezoelectric DOD technology is used with 36 head (128 jets/head) bi-directional application. After printing, the substrate is exposed to a proprietary cold curing ultra violet light system for colour fixation. The machine can be used for printing on textiles, plastic, wood, paper, glass, metal, etc. The price of the machine is 510,000 Euros [62].

Mutoh, a well-known printer manufacturer, developed a series of printers among which the Falcon II RJ-80000 printer displayed at ITMA 2003 was most suitable for textile printing. The machine is based on micro piezoelectric DOD technology. The advantage of this new approach was the ability to vary the drop mass output between 5.4 mg to 41.5 mg thus allowing output of high volumes of colour as required for textile applications. The printer can print at 3-43 sq m/hr with print resolution up to 720 dpi. The printing width depends on the model of the printer and can be between 1.3 to 2.2 metres. 8 colours (CMYK + spot or light colours) are used with different ways of applying the colours such as uni-directional, bi-directional, interweaving or multi passing [62].

The Sapphire textile ink jet printer was a joint venture between Stork digital imaging and Lectra Software Company. This machine is based on piezoelectric drop on demand technology with the ability to vary the mass of the ink drop. The ink is delivered by eight heads (180 nozzles per head) for uni or bi-directional application. Depending upon print resolution, number of passes and usage of variable drop size utility, the production speed can be between 3.1 to 17.6 sq m/hr. The printer can print with a resolution of 360 to 720 dpi with a maximum printing width of 1.65 metres. Specially developed Stork reactive and acid dyes are used for printing inks and are installed on machine in 220 ml cartridges. The machine can also be connected with an external ink system to supply ink from eight 2 litre cartridges [62].

Taeil Systems introduced two printing machines viz., the “d. gen” 740 TX/C Cylinder type and the “d. gen” 740 TX/B Belt type. Both machines are based on piezoelectric drop on demand technology. These machines differ in the conveyor mechanism for fabric transportation. The former uses a cylinder and the latter uses an endless belt. The cylinder drive is most suitable for furnishings, garments and strike-offs, while the belt type is more suitable for knitted and stretch fabrics. The speed can be between 3.5 sq m/hr (for 1440 dpi resolution and 16 passes) to 28 sq m/hr (for 450x 360 dpi resolution and 2 passes). Maximum printing width for the cylinder type is 1.9 metres while that for belt type is 1.8 metres. Specially developed “d. Gen” inks based on reactive dyes, disperse dyes and pigments are used. Six colours CMYK plus orange and blue are used to produce the coloured designs [62].

Mimaki displayed its Tx2-1600 and Tx3-1600 printer models. The main difference between these two models is that Tx3-1600 printer is more advanced and an endless conveyor belt was used for fabric transportation making it more suitable for knitted and light weight fabrics. Another interesting feature in the Tx3-1600 machine was that after each pass, the print head printed on a transparent film positioned between the head and the fabric allowing detection of missing dots. Both machines used Epson heads based on Piezoelectric Drop on Demand technology. Production speeds up to 28 sq m/hr can be achieved. Both the machines can print with resolution of 360 x 360 dpi, 360 x 540 dpi and 720 x 720 dpi on printing width of 1.6 metres. Specially developed “d. gen” inks are used for production of print designs. Mimaki also developed the GP-604 ink jet printer for printing garments. The printer was based on piezoelectric drop on demand technology and can apply 4 colours (CMYK) using 4 heads (each head with 360 nozzles) [62].

Gali Italia srl introduced the GaliFlex-Print machine also based on Piezoelectric Drop on Demand technology. The machine can print at speed up to 29 sq m/hr with printing width of up to 1.860 metres and the resolution up to 720x720 dpi. A-Tex Worldwide displayed two machines; A-Tex print and A-Tex print DPM, both based on piezoelectric technology. The former machine can print very fine images with 1440 dpi resolution while the latter is a high speed printer that uses 6 colours and can print at a speed up to 60 sq m/hr.

The QUALIJET La Meccanica and JETPRINT printing machines are based on Piezoelectric Drop on Demand technology. Both machines use a continuous printing blanket for fabric transport and are installed with continuous blanket washing and drying system. Tiara Opal 46 and 63 models are two paper printing machines based on Piezoelectric Drop on Demand technology. They are used for transfer printing and can print at speeds of 6.6 sq m/hr with 360 dpi resolution and 3.3 sq m/hr with 720 dpi resolution [62].

Color Wings developed two ink jet printing machines namely Texjet 156 and Texjet 254. The Texjet 156 printer is based on thermal DOD technology and is suitable for printing flags and signage. The production speed can be between 12 to 30 sq m/hr with maximum printing width of 1.6 metres and the machine can print with up to 300 dpi resolution. Eight colours based on reactive dyes, disperse dyes and pigments can be used. The specialty of this machine was its ability to apply water based sublimation disperse dyes directly (rather than via transfer paper) onto synthetic fabrics. Pre-treatment of fabrics was not required and after printing, fixation was carried out on flat bed heat press without further post-treatment. It was claimed that with these printers, 3 to 4 colours on a white background with 50% coverage would cost around 3.70 Euro/sq metre with a production output of 12 sq m/hr [62].

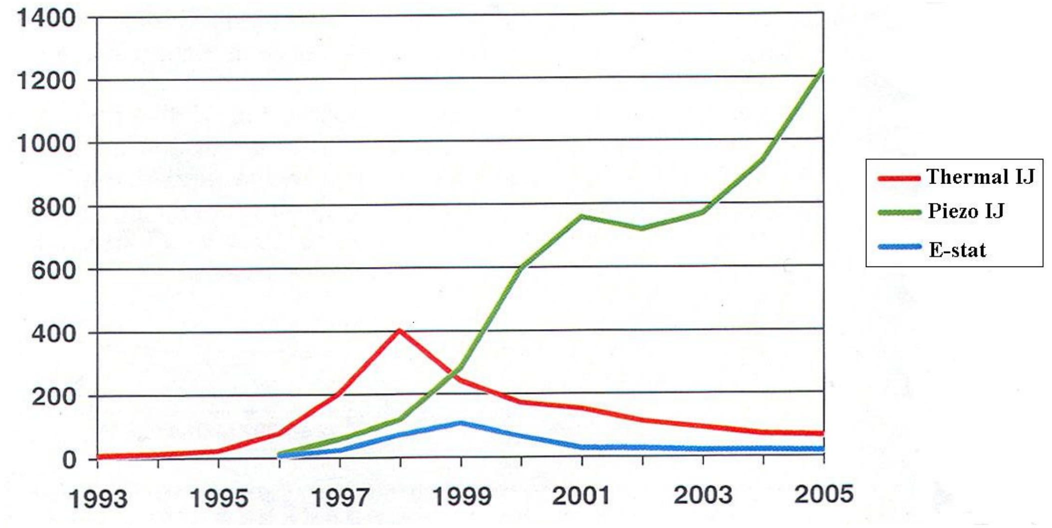
The Texjet 254 In-line system comprised of printing followed by Sublifix 254 thermal fixing unit. The machine is based on valve ink jet printing Drop on Demand (VIP-DOD) technology supplied by Printos. This unique technology has been adapted from previously coarse Drop on Demand valves used for carpet printing to print at finer resolution. With this approach a relatively high production speed can be achieved without the use of special inks. The machine was claimed to print at resolution of 2580 dpi and is suited for pile fabrics. The machine can print at a production speed of 50 sq m/hr with maximum printing width of 2.5 metres. Eight built in print heads are used to deliver eight colours with colour mixing options allowing the user to achieve almost any desired shade. The machine is claimed to be suitable for all textile substrates and uses reactive, acid sublimation disperse dyes and pigments. The fixation unit, placed immediately after the printing stage, can operate at temperatures from 160-210°C for fixation of pigments and sublimation disperse dyes. The cost of this machine was around 375,000 Euros [62].

Another different approach was introduced in the Chromotex printing machine developed by Zimmer. The machine used a specially developed print head containing fine nozzles and vibrating needles that produce fine stream of drops which can be directed on fabric to produce the required design. With this approach, high volumes of ink can be applied to the fabric compared with other technologies and instead of applying inks in pixels or dots per inch, overall blotch colouration can be achieved without the need to form a raster. The machine can print coloured patterns that otherwise are difficult to print at high speeds of up to 140 sq. m. per hour on up to 2.25 m wide fabric. The machine can print with 100-120 dpi resolution on thick (up to 45 mm), pile, brushed, fur or bulky fabrics. The designs are produced using either four CMYK colours or four pre mixed colours but are not sharp compared to other technologies as the nozzles are quite large. Inks produced by Dystar based on cationic, disperse and acid dyes are used for the machine while inks based on reactive dyes and pigments are being developed. The price of this machine was quoted to be around 400,000 Euros [62].

It was evident from ITMA 2003 that ink jet printing has become the industry agreed direction for both sampling and industrial production of printed textiles. It was also acknowledged that the successful application of this technology for textile printing depends on the combination of hardware, software, inks and fabric presentation. Machines with the production speed ranging between 26-150 sq m/hr and with print resolution between 50-720 dpi were displayed at ITMA 2003. The costs of the machines were between 30,000 to 750,000 Euros. In terms of technology, piezoelectric drop on demand again dominated over other technologies while some completely new approaches were introduced [62].

Initially, thermal drop on demand technology developed by Canon and Hewlett Packard and offered to the textile markets by machine manufacturers like Encad and Colorspan took the lead. Printers for textiles based on Electrostatic (E-Stat) technology showed smaller but nearly parallel growth. Though not an ink jet technology, electrostatic printing was the only other digital method available for wide format printing. This was used for printing mainly polyester based textile flags, banners and to a limited extent, apparel and interior textiles. It was piezoelectric Drop on Demand technology which surpassed both these technologies and is still the dominant method for textile applications [16]. Figure 2-7 below shows the worldwide trends in the current positions of ink jet printers by technology for textile applications.

Figure 2-7 Digital textile printer placements by technology [16]



2.3 Classification of Ink Jet Inks

Depending upon the types of base and colourant used, ink systems for textile ink jet printing are classified as shown in Figure 2-8. The most widely used ink jet inks are aqueous or water based. Water is the base of choice because of its viscosity, ionic nature, safety and cost. It is also best vehicle in case of thermal ink jet inks due to the basic vapour bubble formation process. A typical composition for water based inks is shown in Table 2-1.

Figure 2-8 Classification of ink jet inks [48]

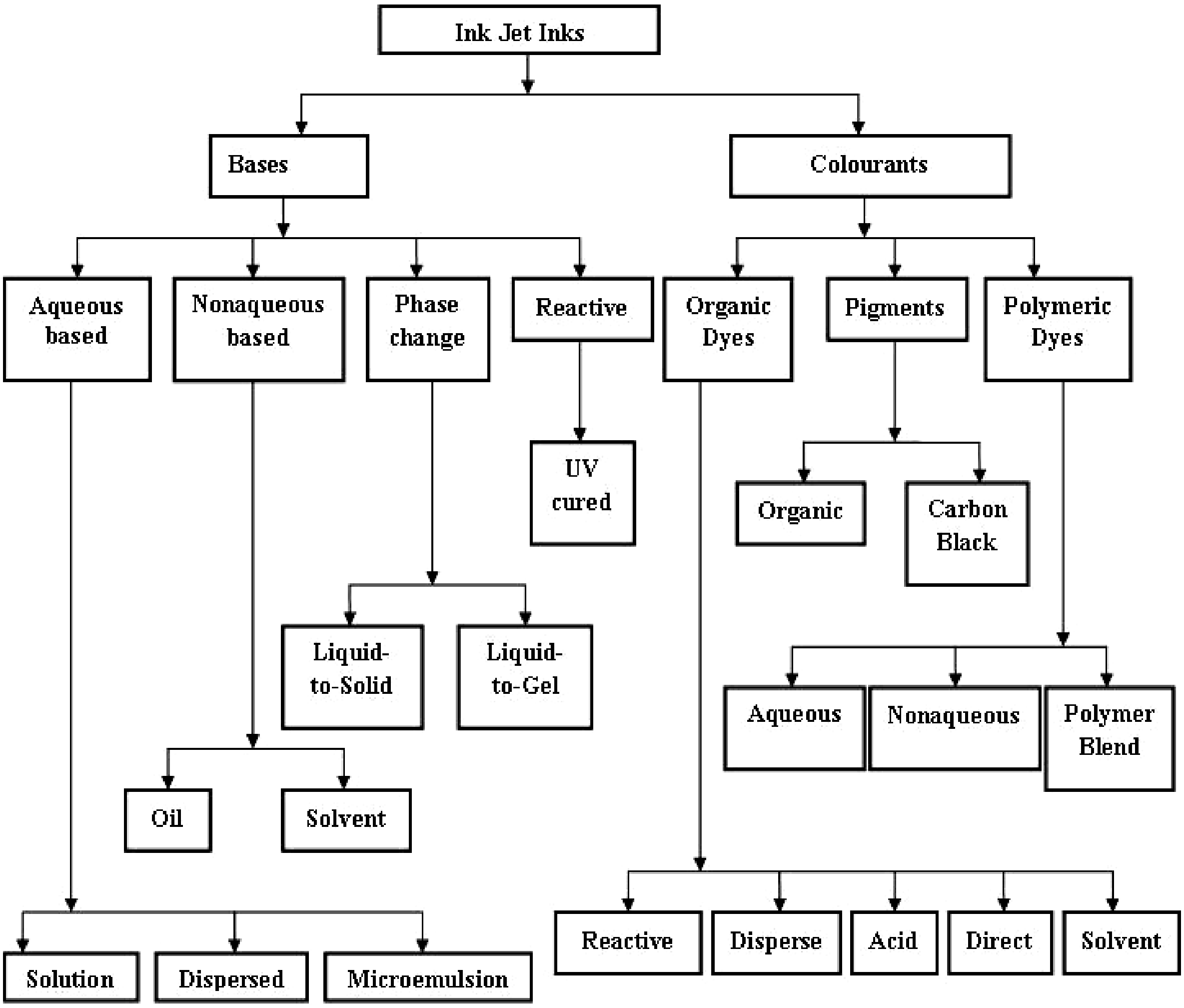


Table 2-1 Typical composition of water-based ink-jet inks [48]

Component	Function	Concentration (%)
Deionised water	Aqueous carrier medium	60-90
Water soluble solvent	Humectant, viscosity controller	5 – 30
Dye or pigment	Provides color	1 – 10
Surfactant	Wetting agent, penetrating agent	0.1 – 10
Biocide	Prevents biological growth	0.05 – 1
Buffer	Controls the pH of ink	0.1 - 0.5
Other additives	Chelating agent, Binder, defoamer, etc.	> 1

2.4 Ink Jet Inks Properties

Ink jet inks must have suitable properties, as listed in Table 2-2, in order to ensure proper functioning of the printer head and to achieve sharp prints on textiles with acceptable fastness properties and resultant fabric hand.

Studies have shown that variations in physical properties such as viscosity and surface tension cause variations in drop sizes and drop velocities at the nozzle exit [71]. This causes inconsistency in drop generation and causes satellite drops and results in poor print quality. Variations in drop size also affect the degree of saturation of the fabric and hence resulting in shade variations. Therefore, the physical properties of the ink jet inks must be carefully controlled within a specific range for stable drop formation, good jettability and good print quality.

Table 2-2 Property requirements of ink jet inks for textile printing [70]

Physical	Printing	Functional
Viscosity	Good optical density	Machine Compatibility
Surface tension	Uniform spreading	Stable drop formation
Particle Size	No feathering	No particle contamination
pH	Fast drying or set time	No nozzle clogging
Specific gravity	Good fading resistance	Low corrosion
Colour	Good wash fastness	Long shelf life
Dye purity	Good rub fastness	No biological growth
Conductivity	Good smear resistance	No chemical hazards
	Acceptable hand	No long term health problems
	Able to be printed on textiles	

Generally, a commercially viable ink jet ink should have a viscosity lower than 20 cps (except for valve jet), although it is quite common for an ink jet ink to have a viscosity up to 30 cps. Ideally, ink jet inks should have a surface tension in the range of 25-60 dynes/cm [72]. For pigment based inks, a particle size of 0.5 microns or below is desirable as this allows for improved dispersion stability, optical density, colour gamut, gloss and light fastness [26].

Table 2-3 lists the requirements of ink jet inks for different printers in terms of physical properties.

Table 2-3 Indicative ink jet ink requirements [71]

Ink Property	CIJ Binary	CIJ Multi-deflection	DOD Piezo	Valve-jet	Office Piezo	Office TIJ
Viscosity (cps)	~ 1.5	1-10	5-30	100	~ 1.5	1-3
Surface Tension (dynes/cm)	> 35	25-40	>32	> 24	>35	>35
Maximum Particle Size (microns)	1	3	1	5	1	0.2
Conductivity (microsiemens)	Yes >500	Yes >1000	No	No	No	No

2.5 Dye Based Ink Formulations

As already discussed in chapter 1, the development of aqueous dye based formulations has created maximum interest especially those formulations based on reactive dyes. Dyes containing the mono-halogen-triazine reactive group (Procion P-Zeneca) were chosen because approximately 85% of conventional textile printing is done with these dyes on cellulosic fabrics. In 1991, STORK introduced the first commercial textile ink system based on Procion P type reactive dyes. These reactive dyes and the pre-treatment process required were developed by ZENECA [73-74]. Ink formulations based on reactive dyes such as Remazol liquid dyes, Cibacron liquid dyes and Levafix liquid dyes and those based on Acid, Direct, Liquid Naphthol and Disperse dyes have also been formulated and are available commercially [20,42,62,73] .

Typical process routes for ink jet printing with reactive, acid and disperse dyes on textile substrates are illustrated in Table 2-4, 2-5 and 2-6 respectively [20].

Table 2-4 Typical process route for IJP of 100% cotton with reactive dyes

Pad with 80-90% WPU	Sodium alginate solution 250 grams, Urea 100 grams, Ludigol® (wetting agent) 25 grams, sodium bicarbonate 25 grams, water to 1000 grams (for viscose rayon, 200 g.L^{-1} of urea is used)
Dry	Under controlled conditions- temperature below 120°C
Ink Jet Print	Using reactive dye ink jet ink formulations
Fixation	Atmospheric Steaming at 102°C for 8 minutes, or Bake Fixation at 130°C for 6-8 minutes. For heat fixation of viscose, use 25 grams/kilo of sodium carbonate.
Wash off	Overflow cold water rinse Rinse in boiling water Soap at boil followed by cold rinse
Dry	

Table 2-5 Typical process route for IJP with acid dye ink jet inks

Pad with 80-90% WPU	Guar Thickener solution 250 grams, Urea 100 grams, Ammominum Tartrate (1:2 solution) 25 grams, water to 1000 grams (for silk fabrics, 250grams/ kilo of sodium alginate is used)
Dry	Under controlled conditions- temperature below 100°C
Ink Jet Print	Using acid dye ink jet ink formulations
Fixation	Atmospheric Steaming at 102°C for 30-45 minutes
Wash off	Specified procedure for the particular acid dye on the nylon, silk or wool fabric
Dry	

Table 2-6 Typical process route for IJP with Disperse dye ink jet inks

Pad	Luprejet HD® 440 grams, (a pretreatment developed to retain print definition), Defoamer 0.20 grams, water to 1000 grams
Dry	Drying not to exceed 100°C
Ink Jet Print	Using disperse dye ink jet ink formulations
Fixation (Specific time/temperatures depends on type of disperse dye used)	High temperature steam (170-180°C) for 6-8 minutes or Thermosol at 190°C for 60 seconds
Wash off	Normal Polyester wash off process including a reduction clear process
Dry	

Since the early 1990’s, Georgia Institute of Technology (USA) has been developing ink formulations for textile ink jet printing. One of the approaches taken was to develop dye based UV curable inks. Such inks consist of a mixture of monomers and oligomers which can be post-polymerised on the fabric. Two problems associated with this approach were high viscosity of ink formulation and unacceptable fabric stiffness. The formulation was improved by addition of reactive diluent such as vinyl acetate. An acceptable formulation comprised aliphatic urethane diacrylate, tetraethylene glycol diacrylate, vinyl acetate, acetone, $LiClO_4$ (Conductivity adjuster), UV initiator and colourants like solvent and/or disperse dyes [75]. Another way to improve fabric hand was to control the polymer structure by thiol-ene polymerisation. A chain transfer agent was used to extend chain segments between branch points [76].

Polymerisable dyes can be defined as dyes having one or more polymerisable double bonds that can participate in polymerisation reaction with themselves by homopolymerisation or by reacting with other compounds in copolymerization. Li [71] reviewed preparations of various polymerisable dyes. In his study, selected reactive and acid dyes were modified to contain polymerisable groups. Inks formulated using these polymerizable dyes and resin components like acrylate and acrylamide showed good colour fastness and acceptable hand on different types of fabrics.

2.6 Pigment Based Ink Formulations

Two major difficulties in formulating the pigment based inks for textile applications are poor dispersion stability and the incorporation of a binder while maintaining the required viscosity profile for a specific print head.

2.6.1 Stabilization of Pigment Particles

Developments in nanotechnology have allowed more convenient methods for preparing nano-scale pigment particles. Significant work has been done with respect to preparation, stabilization and characterization of nano-scale pigment dispersions. Basically, pigment nanoparticles can be prepared in an aqueous media by grinding or milling the bulk pigment powders in the presence of dispersing agents. These dispersing agents can be either anionic, cationic or polymeric surfactants or a combination of them. Generally, it is believed that during milling, the surface of the nanoparticles formed is immediately covered by the surfactant molecules through adsorption and then stabilized as individual particles with the desired size [77-78]. In practice, the pigments, a surfactant and a solvent are mixed together or added in a stepwise manner to a grinding mill containing rigid, inert grinding media, such as ceramics, metals, glasses, plastics or most preferably, polymeric resins in the form of spherical beads. Mechanical energy is supplied to the pigment dispersion by shaking or rotating the system. Collision between the milling beads and the pigment causes the breakdown of pigments into smaller particles. The efficiency of size reduction is proportional to the efficiency of energy conversion [79]. Once the large particles are broken down to smaller particles, surfactant molecules will adsorb onto their surfaces, stabilizing the particles and preventing aggregation. The milling and stabilization process continues until the energy transfer between grinding beads and the pigment particles reaches its limiting size. At this point, the particles have been reduced to a limit size.

2.6.2 Mechanisms of Stabilization

Three mechanisms have been proposed to explain the stabilization of aqueous colloidal dispersions, namely, electrostatic, steric and electrosteric. All three stabilization mechanisms originate from the repulsive (coulombic) interactions produced between the surfactant molecules adsorbed on the particle surfaces that keep the particles from approaching and aggregating together. The nature of colloidal stabilization is to reduce the free energy of the particles by covering the particles with a layer of surfactant molecules. Electrostatic stabilization involves formation of an electron double layer on the surface of the pigment particles thus preventing particle aggregation. Steric (or polymeric) stabilization proposed by Napper and other researchers [77-78], involves adsorption of polymeric molecules on the surface of the pigment particles maintaining their separation. Electrosteric stabilization is the combination of electrostatic and steric stabilization [79].

Based upon the above mechanisms, numerous pigment nanoparticle dispersions have been prepared and used in ink jet ink formulations, mostly, for paper printing. However, for textiles, most of the work done on pigment based ink formulations are of a proprietary nature and very little has been published in the literature.

2.6.3 Review of Previous Work

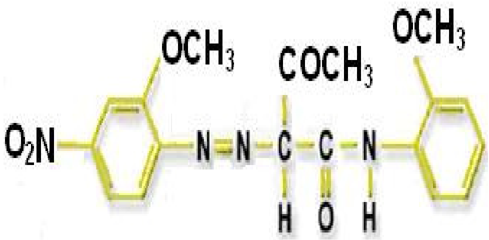
High colour strength requires the pigment based ink jet inks to be transparent and not scatter light. For this to be so the pigment particles must be less than half the shortest wavelength of visible light (less than 200 nm). Also, with the particle size less than 200 nm, the image brilliancy and colour gamut are greatly enhanced. However, reduction in pigment particle size often results in reduction in light fastness and the image durability as these are related to the particle size and the total surface area [80]. Thus, to achieve a good balance between image brilliancy and image durability at small particle sizes, pigment chemistries with inherent high light and weather stability must be selected. Biry and Sieber [81] have reviewed the requirements for pigmented ink jet inks and provided suggestions on optimum pigment selection in terms of chemistry, particle size, surface modification and purity.

Mendel *et al.* [28, 29] discussed the effect of particle size of cyan pigmented inks on dispersion stability, optical density, colour gamut, gloss and light fastness. In this study, two cyan pigmented inks with significantly different particle size distributions viz., one cyan ink with average or mean particle size of 16 nm and the other with mean particle size of 122 nm were prepared. It was found that neither ink showed particle size growth when subjected to freeze/thaw cycling as well as incubation for extended periods at 60°C. The optical density and colour gamut of the 16 nm cyan ink was significantly higher than the 122 nm cyan ink, but the final gloss value was better with the ink with the higher mean particle size. With respect to light fastness, no significant fading was observed with either of the inks after 8 weeks of high intensity exposure to light.

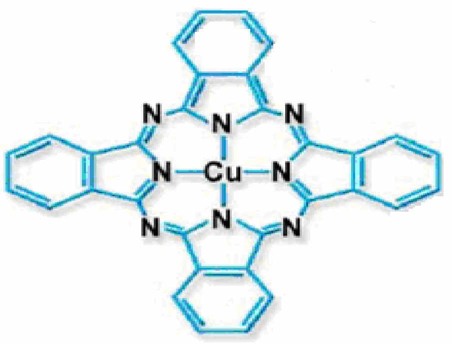
Little has been published on the type of pigments used for formulating pigment based inks for textile ink jet printing. However, there is no reason to believe that the pigments used in ink jet ink formulations for textile printing are different to those used in commercial ink paper printers. Typical pigments commonly used in aqueous and solvent based ink jet inks are shown in Figure 2-9 below.

Figure 2-9 Typical pigments used for ink jet printing

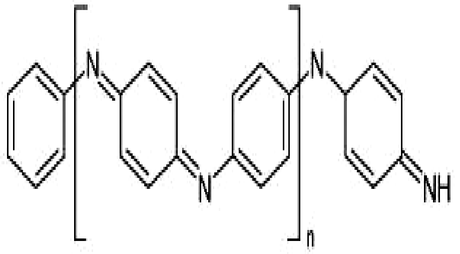
C.I. Pigment Red 122 (dimethyl quinacridone)



C. I. Pigment Yellow 74 (monoazo)



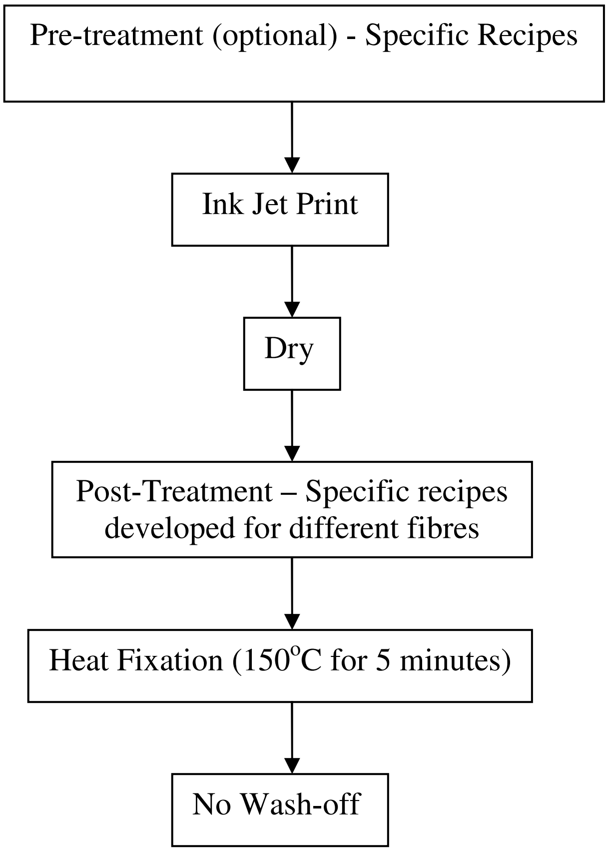
C.I. Pigment Blue 15 (Copper Phthalocyanine)



C.I Pigment Black 1(Aniline Black)

Hees *et al.* [5] outlined developments in pigment ink jet printing of textiles and the approach taken by BASF in developing pigment ink jet systems for textiles. The limitations of developing pigment based ink jet systems for piezo and thermal DOD print heads due to viscosity requirements and binder incorporation were discussed. BASF has developed binder-free pigmented ink jet formulations (Helizarin® P) for low viscosity piezo DOD print heads and the Helizarin® H range for 600 dpi thermal DOD print heads. The Helizarin® P ink range comprises ten colours providing a broad colour gamut. It was claimed that with Helizarin® inks the required colour strength and gamut, runnability and fastness properties could be achieved if a specific post-treatment is followed. The post-treatment is applied by a screen application rather than by padding and is summarized in Figure 2-10.

Figure 2-10 Process route for Helizarin$^{\circledR}$ textile ink system



Ink jet inks have a viscosity in the range of 5 to 30 cps compared to that of 5000 cps of a printing paste. When jetted onto a fabric, the low viscosity ink wicks along the fibres and yarns. This results in a poor image quality. In order to obtain brilliant colours with clear contours and to prevent ink running on and into the fabric, the textile fabric can be pre-treated with a thickener. This can result in an unacceptable handle. Hees *et al.* [83] described a product (Luprejet HD$^{\circledR}$-BASF) which can be used as pre-treatment for textile ink jet printing. The pre-treatment is recommended for direct ink jet printing of polyester with Bafixan$^{\circledR}$ (Disperse) inks and of cotton and cotton blends with Helizarin$^{\circledR}$ (pigment) inks. Almost all textile fibres for ink jet printing with Helizarin$^{\circledR}$ (pigment) inks can be pre-treated with this product. The advantages claimed are clear contours, no ink running, increased colour intensity and brilliance and a soft handle. In the case of fabrics printed with Helizarin$^{\circledR}$ inks, the mode of operation is that the pre-treatment acts like a filter, absorbing the ink medium and keeping the pigments on the fabric surface. This prevents the penetration of pigments into the textile material and thus improves the yield and colour intensity of the prints.

Fan *et al.* [82] studied pre-treatments for woven and knit cotton print fabrics to improve digital print quality using β-cyclodextrin dispersed in a UV-curable acrylic emulsion. The fabrics were pre-treated with two recipes containing different amounts β-cyclodextrin, polyethylene diacrylate (a UV-curable resin) and 2-hydroxy-2-methyl-1-phenyl propanone (a photoinitiator) and cured with different intensities of UV radiation. Different test patterns were then printed using a HP Deskjet 820CSE printer. Print qualities such as line width and colour variation were determined. Print qualities comparable to photographic paper were achieved with a composition of 10% β-cyclodextrin and 90% resin subsequently cured with 118Watt/cm UV intensity at 6 m/min. The fabrics were stiff and harsh and were unsuitable for apparel. It was suggested that fabrics pre-treated according to this study would be suitable for other applications such as luggage, umbrellas, tents, raincoats and convertible tops.

A new approach of using novel multifunctional polymeric dispersing agents (MFDA) instead of textile binders has been reported in the literature [84]. The MFDA consists of hyper-branched polymers derived from polyacrylic esters, polyacrylamides, polyurethanes or polyvinyl alcohol, etc together with dispersing agents for steric or electrostatic stabilisation. It is claimed that the MFDA based pigmented inks meet the requirements of low viscosity piezo print heads. This approach has been shown to achieve the fastness performance and colour yields with textile ink jet printers without the need for a conventional binder.

The transfer of an image, especially using sublimable disperse dyes on polyester, by application of heat and/or pressure is well known. In 1997, Bishop, *et al.* [85] invented a method of transferring ink jet printed images onto 50% polyester/50% cotton fabrics. The patent describes the preparation of an ink jet ink set comprising heat transferable cyan [2-(N-methylcarbamyl)-4-(4-N,N-di-ethylaminophenylimino)-1,4-naphthoquinone], magenta [N-ethyl-N-benzyl-3-acetamido-4-(3-methyl-4-cyanoisothiazol-5-ylazo)-aniline] and yellow [-phenyl-3-N,N-dimethylamino-4-(4-N,N-diethylaminobenzylidene)-pyrazoline-5-one] pigments. The images were ink jet printed onto bond paper and then transferred to the fabric at approximately 176°C for 16 seconds using a commercial heat press. The process was repeated for fabric coated with a low Tg (<50°C Tg) polymer. Polymers or plasticized polymer layers with a Tg less than 50°C (for example polycarbonates, polyvinyl chlorides, polyesters and polyvinyl butyral) can be used for coating. It was claimed that improved wet fastness, higher image density and sharpness could be achieved on the polymer coated fabrics compared to the uncoated fabrics.

Ciba Specialty Chemicals has developed the Irgaphor TBI-HC2 range; an eight colour pigment based inks suitable for ink jet printing on almost all the textile substrates [62].

Toxot has developed water based pigmented ink system that can be applied by a CIJ printer and which requires, after curing, no further treatment. These inks are based on UV or thermally curable binders and can be printed on cotton, polyester and P/C blended fabrics. Washing and rubbing fastness comparable to conventionally printed fabrics can be achieved with these inks [86]. In 2004, Trident, a leading provider of piezoelectric ink jet print-heads and inks introduced a range of water based pigmented inks (FabricFast™). These inks can be used in any colour textile printer with an Epson piezoelectric ink jet print head such as Mimaki, Roland, Mutoh and Stork printers. It was claimed that the inks can be used on cotton, P/C blends, nylon, rayon and silk with simple heat fixation for 3 minutes at 150°C. In 2006, Trident released the 12 colour FabricFast Ultra™ ink range. The new range was claimed to be an improvement over the FabricFast™ inks in terms of brilliancy of colours and wash fastness [87]. The compositions of the inks are as shown in Table 2-7.

Table 2-7 Compositions of Trident inks

Components	**Percent (%)**	
	FabricFast™ inks	**FabricFast Ultra™ inks**
Proprietary Pigments	1-20	20-60
Proprietary organic materials	15-20	
Diethylene glycol	10	< 20
Glycerol	10	--------
Water	Balance	Balance
pH	Approximately 7.0	Approximately 7.0
Viscosity @ 25^{0}C	Approximately 4 cps	Approximately 4 cps

It is important to have an understanding of the stability of a pigmented ink before testing the ink in a particular print-head. This is to ensure robust printer performance. Conventional techniques for determining ink stability involve measurement of physical properties of the ink and the pigment particle size various accelerated ageing trials. A typical example is freeze/thaw cycling which involves trials at room temperature and raised temperatures for up to six weeks.

Sime and Bentley [88] have suggested a new analytical technique known as sedimentometry using a Turbiscan system to characterize the stability of difficult-to-disperse pigment ink jet systems. Sedimentometry is a sensitive technique and does not require dilution contrary to the typical light scattering methods for particle size analysis. The dispersions or inks are used as received and scanned through a vertical column using near infra red light. The scan times of up to 2 hours can be useful in screening the ink formulations while 24 and 48 hours of scanning provide in-depth information about changes in particle size and settling rates. Also, the sample scanned previously can be re-scanned the next day to gain the information about thermal stability normally achieved through accelerated ageing. Sedimentometry also provides an understanding about the differences between physical and chemical stability. In this study, inorganic pigments, metallic pigments and ceramic inorganic pigments with particle size typically over one micron and in some cases over 5 microns were chosen as examples of difficult-to-disperse materials. Results obtained using sedimentometry showed that a range of difficult to disperse materials can be efficiently dispersed into a low viscosity ink jet ink and can be reliably printed in a production environment. Sedimentometry can also provide an understanding of the rate and mode of settling and agglomeration and the effect of ink components on stability. Such information allows for faster and more efficient formulation of inks [88].

Canon developed the BJC-7000 ink-jet printer to capitalize on their new process known as Plain Paper Optimized Printing (P-POP). In this new printer, the black print-head contains black ink and a pre-coat fluid which is applied to the paper surface a few microseconds before dye-based ink drops hit the paper. The pre-coat fluid is clear and is believed to contain a compound that aggregates with the dye, thus fixing the dye instantly on the surface of paper. This unique P-POP process provided excellent water fastness of the printed image and also fixed the ink on the top surface of the paper, making the plain paper perform as if it were a coated media. It is believed that the P-POP process could become one of Canon's significant technological breakthroughs provided it does not affect the overall reliability of the system in any way [89]. This approach is yet to find application into textile printing.

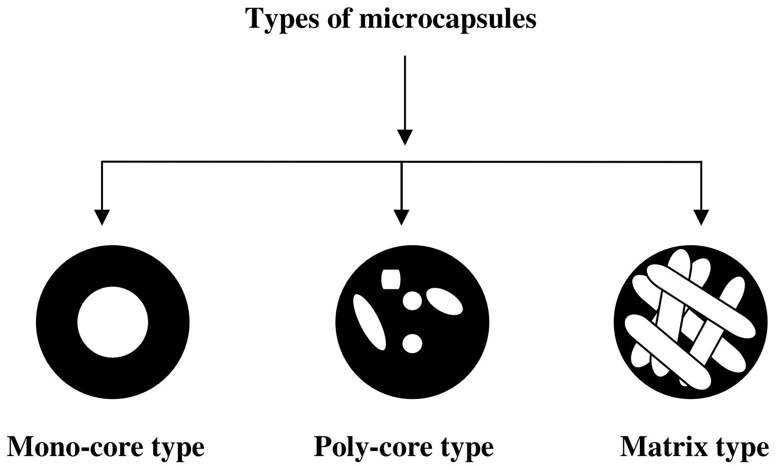
It is commonly accepted that pigmented ink jet inks, due to their aggregating behaviour, clog the nozzles and are detrimental to the performance of the printer. Initially, a properly dispersed ink jet ink does not contain particles larger than the nozzle diameter (usually at least 10 microns) and hence is less likely to clog the nozzles. Also, ink drying in the nozzles also causes jet deviation and leads to clogging of nozzles. This is true also for dye based inks [90]. Conventionally, the pigment dispersion stability was achieved using a dispersing agent. Recently, techniques such as micro-encapsulation and surface modification are being increasingly used and explored to achieve more stable pigment dispersions.

2.6.3.1 Micro-encapsulation

Micro-encapsulation is a process of entrapping small solid particles, liquid droplets or gas bubbles in a covering or coating. The particles formed by micro-encapsulation may have diameters from several nanometres (nanocapsules or nanoparticles) to several hundred micrometres (microcapsules or microparticles). The material used to encapsulate the particles is referred to as the carrier, coating, membrane, shell or wall. The material encapsulated is called the core, nucleus, fill, internal phase or payload. The coating material can be wax, fat, hydrogel, inorganic oxides, lipids and synthetic polymer or natural polymers. Most often, polymers are used as the coating materials. The core material may be pigments, dyes, drugs, flavours, fragrances, live cells, enzymes, adhesives, agrochemicals, metal oxides, fillers and other inorganic particulates. Through selection of appropriate core and coating materials, microcapsules with a variety of functions can be prepared.

Sometimes, the terms microcapsule and microsphere are used synonymously, although the former is used for loaded particles and the latter is usually reserved for empty spherical particles. The most significant feature of microcapsules is their microscopic size with large surface area. The microcapsules can have a variety of structures. The material to be encapsulated may form a core within a coating of polymer but usually is dispersed throughout the polymer particles. The microcapsules may be spherical or irregular in shape. According to morphology, microcapsules can be classified into three basic categories as mono-core, poly-core and matrix type (Figure 2-11).

Figure 2-11 Classification of microcapsules according to morphology



Control of the morphology and internal structures is important and is governed by the protocols and the methods of micro-encapsulation employed [91]. In general, micro-encapsulation may be used to control optical, chemical or physical properties of colloidal particles for numerous applications.

Complex coacervation developed by Green in the 1930s, was the first micro-encapsulation process [92]. In the 1950s, Green and Schleicher developed carbonless copy paper, the first industrial product employing a micro-encapsulation technique. The microcapsules used in this product were prepared by complex coacervation of gum Arabic and gelatin [93]. Since then, various techniques have been developed to carry out micro-encapsulation for various industrial applications. Basically, the micro-encapsulation process can be classified into five categories: polymerisation, emulsification, phase separation, spray drying and grinding.

1. Polymerisation

I) Emulsion Polymerization

Emulsion polymerization involves dispersing a core material in a monomer phase, dispersing the monomer phase containing the core material in an aqueous medium to form a dispersion and then agitating the resultant dispersion during polymerisation to encapsulate the core material. Emulsion polymerisation has been employed to encapsulate pigments [94], magnetic iron oxide [95], hydrophilic and hydrophobic magnetic latex particles [96], etc.

II) Suspension Polymerization

In this process, a core material is dispersed in a monomer phase containing at least one water-insoluble homopolymer or copolymer in monomers. This dispersion is suspended in aqueous medium and then the monomers are polymerised to encapsulate the core material. Magnetic beads of vinyl aromatic polymers [97], toner particles [98] and iron oxide particles [99] have been successfully encapsulated using suspension polymerization.

III) Interfacial Polymerization

In this process, the aqueous or organic phase to be encapsulated contains a core material and the water or solvent soluble monomer. The phase is then emulsified in an organic or water phase which contains a second monomer. The reaction occurs at or near the interface forming a polymeric membrane to encapsulate the core material. The Schotten-Baumann reaction between an acid halide and a compound containing active hydrogen forms the basis of interfacial polycondensation reactions. Interfacial polymerisation has been used for micro-encapsulation of aqueous erythrocyte hemolysate [100] and asparaginase [101] using a nylon 6,10 membrane. Preparation of nylon 6,10 microcapsules via interfacial polymerisation for controlled drug delivery systems has also been reported [102].

2. Phase Separation Process

Complex coacervation is one typical example of phase separation process. This process is used for encapsulation of water immiscible core materials in aqueous media. Any pair of oppositely charged polyelectrolytes capable of forming a liquid complex coacervate can be used for encapsulation by this process. For example, a water immiscible core material is dispersed in a warm gelatin solution and mixed with a gum arabic solution to induce complex coacervation between the gum arabic and gelatin. The complex coacervate adsorbs on the core material forming microcapsules. The coating of complex coacervate is gelled by cooling and is then cross-linked with glutaraldehyde or formaldehyde to form capsules [93].

Polymer-solvent incompatibility is another example of phase separation process. In this process, a core material insoluble in the solvent is dispersed in a solvent and a polymer soluble in the solvent is preferentially adsorbed by the dispersed core material. The polymer encapsulates the dispersed core material thereby forming microcapsules. The wall of microcapsule is solidified by addition of a non-solvent or a cross-linking agent. The encapsulation mechanisms involved in this process are still not well understood.

3. Emulsification

Emulsification is a physical process involving 1) preparation of dispersion of a core material in a polymer solution 2) emulsification of the dispersion in water or other organic solvent to form water in oil or oil in oil dispersion and 3) removal of liquid from the dispersed second phase by heating the system to solidify and to encapsulate the core material. Polymer encapsulated particles for electrophoretic displays [103], pressure fixable toner particles [104] and pigment encapsulated latex aqueous colourant dispersions for writing inks, cosmetic applications and textiles [105] have been successfully prepared by emulsification technique.
However, the difficulty in removing the surfactant from the encapsulated particles may cause changes in the properties of the particles. In case of small particulates such as dye or pigment, diffusion of the core material from the dispersed second phase to the continuous phase during heating causes inefficient encapsulation.

4. Spray Drying

In 1927, spray drying was commercially employed to encapsulate flavours with gum arabic. Since then it has become a low cost process capable of producing a range of microcapsules with good yields. In this approach, a coating material is dissolved in a carrier solvent (organic solvents or water). Then the material to be encapsulated is dispersed in the carrier solution and emulsified using a surfactant to form oil-in-water emulsion. This emulsion is sprayed into a hot drying chamber in the form of small droplets with high surface area. In the drying chamber, the water is rapidly evaporated from the droplets to form a dry powder [106].

5. Grinding

In grinding, a mixture of a core material and a coating material is plasticized either by adding a solvent to form a solution or by heating the mixture to form a melt. After this, the solvent is removed from the solution or the melt is cooled to form a solid mass. The solid mass is then broken into small particles by mechanical shearing in which the core material is encapsulated. This is an easy process of encapsulation and has been used for manufacturing toners for many years [107-109].

In addition to the techniques described above, micro-encapsulation can be carried out by various other processes such as electrostatic encapsulation [110], desolvation [111], vapour deposition [112] centrifugal encapsulation [113], biliquid column process [114], fluidized-bed coating [115] or gelation encapsulation [116].

Micro-encapsulation techniques have been employed for various commercial applications but few studies have been published in the literature especially those related to application of micro-encapsulation for preparing pigment based inks. Compared with inks containing water-soluble dyes, aqueous pigment based inks are characterized by excellent wash fastness and light fastness. Generally, such aqueous pigment inks are prepared by dispersing a pigment in an aqueous medium (normally water) with the aid of a dispersant, such as a surface active agent or a polymeric dispersant. Such pigment dispersions are not always sufficient in dispersibility and dispersion stability. Micro-encapsulation has been mainly employed to improve the dispersion stability of pigment based ink jet inks and, as the literature suggests, the preferred method for micro-encapsulation of pigments is emulsion polymerisation.

2.6.3.1.1 Emulsion Polymerisation

Emulsion polymerisation occurs between two immiscible liquid phases, an aqueous continuous phase and non-aqueous discontinuous phase of monomer and polymer resulting in a final product referred to as latex or resin emulsion. This emulsion is often directly used without prior separation of the polymer from the water and the other components.

Cheng *et al.* [117] described the preparation of four different polymer latexes by emulsion polymerisation. The properties of the latexes prepared in that study are shown in Table 2-8.

Table 2-8 Physical properties of latexes

Types of latex	Average particle size (nm)	Weight average molecular weight	Glass transition temperature (Tg) (°C)
Ionic sulphonate polymer latex	171	51,500	39
Epoxy polymer latex	145	36,000	38
High Tg polymer latex	250	449,000	85
polymer latex with a non-ionic surfactant with HLB value of 18.7	385	660,000	55

Pigmented ink jet inks using the above latexes were prepared for thermal ink jet print head technology. Each ink comprised a carbon black pigment dispersion (Cabojet 300), Sulfolane, 2- pyrrolidinone, a non-ionic surfactant, water and 1% wt of one of the above lattices. An ink with the same composition but without the latex was prepared as a reference. The polymer latex was found to improve the stability of the inks and acted as a binder with carbon black colourant or other colour pigments. Addition of latex also improved the optical density, smear resistance, film hardness and humidity resistance. However, the inks formulated in this study were printed on paper. Nevertheless, this study presented the concept of developing ink jet inks containing latex for thermal ink jet technology. Based on the same concept, pigmented ink jet inks can be formulated for printing of textile substrates.

Tsutsumi *et al.* [118] developed a new emulsion colourant system to overcome limitations of pigmented inks such as poor rub resistance, poor jetting reliability and lack of clear colour. The colourant system is a water based polymer emulsion containing a water insoluble dye. The inks based on this emulsion colourant showed clear colour, rub resistance similar to water soluble dye based inks and wash fastness, sharpness like pigmented inks.

The emulsion colourant based inks also showed high optical density compared to dye based and pigment based inks but caused clogging of the print head nozzle thereby reducing jetting reliability. To solve this problem, Sawada *et al.* [119] evaluated various humectants such as alcohols, ethers, amino acids and their derivatives, etc. It was found that addition of water soluble amino acids and their derivatives especially glycine derivatives significantly improved the jetting reliability. Within glycine derivatives, N-methyl glycine, N, N-dimethyl glycine and N, N, N-trimethyl glycine were found to be very effective in improving jetting reliability of emulsion colourant based ink as well as pigmented ink. Moreover, addition of glycine derivatives increased the optical density and rub resistance of inks.

Tanaka *et al.* [120] prepared and investigated the characteristics of aqueous dispersions of micro-encapsulated pigments and their application to ink jet inks. The encapsulation polymers were synthesized using an automated polymerisation apparatus. The pigment dispersions were prepared by mixing pigment, encapsulation polymer (as solution of 2-butanone), base (usually sodium hydroxide) and deionized water. This pre-mix was dispersed using a paint shaker or bead mill. The 2-butanone was distilled off and dilute hydrochloric acid was added to the dispersion to deposit the polymer on the pigment surface. The mixture was then filtered, washed several times with deionized water and re-pulped by adding base. The coarse particles were removed from the dispersion by centrifuge. Inks were formulated with dispersions containing micro-encapsulated pigments for both piezoelectric type printers and thermal type printers. Inks were also formulated with dispersions containing polymeric dispersants to compare dispersibility and dispersion stability. It was found that the dispersions containing micro-encapsulated pigments were excellent in dispersibility with a mean diameter of around 100 nm. The dispersions were stable over one year under ambient conditions and were superior to dispersions containing polymeric dispersants. The dispersions showed excellent stability to water- soluble solvents such as ethanol, 2-propanol, ethylene glycol, ethoxyethanol, dimethyl formamide and 1-methylpyrrolidine-2-one. The inks formulated from dispersions containing micro-encapsulated pigments showed excellent print qualities, good gamut and colour reproduction, excellent water fastness, abrasion resistance and marking-pen-ink-resistance. This study showed that the dispersions containing micro-encapsulated pigments have great potential of application in the formulation of ink jet inks [120].

Tsuru *et al.* [121] analysed the colour reproducibility of micro-encapsulated pigment dispersions. Three different pigment dispersions, one consisting pigment encapsulated in water insoluble polymer, the second consisting of pigment encapsulated in water soluble polymer and the third consisting of pigment dispersed in a dispersion were prepared for this study. The dispersion containing pigment encapsulated in water insoluble polymer was prepared as follows: the polymer of styrene (ST), lauryl methacrylate (LMA) and methacrylic acid (MAA) was prepared by solution polymerisation in 2-butanone (ST/LMA/MAA with ratio of 40/40/20 wt%, MW=30,000) and was neutralized using sodium hydroxide. The neutralized polymer (30 grams) and 70 grams of pigment (C. I. Pigment Blue 15:3 or C. I. Pigment Red 122) were mixed with 500 grams of water. This pre-mix was dispersed using a bead mill. The resulting dispersion was then concentrated to 20%. The other two dispersions were prepared in a similar way. The encapsulated colourants with different polymer to pigment ratios were prepared. Ink jet inks were formulated consisting of 5% of encapsulated pigment, 10% of 2-pyrrolidinone, 10% of glycerin and the rest of water. The pigments encapsulated with water insoluble polymer were found to have a smaller particle diameter, lower viscosity and better ink stability than the other colourants prepared in this study. It was also found that the colour reproducibility and colour quality of the printing was improved by using encapsulated pigment ink jet inks and by reducing the ratio of pigment in the colourant.

Chovancova *et al.* [122] investigated different Epson ink jet printers and their corresponding ink sets in terms of printability, ink/printer/substrate (paper) interactions, particle size analysis, colour gamut comparisons, colour profile accuracy of printers, light fading tests and operating costs of ink/media sets. Table 2-9 shows the types of printers and ink sets used in the study.

Table 2-9 Types of ink jet printers and their corresponding ink sets

Ink Jet Printer	Corresponding Ink Set
Epson Stylus® Pro 5000	Dye based
Epson Stylus® Pro 5500	Pigment based Archival
Epson Stylus® Pro 2200	Pigment based 7-colour UltraChrome™

Both the Archival and UltraChrome™ ink systems, recently developed by Epson, contain pigment particles each encapsulated in a resin. It was claimed that this new technology offered various advantages over conventional pigment and dye based inks. The advantages include more uniform particle shape and size, large colour gamut, enhanced gloss and optical density, enhanced light fastness and support for a wider range of substrates. The results of this study showed that the new technology of manufacturing pigment based inks that involve encapsulation of pigment particles in specific resins enables the colour gamut to approach that of dye based inks. The particle size of the pigment based inks were small enough to provide the colour range comparable to dye based inks and reached the colour gamut of digital silver halide photo on conventional photo paper. The price/performance of the Epson Stylus® Pro 2200 printer and UltraChrome™ ink set was found to be very impressive. The pigment based inks showed better light fastness compared to dye based inks. Substrates treated with optical brighteners showed a shift towards yellow as the optical brighteners started losing their effect irrespective of type of inks used for printing [122].

Nakamura *et al.* [123] disclosed a process of making microencapsulated pigments in which the pigment particles, having hydrophilic group on their surface, were coated with a polymer by emulsion polymerization. An aqueous dispersion of these microencapsulated pigments was prepared and then used to prepare ink jet inks. It was claimed that the ink jet inks showed excellent dispersion stability and ejection stability and were capable of forming images with excellent fastness, abrasion resistance, colour development, and high density with little feathering.

Resin-pigment systems are a two phase system and offer a special challenge for ink jet printing due to the fact that both pigments and resins are insoluble in water or organic solvents. Despite the problems such as agglomeration, high viscosity, particle size instability and phase separation, resin-pigment systems can be formulated for different ink jet engines which can give acceptable performance on printed fabrics. It is possible to produce small particle polymer lattices containing up to 50% solids suspended in water via emulsion polymerization. Polymer structures in these lattices can be varied to achieve desired properties of cured resin on the substrate. These two phase ink systems can be tailored to contain particle sizes in the nanometre range with low viscosities at 50% solids [124].

Tian [125] showed that such pigment-resin systems containing small particle polymer lattices can be deposited on textiles by ink jet printing and can be thermally cured on the fabric. In another study, lattices containing modified acrylic, acrylonitrile-butadiene copolymer, nitrile-butadiene copolymer and modified butadiene copolymer were obtained, screened depending upon the cured film properties and printed on cotton, P/C blend and silk fabrics using the TOXOT CIJ printer. Evaluation of printed samples showed that pigment based polymer lattices can be a promising approach for textile ink jet printing [73].

Tincher and Yang [124] carried out a study in which a range of silk fabrics were printed with the TOXOT Jamine™ 1000 S4 continuous ink jet printer using pigmented ink with sub-micron particle size lattices of polymer resins. C.I. Pigment Red 184 (Hostafine Rubine F6B) was used for this study. Two polymer compositions were selected and the polymer lattices were prepared by a proprietary process to give stable, nanometre range particles of acrylate copolymers with different ratios of butyl acrylate to methylmethacrylate to control glass transition temperature (Tg). The two resins prepared had Tg's of -10 and -21°C. The lattices showed viscosities in the range of 12-13 cps at approximately 30% solids. Results showed that inks with high pigment loading of 5-9% and resin content of 15-20% could be successfully jetted. Increase in solids level increased the viscosity, limiting good drop formation. Addition of urea (approximately 2.5%) to the ink formulation reduced the viscosity, improved jetting characteristics of ink and reduced the clogging of the recycle line by minimizing the rate of water evaporation. Printed silk samples were thermally cured and tested for bending rigidity and crock fastness properties. Inks with up to 20% solids and with resin to pigment ratios of 2.5 or above gave acceptable hand and crock fastness. To achieve good balance between hand and crock fastness for silk fabric printing, resins with Tg's near -15°C were recommended.

As can be seen from the above discussion that emulsion polymerization has been extensively utilized for the formulation of ink jet inks compared to other micro-encapsulation techniques. The present study intends to utilize the complex coacervation micro-encapsulation technique for the formulation of ink jet inks.

2.6.3.2 Surface Modification

Most of the commercially available pigment based inks rely on conventional dispersant technology in which the pigments are milled or subjected to other forms of shear in presence of suitable dispersants to yield pigment dispersions of desired particle size distribution and colloidal stability. The inherent limitations of using polymer or surfactant as dispersants are poor stability, low surface tension and high viscosity, possible interference of dispersants with other ink components, contamination and particle size restriction as dispersions of small pigment particles require large amounts of surfactants for stabilization.

The modification of pigments by treating their surface tends to improve various ink properties such as pigment dispersion, colour strength, hue, gloss, transparency, rheology and deflocculation and is well known in all the major application areas for organic pigments [87]. Surface treatment of pigment with its own derivatives has been very successful in ink applications.

Daplyn and Lin [72] reported preparation of three different pigment dispersions and formulations of ink jet inks from the prepared dispersions. The ink formulations comprised 2% pigment dispersion, 15% thermal curing binder, 5% ethylene glycol, 5% isopropyl alcohol and 73% water. The ink formulations were evaluated for their suitability for jet printing on textile fabrics. Results of this study showed that ink formulation containing a surface modified pigment (Cabot Magenta IJX 266) was most suitable for ink jet printing. This was attributed to the pigments smaller particle size, lower viscosity and stability to the freeze-thaw cycles and pH changes. It was suggested that the other two pigments viz., Clariant Toner Magenta E02 and the Microlith Magenta B-WA may cause blocking of print head nozzles due to relatively lower stabilities. Prints on cotton fabrics were found to have better image qualities compared to those on polyester fabrics, due to high absorbency of cotton.

Grant [126] described the designing of water based pigmented jet inks for Drop on Demand (DOD) and Continuous ink jet (CIJ) print heads. Series of inks were formulated for textile applications (Table 2-10). Generally, pigment dispersions consist of a traditional dispersant for stabilization. In this study, the pigment dispersions used for ink formulations consisted of modified pigment with a stabilizing group directly attached to it without the need of a dispersant. Commercial acrylic, styrene-acrylic and acrylic copolymer emulsions with suitable particle size were selected to cover a range of molecular weights and glass transition temperatures. Four thickeners viz. PG (propylene glycol), PVP (polyvinyl pyrrolidone), PEG (polyethylene glycol) and PU (polyurethane) were used to meet the viscosity requirements of the DOD print heads. The ink formulations were applied to cotton and cured at 150°C for 3-4 minutes.

Table 2-10 CIJ and DOD ink jet ink formulations

Ink Component	**CIJ CMYK**	**DOD CMYK**
Polymer emulsion	8-14 %	8-14%
Water	Balance	Balance
Surfactant	0.05-1%	0.05-1%
Humectant	5-10%	5-10%
Conditioning agent	0.25-0.5%	0.0%
Thickener	0.0%	0.5- 5%
Cross-linker	0.5-1%	0.5-1%
Pigment dispersion	2-5%	2-5%
Particle size	<1 micron	<1 micron
Viscosity	3-5 cps @ 25°C	10-14 cps @ 25°C
Surface tension	30-35 dyne/cm	30-35 dyne/cm

Results showed that inks containing an acrylic copolymer emulsion combined with a cross linker distinctly improved wash fastness, dry and wet crock fastness and hand compared to other emulsions. Propylene glycol showed superior performance in terms of wash fastness, dry and wet rub fastness and hand. Incorporation of emulsion polymers and thickeners with high Tg's (glass transition temperatures) gave a stiff hand. The black DOD ink formulation was found to be stable over a period of three months at 25°C and 40°C.

Cabot Corporation has developed a proprietary technology to modify pigment surfaces by attaching various ionic functional groups such as sulphonate ($-SO_3^-$), carboxylate ($-COO^-$) or ($-R_4N^+$) to impart electrostatic stabilization and desired physicochemical properties to aqueous pigment dispersions. This technology eliminated the need for conventional dispersants. The technology was first utilized for surface modification of carbon black pigments which resulted in commercial products such as CAB-O-JET® 200 and CAB-O-JET® 300 black pigment dispersions [127-128].

Yu and Gottberg [129] described a novel colour pigment dispersion set for aqueous ink jet ink applications that comprised of surface modified copper phthalocyanine blue pigment (IJX™ 253, PB 15:4), Quinacridone red pigment (IJX™ 266, PR 122) and monoazo yellow pigment (IJX™ 273, PY 74). These dispersions were prepared using Cabot surface modification technology [130-131]. It was demonstrated that surface modification of colour pigments with ionic groups provides stable dispersions with favourable physical characteristics for formulation of aqueous ink jet inks.

Titration has been used as a quantitative tool to evaluate pigment particles bearing weak acid or base functional groups. The level of surface modification can be determined by measuring the value of total titratable groups in mmol/grams pigment. The dissociation constants (pK_a or pK_b) derived mathematically from the titration curve provide understanding about the colloidal stability as a function of pH. Poor determination of functional groups reported in previous studies about titration of pigment particles made the data interpretation difficult. Cabot's surface modification technology of introducing specific functional groups to the pigment particles has allowed for systematic investigation of stability of pigment dispersions. An understanding of the nature and concentration of surface charge groups and the charge density as a function of pH is helpful in formulation, troubleshooting and failure mode analysis of pigmented inks. Yu and Gottberg [132] investigated surface modified carbon black pigments by potentiometric titration. The effect of ionic strength, ink jet ink components and nature of surface functional groups were studied and related to the pigment stability. The discrepancy between experimental pK and functional group pK was explained using a diffuse double layer (DDL) correction model. Potentiometric titration was found to be effective in order to understand the stability of pigment dispersions.

Kiatkamjornwong *et al.* [133] investigated print qualities of cotton fabric printed by ink jet printing and screen printing. The cotton fabric to be printed by ink jet printing was pre-treated with 3%wt polyethylene oxide (2 to 3 million Dalton molecular weight) solution. Pigmented ink jet inks prepared in this study were composed of 4%wt of each pigment dispersion (cyan, magenta, yellow and black), 10%wt diethylene glycol, 15%wt glycerin, 16.49%wt acrylic binder with pigment to binder ratio of 1:2 and deionized water. The pH of the inks was adjusted to 9.0 using sodium hydroxide. The inks were filtered through a 0.5 micrometre pore size filter and printed on cotton using an Epson Stylus 3000 ink jet printer. The screen ink was composed of 10%wt pigment dispersion (cyan, magenta, yellow and black), acrylic binder with pigment to binder ratio of 1:2 and fume silica to increase the viscosity required for screen printing. The viscosity and flow behaviour of both ink jet inks and screen inks were found to be acceptable. The particle size distribution and viscosity of ink jet inks were slightly increased during ambient storage of two months. It was found that both inks showed the same colour saturation, colour gamut and ink tone reproduction. The colour gamut volume, stiffness, air permeability and crock fastness of ink jet printed fabrics were superior to those of fabrics printed with screen inks. The ink jet printed pre-treated fabric showed improved colour gamut volume and colour saturation compared to the untreated fabric. The three pass ink jet printing on pre-treated cotton fabric increased colour gamut, colour gamut volume and colour saturation.

Kiatkamjornwong *et al.* [134] studied the effect of pigment dispersion techniques such as surface modification and micro-encapsulation on ink jet printing of silk fabric. Four colour (cyan, magenta, yellow and black) surface modified pigment dispersions and micro-encapsulated pigment dispersions were used for ink jet ink formulations (Table 2-11). The properties of both types of inks were: viscosity 3.5-5 mPas, surface tension 38-45 mN/m and particle size 220-230 nm. To examine stability, inks were stored at ambient room temperature for 12 weeks. It was found that after storage, the particle size and viscosity of inks increased by 2-15% and 20-40% respectively. Silk fabric was pre-treated with 10% Sanfix 655 (cationic acrylate polymer) and 10% urea solution at 100% wet pick up and then dried at 80°C for 10 minutes.

Table 2-11 Formulation of ink jet inks

Components	Concentration (% weight)
Pigment dispersion	4.0
Diethylene glycol	10.0
Glycerol	10.0
Urea	5.0
Binder	8.0
Deionized water	63.0
Total	100.0

Both untreated and pre-treated silk fabrics were ink jet printed with both types of inks using an Epson Stylus colour 3000 printer. The pre-treated silk fabrics showed high optical density compared to the untreated fabrics. When compared with microencapsulated pigment inks, the surface modified pigmented inks provided high optical density, good tone reproduction, better colour gamut and gamut volume on both untreated and pre-treated silk fabrics.

Chitosan, a biopolymer derived from chitin was further reviewed to gain an understanding of its applicability into the ink jet printing of textiles.

2.7 Chitin

Chitin is the second most abundant polysaccharide on earth after cellulose. It is found in the shells of crustaceans such as crabs, shrimps and lobster, in the exoskeleton of insects and molluscs and in the cell walls of certain fungi [135, 136]. Chitin was first isolated by Braconnot [137] in 1811 and called it fungine. Later, in 1823, Odier found it in insects and named it as chitin [138]. Chitin is mostly produced from crab and shrimp shells which are dumped as huge wastes by the seafood industry. The crustacean shell waste contains 30-50% calcium carbonate, 30-40% protein and 20-30% chitin on a dry mass basis [139].

2.7.1 Isolation and Preparation of Chitin

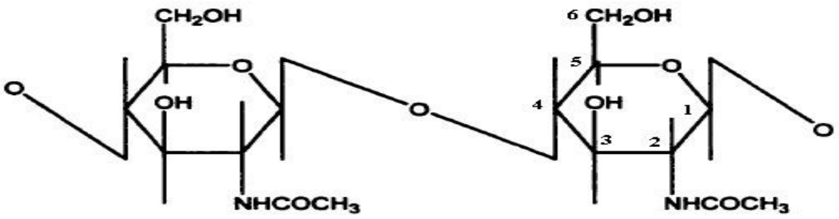
The preparation of chitin from crustacean shell waste involves three basic steps:-

1. Demineralization of calcium carbonate and calcium phosphate by acids like dilute HCl, HNO_3, H_2SO_4, CH_3COOH and HCOOH at room temperature [140, 141].
2. Deproteinization with NaOH, Na_2CO_3, KOH, K_2CO_3, Na_2SO_3, $NaHSO_3$, $CaHSO_3$, Na_3PO_4 and Na_2S. Dilute sodium hydroxide at elevated temperature (65-100°C) is preferred. The use of enzymes has also been reported in the literature [142, 143].
3. Decolouration using ethanol, acetone, warm 50% aqueous acetic acid or by bleaching with NaOCl, H_2O_2, SO_2, $Na_2S_2O_4$, $NaHSO_4$ and $KMnO_4$ [140, 141].

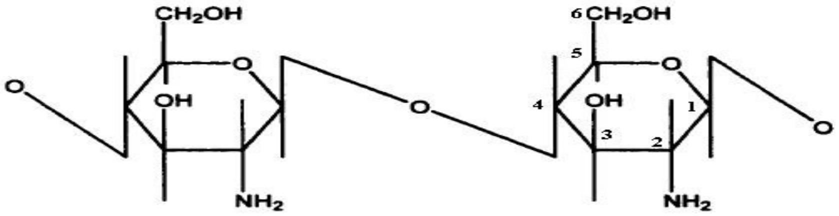
2.7.2 Structure of Chitin, Chitosan and Cellulose

Chemically, Chitin is a homopolymer of 2-acetamido-2-deoxy-β-D-glucopyranose with some of the glucopyranose residues existing as 2-amino-2-deoxy-β-Dglucopyranose. Its molecular weight, purity, and crystal morphology are dependent on their sources [144]. It occurs naturally as one of three crystalline polymorphic forms; α-, β- or γ-chitin differing in chain packing in crystalline regions [145]. α-chitin has anti-parallel chains, β-chitin has a parallel stack structure while arrangement of two parallel chains and one anti-parallel chain has been suggested for γ-chitin. Both α- and β-chitins possess $C{=}O\cdots\cdots H{-}N$ intermolecular hydrogen bonds, but the intermolecular hydrogen bonds between $-CH_2OH$ groups are present in the α-chitin and absent in the β-chitin [146]. Therefore, β-chitin swells easily in water to produce hydrates unlike α-chitin, which has a strong three-dimensional hydrogen bond network. β-chitin is found in squid and marine diatoms and is rare while α-chitin is most abundantly found in crustaceans, insects, and fungi. Hence, chitosan is commercially prepared from α-chitin. The molecular structure of chitin, chitosan and cellulose are shown in Figure 2-12.

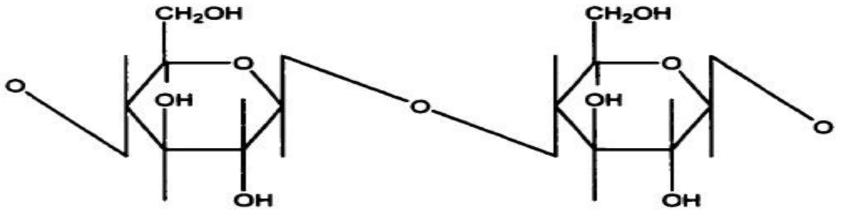
Figure 2-12 Molecular structure of chitin, chitosan and cellulose



CHITIN



CHITOSAN



CELLULOSE

Chitin, chitosan and cellulose are naturally occurring *β*-1, 4-linked linear polysaccharides. Chitin has the same backbone as cellulose, but it has an acetamide group on the C-2 position instead of a hydroxyl group. Chitin is a homopolymer of 2-acetamido-2-deoxy-*β*-D-glucopyranose, although some of the glucopyranose residues exist as 2-amino-2-deoxy-*β*-Dglucopyranose.Chitosan is the *N*-deacetylated derivative of chitin and the majority of its glucopyranose residues are 2-amino-2-deoxy-*β*-D-glucopyranose.

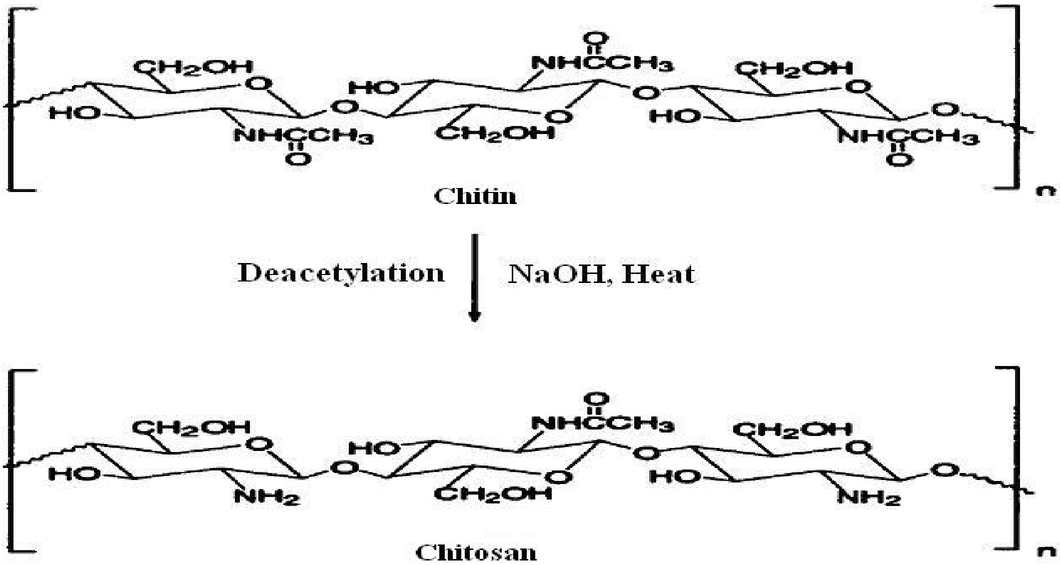
2.8 Chitosan

Chitin is a semicrystalline polymer with extensive inter- and intra-molecular hydrogen bonding. Hence, it is difficult to dissolve chitin in organic solvents or dilute acids under mild conditions. When chitin is deacetylated by over about 60%, it can easily be dissolved in dilute aqueous acids and is referred to as chitosan or deacetylated chitin. Thus, chitosan is the collective name given to the polymers that are deacetylated from chitin. The only difference between chitosan and chitin is the degree to which the former is deacetylated. Chitosan was first discovered in 1859 by Rouget while boiling chitin with concentrated potassium hydroxide solution that resulted in the deacetylation of chitin [147]. In 1934, Rigby [140] obtained two patents, one for chitosan production from chitin and other for making films and fibres from chitosan. Clark and Smith [148,149] reported the first X-ray pattern of chitosan fibre. The first review on chitin and chitosan was published by Muzzarelli in 1977 [135]. Due to its versatile physical and chemical properties, unique cationic nature, biodegradability, biocompatibility, non-toxicity and antimicrobial activity, chitosan has been extensively investigated for wide range of applications for the last three decades. Chitosan is seen as a new functional material with high application potential in various fields. Chitosan has been found to have applications in areas like food processing, cosmetics, biotechnology, agriculture, fibre formation, pharmaceuticals, medical applications, wastewater treatment, paper production, textile dyeing, printing, finishing [150-154] and textile ink jet printing [351-354].

2.8.1 Production of Chitosan

Chitosan is found in some fungi but in limited quantities. Hence, chitosan is commercially produced by alkaline deacetylation of chitin [136]. The purpose of deacetylation is to produce chitosan that is readily soluble in dilute acetic acid. Deacetylation can be defined as a process that involves reaction of chitin with aqueous 40-50% NaOH solution at 100°C or higher for at least 30 minutes to hydrolyze the N-acetyl linkages. Repeating the process can give deacetylation values of up to 98% but it is difficult to achieve complete deacetylation with such a heterogeneous process. Mima *et al.* prepared chitosan with up to 100% deacetylation by alkaline treatment of chitosan in gel form instead of powder form [155]. Figure 2-13 illustrates a typical deacetylation process. It can be seen that chitin is mostly comprised of acetamide groups while chitosan is a copolymer containing acetamide and primary amino groups.

Figure 2-13 Deacetylation process



The production of chitin and chitosan generates large quantities of liquid chemical waste. For large-scale chitosan production, the deacetylation process needs to be simplified while maintaining the desired features of chitosan. Reducing the number of steps makes the process more economically feasible and eco-friendly. The simplified and traditional chitosan production schemes are shown in Figure 2-14 and Figure 2-15, respectively. 6.3 kg of HCl and 1.8 kg of NaOH along with nitrogen, process water (0.5t) and cooling water (0.9t) are required to produce 1 kg of 70% deacetylated chitosan from shrimp shells [156]. No *et al.* used autoclaving (15 psi/ 121°C) to prepare chitosan and achieved effective deacetylation with 45% NaOH for 30 minutes with solid:solvent ratio of 1:15 [159].

Figure 2-14 Simplified chitosan production scheme [158]

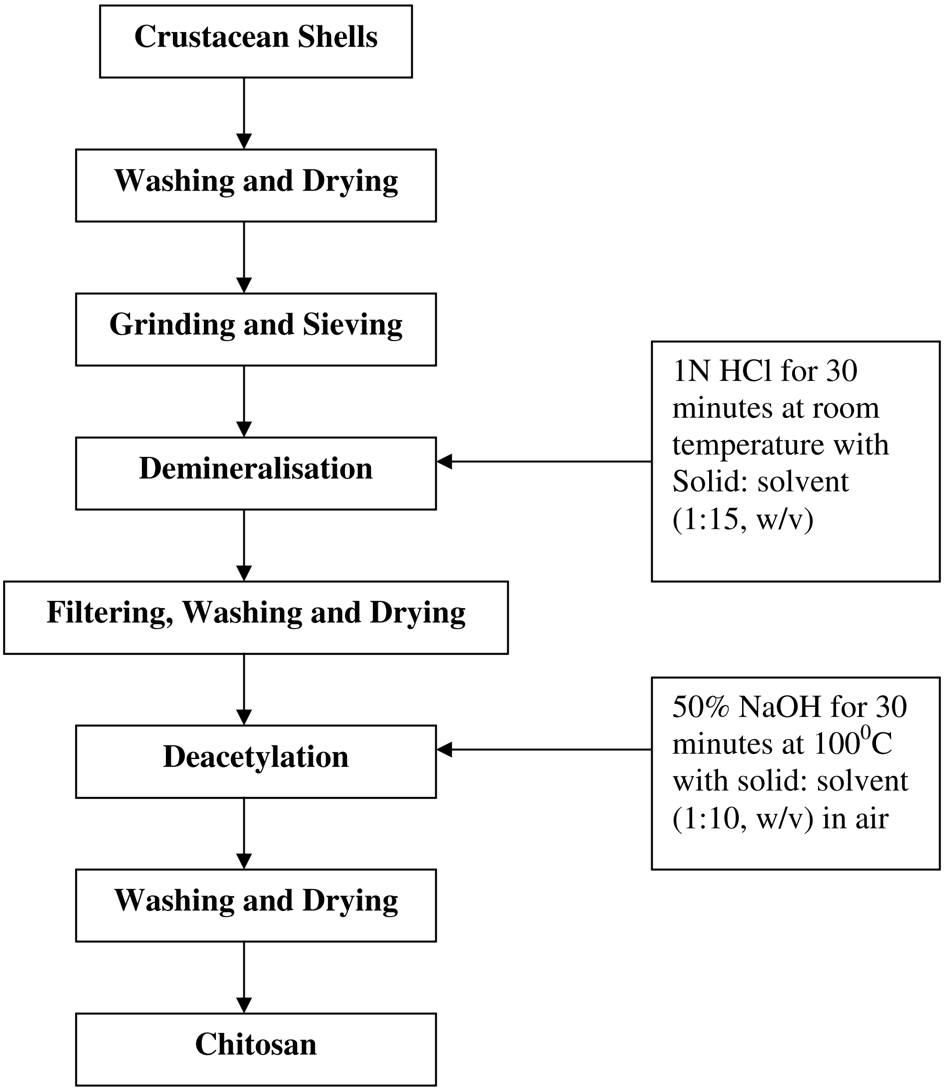
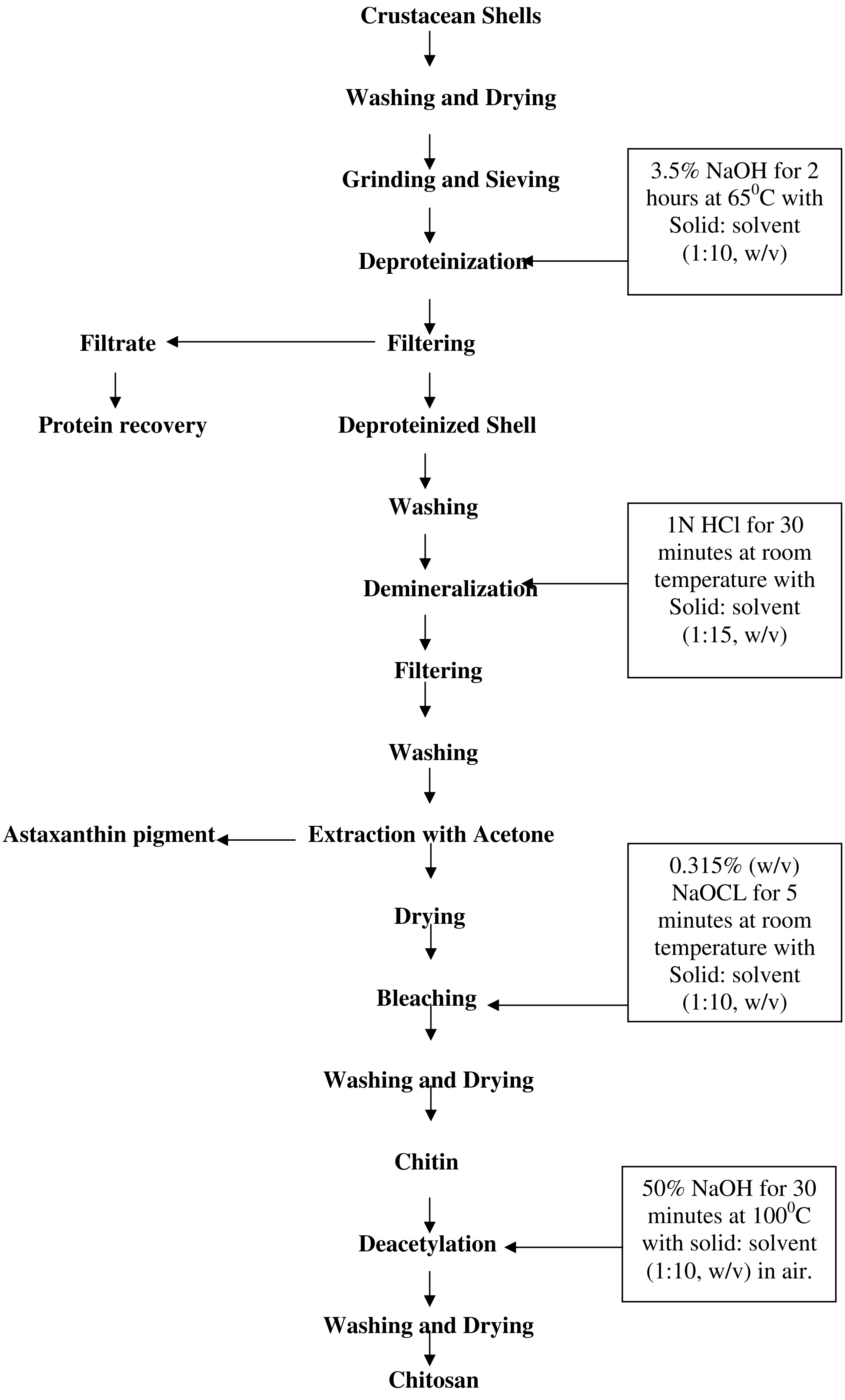
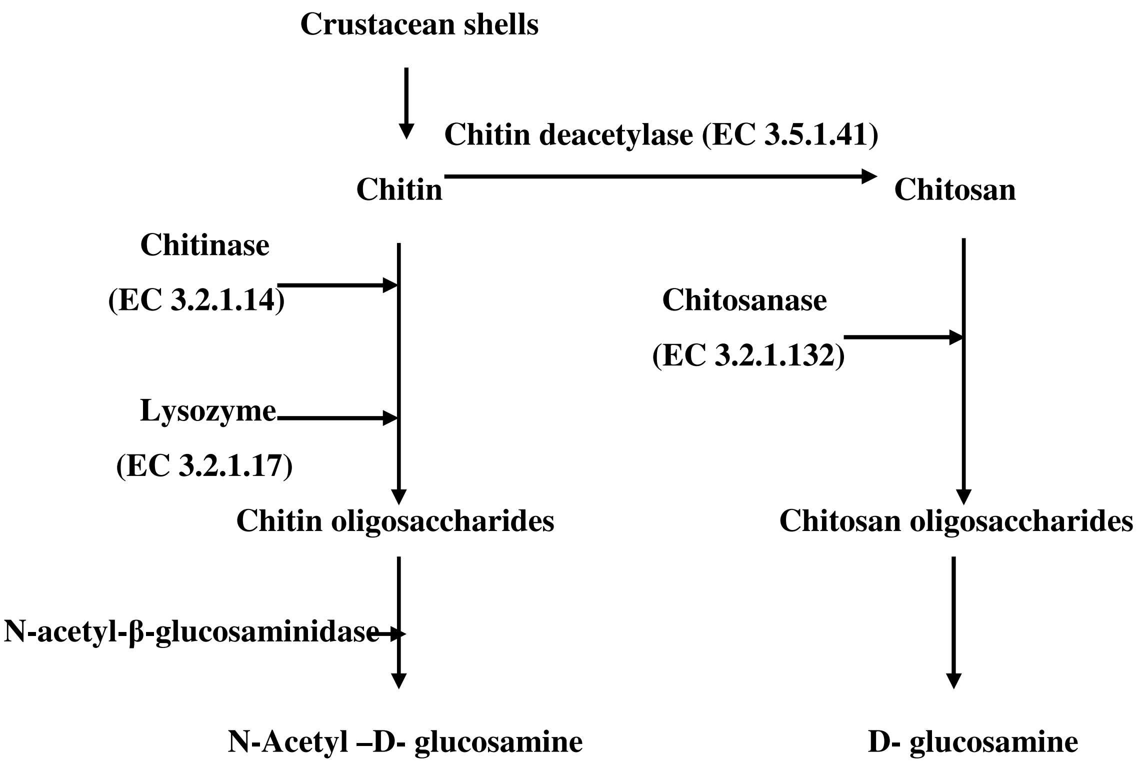


Figure 2-15 Traditional chitosan production scheme [157]



Hirano achieved enzymatic conversion of chitin to chitosan using chitin-N-deacetylase and prepared chitin and chitosan oligosaccharides by catalysis using set of enzymes. As shown in Figure 2-16, chitinase and lysozyme catalyze the hydrolysis of chitin while chitosanase catalyzes chitosan to produce oligosaccharides of chitin and chitosan [160].

Figure 2-16 Enzymatic preparation of chitosan and oligosaccharides of chitin and chitosan [160]



Several countries such as Norway, Mexico and Chile possess huge crustacean resources still to be exploited while chitin and chitosan are now being commercially produced in Japan, United States, India, Poland, Norway and Australia.

2.8.2 Physicochemical Characteristics of Chitosan

2.8.2.1 Degree of Deacetylation (DD)

Basically, the deacetylation process involves the removal of acetyl groups from chitin molecules. The degree of deacetylation is defined as the average number of D-glucosamine units per 100 monomers expressed as a percentage. It determines the content of free amino groups (-NH2) in the chitosan and is one of the most important chemical characteristics that influence the physicochemical properties, biological properties, antibacterial activity and applications of chitosan [135,161-162]. Depending on the production method and species used, the degree of deacetylation ranges from 56% to 99%. For good solubility, the degree of deacetylation should be at least 85% [163].

The degree of deacetylation can be obtained directly by determining amino group content of a chitosan sample or indirectly by determining acetyl content (degree of N-acetylation). Acid-base titration is one of the simplest methods to determine DD which involves dissolving a known amount of chitosan in an excess of dilute acid (e.g. hydrochloric acid), titrating it with a standard sodium hydroxide solution and measuring the pH to determine the stoichiometry. Domardo and Rinaudo questioned its accuracy because of the precipitation of chitosan in the neutral pH range which results in slow and unstable pH reading and suggested conductometric titration as an alternative [164]. Other methods used to determine the DD are IR spectroscopy [165-169], UV spectroscopy [170], circular dichroism [171], 1H NMR spectroscopy [172,173], 13C solid-state NMR spectroscopy [174], gel permeation chromatography [170], titration methods [168,174-177], residual salicylaldehyde analysis [168], equilibrium dye adsorption [178], elemental analysis, acid degradation followed by HPLC [179], thermal analysis [180], and pyrolysis-mass spectrometry [181].

2.8.2.2 Molecular Weight (MW)

The molecular weight of chitosan is another important property that determines its suitability for a particular application. The MW of chitin and chitosan varies with the sources and the methods of preparation. MW of native chitin is usually larger than one million daltons while that of commercial chitosan product ranges from 100,000 to 1,200,000 daltons [161]. MW of chitosan is one of the most important factors affecting its antimicrobial activities [182]. Viscometry [183-187], gel permeation chromatography [188-191] and light scattering spectrophotometry [164,192-193] are preferred methods for determining MW of chitosan.

Application of chitosan as a textile finish has shown to increase the stiffness of the fabrics, thereby affecting the feel and handle. Hence, for textile applications, it is preferable to use chitosan with a molecular weight that does not affect the hand of the fabrics. In the present study, the effect of MW on the film forming ability of chitosan and on the handle of textile substrates especially cotton will be assessed.

2.8.2.3 Viscosity

Viscosity of chitosan solution is another property that determines its commercial applications and is affected by the degree of deacetylation, molecular weight, concentration, ionic strength, pH, and temperature [161]. The viscosity of chitosan increases with an increase in molecular weight and concentration of chitosan, while it increases with decrease in pH in acetic acid and decreases with decreasing pH in HCl. Moreover, the antimicrobial activity of chitosan is also affected by its viscosity. Cho *et al.* [194] found that the antimicrobial activity of chitosan against *Escherichia coli* and *Bacillus sphaericus* increased with decreasing viscosity from 1000 to 10 cP. The viscosity of chitosan solution stored at 4^0C was found to be relatively stable.

No and Meyers [195] studied the effect of treatments such as grinding, heating, freezing, autoclaving, ultrasonification and ozonation on the viscosity of chitosan. The viscosity was affected by all the treatments and, except for freezing, decreased with increasing treatment time and temperature. No *et al.* [196] found that the viscosity decreased from 248 to 32 cP with increasing deproteinization time from 0 to 30 minutes.

Viscosity can be used to determine the molecular weight of chitosan. No and Meyers [197] found that the chitosan viscosity can be accurately estimated from the linear regression equations by measuring flow times using pipettes. This method was proposed as an alternative for routine analysis and does not require a viscometer.

2.8.2.4 Solubility

Due to extensive inter- and intra-molecular hydrogen bonding, chitin is insoluble in water, dilute aqueous salt solutions, dilute acids and most organic solvents. Chitin is depolymerised by strong mineral acids and is partially soluble in mixtures of dimethylacetamide (DMAc) and lithium chloride (LiCl) [163]. The poor solubility of chitin is the major hindrance in its application potential, although various applications of chitin and modified chitins especially, as raw material for synthetic fibres, have been reported in the literature [156]. The majority of the solvents found to dissolve chitin are either toxic, corrosive or possess mutagenic properties. Due to this limitation, chitosan is preferred over chitin for commercial applications.

Both, chitin and chitosan are insoluble in neutral water. However, water-soluble chitin can be prepared by either homogeneous deacetylation of chitin [198] or homogeneous *N*-acetylation of chitosan [199, 200]. Water solubility is obtained by homogeneous reaction instead of heterogeneous reaction and only when the DD of chitin is about 0.5. The homogeneous reaction produces a random copolymer of *N*-acetyl-D-glucosamine and D-glucosamine units while the heterogeneous reaction yields a block copolymer of these two units. X-ray diffraction studies revealed that the random copolymer was almost amorphous whereas the block copolymer was highly crystalline although the degree of deacetylation of the two polymers was same. The water-solubility was attributed to the enhanced hydrophilicity due to random distribution of acetyl groups and the destruction of the tight crystalline structure of chitin [198, 200].

The solubility of chitosan is very important for its commercial applications as a textile finish, fibre or film former and for its chemical modification. Chitosan dissolves in dilute organic and mineral acids by protonation of free amino groups below pH 6.5. This imparts a cationic nature to chitosan which then makes it suitable for a wide range of applications. Chitosan is soluble in dilute nitric and hydrochloric acids, marginally soluble in phosphoric acid and insoluble in any concentration of sulphuric acid at room temperature [201]. Acetic acid is the most preferred solvent for research and applications of chitosan. A list of solvents for chitin and chitosan is available in the literature [202]. Both the degree of deacetylation and the molecular weight affect the solubility of chitosan [203]. Generally, the solubility of chitosan and chitin decreases with increasing MW. Oligomers of chitin and chitosan with degree of depolymerisation (DP) ≤ 8 are soluble in water irrespective of pH [204].

2.8.2.5 Colour

The colour of chitin and chitosan is associated with the carotenoid pigment whose main component is astaxanthin [157, 205-206]. The carotenoids are strongly bound with proteins in the epithelial layer of the exoskeleton of chitin. The carotenoid level in crustacean is very low and varies depending on dietary pigment availability, crustacean size, its maturation, and genetic differences [207]. The average values of pigment concentration found in the shell waste from crab, shrimp and Louisiana crawfish were estimated as 139, 147 and 108 ppm, respectively [157, 205].

2.8.2.6 Chemical Reactivity

Chitosan possesses three reactive groups, viz., primary (C-6) and secondary (C-3) hydroxyl groups on each repeat unit, and the amino group at the C-2 position on each deacetylated unit. These reactive groups can be chemically modified to alter the mechanical and physical properties, and solubility of chitosan. The typical reactions involving the hydroxyl groups of chitosan are etherification and esterification. The nucleophilic amino group in chitosan allows reactions such as N-alkylation, *N*-acylation and reductive alkylation by reacting chitosan with alkyl halides, acid chlorides and aldehydes or ketones, respectively. Selective O-substitution can be carried out by protecting the amino group during the reaction. Cross-linking or graft copolymerization can also be carried out to modify chitosan [136, 208].

2.8.3 Antimicrobial Property of Chitosan

Chitosan has found applications, as an antimicrobial agent, in various fields like pharmaceutical, food, agriculture and textiles. The antimicrobial activity of chitosan has been attributed to its polycationic nature and several studies showing effectiveness of chitosan against various bacteria and fungi have been reported. Chitosan is more effective against fungi and algae, followed by bacteria. In order to utilize chitosan effectively as an antimicrobial agent for textile applications, it is important to understand the mechanism and the factors affecting its antimicrobial activity.

2.8.3.1 Mechanisms of Antimicrobial Activity of Chitosan

Although the exact mechanism has not yet been proven, several theories have been postulated. The most widely proposed mechanism is that of electrostatic interaction between positively charged chitosan and negatively charged residues at the cell surface of many fungi and bacteria. This alters the cell surface and cell permeability which further causes leakage of intracellular components such as electrolytes, UV-absorbing material, proteins, amino acids, glucose, and lactate dehydrogenase. As a result, the normal metabolism of microorganisms is inhibited leading to the death of these cells [156, 209-213]. Another mechanism suggested in the literature is the inhibition of mRNA and protein synthesis due to interaction of chitosan with DNA of some fungi and bacteria [214-216]. For this to occur, chitosan should have a molecular weight sufficiently low to penetrate into the cell of micro organisms. The above theory contradicted with the observations of Tokura *et al.* [217]. Tokura *et al.* studied the antimicrobial action of chitosan with weight average MW of 2200 and 9300. The chitosan with MW 9300 was stacked on the cell wall and inhibited the growth of E. *coli* while chitosan with MW 2200 permeated into the cell wall and accelerated the growth of E. *coli*. They postulated that the antimicrobial action of chitosan was related to the suppression of the metabolic activity of the bacteria by blocking nutrient permeation through the cell wall rather than the inhibition of the transcription of DNA.

2.8.3.2 Factors Affecting Antimicrobial Action of Chitosan

The antimicrobial activity of chitosan is influenced by various factors such as molecular weight [211, 215, 218, 219, 221, 222, 224, 227], degree of deacetylation [215, 223, 225, 228], pH [212, 214, 215, 220] chain length [223], type or species or strains of micro-organisms tested [225-226], temperature [212], cations and polyanions [156, 209, 212], concentration [229-231], type of chitosan (parent or derivative), substrate and/or nutrient composition and environmental conditions [232].

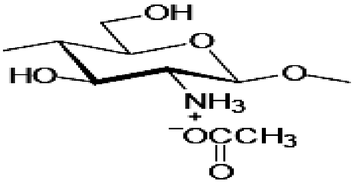
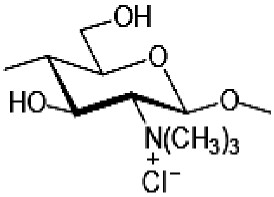
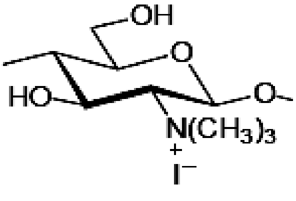
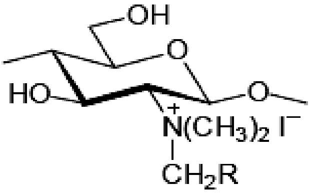
2.8.4 Derivatives of Chitosan

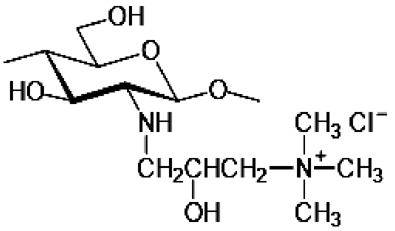
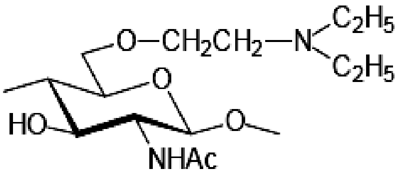
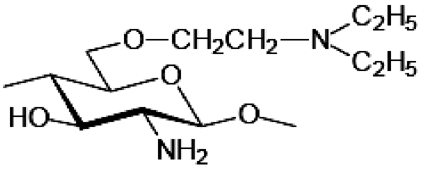
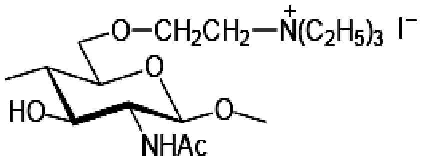
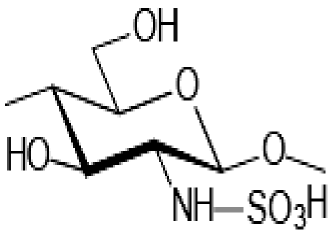
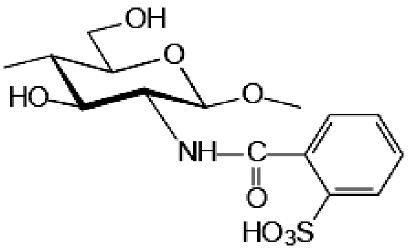
Due to the loss of its cationic nature at pH above 6.5, chitosan exhibits poor solubility. Hence, its applicability, as well as antimicrobial activity is limited to acidic conditions. By utilizing the reactivity of the primary amino group and the primary and secondary hydroxyl groups of chitosan, various derivatives of chitosan were prepared with goals to dissolve it in water over the entire pH range and to broaden its applicability.

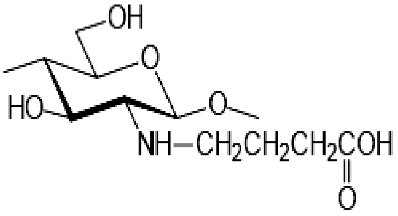
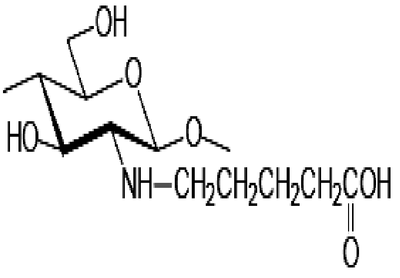
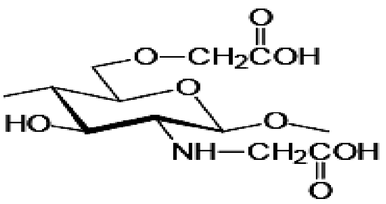
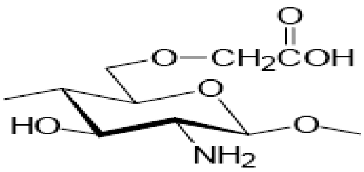
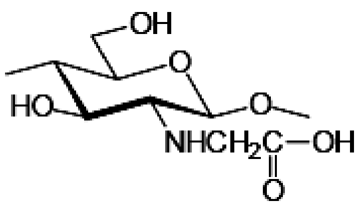
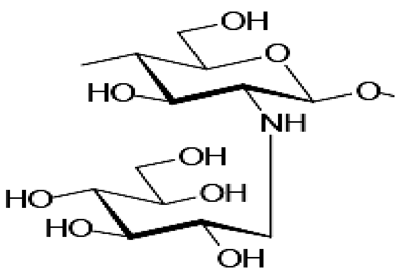
For textile applications, water soluble chitosan derivatives would be more preferable than acid soluble chitosan. Shin *et al.* [233] reported preparation of a water soluble chitosan oligomer for finishing polypropylene nonwoven fabrics to impart antimicrobial activity against *E. coli* and *S. aureus*. Water soluble chitosan lactate and chitosan hydroglutamate were found to exhibit strong antimicrobial activity against *E. coli* and *S. aureus* [211]. Synthesis of water soluble chitosan derivatives with substituted oxiranes has been reported [234]. Water soluble chitosan with 50% deacetylation can be prepared by homogeneous processing. Under homogeneous conditions, the uniform distribution of N-acetyl groups decrease the polymer crystallinity, thereby increasing water solubility [198]. Chitosan can also be rendered water soluble by chemical reactions such as alkoxylation [235], carboxymethylation [236], acylation [237] and graft polymerisation [238].

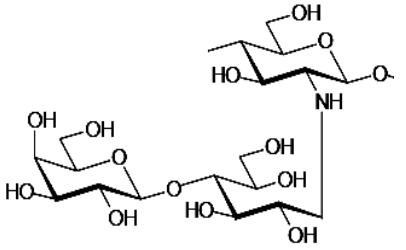
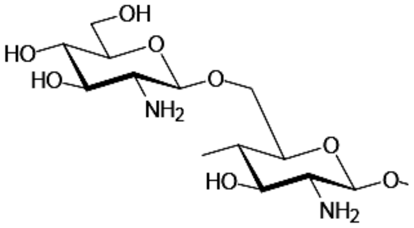
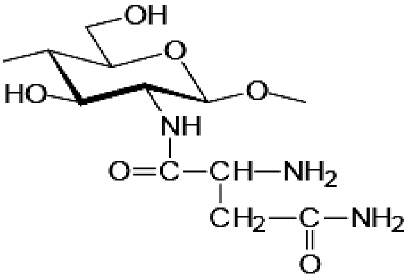
Some of the chemically modified chitosan derivatives are shown in Table 2-12.

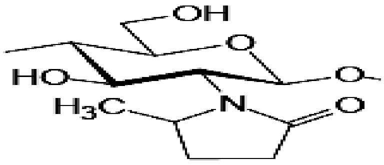
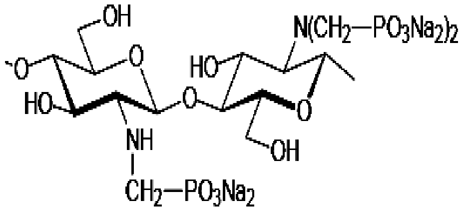
Table 2-12 Derivatives of chitosan [136, 208-209]

Description of Chitosan Derivatives	Examples
Chitosan Salts such as acetate, hydrochloride, lactate, hydro glutamate, pyrithione [239]. Simplest forms. Strong antimicrobial activity (pH dependent) against various bacteria and fungi. Precipitate in alkaline conditions [209].	 **Chitosan acetate**
Quaternary Ammonium Chitosan Derivatives TMCC, TMCI, and *N,N,N*-trimethyl chitosan hydroxide (TMCH) are prepared by introducing quaternary ammonium salts onto chitosan backbone via N-trimethylation [240]. Minimum inhibitory concentrations of TMCI with degree of quaternization (DQ) of 0.1-0.2 against several bacteria were lower than unmodified chitosan [223]. TMCI and TMCC are water soluble while TMCH is insoluble in water. Order of antimicrobial activity against *E. coli and Staphylococcus epidermidis*: TMCH < TMCC < TMCI [241]. Quaternized N-alkyl chitosan derivatives are prepared by introducing different alkyl groups (butyl, octyl, and dodecyl) onto the amino groups of chitosan via Schiff base intermediates followed by reduction and quaternization to produce water-soluble chitosan derivatives. Cationic charge and alkyl chain length of the substituent affected the antimicrobial activity [242].	 **N,N,N– trimethyl chitosan chloride (TMCC)**  **N,N,N-trimethyl chitosan iodide (TMCI)**  **Quaternized N-alkyl chitosan derivatives**

HTCC is prepared by reacting chitosan either with glycidyl trimethyl ammonium chloride (GTMAC) [243] or with 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (Quat 188) [244]. Showed high antimicrobial activity against *E. coli*, *S. aureus* and *Pseudomonas aeruginosa*. DEAE-chitin is prepared by introducing diethylaminoethyl group onto the hydroxyl group at the C-6 position of chitin by reacting alkali chitin with *N,N*-diethylaminoethyl chloride hydrochloric acid. It is soluble in water and aqueous acetic acid. DEAE-chitosan and TEAE-chitin are prepared by treating DEAE-chitin with 10% NaOH and ethyl iodide, respectively. All three derivatives showed antibacterial activities against *E. coli* and *S. aureus* in the increasing order of DEAE-chitin (DS 0.81 and DD 0.41), DEAE-chitosan (DS 0.67 and DD 0.73), and TEAE-chitin (DQ 0.47 and DD 0.48) with increasing alkyl chains and cationic charge of the substituent [245].	 **N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTCC)**  **Diethylaminoethyl (DEAE) chitin**  **Diethylaminoethyl (DEAE) chitosan**  **Triethylaminoethyl (TEAE)chitin**
Chitosan Derivatives with Sulphonyl Groups NSCs with different sulphur contents (0.4, 1.7, 2.5, and 3.4%) are prepared by reacting regenerated chitosan (DD 0.69) with different amounts of chlorosulphonic acid in pyridine [249]. NSBCs with various S-contents (1.7, 2.6, 5.3, and 6.2%) are prepared by reacting chitosan with 2-sulphobenzoic acid cyclic anhydride in methanol [250]. In case of both derivatives, bacteria dependent optimal S-content was observed. NSCs with S-contents of 1.7% and 2.5% were most effective against *Salmonella typhimurium* and *E. coli*, respectively. The optimal S-contents for NSBCs were found to be 5.3%, 1.7%, and 2.6% for *S. aureus*, *E. coli*, and *S. typhimurium*, respectively.	 **N-sulphonated chitosan (NSC)**  **N-sulphobenzoyl chitosan (NSBC)**

Carboxyalkylated Chitosan Derivatives NCPC (DC (degree of carboxymethylation) 0.19) and NCBC (DC 0.26) are synthesized by reacting chitosan (MW 2,000,000, DD 0.75) with 4-chlorobutyric and 5-chlorovaleric acid in methanol, respectively. Both the derivatives did not dissolve in water but showed improved solubility in various solvents and antimicrobial activity against *E. coli* and *S. aureus* compared to chitosan [246]. NCBCs (DC 0.26–0.28) are also synthesized by dissolving chitosan in aqueous levulinic acid followed by reduction using sodium borohydride. They are soluble in water below pH 8.5 and are precipitated at pH $\geq$ 8.5 [247]. In an extensive study [248], NCBC was tested against 298 strains of different pathogens and was particularly effective against candidae and gram-positive bacteria. The NOCMC (DC 0.48 to 0.98) and OCMC (DC 0.42 and 0.73) are synthesized by reacting chitosan with monochloroacetic acid at different reaction conditions. The antimicrobial activity of both the derivatives was measured using optical density methods. NOCMC did not show any antibacterial activity, whereas OCMC was more effective than chitosan against *E. coli* [215]. The NCMC will be discussed later in detail.	 **N-carboxypropyl chitosan (NCPC)**  **N-carboxybutyl chitosan (NCBC)**  **N, O-carboxymethyl chitosan (NOCMC)**  **O-carboxymethyl chitosan (OCMC)**  **N-carboxymethyl chitosan (NCMC)**
Carbohydrate-branched Chitosan Derivatives DGC (DS 0.15) and DLC (DS 0.15) are water-soluble carbohydrate-branched chitosan derivatives. They effectively inhibited *Bacillus circulans* at concentrations below 400ppm but were not effective against *E. coli*. The DLC	 **1-deoxy-1-glucit-1-yl chitosan (DGC)**

showed overall higher antimicrobial activity against *B. circulans* than DGC [251]. Kurita *et al.* [252] prepared D-glucosamine-branched chitosan (DS 0.45) by introducing D-glucosamine branch onto the hydroxyl group on the C-6 position of chitosan by a series of regioselective reactions through *N*-phthaloyl chitosan. It is readily soluble in neutral water at DS > 0.3 and swells in common organic solvents. It showed higher growth suppression against *Bacillus subtilis*, *S. aureus*, and *Candida albicans* compared to unmodified chitosan. The authors suggested its use as water soluble antimicrobial agent in the fields of cosmetics, pharmaceutics, biomedical use, food processing, and textiles.	 **1-deoxy-1-lactit-1-yl chitosan (DLC)**  **D-Glucosamine-branched chitosan**
Chitosan-Amino Acid Conjugates Synthesized by reacting low MW chitosan (MW < 10,000) with Boc-amino acid derivatives followed by de-protection of the Boc group. The chitosan-asparagine conjugate (DS ~ 0.70) showed high bactericidal activity against *E. coli* than unmodified chitosan. Chitosan derivatives *N*-conjugated with different amino acid groups, such as glycine, alanine, aspartic acid, cysteine, and methionine showed lower antibacterial activity than chitosan.	 **Chitosan-asparagine conjugate**
Iodine Complexes of Chitosan or its Derivatives Prepared by exposing chitosan or its derivatives to iodine vapours caused by sublimation of elementary iodine at room temperature or above [253]. This method eliminated the use of toxic organic solvents [254].Chitosan-iodine complexes with iodine content <50% (w/w) can be dissolved in dilute aqueous acids, such as acetic and glutamic acid, in which the iodine remains stable in the form of a soluble complex with chitosan. The chitosan-iodine complex both in its dry state and in solution showed a significant bactericidal action against numerous microorganisms that commonly infect the skin and wounds.	

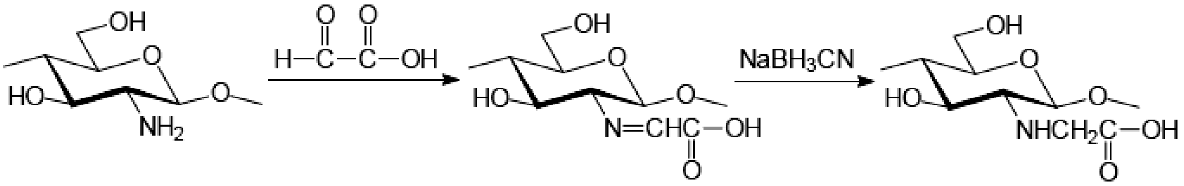
Miscellaneous Chitosan Derivatives MPC (DS 0.27) and NPMC with monosubstituted (DS 0.24) and disubstituted (DS 0.14) units are effective against *Saprolegnia parasitica*. Their amphoteric nature might have lead to the effective interaction with surface components of the *S. parasitica* cell wall, leading to increased permeability and consequent cellular leakage and death of the cells [255].	 **5-Methylpyrrolidinone chitosan (MPC)**  **N-phosphonomethyl chitosan (NPMC)**

Among the above mentioned derivatives, N-carboxymethyl chitosan, one of the carboxyalkylated derivatives of chitosan is of particular interest and is related to this research. NCMCH was selected as it is soluble in water over entire pH range.

2.8.5 N-Carboxymethyl Chitosan

Carboxyalkylation of chitosan is one of the methods to improve the solubility of chitosan. Muzzarelli *et al.* [256] prepared N-carboxymethyl chitosan (NCMC) by treating an aqueous suspension of chitosan with glyoxylic acid followed by reduction with sodium cyanoborohydride ($NaBH_4$) and pH adjustment (Figure 2-17).

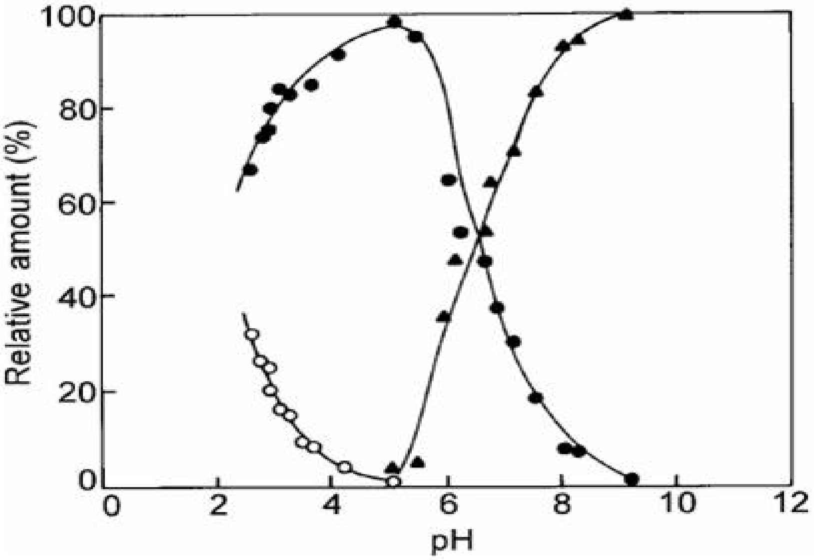
Figure 2-17 Synthesis of N-carboxymethyl chitosan



Briefly, chitosan is stirred in water and glyoxylic acid is added to give a clear solution. When $NaBH_4$ was added, the solution became cloudy between pH of 4 to 6. At pH 7, the solution started to clear. At pH 8, the solution was clear. In this derivative, the carboxymethyl group was substituted exclusively on the amino group of glucosamine unit. The NCMCs were obtained as white, free flowing powders and were reported to be soluble in water at all pH values, irrespective of their degree of substitution (DS) that ranged from 0.25 to 1.0. NCMC prepared in this study was found to be suitable as a chelating agent.

A distinctive feature of carboxyalkylated chitosan is its amphotericity. According to Delben *et al.* [257], NCMC exists in three different forms depending on pH. At pH ~5, only the monodissociated (–NH–CH_2–COOH ↔ –N^+H_2–CH_2COO^-) form exists and at pH > ~ 9, only the fully dissociated (–NH–CH_2COO^-) form exists. Between the two pH values, NCMC exists as a mixture of mono and fully dissociated forms. As the pH decreases below ~ 5, NCMC exists as a mixture of monodissociated and fully protonated (–N^+ H_2–CH_2COOH) forms and the amount of the latter increases with decreasing pH (Figure 2-18).

Figure 2-18 Relative amounts (%) of three forms of NCMC in water at 25^0C as a function of the pH (4.8 x 10^{-3} M NCMC): o, fully protonated; •, monodissociated; ▲, fully dissociated [257].



Muzzarelli [255] reported that NCMC with degree of carboxyalkyation (DC) 0.27 was significantly effective in depressing the radial growth of *Saprolegnia parasitica* while, Cuero *et al.* [258] observed that aqueous solutions of NCMC suppressed the growth of *Aspergillus flavus* and *A. parasiticus*.

2.8.6 Depolymerisation of Chitosan

The effectiveness of chitosan and its derivatives for a particular application has been found to be dependent on their molecular weight and degree of deacetylation [261]. The molecular weight of chitosan produced commercially from crab and shrimp waste shells is usually in the range of 10^5 – 10^6 and the viscosity is of the order of 1500 centipoise [163, 259-260]. Depolymerisation is a process of preparation of low molecular weight chitosan from high molecular weight chitosan. It can be achieved by chemical, physical and enzymatic methods. Chemical depolymerisation using hydrochloric acid, nitrous acid, phosphoric acid and hydrogen fluoride has been attempted. This is a common and fast method but has some drawbacks such as low yield, high cost, production of large amount of monomeric D-glucosamine and environmental pollution [262]. The enzymatic depolymerisation with chitosanase [221] or protease [263] is milder and easy to control but is expensive. Oxidative depolymerisation using ozone [264], sodium nitrite [265] and hydrogen peroxide [266-267] has also been reported. Physical methods such as ultrasonification [268], irradiation [269] and autoclaving [270] have been attempted by researchers. Depolymerisation of chitosan by autoclaving at 121^{o}C for 15 minutes was found to be a simple, timesaving and homogenous process. This process of depolymerisation will be utilized in the present study.

2.8.7 Application of Chitosan in Paper Printing

Kohler *et al.* [326] tested light fastness of polyethylene base paper coated with gelatine/chitosan mixtures and compared them with gelatine coated papers containing other dye fixing agents. They found that chitosan/gelatine coatings improved dye fixation on the paper and kept the light fastness of the printed image at the high level observed for pure gelatine coatings. At 6% by weight concentration of chitosan, the image quality and dry time remained unaffected while the dye fixation was comparable to a commercial high end porous paper and was better than a gelatine coating containing 17% quaternary amine. They assumed that the improvement in the dye fixation by the chitosan containing coating formulations was related to the film forming properties of chitosan.

Gore [354] formulated pigment based ink jet inks containing a polystyrene-maleic anhydride polymer system that reacts with a fixer fluid containing chitosan salt such as chitosan acetate (5000 weight average molecular weight). A gel precipitate is formed on the substrate by the interaction of the chitosan in the fixer fluid and the reactive polymer system in the ink. It was claimed that the gel formed a protective film on the substrate providing benefits such as increased drying time, smear fastness, smudge fastness and water fastness. Although it was suggested that the above invention can be used for various substrates including textiles, the invention was demonstrated specifically on the paper substrate.

2.8.8 Application of Chitosan in Textiles

Over the past 20 years, chitosan has been evaluated for numerous textile applications. The application of chitosan in textiles includes production of man-made fibres [150], cotton dyeing [271-278], silk dyeing [137, 279-281, 298], wool dyeing [282- 283], polypropylene dyeing [319], durable press finishing [284-295], wool finishing [296-304], antimicrobial finishing [233, 305-318], antistatic finishing [320-321], de-odourising finishing [322], sizing [323], textile printing [153, 324-325] and recently, textile ink jet printing [351-354].

2.8.8.1 Application of Chitosan in Textile Printing

Bahmani *et al.* [153] examined the performance of chitosan (MW 171,000) as a combined thickener and binder in pigment printing. Polyester/cotton and 100% polyester fabrics were printed with chitosan/pigment printing paste, dried at room temperature and cured at 150^{0}C for 6 minutes. They found that the fabrics printed with chitosan printing paste gave a comparable colour fastness to the fabrics printed with commercial printing paste (Alcoprint system). However the fabrics printed with the chitosan printing paste showed poor colour strength (K/S) and were stiff. It was proposed that the poor colour strength was due to reduced stability of the pigment dispersion in chitosan paste at pH 4. It was suggested that the addition of appropriate auxiliaries could minimize the stiffness of the fabric and further studies would be necessary to improve the poor colour strength.

Hakeim *et al.* [324] studied the effect of chitosan pre-treatment and its depolymerised grades on printing of cotton with the natural colour, curcumin. They prepared chitosan samples with different molecular weights using sodium nitrite in acidic medium. The cotton fabrics were pre-treated (pad-dry-cure) with the chitosan samples and then printed with curcumin. The colour yield (K/S) of cotton fabrics pre-treated with chitosan was higher compared to the untreated samples. This was attributed to the possibility of curcumin behaving as a direct dye due to its structure features. The interaction between the dye and the fabric might have increased due to presence of amino groups of chitosan via hydrogen bonding. Another possibility could be the formation of salt side linkage between the protonated amino groups of chitosan and the dye. The colour yield increased with increasing molecular weight of chitosan which could be due to increase in amino group content. The fabric stiffness only became acceptable at low molecular weights of chitosan. The wet and dry rub fastness of the printed cotton fabrics was good.

Abou-Okeil *et al.* [325] studied the effect of chitosan pre-treatment on the printability of wool fabric. The wool fabric was pre-treated with chitosan of different molecular weights followed by mordanting with copper sulphate and then printing with a natural dye (2-hydroxy-1,4-naphthoquinone). The purpose of the chitosan pre-treatment was to increase the copper (II) binding of the wool fabric which would result in the reduction of metal ions in the effluent. It was found that copper (II) uptake increased with increase in the molecular weight and concentration of chitosan applied. The colour strength (K/S) and the wash fastness of the chitosan pre-treated printed wool samples increased compared to the untreated wool samples.

2.8.8.2 Application of Chitosan in Textile Ink Jet Printing

Choi *et al.* investigated a medium viscosity (~150 mPa.s) chitosan to replace sodium alginate in the pre-treatment print paste for digital ink-jet printing of cotton fabric. Cotton fabric was padded (80% WPU) with pre-treatment print paste containing suitable amounts of chitosan, urea and sodium bicarbonate and cured at 150°C for 90 seconds. The pre-treated fabric was ink jet printed with reactive dye based four colour ink system using Mimaki Tx2-1600 digital ink-jet printer. The printed fabrics were air dried and steamed at 110°C for colour fixation. The colour fastness properties of the printed fabrics were found to be satisfactory while the outline sharpness of the prints was enhanced by the chitosan pre-treatment. However, the colour yield was not as good as that achieved with sodium alginate based pre-treatment print paste [351].

Yuen *et al.* [352-353] postulated that the reduction in the colour yield in the above study was due to the neutralisation effect between acetic acid in the chitosan stock solution and sodium bicarbonate in the pre-treatment print paste. The neutralisation effect might have reduced the amount of sodium bicarbonate and might have increased the amount of neutralisation product i.e. water. Therefore, during the steaming process, the decreased amount of sodium bicarbonate reduced the fixation of reactive dyes with the fibre while the increased amount of water imposed a higher risk of hydrolysis of reactive dyes. This in turn reduced the colour yield. To improve the colour yield, Yuen *et al.* [352-353] modified the pre-treatment method by applying chitosan separately on the cotton fabric for digital ink jet printing with reactive dyes. The proposed two-bath method included (1) padding of cotton fabrics with chitosan solution (80% WPU) and curing at 170°C for 90 seconds. (2) padding of chitosan pre-treated fabrics with a pre-treatment paste containing 10 grams of urea and 8 grams of sodium bicarbonate in 150 grams of deionised water. The fabrics were padded with 80% WPU, dried at 80°C and subsequently conditioned. High colour yield was achieved with the developed two-bath method. However, chitosan slightly reduced the tensile strength of the digital ink jet printed cotton fabric.

2.9 The Hypothesis for Using Chitosan in Ink Jet Printing of Textiles

Chitosan has been extensively used for preparation of microspheres, microcapsules, nanocapsules and nanoparticles using various micro-encapsulation techniques especially complex coacervation processes [327-328]. Chitosan has one primary amino and two free hydroxyl groups for each C_6 building unit. Due to the easy availability of free amino groups in chitosan, it carries a positive charge and thus, in turn, can react with many negatively charged surfaces/polymers [329]. A recent study has shown that chitosan can be used as a textile binder for pigment printing [153]. Recent developments in nano-technology and surface modification technology have made available surface modified pigment nanoparticles.

Chitosan has also been extensively investigated as fibre and film former [150]. It has been reported that chitosan has good film forming ability due to intra- and intermolecular hydrogen bonding [330]. Rippon [272] postulated that the affinity of chitosan to cotton may be due to van der Waals' forces between them because of the similar structures of chitosan and cotton. The binding of the chitosan to cellulose may be also due to cross-linking by formation of Schiff base between cellulose's reducing end (–CO–H) and the amino group of chitosan [331].

Based upon these facts, the author of the present work developed the concept of microencapsulating surface modified carbon black nanoparticles with chitosan via the complex coacervation process. The hypothesis is that the surface modified pigment nanoparticles may be adsorbed, physically entrapped or attached with chitosan either by ionic interaction or by formation of an amide linkage. This approach can be rationalised as follows: Surface modified carbon black pigment nanoparticles are negatively charged due to carboxylated functionality ($-COO^-$) while chitosan is positively charged in weakly acidic conditions due to protonation of the amino group on the glucosamine unit [127-128, 329]. When mixed together, electrostatic interaction via the amide linkage would take effect between oppositely charged species and chitosan would be adsorbed on the surface of pigment nanoparticles.

The chitosan/pigment nanoparticles prepared according to above process could then be used to formulate ink jet inks for ink jet printing of textiles. The film forming ability of the chitosan would then act as an efficient binder for the pigment. Hence, chitosan would serve as a multi-functional one step application approach for binding pigments on textile fibres.

In a previous study [351], chitosan has been used to replace sodium alginate in the pre-treatment print paste for digital ink jet printing of cotton fabric with reactive dye based inks. Chitosan has also been applied via two-bath pre-treatment method to improve colour yield of reactive dye based inks on ink jet printed cotton fabric [352-353]. In the present study, chitosan was applied via a post-treatment method as a binder for fixation of pigment based inks printed digitally on cotton fabric. It was postulated that a chitosan post-treatment may fix the pigmented inks printed on cotton fabric by forming a film on fabric surface, thereby entrapping or encapsulating the pigments.

2.10 Objectives of the Present Study

The present study was carried out with two specific objectives:

1. To investigate and develop a chitosan-based post-treatment method for the fixation of pigment based ink jet inks digitally printed onto cotton fabric.
2. To formulate ink jet inks using chitosan encapsulated pigment nanoparticles for the basis of a one-step binder and pigment application.

Both of these two objectives are novel. Firstly no reports have been published in the literature concerning chitosan-based post-treatment for the fixation of pigmented inks on digitally printed cotton fabric. With this approach, it should be possible to use existing pigmented inks, which are those intended for paper printing, to be fixed on cotton fabric via the chitosan post-treatment. The post-treatment may also offer possibilities for other natural and synthetic fabrics. Secondly, ink jet inks containing surface modified pigment/chitosan nanoparticles are similarly not known. Co-application of such a pigment binder combination could provide important developments in ink jet printing technology. The knowledge and information achieved from this study will, therefore, provide an understanding of the novel application of chitosan as a post-treatment for pigment ink jet printed fabrics and on the mechanisms and efficacy of the potential one-step pigment jet print and bind process based on chitosan.

CHAPTER III EXPERIMENTAL

In this chapter, the experimental design, the materials used and the methods employed are presented and, where necessary, are discussed.

3.1 EXPERIMENTAL DESIGN

This study has two broad objectives:

1. Application of chitosan as a post-treatment for cotton fabric ink jet printed with pigment based inks.
2. Formulation of pigment based inks containing chitosan for ink jet printing of cotton fabric.

The experiments were carried out for the following purposes:

1. To determine degree of deacetlyation of chitosan samples and its derivatives using FT-IR Spectroscopy.
2. To carry out preliminary assessments of the applicability of chitosan and its derivatives for the fixation of pigment based ink jet inks on cotton.
3. To study the factors affecting the fixation of pigment based ink jet inks on cotton fabric post treated with chitosan and to (simultaneously) optimize the application conditions of chitosan post-treatment.
4. To develop a chitosan based post-treatment especially for cotton fabric ink jet printed with pigment based ink jet inks, which can overcome the limitations associated with chitosan.
5. To assess the anti microbial activity of ink jet printed cotton fabric treated with chitosan.
6. To formulate ink jet inks containing chitosan for ink jet printing of cotton fabric.

3.2 MATERIALS

3.2.1 Textile Binders

Three commercial thermally curable textile binders (CHT (Germany)) were selected to cover the principal classes of binders used by industry and for comparative assessment with chitosan. Their characteristics are listed in Table 3-1.

Table 3-1 Characteristics of textile binder emulsions

Binder	Chemical nature	Ionic Character	pH value
Tubicoat DB 314	Butadiene containing copolymer	Anionic	7-8
Tubiprint binder AUS	acrylic acid esters	Anionic	3-5
Tubiprint binder AS30	acrylate-styrene copolymer	Anionic	6.0

3.2.2 Chitosan Samples

Five commercially available forms of chitosan (CH) were used in this study. Their source and basic properties as specified by the supplier are shown in Table 3-2. All the chitosan samples were known to have been produced from crab shell.

Table 3-2 Chitosan samples

Chitosan Sample	Supplier	Degree of Deacetlyation (DD %)	Molecular Weight	Viscosity (centipoise) (1% solution in 1% acetic acid)
CH90 (Chitosan oligosaccharide prepared by enzymatic hydrolysis of chitosan)	Sigma-Aldrich, Australia	> 90%	< 5000	~ 6 at 25 ºC
CH95 (low molecular weight)	Sigma-Aldrich, Australia	95%	~150,000	24 at 25ºC
CH98 (medium molecular weight)	Sigma-Aldrich, Australia	98%	>375,000	> 200
CH82 (medium molecular weight)	India Sea Foods, India	82%	not specified	292 at 20ºC
NCMCH82 (N-carboxymethyl chitosan-water soluble derivative)	India Sea Foods, India	82%	not specified	not specified

3.2.3. Fabrics

Twelve commercial woven fabrics of different weights, weave and fibre composition were used and are listed in Table 3-3. The desized, scoured and bleached heavy cotton (189 g/m^2) if not otherwise specified was used in all cases. The fabric samples, if not specified, were used as received.

Table 3-3 Fabric description

Fabric Type	Weight in g/m^2	Type of Weave
Heavy cotton	189	Plain
Light cotton	110	Plain
Greige cotton	125	Plain
Desized cotton	124	Plain
Scoured cotton	124	Plain
Heavy un-mercerized cotton	276	Twill
Heavy mercerized cotton	276	Twill
50/50% Polyester/cotton	110	Plain
100% Polyester	50	Plain
Wool	230	Twill
Silk	25	Plain
Viscose	62	Plain

3.2.4. Surface Modified Pigment Dispersions

Surface modified pigment dispersions supplied by Cabot Corporation (USA) were used and their properties are given in Table 3-4. These dispersions were used to formulate the ink jet inks for ink jet printing on cotton fabric.

Table 3-4 Properties of pigment dispersions

Trade name	Cabojet 250C Cyan	Cabojet 260M Magenta	Cabojet 200 Black	Cabojet 300 Black
Colour Index	Pigment Blue 15:4	Pigment Red 122	Pigment Black 1	Pigment Black 1
Chemical Structure	Copper Phthalocyanine	Dimethyl Quinacridone	Aniline black	Aniline black
Percent Solids	11.7%	10%	19.9%	14.9%
Mean particle size (nm)	100	120	130	130
Surface functionality	Sulphonated	Sulphonated	Sulphonated	Carboxylated
pH	7.0	7.0	7.5	7.0 – 7.5
Viscosity (cP)	2.1	2.0	5.0	4.0
Surface Tension (dynes/cm)	70.3	70.1	69.0	67.3

All the other solvents, materials, chemicals and reagents used in this study were of analytical grade. Deionized water was used for preparation of chitosan solutions and formulation of ink jet inks.

3.3 METHODS

3.3.1 Determination of Degree of Deacetylation (DD) by FTIR Spectroscopy

The DD of commercial chitosan samples was determined using a Perkin Elmer AutoImage Spectrometer and according to procedures described by Domszy and Roberts [168], Baxter *et al.* [169] and Raut [250]. The instrument control and data handling was done using AutoImage Software. The data for each sample was collected with following instrument parameters: Gain: 1, Resolution: 4 cm^{-1} and Scans: 32. The KBr pellet for each sample was prepared by mixing a known amount of chitosan with a known amount of KBr. The pellet was placed directly in the beam and the spectrum was recorded for each sample.

Abbreviation:

CH90: Chitosan sample with DD >90%
CH95: Chitosan sample with DD95%
CH98: Chitosan sample with DD98%
CH82: Chitosan with DD82%
CMCH82: Carboxymethyl chitosan with DD82%

The protocols proposed by researchers mentioned above and used for calculation of DD of chitosan samples are as follows (Table 3-5):

Table 3-5 Proposed protocols for calculation of DD

Researcher	***Protocol***
Domzy and Roberts [168]	$DD = 100 – [A_{1650}/A_{3450} X 100/1.33]$
Baxter [169]	$DD = 100 – [A_{1655}/A_{3450} X 115]$
Raut [250]	$DD = 118.883 – [40.1647 X A_{1655}/A_{3450}]$

3.3.2 Preliminary Experiments for Assessment of Chitosan and its Derivative for Fixation of Pigment Based Ink Jet Inks

For preliminary experiments, the medium molecular weight commercial chitosan sample (CH82) and its water soluble derivative (NCMCH82) were selected. These chitosan samples were compared with commercial textile binders for fixation of pigment based ink jet inks on cotton fabric (189 g/m^2).

3.3.2.1 Preparation of Solutions of Commercial Binders

The binder solution was prepared by mixing 5 gm of binder emulsion in 100 ml of deionized water. The solution was magnetically stirred for 30 minutes to give homogeneous solution with the emulsion concentration of 50 $g.L^{-1}$ (grams per litre). This procedure was followed for all the three binders listed in Table 3-1.

3.3.2.2 Preparation of Solutions of Chitosan and its Derivative

Solutions of different concentrations (5 $g.L^{-1}$, 10 $g.L^{-1}$, 15 $g.L^{-1}$ and 20 $g.L^{-1}$) of chitosan (CH82) were prepared in 1% (v/v) acetic acid solution. The solutions were stirred for four hours by magnetic stirring to ensure complete dissolution of chitosan. 20 gm of N-carboxymethyl chitosan (NCMCH82) was added to 1000 ml of deionised water and stirred magnetically until the solution became homogeneous. The pH of the N-carboxymethyl chitosan solution was found to be 9.5. The pH was adjusted to 5.0, 7.0 and 9.0 using 2N acetic acid.

3.3.2.3 Ink Jet Printing of Cotton Fabric

All samples were ink jet printed with HP pigment based black ink except stated otherwise. The fabric samples (17 cm x 25 cm) were taped with a sticky tape on A4 size white bond paper as a backing material. A solid 15 cm x 20 cm rectangle with maximum print quality of 600 x 600 dpi (dots per inch) was printed using a Hewlett Packard (HP) 880C Deskjet printer. The print head is based on thermal Drop on Demand technology. The aqueous pigmented black ink supplied along with the printer by manufacturer was used for printing. The composition of the ink [332] is shown in the Table 3-6.

Table 3-6 Composition of the HP pigment based black ink

Component	Percent by Weight
Carbon black pigment	<5
Water	>70
Isopropyl alcohol	<2.5
2-pyrrolidone	<15

Cotton fabric samples were also printed as described above with Epson Stylus C65 printer based on piezoelectric Drop on Demand technology. The CMYK pigment based ink set [333] supplied along with the printer by the manufacturer was used for printing. Table 3-7 shows the compositions of CMYK inks.

Table 3-7 Composition of the Epson pigment based four colour inks

Component	Percent by Weight			
	Cyan	**Magenta**	**Yellow**	**Black**
Proprietary pigment Colourants	<5	5-10	5-10	<5
Proprietary Organic materials	10-15	15-20	10-15	15-20
Glycerol	15-20	10-15	10-15	10-15
Water	Balance	Balance	Balance	Balance

3.3.2.4 Post-Treatment of Ink Jet Printed Fabrics

3.3.2.4.1 Post-Treatment with Textile Binders

The ink jet printed cotton samples were padded separately with three binder solutions of different concentrations using a laboratory padder at 100% pick-up. The samples were dried at 110 ºC and cured at 150ºC for 5 minutes using Werner Mathis laboratory curing machine.

3.3.2.4.2 Post-Treatment with Chitosan and N- Carboxymethyl Chitosan

The ink jet printed cotton samples were padded with different concentrations of chitosan (CH82) solutions with 80% wet pick up, air dried and cured at 150ºC for 5 minutes. The same procedure was followed for application of N-carboxymethyl chitosan (NCMCH82).

3.3.2.4.3 Optical Microscopy

The migration of the pigments on the fibre surface after washing was examined using Zeiss Ultraphot microscope (Germany). The optical micrographs after padding and after washing were captured using a 3 MP (mega pixel) camera with 1280 x 1024 resolutions. PixeLINK Capture SE software was used for the analysis of the optical micrographs.

3.3.2.5 Spreading of Pigment Based Inks

The spreading of pigment based inks on cotton fabric was observed visually after chitosan post-treatment. Cotton fabric samples (17 cm x 25 cm) were taped with a sticky tape on A4 size white bond paper as a backing material. Three solid 5 cm X 10 cm rectangles with maximum print quality of 600 x 600 dpi (dots per inch) were printed using a Hewlett Packard (HP) 880C Desk jet printer and an Epson Stylus C65 printer. A dye based magenta ink supplied by the HP printer manufacturer was used for comparison. All the ink jet printed cotton samples were then padded with 1% chitosan solution (80% wet pick up), air dried and then cured at 150ºC for 5 minutes. The fabric samples printed with pigment based inks and post treated with chitosan were visually observed and compared with the fabric sample printed with dye based ink and post treated with chitosan. The aim of this subjective assessment was to visually observe to what extent pigment based inks spreads on the fabric as a result of chitosan post- treatment.

3.3.2.6 Colour Measurement of Ink Jet Printed Fabrics

The colour characteristics of printed samples were evaluated using a HunterLab colorQUEST II Reflectance Spectrophotometer with following settings: illuminant D65 and 10º Standard observer, Specular component included, Port size 30mm, reflectance mode. Premier Colorscan software was used for colour measurement.

3.3.2.6.1 Colour Strength (K/S)

The colour strength (K/S value) of dyed or printed fabrics is a measure of dye or pigment concentration on the fabric. It is calculated by measuring the K/S values of the dyed or printed fabrics with a spectrophotometer under a reflectance mode. This method was defined by Vickerstaff as “Direct Colourimetric Estimation”. The principle is based on Kubelka-Munk theory which gives the relationship between the K/S and R (reflectance) [349]. In the present study, the colour strength of the printed samples was calculated using the Kubelka-Munk equation:

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

Where, R= Reflectance of an incident light from the material,

K= Absorption Coefficient of the material

S= Scattering Coefficient of the material

All the K/S values in the present study were determined at the maximum absorption wavelength (λ_{max}) at which the reflectance value is the lowest.

3.3.2.6.2 Degree of Fixation (DF %)

The degree of fixation was calculated using following equation:

$$\mathbf{DF\% = \frac{K/S\ after\ washing^{*}}{K/S\ before\ washing^{*}} \times 100}$$

* Washing was carried out according to ISO 105-C06: 1994 (E) method [334]. C1M test conditions were used. The results of one C1M (multiple) test is considered equivalent to approximately five domestic or commercial launderings at temperatures not exceeding 60 ºC. No steel balls were used for fabrics made up of wool and silk. The test conditions are listed in the Table 3-8 below:

Table 3-8 Test conditions

Test Number	Temperature (^{0}C)	Liquor Volume (ml)	pH of the Soap Solution	Wash Time (minutes)	Number of Steel Balls
C1M	60	50	10.5 ± 0.1	45	50

3.3.2.6.3 Shade Difference

To measure the shade difference of the samples before and after washing, CIELAB L^* (lightness), a^*, b^* and C^* (chroma) were measured using spectrophotometer specified above. Colour Difference (ΔE^*) and Hue Difference (ΔH^*) were calculated using following equations:

$$\text{Colour Difference, } \Delta \mathbf{E}^* = \sqrt{(\Delta \mathbf{L}^*)^2 + (\Delta \mathbf{a}^*)^2 + (\Delta \mathbf{b}^*)^2}$$

$$\text{Hue Difference, } \Delta \mathbf{H}^* = \sqrt{(\Delta \mathbf{E}^*)^2 - (\Delta \mathbf{L}^*)^2 - (\Delta \mathbf{C}^*)^2}$$

3.3.2.7 Colour Fastness of Printed Fabrics

3.3.2.7.1 Colour Fastness to Rubbing

Fastness to rubbing of printed fabrics was assessed according to ISO 105-X12:1993. The tests were carried out on an AATCC crock meter- Model CM-5 (Atlas Electric Devices Company). Two fabric samples, one for dry rub and one for wet rub testing were cut into size 10 cm X 5 cm. A white cotton lawn (5 cm X 5 cm) was mounted on the tester and rubbed against the printed fabric samples for 10 cycles. The amount of colour transferred from the printed sample to the white cotton lawn was evaluated using ISO Gray Scales. The fabrics were ranked from 1 to 5 for staining, 5 being the best (no ink transfer) and 1 the worst. Three observers were selected for evaluation and rating of the staining and the average value were reported.

3.3.2.7.2 Colour Fastness to Laundering

The colour fastness to laundering was evaluated according to ISO 105-C06:1994 (E). C1M test conditions used were as follows: Temperature 60 ºC, pH of detergent solution 10.5, Time: 45 minutes. Number of Steel balls used: 50. No steel balls were used for silk and wool fabrics. The tests were carried out on an Atlas Launder-O-meter (Atlas Electric Devices Company). The test specimen was cut into size of 5.0 X 10.0 cm and was stitched at four sides with a multifibre (DW) fabric. Colour change and staining of the washed samples were evaluated using ISO Gray Scale for colour change and staining, respectively. The ECE Reference Detergent without optical brightener was used and its composition is shown in Table 3-9:

Table 3-9: Composition of ECE reference detergent

Composition	Mass fraction (%)
Linear sodium alkyl benzene sulphonate (mean length of alkane chain C11.5)	8.0 ± 0.02
Ethoxylated tallow alcohol (14 EO)	2.9 ± 0.02
Sodium soap, chain length $C_{12} – C_{16}$:13% - 26% $C_{18} – C_{22}$:74% - 87%	3.5 ± 0.02
Sodium tripolyphosphate	43.7 ± 0.02
Sodium silicate (SiO_2/Na_2O = 3.3/1)	7.5 ± 0.02
Magnesium silicate	1.9 ± 0.02
Carboxymethyl cellulose (CMC)	1.2 ± 0.02
Ethylene diamine tetra acetic acid (EDTA), sodium salt	0.2 ± 0.02
Sodium sulphate	21.2 ± 0.02
Water	9.9 ± 0.02

3.3.3 Factors Affecting the Degree of Fixation of Pigment Based Inks

For this set of experiments, HP pigment based black ink was used for ink jet printing on cotton fabric except as stated otherwise. Ink jet printing was carried out using Hewlett Packard (HP) 880C Desk jet printer with maximum print quality of 600 X 600 dpi (dots per inch). The cotton samples were printed as described in Section 3.3.2.3.

3.3.3.1 Effect of Molecular Weight (MW) of Chitosan on Degree of Fixation

In order to assess the effect of molecular weight on the degree of fixation, three chitosan samples with different molecular weight were chosen and are listed in the following Table 3-10. These chitosan samples were applied to the ink jet printed cotton fabric using two application methods, viz., pad-dry-cure method and pad-batch method. The former is commonly used for application of chemical finishes to textile fabrics while the latter is used for chemical pre-treatments of fabrics and for dyeing of cotton with reactive dyes.

Table 3-10 Chitosan samples with different molecular weight

Description	Degree of Deacetylation (DD %)	Molecular Weight (MW)	Viscosity in cps at 25^0C (as specified by the supplier)	Calculated Viscosity in cps at 25^0C (1% concentration)
CH90 Chitosan oligosaccharide	>90%	<5000	6	6
CH95 Low MW Chitosan	95%	150,000	43	24 cps
CH98 Medium MW Chitosan	98%	>375,000	>200	>200 cps

The general outline of the two processes is shown in Figure 3-1 and 3-2, respectively.

Figure 3-1 Pad-dry-cure process

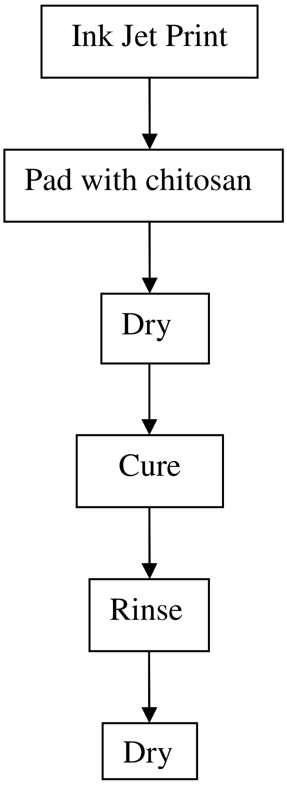
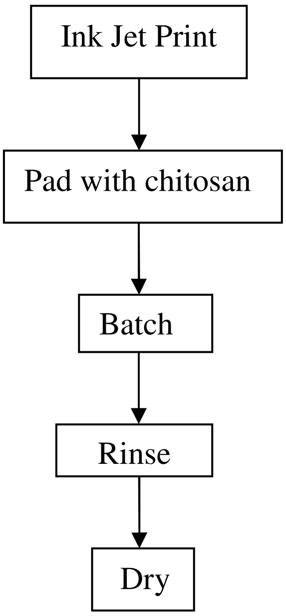


Figure 3-2 Pad-batch process



3.3.3.1.1 Pad-Dry-Cure Method

The padding solutions were prepared by dissolving 1 gm of the respective chitosan sample of different molecular weight in 100 ml of 1.5% (v/v) acetic acid to give a concentration of 10 $g.L^{-1}$. The padding solutions were stirred magnetically for 4 hours to ensure complete dissolution of chitosan samples.

The ink jet printed cotton samples were then padded with the chitosan solutions at 80% WPU on a laboratory padding machine (Ernst Benz AG).The padded samples were dried at 50°C for 5 minutes and then cured in a laboratory stenter (Werner Mathis AG) for 5 min at 150°C. The post-treated ink jet printed fabrics were rinsed with tap water until neutral to pH paper and air dried.

3.3.3.1.2 Pad-Batch Method

The ink jet printed cotton samples were also padded with each padding solution of chitosan (as described in Section 3.3.3.1.1) at 80% WPU and were kept in tightly sealed plastic bags at room temperature (23 ±2ºC) for 24 hours. After this, the samples were rinsed with tap water until neutral to pH paper and air-dried.

3.3.3.1.3 Determination of Viscosity Average Molecular Weight (M_v)

Chitosan solutions of different concentrations, viz., 0.0625, 0.125, 0.25, 0.5 and 1.0% in 0.1M acetic acid – 0.2M NaCl (1:1, v/v) were prepared. During preparation, all the solutions were magnetically stirred for 4 hours to ensure proper dissolution of chitosan and were filtered using Whatman filter paper grade 4. The Ubbelohde-type capillary viscometer (Canon-Fenske, No.OB) was used to measure the flow time of the solutions flowing through the capillary maintained at 25°C in a constant temperature water bath. The flow times of chitosan solutions at each concentration and of the solvent were recorded in triplicate and the average value calculated. The specific viscosity (η_{sp}) were calculated using following equation,

$$\eta_{sp} = \frac{t - t_s}{t_s}$$

Where t is a sample flow time and t_s is a solvent flow time.

The intrinsic viscosity [η] was obtained by extrapolating the linear regression of a Huggins plot of η_{sp}/c versus c, where c is concentration of chitosan solution (%), to zero concentration. The viscosity average molecular weight was calculated using the Mark-Houwink equation which determines relationship between intrinsic viscosity and molecular weight.

$$[\eta] = K\,(M_v)^a \text{ ----------- Mark-Houwink Equation}$$

Where, K and a are constants for a given solute-solvent system and temperature. The values of “K” and “a” used were 1.81 x 10^{-5} and 0.93, respectively [196].

3.3.3.2 Effect of Application Method of Chitosan on Degree of Fixation

Chitosan sample with molecular weight of 150,000 was used and was prepared as described in Section 3.3.3.1.1. The procedures were same as described in Section 3.3.3.1.1 and 3.3.3.1.2. For pad-dry-cure method, three different curing temperatures (110 ºC, 130 ºC and 150 ºC) were selected and for pad-batch method, the fabric samples were batched for three different durations (3 hours, 12 hours and 24 hours). The two methods were then compared in terms of whiteness index, degree of fixation, colour difference and colour fastness to wash and rubbing.

3.3.3.2.1 Whiteness Index

Heat causes degradation of cellulose through oxidation and chain scission. The aldehyde groups present in the oxidized cellulose are known to cause yellowing [335]. Moreover, studies have shown that chitosan causes yellowing of fabrics during heat treatment and that the yellowing varies from one chitosan sample to another [153, 324]. Therefore, the whiteness index of the fabrics treated with both, pad-dry-cure and pad-batch method, was determined.

The CIE-Whiteness Index for each fabric sample was measured using a Datacolor 600 spectrophotometer. Datacolor Tools version 1.1.1 software was used to calculate the whiteness index. The spectrophotometer settings were as follows:

Illuminant : D65/10^o
Reflectance Mode
Specular Component Included
Port Plate Size: 3 cm
UV-Filter Out
Measurement: Polychromatic

Each fabric sample was folded twice and three scans were performed at different places on the fabric surface. The average value was recorded.

The degree of fixation, colour difference and colour fastness to laundering and rubbing were evaluated according to procedures described in Sections 3.3.2.6.2, 3.3.2.6.3 and 3.3.2.7, respectively.

3.3.3.3 Effect of Concentration of Chitosan (MW 150,000) on Degree of Fixation

Seven concentrations (between 0.3 and 10 g.L^{-1}) of chitosan sample (MW 150,000) were prepared by dissolving chitosan in 1.5% (v/v) acetic acid. The solutions were stirred for 4 hours using magnetic stirrer. The ink jet printed cotton samples were padded with above prepared solutions at 80% WPU. The padded samples were dried at 50°C for 5 minutes and then cured in a laboratory stenter (Werner Mathis AG) for 5 min at 110°C. The post treated ink jet printed fabrics were washed with tap water until neutral (to pH paper) and air dried. The degree of fixation, colour difference and colour fastness to laundering and rubbing were evaluated according to procedures described in Sections 3.3.2.6.2, 3.3.2.6.3 and 3.3.2.7, respectively.

3.3.3.4 Effect of pH on Degree of Fixation

To study the effect of pH on degree of fixation, 3 grams of chitosan (MW 150,000) was dissolved in one litre of 1.5% (v/v) acetic acid to give solution with a concentration of 3 g.L^{-1}. Six different pH values (4.0, 5.0, 6.0, 7.0, 8.0 and 9.0) were selected and the pH was adjusted using 1N NaOH. The pH readings were noted using Leeds and Northrup 7411 pH meter at 21^{0}C. The pH values were also measured using Ajax Finechem pH paper. Ink jet printed cotton samples were treated with chitosan solution of different pH values by pad dry cure method as described in Section 3.3.3.1.1.

3.3.3.5 Effect of Depolymerisation of Chitosan on Degree of Fixation

Depolymerisation of chitosan (MW 150,000) was carried out by an autoclaving process at 121^{0}C and 120 Kpa as it is simple, time-saving and a homogeneous process. Briefly, solutions of chitosan at two concentrations (1 g.L^{-1} and 10 g.L^{-1}) were prepared in 1.5% (v/v) acetic acid. 200 ml of each chitosan solution was transferred to 250 ml of screw-capped glass bottles. These samples were introduced in an autoclave (SILTEX steam sterilizer) at 70°C and the temperature was raised to 121°C after closing the chamber. The samples were treated for 15 minutes and after autoclaving the bottles were immediately cooled in running tap water. The viscosity in centipoise (cps) of the chitosan solutions before and after autoclaving was determined by Shell Efflux Cup No.2.0 at 25^{0}C. The decrease in the viscosity was calculated using following formula:

$$\text{Viscosity decrease (\%)} = \frac{\mathbf{V_1 - V_2}}{\mathbf{V_1}} \mathbf{\times 100}$$

Where, V_1 = viscosity before autoclaving; V_2 = viscosity after autoclaving for 15 minutes.

After depolymerisation, the chitosan solutions were directly applied to ink jet printed cotton fabrics by the pad dry cure method described in Section 3.3.3.1.1. The whiteness index, degree of fixation, colour difference and colour fastness to laundering and rubbing were evaluated according to procedures described in Sections 3.3.3.2.1, 3.3.2.6.2, 3.3.2.6.3 and 3.3.2.7, respectively.

3.3.3.6 Effect of Plasticizer on Degree of Fixation

A chitosan (MW 150,000) solution was prepared by dissolving it in 1.5% (v/v) acetic acid to give final concentration of 3 g.L^{-1}. Glycerol was used as plasticizer and was added to the chitosan solution at three concentrations 20%, 60% and 100% (wt/wt). The glycerol content was based on the chitosan weight. The ink jet printed cotton fabrics were treated with above glycerol containing chitosan solutions by pad dry cure method as described in Section 3.3.3.1.1.

3.3.3.7 Effect of Textile Softeners on Degree of Fixation

Three commercial textile non-ionic softeners supplied by CHT, Germany are listed in Table 3-11. The softeners were selected because of their non ionic nature (to avoid interaction with cationic chitosan) and to cover the three principal softener classes used in industry.

Table 3-11 Textile softeners

Trade Name	Chemical Nature	pH
Tubisoft PCE	Ester softener	4-5
Tubisoft SEM	Silicone softener	4-5
Tubigat WAF 20	Multifunctional, consists of fixing agent, emulsifier and softener	9-10

A chitosan (MW 150,000) solution was prepared by dissolving it in 1.5% (v/v) acetic acid to give final concentration of 3 g.L^{-1}. The chitosan solutions were prepared by adding each softener at three different concentrations 10%, 50% and 100% (wt/wt) based on chitosan mass. The ink jet printed cotton fabrics were treated with softener containing chitosan solutions by pad dry cure method as described in Section 3.3.3.1.1.

3.3.4 Performance Properties of Ink Jet Printed Cotton Treated with Chitosan

The cotton fabrics ink jet printed with pigment based inks and post treated with 3 g.L^{-1} chitosan (MW 150,000) were evaluated for the following performance properties; stiffness, tensile strength and extension at break. The post-treatment with chitosan was carried out by pad-dry-cure method as described in Section 3.3.3.1.1. The stiffness of the cotton fabric samples (189 g/m^2) was evaluated using a SHIRLEY Stiffness Tester serial no. 133 (England) according to standard procedure of cantilever method (ASTM D1388-96). The samples were tested in warp direction. The stiffness was expressed in terms of flexural rigidity.

For tensile strength and extension at break testing, four cotton fabrics light cotton (110 g/m^2), heavy plain cotton (189 g/m^2), un-mercerized twill cotton (276 g/m^2) and mercerized twill cotton (276 g/m^2) were selected. The samples were tested using Instron series IX automated materials testing system 2.0. The Australian Standard AS4878.6-2001-(strip test) was used and the samples tested in the warp direction.

3.3.5 Laundering Durability of Ink Jet Printed Cotton Fabrics Post Treated with Chitosan

The cotton fabric (189 g/m^2) ink jet printed with HP pigment based black ink was post treated with 3 g.L^{-1} chitosan (MW 150,000) by the pad-dry-cure method as described in Section 3.3.3.1.1. The laundering durability of chitosan post treated cotton fabric for fixation of pigment based ink (HP black ink) was assessed according to ISO 105-C06: 1994 (E) method using an ATLAS Lauder-O-meter. C1M (multiple) test conditions were used. One cycle of C1M test is considered equivalent to approximately five domestic or commercial launderings at temperatures not exceeding 60 ºC. The ECE reference detergent without optical brightener was used. The ink jet printed and chitosan post treated cotton fabrics were subjected to 2, 4, 6, 8 and 10 laundering cycles which were equivalent to 10, 20, 30, 40 and 50 domestic launderings respectively.

3.3.6 Characterisation of Film Forming Ability of Chitosan

Scanning electron microscopy (SEM) was used to characterize the film formation and to observe the morphology of the chitosan treated cotton fabrics. An FEI Quanta 200 ESEM (Environmental scanning electron microscope) was used to obtain the images of the untreated and chitosan treated cotton fabrics.

3.3.7 Chemical Interaction between Chitosan and Cotton Fabric

3.3.7.1 Determination of Carboxyl Group Content in Cotton

Four different cotton fabrics were selected as shown in the Table 3-12 for determination of carboxyl group content in them.

Table 3-12 Fabric samples

Cotton Fabric Samples	Description
Heavy cotton fabric (189 g/m^2)	Desized, scoured and bleached
Light cotton fabric (110 g/m^2)	Desized, scoured and bleached
Cotton fabric (124 g/m^2)	Desized, scoured and bleached once
Cotton fabric (124 g/m^2)	Desized, scoured and bleached twice

The bleached cotton fabric (124 g/m^2) was bleached again with 7% (owf) hydrogen peroxide (strength 3%) for one hour at 90^{0}C. The bleaching was carried under acidic conditions at pH 5.0. This mild oxidation was carried out to generate more, new terminal aldehyde groups that impart a reducing oxycellulose character to the cotton [350].

The carboxyl group content in the above cotton fabrics was qualitatively determined by methylene blue test method. In brief, cotton samples (1 gram) were placed in separate conical flasks containing 50 ml of 1% methylene blue (C. I. Basic Blue 9) dye solution and shaken for 5 minutes at room temperature. The samples were then thoroughly rinsed with cold water and air-dried. The reflectance for all the samples with a standard illuminant D65 and 10^0 observer was measured using Datacolor 600 Spectrophotometer with datacolor Tools version 1.1.1 software. The K/S value, which depends on the presence of carboxyl groups, was calculated using Kubelka-Munk equation (Section 3.3.2.6.1).

3.3.7.2 FTIR-ATR (Fourier Transform Infrared-Attenuated Total Reflectance) Analysis

A Perkin Elmer FTIR spectrometer (1725X) with variable angle ATR accessory was used to provide a measure of the chemical interaction between chitosan and cotton fabric. Desized, scoured and bleached cotton fabric (189 g/m^2) was treated with 3 g.L^{-1} chitosan by pad dry cure method as described in Section 3.3.3.1.1. The FTIR-ATR analysis was performed on both untreated and chitosan treated cotton fabric.

3.3.8 Chitosan Post-Treatment of Different Ink Jet Printed Textile Fabrics

Different fabrics listed in Table 3-13 were ink jet printed with HP pigment based black ink. All the fabrics were then post treated with 3 g.L^{-1} chitosan (MW 150,000) by the pad dry cure method as described in Section 3.3.3.1.1. Prior to ink jet printing and chitosan application, all the fabrics were washed with 1 g.L^{-1} non-ionic detergent (Kierlon NB-MFB, BASF) for 30 minutes at 60^{0}C, rinsed with warm water and air-dried.

The desized cotton fabric was prepared by treating greige cotton fabric (125g/m^2) with 10 ml Enzylase U50, 40 ml of 10% sodium chloride and 12 ml of Teric N10 wetting agent

(10% solution) in 1 litre water at 60^0C for 30 minutes. The scoured cotton was prepared by treating the enzyme desized fabric with 3% NaOH (owf) and 0.05% non-ionic detergent (Kierlon NB-MFB, BASF) with 1:20 M:L ratio. The desized fabric was entered in the scouring liquor at 40^0C and the temperature was increased to 90^0C. At 90^0C, the fabric was scoured for another 30 minutes and then was rinsed twice with hot water and twice with cold water and finally air-dried.

Table 3-13 Fabric description

Fabric Type	Weight in g/m^2	Type of Weave
Desized, scoured and bleached heavy cotton	189	Plain
Desized, scoured and bleached light cotton	110	Plain
Desized cotton	124	Plain
Scoured cotton	124	Plain
50/50% Polyester/cotton	110	Plain
100% Polyester	50	Plain
Wool	230	Twill
Silk	25	Plain
Viscose	62	Plain

3.3.9 Fixation of Epson CMYK Inks with Chitosan Post-Treatment

Cotton fabric ((189 g/m^2) samples were printed with Epson CMYK inks as described in Section 3.3.2.3. These samples were then post treated with 3 g.L^{-1} chitosan (MW 150, 000) as described in Section 3.3.3.3.

3.3.10 Antimicrobial Activity of Ink Jet Printed and Chitosan Post Treated Cotton Fabric

Cotton fabric (189 g/m^2) was ink jet printed with HP pigment based black ink. After ink jet printing, the fabric was treated with 3 g.L^{-1} chitosan (MW 150,000) dissolved in 1.5% acetic acid by pad-dry-cure method as described in Section 3.3.3.3. The chitosan post-treated fabric was rinsed thoroughly in warm tap water and air-dried. The post-treated fabric was then subjected to different number of launderings according to ISO 105-C06: 1994 (E) C1M test method using ECE reference detergent without optical brightener.

The antimicrobial properties of the ink jet printed and chitosan post-treated cotton fabrics were evaluated according to ASTM E2149-01 [345] with a slight modification. This is a quantitative method designed to evaluate antimicrobial activity of samples treated with non-leaching antimicrobial agents under dynamic contact conditions. *Klebsiella Pneumoniae*

(ATCC 13883), a Gram-negative bacteria commonly found on the human body was chosen as a test organism. The test culture was suspended in a 5 ml nutrient broth, spread on a nutrient agar plate and incubated at 37^0C for 24 hours. Two single colonies were picked with an inoculating loop, suspended in a 5 ml nutrient broth and incubated at 37^0C for 18 hours. The culture solution was diluted to a final concentration of $7.5 \times 10^5 - 1.5 \times 10^6$ CFU/ml. This solution was used as a working bacterial solution. The untreated cotton fabric (control) and the ink jet printed and chitosan post-treated cotton fabrics subjected to different laundering cycles were used for the test.

Each fabric (1±0.1 gram) was cut into small pieces (1 x 1 cm). These fabric pieces were transferred to a 250 ml conical flask containing 70 ml of sterilised saline solution and 5 ml of working bacterial solution ($7.5 \times 10^5 - 1.5 \times 10^6$ CFU/ml). All the flasks were capped and shaken on a rotary wrist action shaker at 37^0C for 1 hour. After shaking, 10µl of the test solution was extracted, diluted and spread on a nutrient agar plate. The plates were incubated at 37^0C for 24 hours and the surviving cells counted. The average values of the duplicates were converted to the average colony forming units per millilitre (CFU/ml) of buffer solution in the flasks by multiplying by the dilution factor. The antimicrobial activity was expressed in terms of % reduction in the number of colonies and was calculated using the following equation:

$$\textbf{Reduction (\%)} = \frac{\textbf{(B-A)}}{\textbf{B}} \times \textbf{100}$$

Where,

A = surviving cells (CFU/ml) in the flasks containing chitosan treated cotton samples after 1 hour contact time

B = surviving cells (CFU/ml) in the flasks containing untreated cotton samples (control) after 1 hour contact time

3.3.11 Formulation of Ink Jet Inks Containing Chitosan

Two approaches were taken to formulate pigment based ink jet inks containing chitosan:

1. Direct incorporation of chitosan in the ink,
2. Preparation of chitosan encapsulated surface modified carbon black pigment nanoparticles and formulation of ink jet ink using the same.

3.3.11.1 Direct Incorporation of Chitosan to Formulate Pigment Based Ink Jet Inks

Chitosan (MW 150, 000) and the pigment dispersions listed in Table 3-4 were selected for the formulation of the ink jet inks.

3.3.11.1.1 Preparation of Chitosan Solution

A stock solution of 0.1% chitosan was prepared by dissolving 1 gm of chitosan in 1000 ml of 1.5% (v/v) acetic acid solution. Deionized water was used to prepare the chitosan solution.

3.3.11.1.2 Preparation of Pigment Dispersions

To formulate ink jet inks, the supplied pigment dispersions were further diluted by mixing 1% of each pigment dispersion with 99% of deionized water. These dispersions were magnetically stirred for one hour before use.

3.3.11.1.3 Preparation of Ink Jet Ink Formulations

A known amount of chitosan stock solution was added to deionized water while magnetically stirring the solution at a constant speed. After stirring for 20 minutes, glycerol was added followed by isopropyl alcohol. The solution was further stirred for 5 minutes and to this solution, a known amount of pigment dispersion prepared as described in Section 3.3.11.1.2 was added. The solution was further stirred for one hour. The pH of each ink formulation was found to be 4.0. Table 3-14 lists the four ink formulations prepared as described above. For the ink formulations without chitosan, the ink composition was adjusted with deionised water.

Table 3-14 Composition of ink jet ink formulations containing chitosan

Component	Percent (%)			
	Cyan 250C	Magenta 260M	Black 200	Black 300
Pigment dispersion	4	4	4	4
Chitosan	16	16	16	16
Isopropyl alcohol	5	5	5	5
Glycerol	5	5	5	5
Deionized water	70	70	70	70

Isopropyl alcohol is commonly used in ink formulations as a water miscible organic solvent. It was selected because it encourages bubble formation (an important requirement in thermal ink jet technology), inhibits foaming, acts as a degassing agent by enhancing removal of contaminant gases from ink jet ink, maintains appropriate surface tension of the ink, enhances uniform ink dot formation and enhances bonding of the ink with the substrate.

Glycerol was chosen as a high-boiling water miscible organic solvent. A high-boiling water miscible organic solvent is a solvent with a boiling point greater than that of water (> 100^0C) at 1 atmospheric pressure. The water and the high-boiling water miscible organic solvent form a eutectic mixture. The high-boiling water miscible solvent is believed to control the rate of evaporation of water from the ink and consequently maintains uniform dispersion of the pigment in the ink, even during and after formation of ink droplets. Glycerol also serves as a humectant which prevent clogging and plugging of jetting nozzles in ink jet printers [346].

3.3.11.1.4 Characterisation of Ink Jet Ink Stability

As mentioned in the literature review, the stability of ink jet inks is vital for the efficiency and economy of ink jet printing. Generally, the ink stability is evaluated by monitoring relevant properties of the ink over a period of time. In the present study, the ink stability was characterised in terms of change in particle size distribution, freeze/thaw cycling, pigment sedimentation and change in viscosity over a period of one month. Particle size distribution of the ink jet inks were measured immediately, one week and four weeks after the preparation of inks, using dynamic light scattering ALV particle size analyser. ALV Correlator Software Version 3.0 and ALV-Correlator Distribution Function Fit were used for the particle size analysis. For convenience, the particle size distribution for all the samples analysed by ALV particle size analyser were reported as mean particle size in the present study.

Freeze/thaw cycling was carried out by holding the inks for 24 hours at 20°C, followed by 24 hours at 60°C [29]. This whole process formed one cycle and was repeated four times. The inks after each cycle were tested for the change in the particle size distribution and were also examined visually for any pigment sedimentation.

The change in the viscosity of each formulated ink was measured using Shell Efflux Cup Number 2.0. Briefly, 200 ml of each ink sample was taken in a glass beaker and kept in a water bath maintained at 25°C. The Shell Cup Number 2.0 was submerged in the ink sample for approximately 30 seconds in order to allow the cup to reach the sample temperature. The cup was then lifted vertically out of the ink sample simultaneously starting the stop watch as the cup breaks the surface of the fluid. The time required for the cup to empty was recorded by stopping the watch just as the stream of ink breaks. The average of three readings for each ink sample was taken. The viscosity in centipoise (cp) was directly read from the appropriate conversion charts or calibration drawings.

3.3.11.1.5 Printing of Cotton with the Ink Jet Inks

As an illustration, the magenta inks with and without chitosan were prepared according to the general formulation (Table 3-14). These inks were jet printed on cotton fabric (189 g/m^2) using a HP Deskjet 880C printer based on thermal drop on demand technology. Before loading into the ink cartridges, the ink formulations were filtered through 0.5 micron PTFE (polytetrafluroethylene) LCR™ membrane filter (Millipore). The fabric samples were cut into 17 cm X 25 cm size and were taped with a sticky tape on A4 size white bond paper as a backing material. A solid 15 cm X 20 cm rectangle with maximum print quality of 600 X 600 dpi (dots per inch) was printed on the cotton samples. As the concentration of pigments used in the ink formulations was too low, the fabrics were repeatedly printed (6 pass) to build up the shade to acceptable level. The printed samples were cured in a laboratory stenter (Werner Mathis AG) for 5 min at 110°C.

3.3.11.1.6 Colour Characteristics of Ink Jet Printed Cotton Fabric

Colour characteristics such as colour strength (K/S) and shade difference were measured as described in Section 3.3.2.6.1 and 3.3.2.6.3, respectively. The degree of fixation of inks was calculated according to procedure described in Section 3.3.2.6.2.

3.3.11.1.7 Evaluation of Colour Fastness Properties of Ink Jet Printed Samples

The cotton fabrics ink jet printed with magenta ink formulations were evaluated for colour fastness to rubbing and laundering according to procedures described in Section 3.3.2.7.1 and 3.3.2.7.2.

3.3.11.2 Formulation of Ink Jet Ink using Chitosan Encapsulated Pigment Nanoparticles

For this set of study, chitosan (MW 150,000) and surface modified Cabojet 300 black pigments with carboxylated (COO^-) functionality were used for preparation of nanoparticles.

3.3.11.2.1 Preparation of Nanoparticles

The nanoparticles were prepared using complex coacervation of chitosan and surface modified cabojet black pigments. The complex coacervation was carried out according to the method reported by Mohanraj [348] with a slight modification. Briefly, chitosan solution was mixed with a solution containing the surface modified pigments at room temperature under magnetic stirring to form nanoparticles of desired particle size. Chitosan and surface modified pigments when mixed together undergo complex coacervation due to ionic interactions.

Chitosan solutions were prepared by dissolving various amount of chitosan in 1.5 % (v/v) acetic acid to obtain final chitosan concentrations of 0.1%, 0.3%, 0.5% and 1% (w/v).

Similarly, the carbon black pigment dispersion was diluted with deionised water to give final pigment concentrations of 0.1%, 0.3%, 0.5% and 1% (w/v). Variable volumes of chitosan solution (0.5, 1, 2, 3, 4, 5 ml) were added to 5 ml of pigment solution with magnetic stirring at a constant speed at room temperature for 15 minutes. The particle size distribution of all the samples was measured using dynamic light scattering ALV particle size analyser. ALV Correlator Software Version 3.0 and ALV-Correlator Distribution Function Fit were used for the particle size analysis. The samples were also visually examined for any sedimentation. The ratio that produced chitosan encapsulated pigment nanoparticles with desirable particle size was then used for the formulation of ink jet inks.

3.3.11.2.2 Preparation of Ink Formulation using Chitosan/Pigment Nanoparticles

The ratio of pigment to chitosan with lowest particle size (742 nm) was selected and 24 ml of solution containing chitosan/pigment nanoparticles was obtained according to procedure described in Section 3.3.11.2.1. This solution was filtered through 0.5 micron PTFE (polytetrafluroethylene) LCR™ membrane filter (Millipore) to remove the particles larger than 500 nm and any sediment. The filtered solution containing chitosan/pigment nanoparticles was stored over a period of one week to visually examine any further settling and sedimentation. The ink jet ink containing chitosan/pigment nanoparticles was formulated as given in Table 3-15.

Table 3-15 Composition of ink jet ink formulation containing chitosan encapsulated pigment nanoparticles

Component	Volume (ml)
Solution containing chitosan/pigment nanoparticles	24
Glycerol	5
Isopropyl alcohol	5
Deionized water	66

3.3.11.2.3 Ink Jet Printing with Ink Containing Chitosan/Pigment Nanoparticles

The ink containing chitosan/pigment nanoparticles was ink jet printed on cotton fabric (189 g/m^2) as described in Section 3.3.11.1.5. The cotton fabric was also ink jet printed with a blank ink containing only pigments as a reference. The degree of fixation of inks was calculated according to procedure described in Section 3.3.2.6.2. Colour strength (K/S) was measured as described in Section 3.3.2.6.1. The fastness to rubbing and laundering of the ink jet printed cotton fabrics were evaluated according to procedures described in Section 3.3.2.7.1 and 3.3.2.7.2.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter is organised as follows. The first part deals with the application of chitosan as a post-treatment for ink jet printed fabrics. The second part deals with the formulation of chitosan based ink jet inks.

PART I: CHITOSAN POST-TREATMENT OF INK JET PRINTED FABRICS

4.1 Determination of Degree of Deacetylation (DD) of Chitosan

The importance of determining degree of deacetylation and the methods used for the same has already been discussed in the literature review. Accurate determination of DD using FTIR, the methodology used for calculating the absorbance ratio and the selection of the infrared absorption bands has been an issue of much scientific debate. The peaks found in the absorption spectra are due to the types of bond present. Various researchers proposed different infrared absorption bands for determining DD. The use of a particular absorption ratio depends on and is limited to a particular deacetlyation range [250].

The infrared absorption spectra of all the commercial chitosan samples used in this study are shown in Figure 4-1 (a-e). All the Figures include the peaks with corresponding absorption values (cm^{-1}) used for calculation of DD. The IR absorption spectra pattern for all the commercial chitosan samples and the water soluble chitosan derivative are similar; differing only in the intensity of their bands. Among the chitosan samples (CH90, CH95, CH98, CH82 and NCMCH82), amide bands (at 1655 cm^{-1}) decrease with increasing DD. Similar trends were observed by Miya *et al.* [167] and Raut [250] in their respective studies. The chitosan sample (CH98) whose DD is higher than CH90 and CH95 showed lower absorbance at 1655 cm^{-1}. However, CH82, which had DD of 82% as specified by manufacturer showed lower absorbance than CH90, CH95 and CH98. This anomaly may be due to the different protocol used by the manufacturer to determine DD or the source of chitosan sample or presence of impurities.

Figure 4-1 (a) IR spectra for CH90

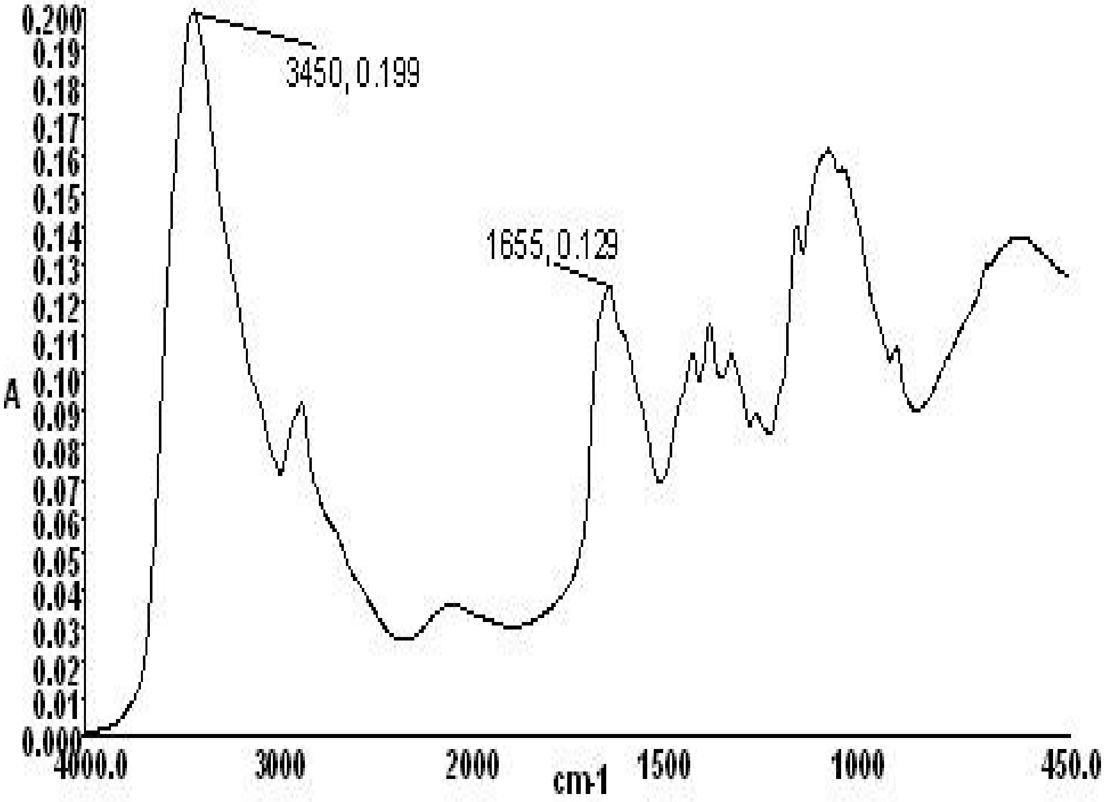


Figure 4-1 (b) IR spectra for CH95

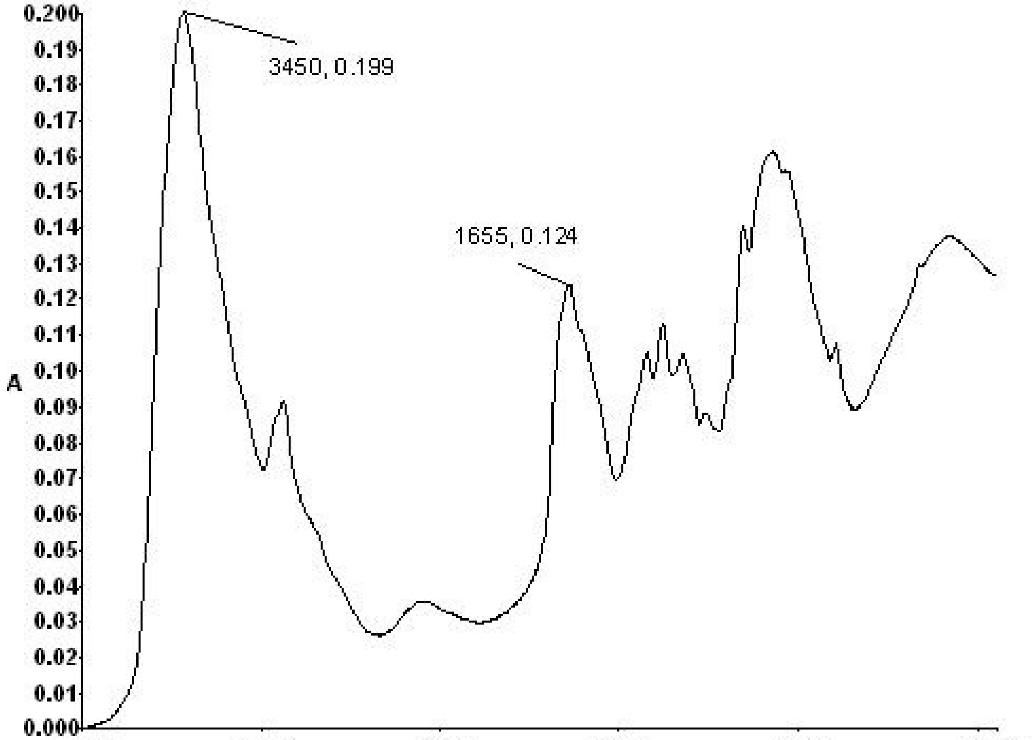


Figure 4-1 (c) IR spectra for CH98

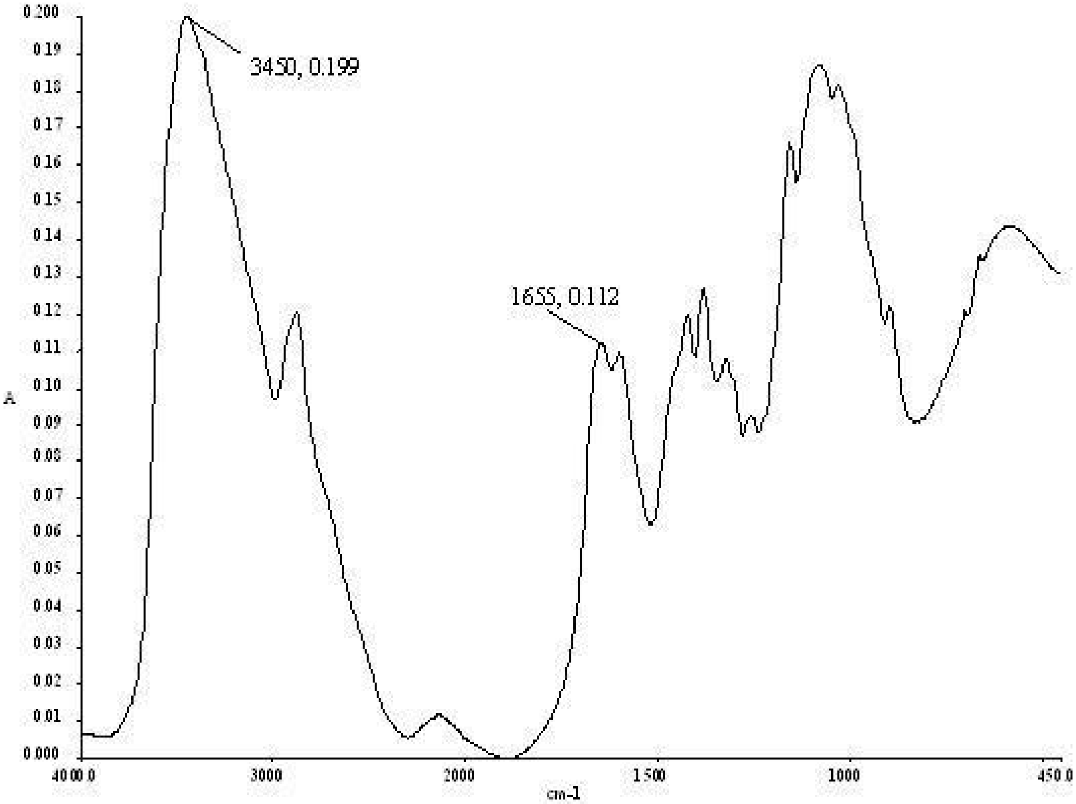


Figure 4-1 (d) IR spectra for CH82

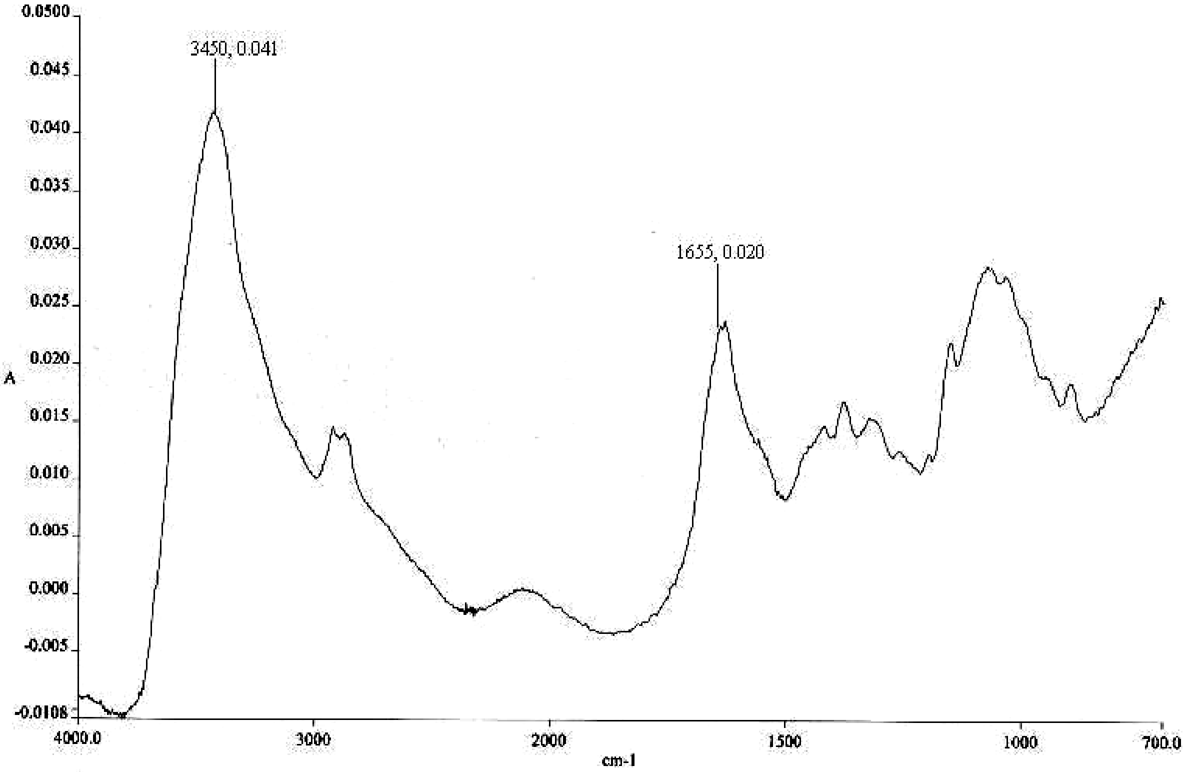
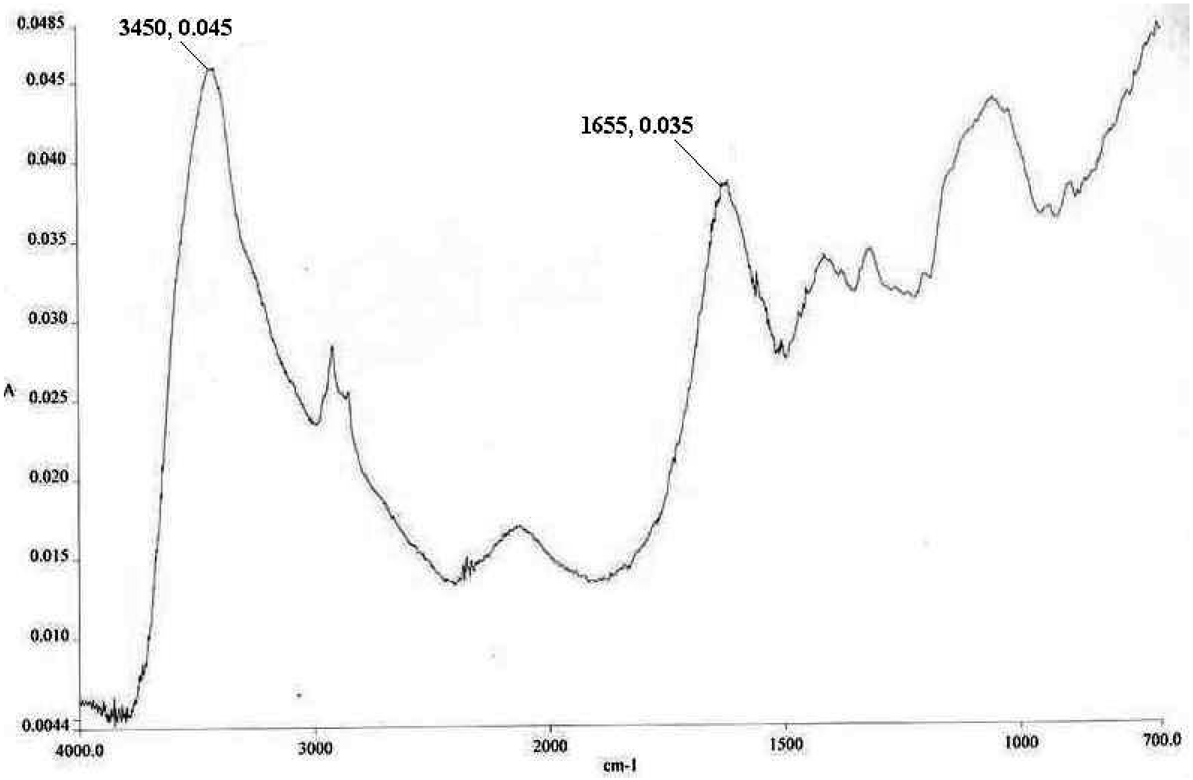


Figure 4-1 (e) IR spectra for NCMCH82



The DD's of chitosan samples calculated using absorbance ratio as per three different protocols and are shown in Table 4-1.

Table 4-1 DD (%) of commercial chitosan samples calculated as per different protocols

DD Specified by supplier	Domzy and Roberts [168]	Baxter [169]	Raut [250]
CH90	51.3	25.5	92.9
CH95	53	28.3	93.9
CH98	57.9	35.6	96.3
CH82	61.5	43.9	99.3
CMCH82	39.9	10.6	87.6

The protocols proposed by Baxter [168] and Domzy & Roberts [169] did not give similar DD (%) values as reported by the supplier. The protocol proposed by Raut [250] was fairly accurate for all the samples except for CH82. This could be due to different sources of chitosan samples. According to Raut, the presence of water in the chitosan samples might interfere with the analysis contributing towards the intensity of the hydroxyl bond. Raut suggested that a consistent equipment setup and thoroughly dried samples would eliminate the inconsistencies during FTIR analysis. In the present study, consistency in the equipment set up and thorough drying of chitosan samples were carefully ensured. The other reason could be the choice of baseline for the amide band I in the formula that uses absorption ratio A_{1655}/A_{3450} for calculation of DD. However, this issue is controversial and it has been found that the absorption ratio A_{1655}/A_{3450} and A_{1555}/A_{3450} give accurate results for chitosan samples with low DD% while A_{1655}/A_{2867} gives accurate results for samples with higher DD%.

Tan *et al.* [251] compared most of the available methods for determination of DD. They advocated first derivative UV-spectrophotometry for determining DD but the limitation of this method is that it requires good solubility of chitosan samples. After decades of research, there is no standard method for the determination of DD of chitosan samples.

FTIR is a fast, easy and fairly accurate method for determination of DD of chitosan samples. In our study, it was found that the protocol proposed by Raut [250] was reasonably accurate for chitosan samples with DD ≥ 90%. This protocol should be further investigated to establish its accuracy in determining DD of chitosan samples over a broad deacetylation range. It would be helpful if the suppliers of chitosan specify the method used for determination of DD and the researchers first corroborate it using the method specified by the supplier and later using FTIR method.

4.2 Assessment of Chitosan and its Derivative for Fixation of Pigment Based Inks on Cotton Fabric

The experiments were conducted as described in Section 3.3.2 to assess the ability of chitosan and its water soluble derivative to fix pigment based inks on cotton.

4.2.1 Spreading of Inks

The ink jet printed cotton fabrics were visually observed for ink spreading after chitosan post-treatment (Table 4-2).

Table 4-2 Spreading of ink after chitosan post-treatment

Fabric samples printed with	*Observation after chitosan post-treatment*
HP dye based magenta ink (Control)	Slight spreading
HP pigment based Black ink	No spreading
Epson pigment based Cyan ink	No spreading
Epson pigment based Magenta ink	No spreading
Epson pigment based Yellow ink	No spreading
Epson pigment based Black ink	No spreading

The HP dye based magenta ink showed slight spreading. No ink spreading was observed in case of the samples printed with either HP black ink or Epson CMYK inks. Contrary to most of the dyes, pigments are insoluble in water. Due to their insolubility, no pigment ink spreading was observed during padding with textile binder solutions and chitosan solutions. This shows that chitosan post- treatment does not affect the print sharpness of cotton fabrics ink jet printed with pigment based inks.

4.2.2 Post-Treatment with Commercial Textile Binders

Cotton samples were ink jet printed with HP pigment based black ink. The samples were then post treated as described in Section 3.3.2.4.1. The colour strength and the degree of fixation of the post treated fabrics are shown in Table 4-3.

Table 4-3 Effect of different textile binders on degree of fixation

Textile Binders (concentration 50 g.L^{-1})	K/S		Degree of Fixation (DF %)
	Before washing	After washing	
Control (without post-treatment)	6.3	1.5	23.8
Tubiprint binder AUS	5.4	3.8	71.2
Tubicoat DB 314	5.7	4.7	81.9
Tubiprint binder AS30	6.3	5.5	87.4

Most commercial pigment binders are copolymers. These are obtained by emulsion copolymerisation of vinyl based monomers. These binders possess side chain functional groups capable of forming films which encapsulate and adhere pigments to fabrics by cross-linking [336].The results obtained demonstrate that the textile binders were able to fix the ink in comparison with the control fabric (without post-treatment). Tubiprint binder AS30 showed the highest degree of fixation while Tubiprint binder AUS showed the lowest among the three. The lower fixation by Tubiprint binder AUS was not surprising as it is an ester. Esters have ability to participate in hydrogen bonding which makes them more water soluble. Hence, the film formed by this binder has moderate water resistance compared to other binders [337].

Tubicoat DB314 is a copolymer containing butadiene which is known to provide flexibility and soft handle to the printed fabrics. Also, butadiene based binders have poor wash fastness and hence the low fixation value compared to Tubiprint binder AS30.

Table 4-4 shows the colourimetric data for unwashed and washed samples treated with the different textile binders. The results are quite obvious as the samples treated with Tubiprint binder AS30 showed low colour difference value due to high degree of fixation and high colour difference in case of Tubiprint binder AUS due to low degree of fixation. From the ΔH^* values, there was almost no change in hue of all the samples. In all the cases, the prints were slightly duller and less yellow than the unwashed counterpart. Tubiprint binder AS30 showed better wash and rubbing fastness compared to other binders used (Table 4-5).

Table 4-4 Effect of binders on colourimetric values of washed and unwashed samples

Textile Binder	Sample	K/S	L^*	a^*	b^*	C^*	ΔE^*	ΔH^*
Tubiprint binder AUS	unwashed	5.4	35.3	0.3	1.6	1.7	4.9	-0.13
	washed	3.8	35.2	0.5	1.6	1.7		
Tubicoat DB 314	unwashed	5.7	33.6	0.8	1.1	1.6	2.4	-0.06
	washed	4.7	33.5	0.4	0.7	1.6		
Tubiprint binder AS30	unwashed	6.3	33.0	0.3	1.6	1.6	1.8	-0.06
	washed	5.5	33.0	0.4	1.5	1.6		

Table 4-5 Wash and rub fastness of the samples post treated with textile binders

Textile Binder	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Tubiprint binder AUS	4-5	2-3	3-4	4-5	4-5	4-5	4-5	4-5	4-5
Tubicoat DB 314	4-5	2-3	3-4	4-5	4-5	4-5	4-5	4-5	4-5
Tubiprint binder AS30	4-5	3	4	4-5	4-5	4-5	4-5	4-5	4-5

a ISO Grey Scale for staining assessment (illuminant D_{65})

b ISO Grey Scale for colour change assessment (illuminant D_{65})

4.2.3 Effect of Binder Concentration on Degree of Fixation

Based upon the previous results, Tubiprint binder AS30 was selected to investigate the effect of its concentration on degree of fixation. The results are shown in Table 4-6. The increase in concentration from 50 to 100 $g.L^{-1}$ increased the degree of fixation of pigments. But the fixation decreased as the concentration was further increased to 150 $g.L^{-1}$. This may have been due to saturation of sites for cross-linking and the removal of the pigments entrapped or loosely held in the unfixed film structure during washing.

Table 4-6 Effect of binder concentration on degree of fixation

Tubiprint Binder AS30 Concentration	K/S		Degree of Fixation (DF %)
	Before washing	After washing	
50 g.L^{-1}	6.3	5.5	87.4
100 g.L^{-1}	5.7	5.5	96.1
150 g.L^{-1}	5.8	5.0	85.7

The colour difference was minimal at 100 g.L^{-1} concentration suggesting minimum loss of pigment and corroborating high fixation (Table 4-7). There was no change in hue at all concentrations but the prints were slightly duller and less yellow than the unwashed samples.

Table 4-7 Effect of Tubiprint binder AS30 concentration on colourimetric values

Tubiprint Binder AS30 (g.L^{-1})	Sample	K/S	L*	a*	b*	C*	ΔE*	ΔH*
50	unwashed	6.3	33.0	0.3	1.6	1.6	1.8	-0.1
	washed	5.5	33.0	0.4	1.5	1.6		
100	unwashed	5.7	33.7	0.8	1.0	1.3	0.7	-0.5
	washed	5.5	32.6	0.8	-0.2	0.8		
150	unwashed	5.8	33.5	0.8	1.1	1.4	1.6	-1.0
	washed	5.0	32.6	0.4	0.3	0.9		

The increase in the binder concentration did not show any significant effect except that the wet rub fastness increased by one point at 150 g.L^{-1} binder concentration (Table 4-8). This is believed to be due to the increase in the amount of binder deposition on the post-treated fabrics.

Table 4-8 Effect of binder concentration on colour fastness of cotton fabric

Tubiprint Binder AS30 (g.L^{-1})	Rubbing Fastness^a		Wash Fastness						
				Staining^a					
	Dry	Wet	Colour Change^b	Cellulose acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
50	4-5	3	4	4-5	4-5	4-5	4-5	4-5	4-5
100	4-5	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
150	4-5	4	4	4-5	4-5	4-5	4-5	4-5	4-5

4.2.4 Effect of Chitosan Concentration (CH82) on Degree of Fixation

Henceforth, Tubiprint binder AS30 (100 g.L^{-1}) was used as control for comparative analysis with chitosan (CH82) and N-carboxymethyl chitosan (NCMCH82).

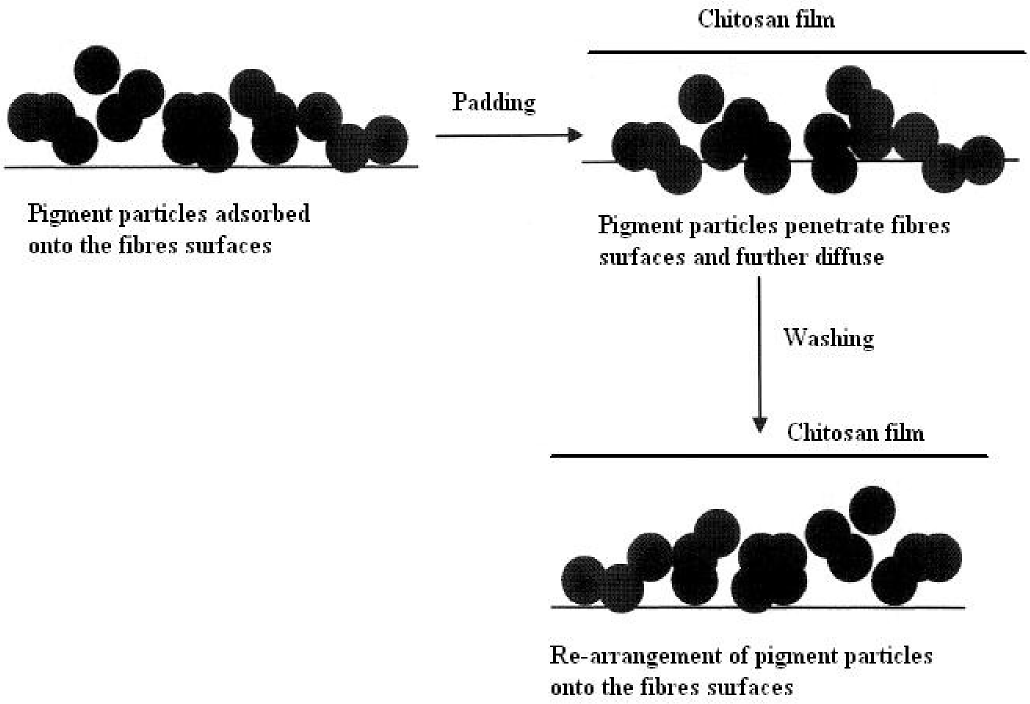
Table 4-9 Effect of chitosan concentration on degree of fixation

Chitosan Concentration	K/S		Degree of Fixation (%)
	Before washing	After washing	
control (Tubiprint AS30)	5.7	5.5	96.1
5 g.L^{-1}	5.2	4.0	76.5
10 g.L^{-1}	5.1	5.4	105.5
15 g.L^{-1}	5.2	5.6	107.7
20 g.L^{-1}	5.5	5.9	107.7

The results from Table 4-9 show that chitosan acts in a manner similar to a conventional binder. That is, it can form clear and strong films thereby encapsulating the pigments on the fabric. The fixation increased with increasing chitosan concentration. This result may be attributed to the increase in the amino groups in chitosan resulting in greater inter chain attraction which may have resulted in denser entanglement network during film formation. The concentration of chitosan from 10 g.L^{-1} and above showed a higher degree of fixation compared to the conventional binder.

The chitosan treated samples showed increased K/S values after washing and therefore higher fixation values exceeding 100%. This may have occurred because during padding the pigments deposited on the fabric surface may have been pressed into the interior of the fabric structure due to pressure of the padding rollers. This may have lead to decreased initial K/S values before washing. Due to mechanical action during washing, the pigments may have migrated back to the fabric surface. Also, the strong film formed by chitosan on the fabric surface may have held the pigment on the fabric surface causing redistribution of pigment on the fabric surface and thereby preventing their loss into the wash liquor (Figure 4-2(a)).

Figure 4-2 (a) Proposed penetration and re-distribution of pigment particles



In order to validate the theory described above, optical micrographs after padding and after washing were obtained and analysed as described in Section 3.3.2.4.3. In the Figure 4-2 (b) and (c), the carbon black pigments can be clearly seen on the surface of the yarns. It is evident that the amount of the carbon black pigments on the surface of the yarns increased after washing due to the pigment migration thereby increasing the K/S value.

Figure 4-2 (b) Optical micrograph of cross-section of yarns after padding

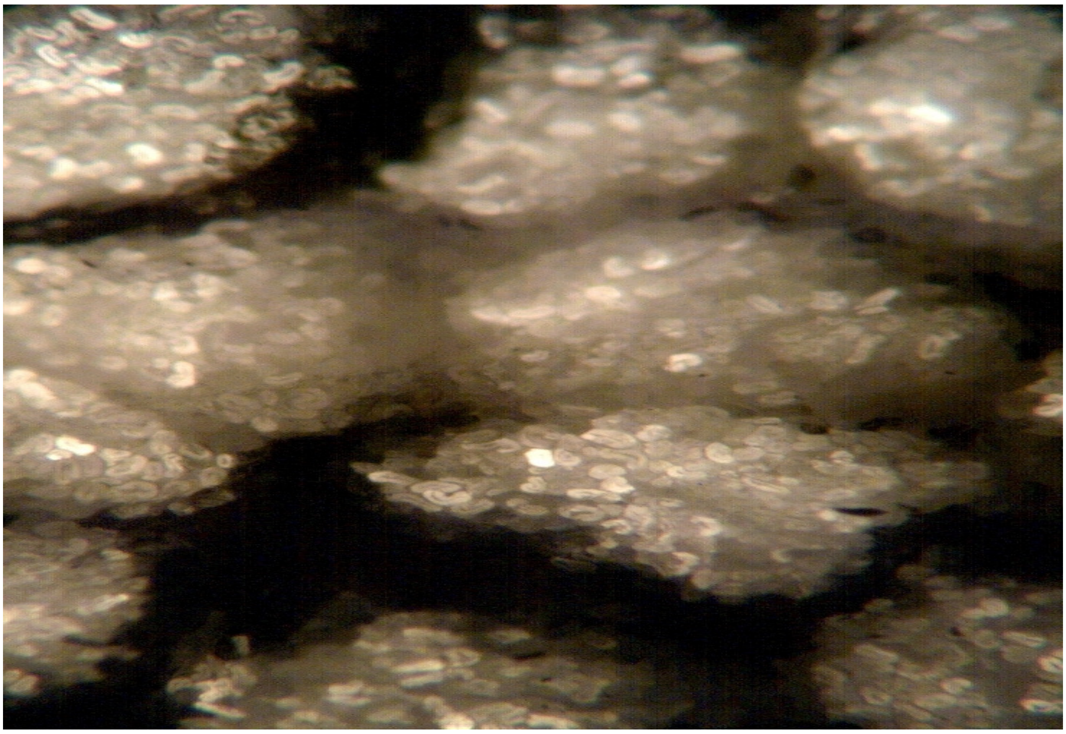
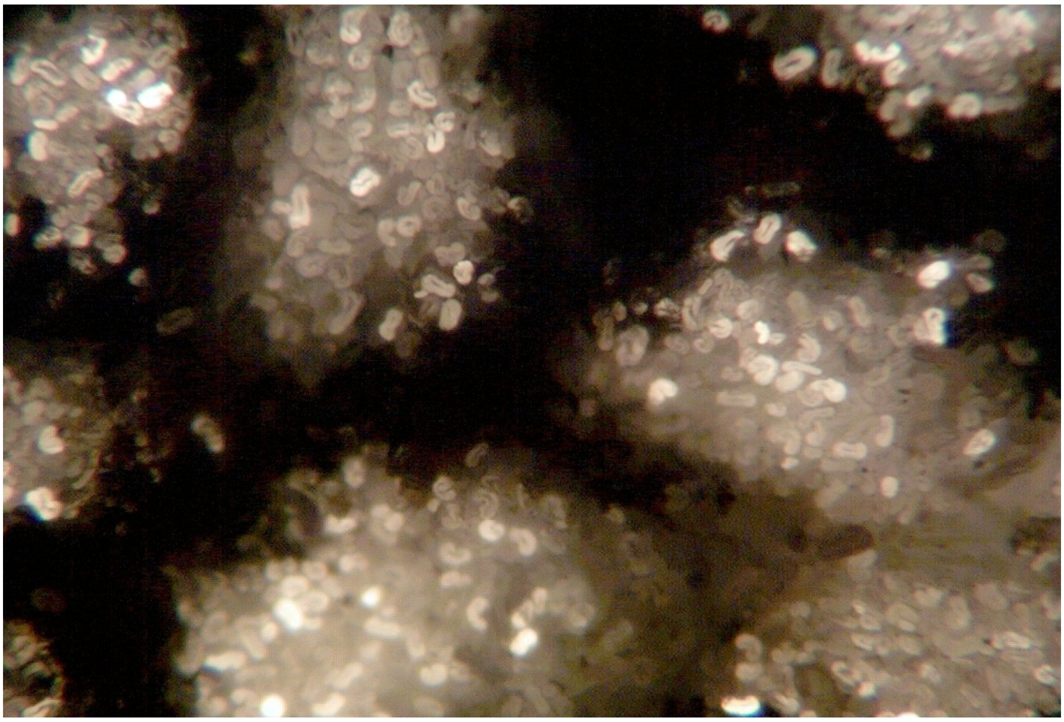


Figure 4-2 (c) Optical micrograph of cross-section of yarns after washing



Another possibility is that chitosan is cationic in nature and may have had attracted the pigments which generally carry an anionic charge on their surface. Chitosan might also have facilitated pigment migration into the interstices of the fabric. On washing, the pigments may have migrated back on the surface thereby increasing the colour strength.

This did not occur in case of Tubiprint binder AS30 as it may not have formed film as strong as chitosan and would have been slightly removed during washing thereby causing some pigment loss. The visual observation of after wash liquor showed that there was no pigment loss in case of samples treated with chitosan at concentration ≥10 g.L^{-1}. However, pigment loss was observed in case of ink jet printed samples treated with 5 g.L^{-1} chitosan and those treated with Tubiprint binder AS30 (control).

Table 4-10 and 4-11 shows the colourimetric data of chitosan treated samples before and after washing, wash and rub fastness respectively. Again there was no change in hue but the prints were brighter and yellower than the unwashed counterparts in case of all the chitosan concentrations except for 5 g.L^{-1} concentration. This might have occurred due to the re-arrangement or re-distribution of pigments on the fabric surface due to mechanical action during washing. In case of 5 g.L^{-1} concentration the colour difference value was too high suggesting marked shade difference. Also, the wet rub fastness was poor. This again is due to insufficient amount of chitosan to provide enough cross-linking to bind the pigments to the fabric. The wet rub fastnesses at other concentration levels were at a near commercially acceptable level.

Table 4-10 Effect of chitosan concentration on colourimetric values

Chitosan Concentration (g.L^{-1})	Sample	K/S	L*	a*	b*	C*	ΔE*	ΔH*
5	Unwashed	5.2	36.1	0.2	2.0	2.0	3.1	-0.10
	Washed	4.0	35.7	0.2	1.7	1.7		
10	Unwashed	5.1	36.2	0.2	1.7	1.7	0.6	0.04
	Washed	5.4	36.3	0.2	1.8	1.9		
15	Unwashed	5.2	36.0	0.2	1.6	1.6	0.9	0.05
	Washed	5.6	36.2	0.2	1.9	1.9		
20	Unwashed	5.5	35.4	0.2	1.8	1.8	0.7	0.05
	Washed	5.9	35.6	0.2	2.0	2.1		

Table 4-11 Effect of chitosan concentration on colour fastness of cotton fabric

Chitosan Concentration (g.L^{-1})	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
5	3-4	2	3-4	4-5	4-5	4-5	4-5	4-5	4-5
10	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
15	4-5	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
20	4-5	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.2.5 Effect of N-Carboxymethyl Chitosan (NCMCH82) on Degree of Fixation

Chitosan (CH82) is soluble in acetic acid. N-carboxymethyl chitosan derivative (NCMCH82) was selected because of its solubility in water at all pH values. It was compared with commercial textile binder (Tubiprint AS30) in terms of degree of fixation. Table 4-12 shows the effect of pH of NCMCN82 padding solution (20 g.L^{-1}) on the degree of fixation.

Table 4-12 Effect of pH of NCMCH82 padding solution on degree of fixation

pH of NCMCH82	K/S		Degree of Fixation (DF %)
	Before washing	After washing	
Tubiprint AS30 (control)	5.7	5.5	96.1
5.0	4.7	3.1	65.1
7.0	5.3	3.9	74.2
9.5	5.2	3.8	73.3

As can be seen the fixation was low compared to the Tubiprint binder AS30. This might be attributed to the water solubility of chitosan derivative. Also, the fixation improved slightly as pH increased from acidic to neutral but increasing the pH further to 9.5 had a negligible effect. N-carboxymethyl chitosan exists in different forms at different pH levels [257]. At pH 7.0, NCMCH exists as a mixture of fully dissociated ($-NH-CH_2COO^-$) and monodissociated ($-NH-CH_2-COOH \leftrightarrow -N^+H_2-CH_2COO^-$) forms. We postulate that one of the forms may have a favourable effect on the film formation. It may also depend on the ratio of these two forms.

4.2.6 Effect of Chitosan (CH82) on Fixation of Epson CMYK Inks

Chitosan (CH82) was used for the post-treatment of the cotton fabric ink jet printed with the Epson four colour inks. Although, highest fixation (107.7%) was achieved with 15 $g.L^{-1}$, 10 $g.L^{-1}$ concentration was selected as there was not much difference in the fixation values between both the concentrations. The Epson inks are composed of pigments encapsulated or coated with a polymer. In order to determine the effect of the coated polymer on the fixation of Epson four colour inks, the inks were ink jet printed on cotton and the fabric samples were subjected to washing after curing at 150 ºC for 5 minutes and also after post-treatment with chitosan by pad-dry-cure (150 ºC for 5 minutes) method. The results are summarised in Table 4-13. It was suspected that the polymer used for encapsulation of the pigments in the Epson inks might fix the inks to the cotton after curing.

Table 4-13 Effect of chitosan post-treatment on fixation of Epson inks

Epson Inks	Degree of Fixation (%)	
	Cured only	Chitosan post-treated
Cyan	6.4	98.5
Magenta	43.1	99.0
Yellow	14.3	99.7
Black	80.8	99.4

As can be seen, the polymer used by the manufacturer for the micro-encapsulation of pigments did not show significant effect on fixation except for the black ink. This may be the case because the polymer used as coating for encapsulation of pigments of the black ink may be different from those used as coating for other pigments. However, chitosan post-treatment significantly enhanced the fixation to almost 100% in case of all the inks. This illustrates the effectiveness of chitosan in enhancing the fixation of inks irrespective of the composition of the inks. The wash and rub fastness of samples printed with Epson inks and post treated with and without chitosan are shown in Table 4-14. Both dry and wet rub fastness was improved to commercially acceptable levels with the chitosan post-treatment. The wash fastness for cyan and yellow ink without chitosan post-treatment was poor, whereas it was good to excellent with chitosan post treated samples.

Table 4-14 Effect of chitosan on colour fastness of samples printed with Epson inks

Epson Inks		Rubbing Fastness[a]		Wash Fastness						
		Dry	Wet	Colour Change[b]	Staining[a]					
					Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Cyan(C)	Cured only	3	1	2	3-4	2	3	3	2-3	3
	Chitosan treated	4	2-3	4-5	4-5	3-4	4-5	4-5	4-5	4-5
Magenta (M)	Cured only	3	2	3	4	4	4	4	4	4
	Chitosan treated	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Yellow (Y)	Cured only	3	1	2	2-3	2-3	2-3	2-3	2-3	2-3
	Chitosan treated	4	2-3	4-5	4-5	4	4-5	4-5	4-5	4-5
Black (K)	Cured only	3	1-2	3-4	4	4	4	4	4	4
	Chitosan treated	4	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

From the above results, it is clear that chitosan can fix, on cotton, commercial pigment based inks developed for paper printing. Furthermore, chitosan post-treatment gave the enhanced fixation of pigment based inks on ink jet printed cotton fabric compared to commonly used commercial textile binders (Table 4-9). This can be attributed to the ability of chitosan to form a coherent, durable binding film thereby encapsulating pigments and holding them to the cotton fabric. N-carboxymethyl chitosan was not as effective as chitosan due to its water solubility. As the chitosan sample used in above set of experiments was of medium molecular weight, the handle was significantly affected and the fabrics were found to be stiff.

4.3 Factors Affecting Degree of Fixation of Pigment Based Ink Jet Inks

Before utilizing chitosan for the formulation of pigment based ink jet inks, it was considered important to further investigate different factors affecting the degree of fixation of pigment based inks with chitosan on cotton fabric.

4.3.1 Effect of Chitosan Molecular Weight (MW) on Degree of Fixation

4.3.1.1 Pad-Dry-Cure Method

The effect of the molecular weight of chitosan on the degree of fixation of the pigments on cotton treated by pad-dry-cure method is shown in Figure 4-3 and Table 4-15. It can be seen that the degree of fixation significantly decreased for chitosan oligosaccharide with molecular weight less than 5000. The fixation was slightly above 100% for chitosan samples with molecular weight 150,000 and >375,000 respectively. Although the degree of deacetylation for all the samples was above 90%, the results suggest that the molecular weight of chitosan significantly affects its film forming ability. In the case of chitosan oligosaccharide, the molecular weight was not sufficient enough to undergo adequate cross-linking for durable film formation.

Figure 4-3 Effect of chitosan MW on degree of fixation, pad-dry-cure method

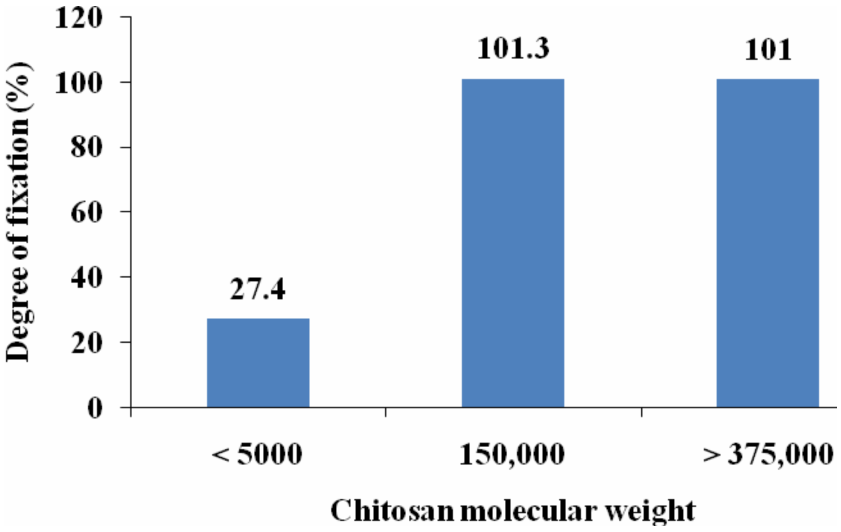


Table 4-15 Effect of chitosan MW on degree of fixation (pad-dry-cure)

Chitosan Sample	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
CH90, Oligosaccharide (< 5000)	5.4	1.5	27.4	19.9
CH95, Low MW (150,000)	5.3	5.4	101.3	0.2
CH98, Medium MW (>375,000)	5.4	5.5	101.0	0.1

Table 4-16 shows the effect of chitosan MW on colour fastness properties of ink jet printed cotton fabric. The results reinforce the proposition that at a low molecular weight (<5000) there is insufficient cross-linking to bind the pigment within the chitosan film.

Table 4-16 Effect of chitosan MW on colour fastness of cotton fabric (pad-dry-cure)

Chitosan MW	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
<5000	3	1-2	1-2	4-5	4-5	4-5	4-5	4-5	4-5
150,000	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
>375,000	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.3.1.2 Pad-Batch Method

The pad-batch method showed similar results to pad-cure method (Figure 4-4 and Table 4-17). The wash and rub fastness results are shown in Table 4-18.

Figure 4-4 Effect of chitosan molecular weight on degree of fixation (pad-batch)

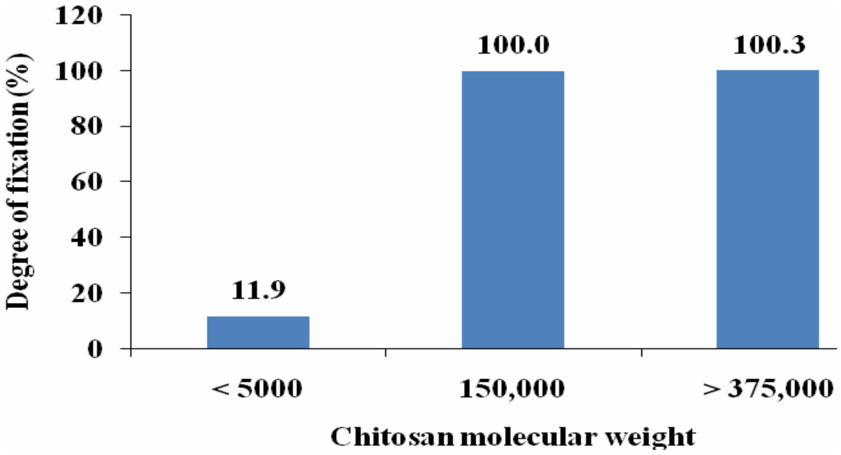


Table 4-17 Effect of chitosan molecular weight on degree of fixation (pad-batch)

Chitosan Sample	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
CH90, Oligosaccharide (< 5000)	5.5	0.7	11.9	32.8
CH95, Low MW (150,000)	5.3	5.3	100.0	0.1
CH98, Medium MW (>375,000)	5.4	5.4	100.3	0.1

Table 4-18 Effect of chitosan MW on colour fastness of cotton fabric (pad-batch)

Chitosan MW	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
<5000	2-3	1-2	1-2	4-5	4-5	4-5	4-5	4-5	4-5
150,000	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
>375,000	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

From this data we conclude that the molecular weight of chitosan had significant effect on the binding ability of chitosan. However, the method of application of the chitosan, viz. pad-dry-cure or pad-batch had no significant effect on the binding ability of the chitosan.

In order to study the effect of chitosan oligosaccharide concentration, ink jet printed cotton samples were further treated with chitosan oligosaccharide at 50 g.L^{-1} concentration with both the pad-cure (150^{0}C) and pad-batch (24 hours) methods. Results are shown in Table 4-19. Increasing the concentration of chitosan oligosaccharide from 10 g.L^{-1} to 50 g.L^{-1} only slightly increased the degree of fixation.

Table 4-19 Effect of concentration of chitosan oligosaccharide on degree of fixation

Method	Concentration (g.L^{-1})	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
		Before washing	After washing		
Pad-Cure	10	5.4	1.5	27.4	19.9
	50	5.2	1.7	33.4	17.2
Pad- Batch	10	5.5	0.7	11.9	32.8
	50	5.0	0.8	16.2	28.9

From the above results, chitosan sample with molecular weight 150,000 was chosen for further evaluation and study.

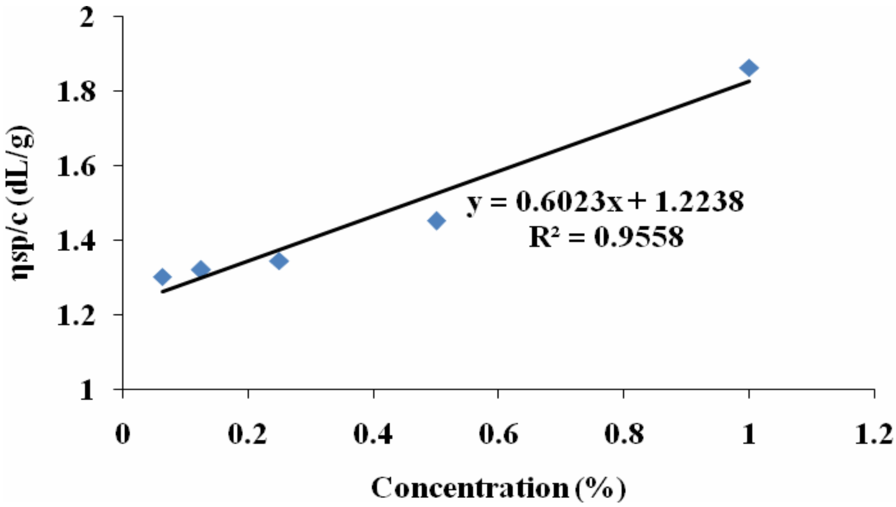
4.3.1.3 Determination of the Viscosity Average Molecular Weight (Mv) of Chitosan

The molecular weight of the chitosan sample chosen for further studies was that as specified by the manufacturer viz. 150,000. Before further studies, it was considered necessary to confirm the actual molecular weight of this sample. The method used for determining the molecular weight has been described previously (3.3.3.1.3). The data for calculation of molecular weight is presented in Table 4.20. The Huggins plot used to determine intrinsic viscosity is shown in Figure 4.5.

Table 4-20 Data for calculation of molecular weight

Concentration of Chitosan (c) (%)	Solvent (without chitosan)	0.0625	0.125	0.25	0.5	1
Time (Seconds)	196.00	211.96	228.36	261.93	338.34	561.38
Specific Viscosity (ηsp)		0.0814	0.1651	0.3364	0.7262	1.8642
ηsp/c		1.3029	1.3208	1.3455	1.4524	1.8642

Figure 4-5 Huggins plot of η_{sp}/c versus c



From the above plot, the intrinsic viscosity, [η] becomes 1.2238 dL/g. The given values of constants, K and a are 1.81 x 10^{-5} dL/g and 0.93, respectively. Substituting these values in Mark-Houwink Equation, the molecular weight is calculated as follows:

Mark-Houwink equation: $\mathbf{[\eta] = K. (M_v)^a}$

$$1.2238 = 1.81 \times 10^{-5} \times (M_v)^{0.93}$$

Therefore, $M_v = 156{,}156$

Rounding to the nearest 1000 gives a MW of 156,000. This value will be used henceforth to describe the MW of CH95 in this study. The calculated viscosity average molecular weight of chitosan sample (CH95) was found to be reasonably close to the value provided by the manufacturer (150,000).

4.3.2 Effect of Application Methods on Degree of Fixation

4.3.2.1 Whiteness Index

The results of the CIE-whiteness index measurement of fabrics treated with chitosan (MW 156,000) by pad-cure and pad-batch methods are shown in Tables 4-21 and 4-22 and plotted in Figures 4-6 and 4-7, respectively. Figure 4-6 shows that the whiteness of the fabrics decreased with increase in the curing temperature. This agrees well with the previous studies [153, 324]. At 110^{0}C, the change in whiteness was minor but at 130^{0}C the loss of whiteness was marked but commercially acceptable. With the pad-batch method, increasing the batching time decreased the whiteness of the fabrics (Figure 4-7). It can be seen from the results of pad-batch method that chitosan alone had an effect on whiteness as no heat was involved in this method. However, the whiteness of the fabrics treated with chitosan by both the application methods was within commercial acceptability.

Table 4-21 CIE-whiteness index of the fabrics (pad-dry-cure)

Curing Temperature (^{0}C)	CIE-Whiteness Index
Untreated fabric (control)	75.09
110	74.46
130	71.93
150	70.37

Figure 4-6 CIE-whiteness index of the fabrics (pad-dry-cure)

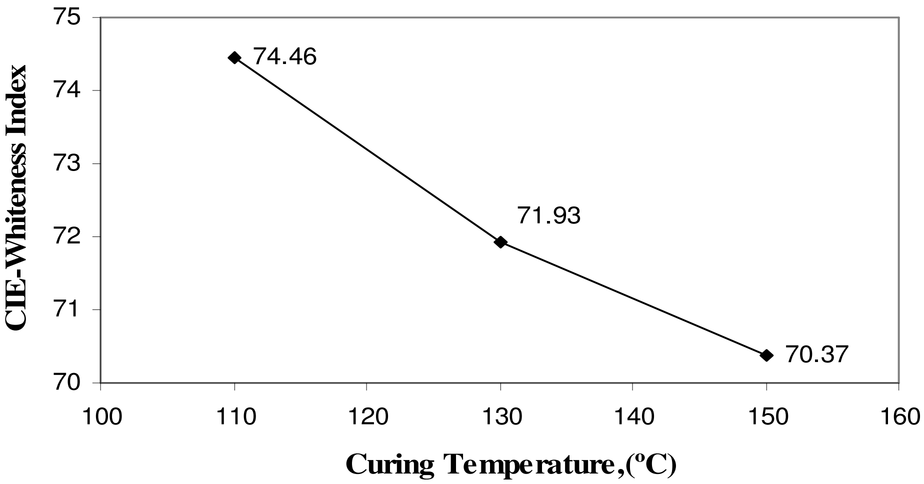
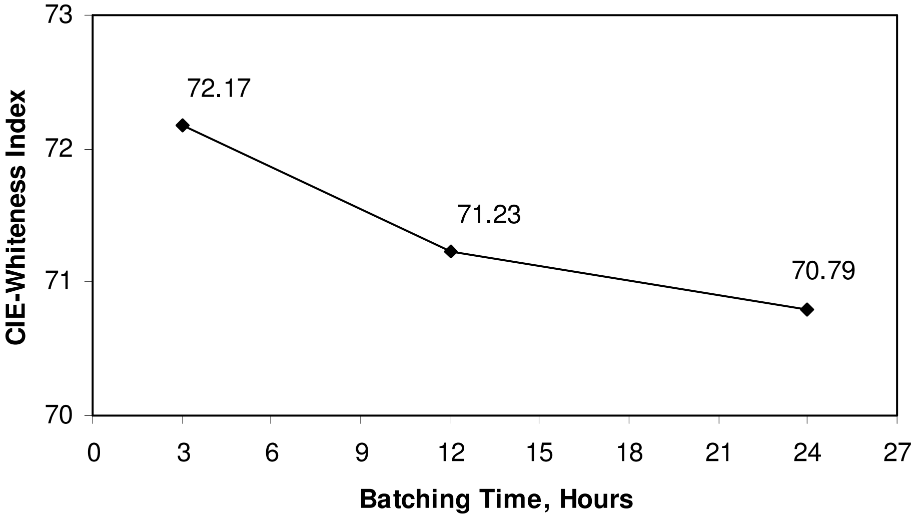


Table 4-22 CIE-whiteness index of the fabrics (pad-batch)

Batching Time (Hours)	CIE-Whiteness Index
Untreated fabric (control)	75.09
3	72.17
12	71.23
24	70.79

Figure 4-7 CIE-whiteness index of the fabrics (pad-batch)



4.3.2.2 Degree of Fixation and Colour Difference

Table 4-23 Degree of fixation and colour difference (pad-dry-cure)

Curing Temperature (^{0}C)	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
110	6.4	7.4	115.4	1.9
130	5.4	5.6	105.0	1.6
150	5.4	6.0	111.8	1.7

Table 4-23 shows the effect of curing temperature on the degree of fixation. At 110^{0}C, the fixation value was highest compared to other temperatures (130^{0}C and 150^{0}C). This was due to high initial K/S value of the fabric sample before washing. During ink jet printing it was observed that not all the ink was retained on the fabric. Some of the ink wicked through the fabric onto the backing paper. We believe that it was due to this that the amount of ink jetted on the fabric by the print head varied slightly from sample to sample. Also, the different

K/S values among the samples and within a sample suggested uneven absorption of inks onto the fabric surface. The other reason might be due to clogging of some nozzles during printing which may have caused reduction in the amount of ink on the fabric samples. The increase in the K/S values and the fixation values after washing are believed to be because of the reason already explained in Section 4.2.4.

The colour difference values were found to be in agreement with the values of degree of fixation. When the unwashed and washed fabric samples were compared visually, the shade of the washed fabric samples appeared darker. This shade difference observed may be due to the re-arrangement of pigment particles on the fibre surface during washing cycle. Most importantly the results show that chitosan can fix the pigmented inks at a curing temperature of 110^0C.

The effect of batching duration on the degree of fixation is shown in Table 4-24.

Table 4-24 Degree of fixation and colour difference (pad-batch)

Batching Duration (Hours)	**K/S**		**Degree of Fixation (DF %)**	**Colour Difference, ΔE**
	Before washing	**After washing**		
3	5.7	6.0	106.0	1.6
12	6.0	6.2	103.7	1.6
24	6.3	7.3	115.7	1.9

As can be seen, there was no marked effect of the batching duration on degree of fixation. Furthermore, the K/S and DF values were effectively the same as those obtained by heat curing the print (Table 4-23). Note that in the pad-batch method used the samples were simply rinsed and then allowed to dry in air under the ambient laboratory conditions viz. 20^0C (see Section 3.3.3.1.1). Results suggest that chitosan is “self cross-linking” which means that it can form a cross-linked network upon exposure to ambient conditions without any application of energy or curing and without the need for a bi-functional cross-linking agent. This may have an important commercial implication in that the cotton fabrics ink jet printed with pigment based inks could simply be “batched” for, say, 3 hours and then air dried to provide a durable print.

The high fixation value for batching duration of 24 hours was again due to initial high K/S value of that sample. Interestingly, the degree of fixation slightly decreased as the batching duration increased from 3 hours to 12 hours despite of high K/S value of the sample batched for 12 hours. This might be due to the variability of ink distribution and absorption on the fabric surface. Also, the migration and redistribution of pigments would have increased with the increase in batching time from 3 to 12 hours. The colour difference values showed similar trend as was seen in case of pad-cure method.

4.3.2.3 Colour Fastness to Laundering and Rubbing

Tables 4-25 and 4-26 show the colour fastness to laundering and rubbing of ink jet printed cotton fabrics post treated with chitosan (MW 156,000) by the pad-cure method and pad-batch methods, respectively. For both the applications, the colour fastness properties were found to be acceptable. The wet rubbing fastness for all the samples post treated with chitosan by both the applications was close to commercial acceptance (industry will accept a wet rub value of 3 for pigment printed fabrics).

Table 4-25 Colour fastness of ink jet printed cotton fabrics (pad-dry-cure)

Curing Temperature (^{0}C)	Rubbing Fastness[a]		Wash Fastness						
	Dry	Wet	Colour Change[b]	Staining[a]					
				Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
110	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
130	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
150	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 4-26 Colour fastness of ink jet printed cotton fabrics (pad-batch)

Batching Duration (Hours)	Rubbing Fastness[a]		Wash Fastness						
	Dry	Wet	Colour Change[b]	Staining[a]					
				Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
3	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
12	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
24	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Two application methods, viz., pad-dry-cure and pad-batch have been compared in terms of whiteness, degree of fixation, colour difference and colour fastness to laundering and rubbing. It was clear from the results obtained that both application methods produced similar results and that both were suitable for the application of chitosan as a surface finish for the fixation of pigment based inks.

4.3.3 Effect of Concentration of Chitosan (MW 156,000) on Degree of Fixation

The effect of chitosan concentration on the fixation of pigment ink jet printed on cotton fabrics are shown in Figure 4-8 and Table 4-27. It can be seen that the degree of fixation of pigmented inks was effectively 100% for chitosan concentrations ranging from 3 g.L^{-1} to 10 g.L^{-1}. The fixation decreased from around 94% to around 82% as the concentration of chitosan was further decreased from 1 g.L^{-1} to 0.3 g.L^{-1}. Hence, the degree of fixation of pigment based inks was markedly affected when the concentration was less than 3 g.L^{-1}.

Figure 4-8 Effect of chitosan (MW 156,000) concentration on degree of fixation

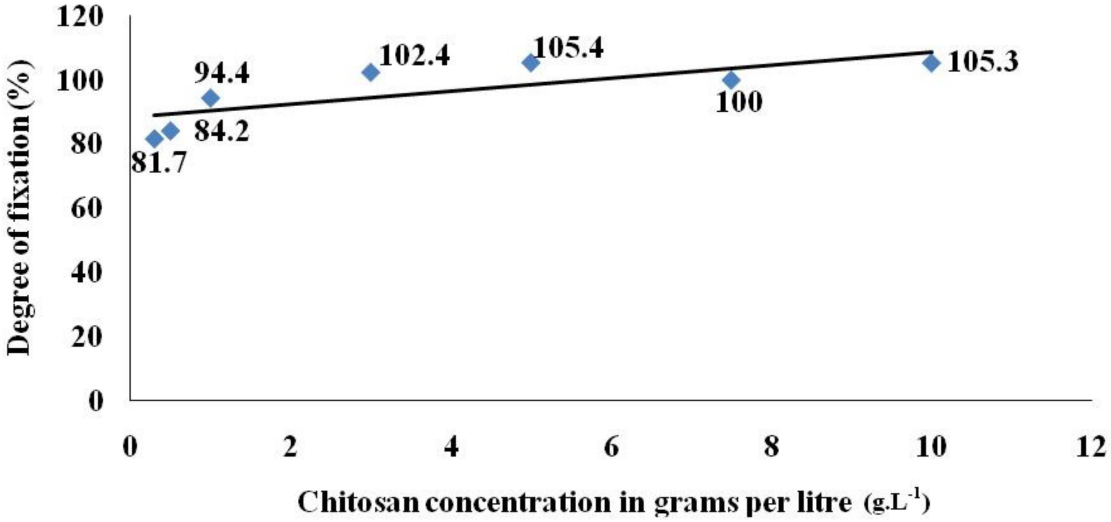


Table 4-27 Effect of chitosan (MW 156,000) concentration on degree of fixation

Concentration of Chitosan (MW 156,000) in g.L^{-1}	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
10.0	5.3	5.5	105.3	1.2
7.5	5.1	5.1	100.0	0.6
5.0	5.4	5.7	105.4	1.3
3.0	5.1	5.2	102.4	0.3
1.0	5.2	5.0	94.4	0.9
0.5	5.0	4.2	84.2	2.7
0.3	5.0	4.0	81.7	3.1

Table 4-28 Effect of chitosan (MW 156,000) concentration on colour fastness

Chitosan Concentration in g.L^{-1} (MW 156,000)	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
10.0	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
7.5	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
5.0	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
3.0	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
1.0	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
0.5	3	2	3-4	3	3	4-5	3-4	4	4
0.3	3	2	3-4	3	3	4-5	3-4	4	4

From Table 4-28, the dry rub fastness decreased as the concentration decreased but was acceptable for concentrations down to 1 g.L^{-1} and further decreased for 0.5 and 0.3 g.L^{-1} concentrations. The wet rub fastness was nearly acceptable for concentrations down to 1 g.L^{-1} whereas, for 0.5 g.L^{-1} and 0.3 g.L^{-1} concentrations, it was found to be poor. The wash fastness was excellent for all concentrations down to 1 g.L^{-1}. For 0.5 g.L^{-1} and 0.3 g.L^{-1} concentrations, the colour change was satisfactory while the staining was acceptable to good. These results demonstrated the suitability of chitosan to bind ink jet printed pigments on cotton at concentration as low as 3 g.L^{-1}.

4.3.4 Effect of pH on Degree of Fixation

The degree of fixation was significantly affected by alkaline pH (Figure 4-9 and Table 4-29). Initially the fixation increased slightly as pH increased from 4.0 to 6.0. At lower pH values the free amino groups of chitosan are highly protonated. Due to this the pigments might have been held more strongly and their migration to the surface been limited. As the pH was further increased up to 6.0, a slight weakening in the protonation may have occurred. As a result, the pigments may have more easily migrated to the fibre surface along with the loosely held chitosan molecules during washing cycle. This contributed to the higher K/S values after washing cycle and hence the increase in the degree of fixation. Also, this could be simply due to variability of the ink distribution and absorption on the fabric surface after washing. After 6.0, as the pH was further increased, the fixation decreased significantly. It is well known that chitosan dissolves in dilute mineral and organic acids by protonation of free amino groups at pH below about 6.5. Above pH 6.5, chitosan exhibits poor solubility due to the deprotonation of amino groups. The poor binding capability beyond pH 6.0 suggested that the film forming ability of chitosan and hence the degree of fixation depends on the cationic nature of chitosan.

Figure 4-9 pH versus degree of fixation

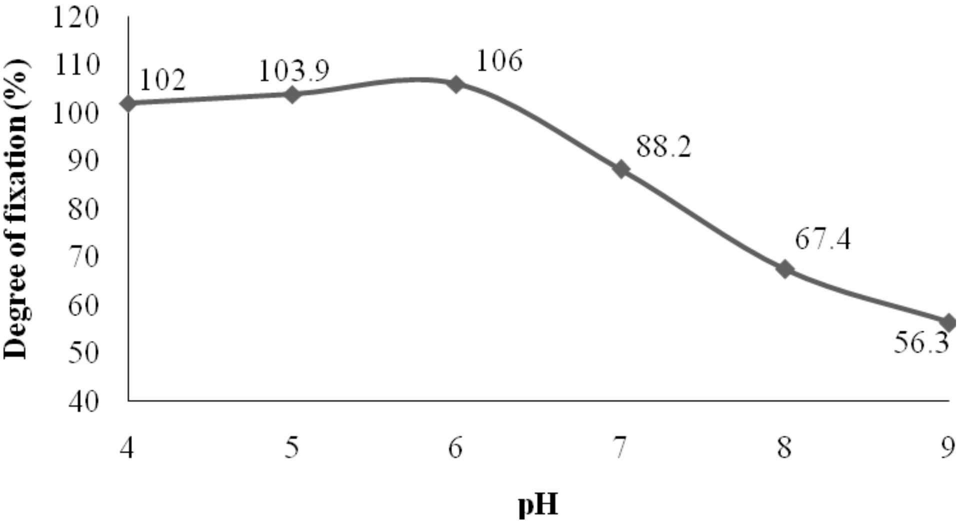


Table 4-29 Effect of pH on degree of fixation

pH of Chitosan (MW 156,000) Pad Solution	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
4.0	5.0	5.1	102.0	0.4
5.0	5.1	5.3	103.9	0.5
6.0	5.0	5.3	106.0	0.6
7.0	5.1	4.5	88.2	4.1
8.0	4.9	3.3	67.4	9.5
9.0	4.8	2.7	56.3	11.7

Similarly there was no significant effect of pH on colour fastness up to pH 6.0. From pH 7.0 to 9.0, there was a decrease in the dry and wet rub fastness. The wash fastness in terms of colour change significantly decreased as the pH increased from 7.0 to 9.0. This was again due to poor binding capability of chitosan beyond pH 6.0. Wash fastness in terms of staining remain unaffected at all pH values (Table 4-30).

Table 4-30 Effect of pH on colour fastness of cotton fabric

pH	Rubbing Fastness[a]		Wash Fastness						
	Dry	Wet	Colour Change[b]	Staining[a]					
				Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
4.0	3-4	2-3	4-5	4-5	4	4-5	4-5	4-5	4-5
5.0	3-4	2-3	4-5	4-5	4	4-5	4-5	4-5	4-5
6.0	3-4	2-3	4-5	4-5	4	4-5	4-5	4-5	4-5
7.0	2-3	1-2	3-4	4-5	4	4-5	4-5	4-5	4-5
8.0	2	1-2	2	4-5	4	4-5	4-5	4-5	4-5
9.0	1-2	1	1-2	4-5	4	4-5	4-5	4-5	4-5

From the studies carried above, the optimum conditions for the application of chitosan on cotton fabric ink jet printed with pigments are listed below:

Chitosan molecular weight: 156,000
Application method: pad-dry-cure method or pad-batch method
Chitosan concentration: 3 grams per litre
pH: 4 to 6

The above conditions were selected for further studies. For convenience, pad-dry-cure method and pH 4.0 were chosen.

4.3.5 Depolymerisation of Chitosan

From the results of Section 4.3.1, the degree of fixation of pigmented inks was found to be dependent on the molecular weight of chitosan. Depolymerisation of chitosan sample (MW 156,000) was carried out (see Section 3.3.3.5) to decrease its molecular weight for further evaluation of the effect of depolymerisation on the degree of fixation.

4.3.5.1 Effect of Depolymerisation on Chitosan Viscosity

The decrease in the viscosity is an indication of decrease in the molecular weight. Viscosity decrease (%) as a result of the depolymerisation process is shown in Table 4-31. The results showed that the decrease in the viscosity increased with increasing chitosan concentration which agreed with No's result [270].

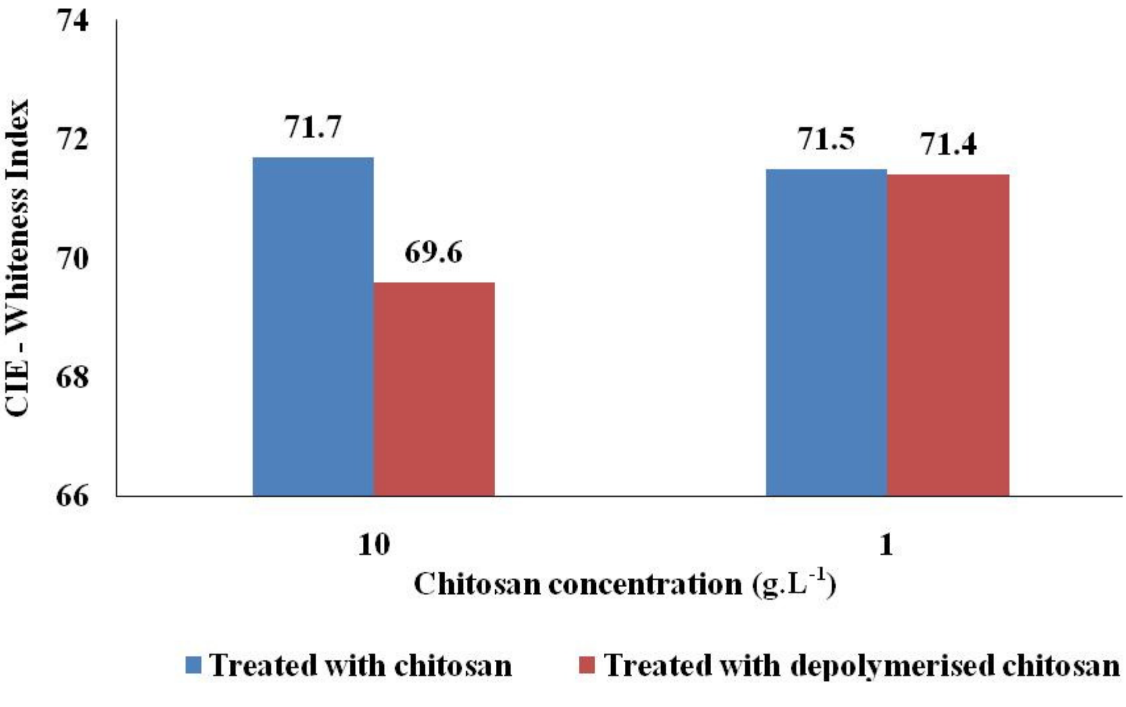
Table 4-31 Effect of autoclaving on chitosan viscosity

Chitosan Concentration ($g.L^{-1}$)	Before Autoclaving		After Autoclaving		Viscosity Decrease (%)
	Drain Time (seconds)	Viscosity (cps) at 25^0C	Drain Time (seconds)	Viscosity (cps) at 25^0C	
10	46	24	17	8	67
1	11	4	10	2	50

4.3.5.2 Effect of Depolymerisation on Whiteness Index of Cotton Fabrics

Depolymerisation of chitosan causes decrease in the molecular weight of chitosan and an increase in the amount of terminal aldehyde groups thereby decreasing the whiteness of the cotton fabrics. An increase in the concentration of chitosan is also known to cause decrease in the whiteness of the cotton fabric [324]. Figure 4-10 shows the effect of depolymerisation of chitosan at 1 $g.L^{-1}$ and 10 $g.L^{-1}$ concentrations on the whiteness of treated cotton fabrics. At 10 $g.L^{-1}$ concentration, the whiteness index of cotton treated with depolymerised chitosan slightly decreased compared to the whiteness index of cotton treated with chitosan. At 1 $g.L^{-1}$ concentration, almost no change was observed in whiteness index of the fabric treated with chitosan and the fabric treated with depolymerised chitosan. This suggested that at 1 $g.L^{-1}$ concentration, depolymerisation of chitosan did not affect the whiteness of the fabric. At 10 $g.L^{-1}$ concentration, the decrease in the whiteness of the fabric was significant. The decrease in the whiteness at 10 $g.L^{-1}$ concentration may be attributed to the increase in the concentration of chitosan or due to the increase in terminal aldehyde groups as a result of depolymerisation of chitosan or both.

Figure 4-10 Effect of depolymerisation on whiteness of treated cotton fabrics



4.3.5.3 Effect of Depolymerisation of Chitosan on Degree of Fixation

Cotton fabrics ink jet printed with pigments were post-treated with chitosan at 1 g.L^{-1} and 10 g.L^{-1} concentrations before depolymerising the chitosan. Similarly, cotton fabrics were post-treated with depolymerised chitosan at same concentrations. Figure 4-11 and Table 4-32 shows the effect of depolymerisation of chitosan at 1 g.L^{-1} and 10 g.L^{-1} concentrations on the degree of fixation of pigments, ink jet printed on cotton fabric.

Figure 4-11 Effect of depolymerisation of chitosan on degree of fixation

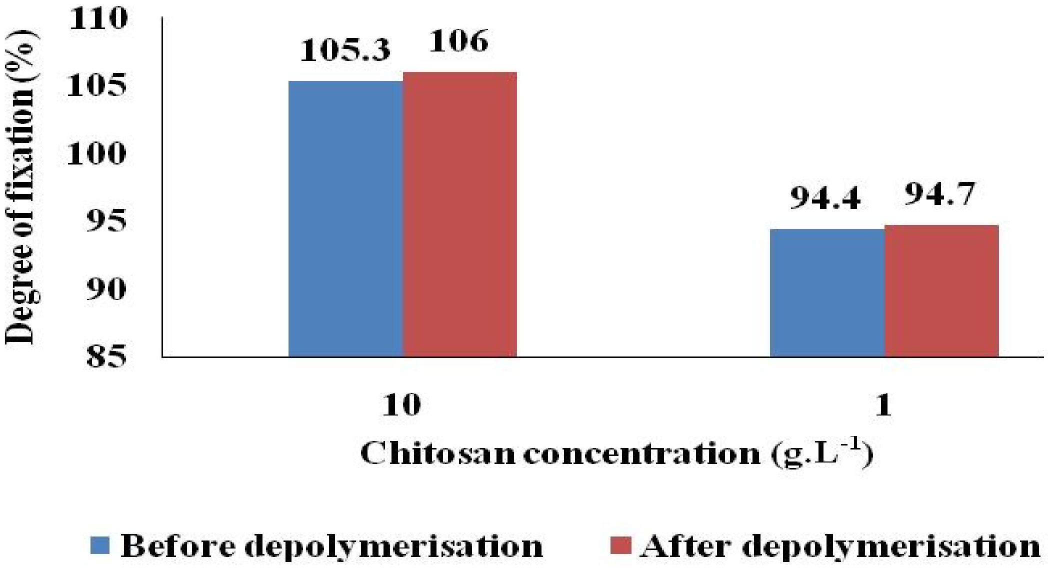


Table 4-32 Effect of depolymerisation of chitosan on degree of fixation

Chitosan Concentration (g.L^{-1})	Degree of Fixation (DF %)	
	Before Depolymerisation	After Depolymerisation
10	105.3	106.0
1	94.4	94.7

From Figure 4-11 and Table 4-32, the fixation values were almost similar before and after depolymerisation of chitosan at both 1 and 10 g.L^{-1} concentrations. This suggested that the depolymerisation of chitosan did not show any marked effect on the fixation of pigments. At both the concentrations, the fixation values slightly increased after depolymerisation. This could be attributed to the ability of the depolymerised chitosan to penetrate inside the fabric structure enhancing the cross-linking between cotton and chitosan and in doing so, would result in better fixation of pigments. At 10 g.L^{-1} concentration, the fixation of pigment before and after depolymerisation of chitosan was above 100%. The reason for fixation above 100%

has been discussed earlier in Section 4.2.4. Also, when the chitosan concentration before and after depolymerisation was decreased from 10 g.L^{-1} to 1 g.L^{-1}, the degree of fixation decreased.

Overall, the results showed that the depolymerisation of chitosan did not significantly affect the fixation of pigment on the cotton fabric. This suggested that chitosan retained its film forming ability even after depolymerisation and that the chitosan samples with molecular weight lower than 156,000 can be explored for fixation of pigments on cotton fabric.

4.3.5.4 Effect of Chitosan Depolymerisation on Colour Fastness of Print

The dry rub fastness (4 and 3-4) was acceptable for fabric samples treated with depolymerised chitosan at all concentrations while the wet rub fastness values (2-3) were unsatisfactory. The fastness to laundering was good at all concentrations (Table 4-33).

Table 4-33 Colour fastness properties of cotton treated with depolymerised chitosan

Chitosan Concentration (g.L^{-1})	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
10.0	4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
1.0	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.3.6 Effect of Plasticizer on Degree of Fixation

Plasticizers such as erythritol, glycerol, sorbitol, etc. have been used to study their effect on the film characteristics of chitosan. In the present study, glycerol was used to assess its effect on degree of fixation and to examine whether it improves the rub fastness of chitosan treated fabrics. Generally, increasing the crystallinity of a film structure promotes intermolecular forces thereby increasing the rigidity and brittleness of the film. Erythritol and glycerol have been shown to decrease the rigidity of the film network of chitosan, producing less ordered film structure and increasing the flexibility of the polymer chains [338]. However, addition of glycerol to chitosan solution did not show any favourable effect on the stiffness of the cotton fabric (results not shown).

The addition of glycerol to the chitosan solution did not affect the degree of fixation (Figure 4-12 and Table 4-34). As the glycerol content increased, there was a slight increase in fixation value which might be attributable to the slight increase in the flexibility of film network thereby increasing the ability of movement of pigments to the fabric surface.

Addition of glycerol did not show any improvement in dry and wet rub fastness while, fastness to washing remain unaffected (Table 4-35).

Figure 4-12 Effect of glycerol content on degree of fixation

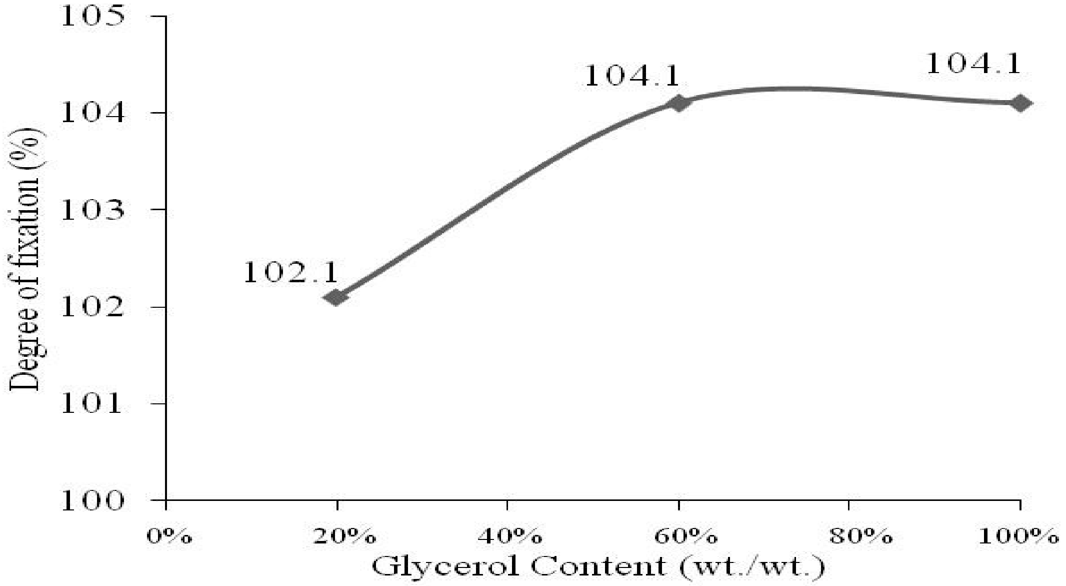


Table 4-34 Effect of glycerol content on degree of fixation

Glycerol Content Based on Chitosan Weight (wt/wt)	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE
	Before washing	After washing		
20%	4.8	4.9	102.1	0.8
60%	4.9	5.1	104.1	1.0
100%	4.9	5.1	104.1	1.0

Table 4-35 Effect of glycerol content on colour fastness properties

Glycerol Content (wt/wt)	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
20%	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
60%	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
100%	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.3.7 Effect of Textile Softeners on Degree of Fixation

It is well known that textile softeners have been found to improve the handle, softness and, to a certain extent, the rub fastness of printed fabrics. In the present study, three commercial non ionic softeners were separately added to the 3 $g.L^{-1}$ chitosan solution to study their effect on degree of fixation and on rub fastness properties of ink jet printed cotton fabrics. The effect of these softeners on the fabric hand in terms of stiffness is discussed in Section 4.3.8.1.

Figure 4-13 Effect of different softeners on degree of fixation

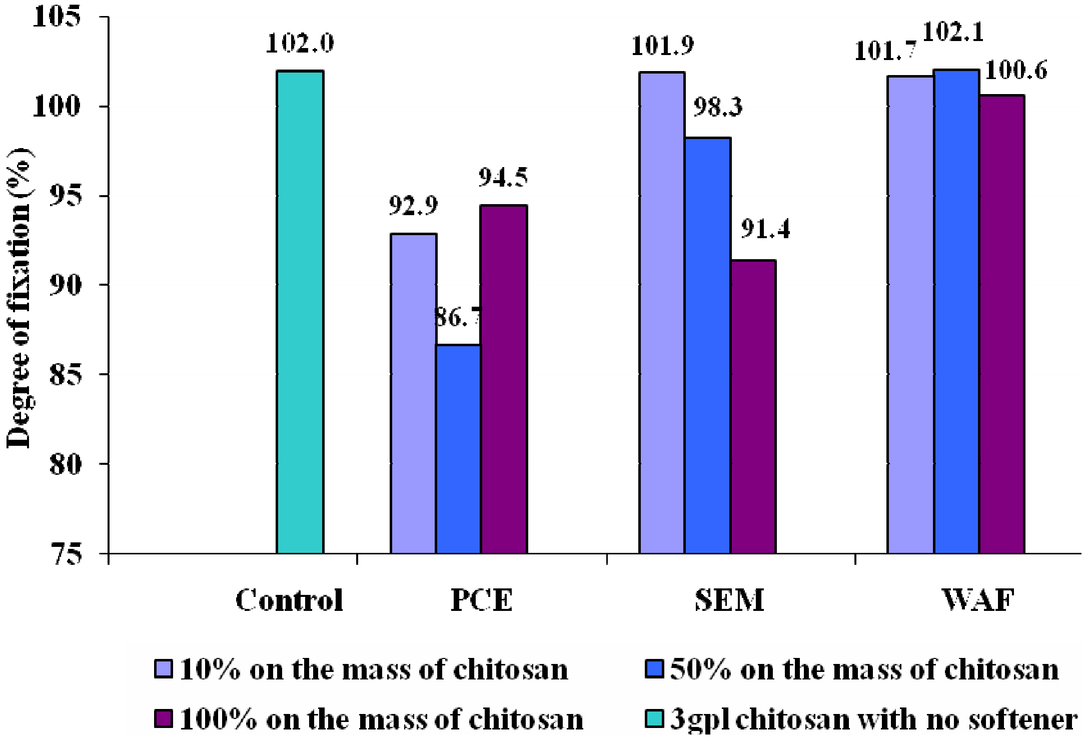


Figure 4-13 show the effect of different softeners at 10, 50 and 100% (on the mass of chitosan) concentrations on the degree of fixation of pigments. The control fabric post treated with 3 $g.L^{-1}$ chitosan without any softener showed 102% fixation. The softener that had the greater effect on fixation was the ester based product Tubisoft PCE. Fixation fell by approximately 7-15% when this product was incorporated into the chitosan post-treatment. This decrease in the fixation may be due to Tubisoft PCE being an ester. Esters have ability to participate in hydrogen bonding making them more water soluble [337]. Hence, due to the incorporation of PCE into chitosan, the water resistance of the film formed by chitosan would have decreased. Tubisoft SEM, a silicone based softener, had no effect when incorporated at 10% on the mass of chitosan. But the fixation decreased as its concentration was further increased. With increasing concentration, Tubisoft SEM may have had an increasing interference with the film formation ability of chitosan. Tubigal WAF did not show any significant effect on the degree of fixation.

Table 4-36 shows that the wash fastness was good in case of all the three softeners. However, there was no significant improvement in the wet and dry rub fastness.

Table 4-36 Effect of softeners on rub fastness properties

Softener Content Based on Chitosan Weight (wt/wt)	Rubbing Fastness[a]					
	Tubisoft PCE		Tubisoft SEM		Tubigal WAF	
	Dry	Wet	Dry	Wet	Dry	Wet
10%	3-4	2-3	3-4	2-3	3-4	2-3
50%	3-4	2-3	3-4	2-3	3-4	2-3
100%	3-4	2-3	3-4	2-3	3-4	2-3

4.4 Performance Properties of Chitosan Post Treated Cotton Fabrics

4.4.1 Stiffness

The fabric handle (the way it feels) is an important aesthetic property and is relatively subjective. Chitosan has been known to affect the fabric handle. No study so far has been undertaken to address this issue. It is desirable that the flexural rigidity (a measure of fabric stiffness) of the ink jet printed and chitosan post treated fabric sample should be as close as possible to that of unprinted and untreated reference material.

Figure 4-14 shows the effect of depolymerised chitosan on the stiffness of ink jet printed cotton fabric. It can be seen that ink jet printing alone resulted in increase in the stiffness due to the deposition of pigments. Post-treatment with chitosan (MW 156,000) as well as depolymerised chitosan at both 1 $g.L^{-1}$ and 5 $g.L^{-1}$ concentration further increased the stiffness of the fabric. It was clear that concentration of chitosan had a significant effect on the stiffness. Depolymerisation of chitosan, to give a lower molecular weight resulted in the decrease in the stiffness. The value of stiffness for fabric treated with depolymerised chitosan at 1 $g.L^{-1}$ concentration was comparable to the value for ink jet printed cotton. This suggests that an acceptable handle, relative to a printed only control can be achieved by choosing appropriate concentration and molecular weight of chitosan for its specific application.

Figure 4-14 Effect of depolymerised chitosan on fabric stiffness

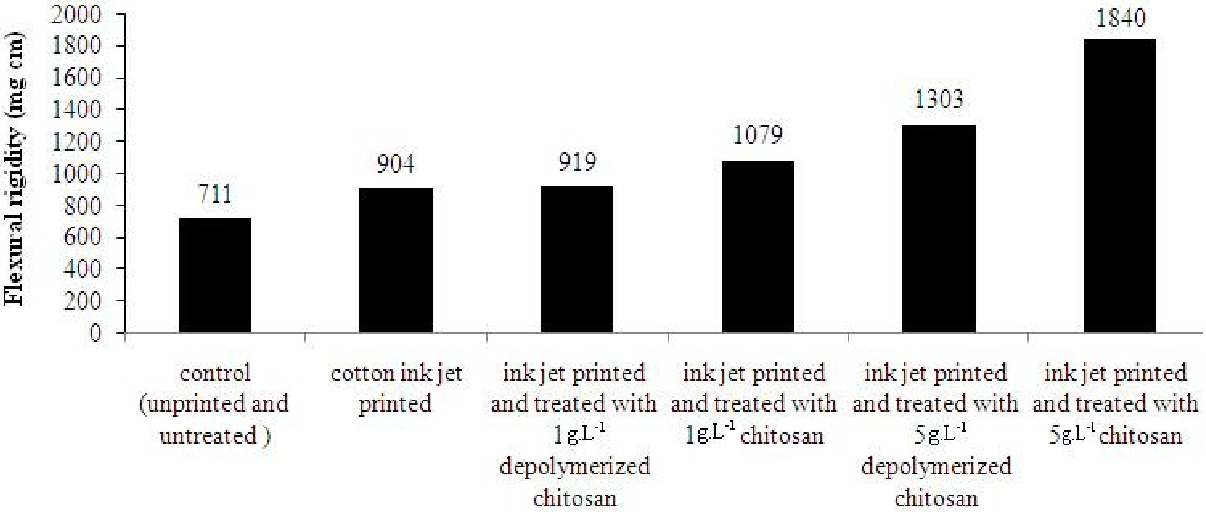


Figure 4-15 shows effect of ester-type PCE softener on the stiffness of ink jet printed cotton fabric. Post-treatment of ink jet printed fabric with 3 g.L^{-1} chitosan increased the stiffness of fabric to 1210 mg cm. Addition of Tubisoft PCE softener at 10% (wt/wt) concentration to the chitosan solution decreased the stiffness of fabric to a value (912) comparable to that of ink jet printed fabric (904). As the PCE content was further increased, the stiffness of the fabric increased. This may be due to an increase in the amount of surface deposition of Tubisoft PCE. However, the stiffness values were lower compared to the value of the fabric sample treated only with chitosan without any softener.

Figure 4-15 Effect of Tubisoft PCE softener on fabric stiffness

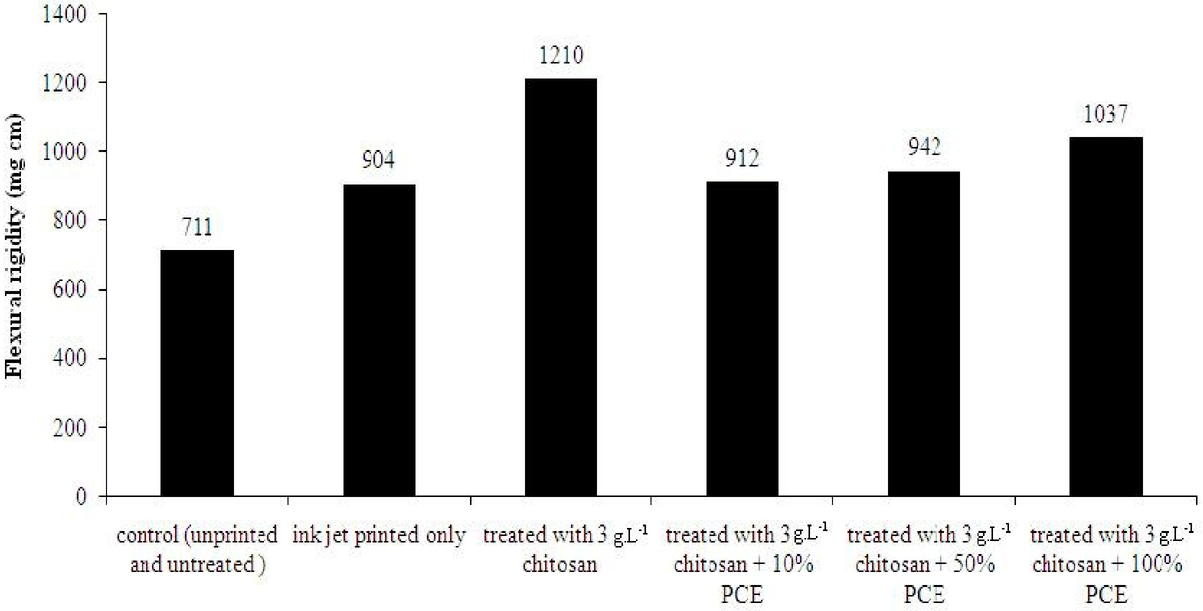


Figure 4-16 shows the effect of the silicone based SEM softener on the stiffness of ink jet printed cotton fabric. The SEM softener, when incorporated at 10% on the mass of chitosan increased the fabric stiffness. This may be due to an increase in the amount of surface deposition of the SEM softener. It is believed that the incorporation of SEM softener at 10% concentration is not sufficient enough to decrease the rigidity of the film network of chitosan. It was expected that a further increase in the SEM content should increase the stiffness due to increased surface deposition as was observed in the case of Tubisoft PCE softener. But, further increase in the SEM content decreased the stiffness. The increase in the SEM content may have increased the flexibility of the chitosan polymer chains, thereby decreasing the fabric stiffness. The fabric treated with 3 g.L^{-1} chitosan containing SEM softener at 100% concentration showed slightly lower stiffness value (1174 mg cm) compared to the value (1210 mg cm) of the fabric sample treated only with chitosan without any softener.

Figure 4-16 Effect of silicone SEM softener on fabric stiffness

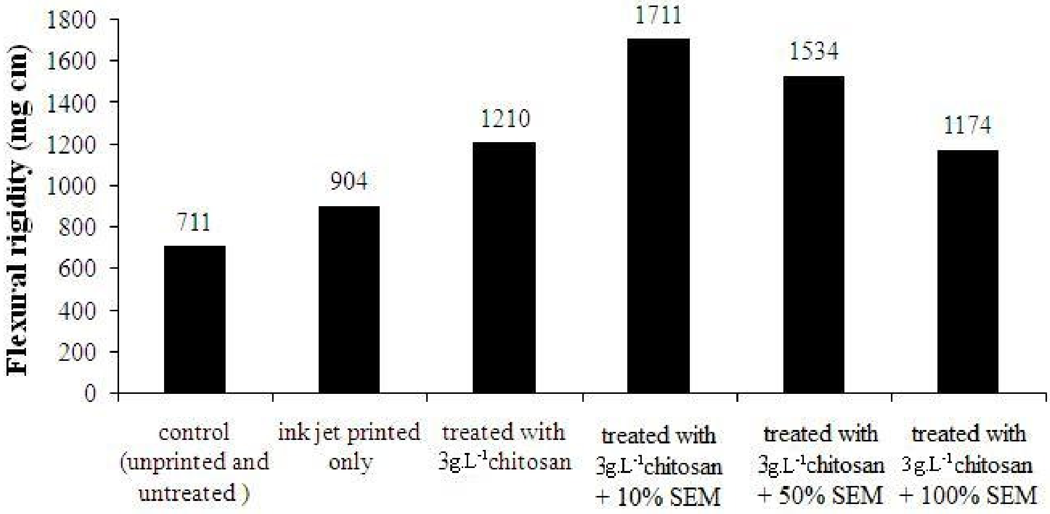
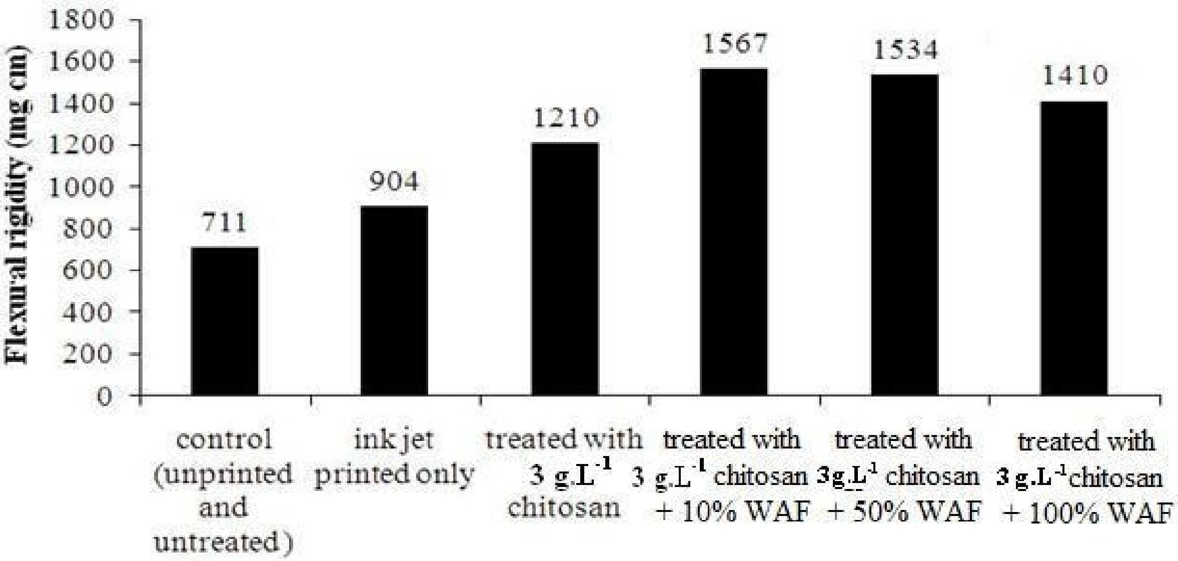


Figure 4-17 shows the effect of Tubigal WAF softener on the stiffness of ink jet printed cotton fabric. The stiffness value increased from 904 mg cm to 1210 mg cm when the ink jet printed fabric was post treated with 3 g.L^{-1} chitosan without softener. Addition of WAF softener at 10% on the mass of chitosan increased the stiffness of the fabric to 1567 mg cm. This increase in the stiffness may again be attributed to the increase in the amount of surface deposition of the WAF softener. But, further increase in the content of WAF softener decreased the stiffness. The Tubigal WAF softener showed almost similar trend as that of silicone based Tubisoft SEM softener. However, the stiffness value (1410 mg cm) for the fabric treated with 3 g.L^{-1} chitosan containing WAF softener was higher than the stiffness value (1210 mg cm) of fabric treated only with chitosan without the softener.

Figure 4-17 Effect of Tubigal WAF softener on fabric stiffness



In summary, incorporation of Tubisoft PCE softener showed the most favourable effect on the stiffness of the fabric, among the three commercial softeners. In the case studied, the application of depolymerised chitosan produced handle equivalent to that of ink jet printed control sample (Figure 4-14).

4.4.2 Tensile Strength and Extension at Break

All the cotton samples post treated with chitosan by pad-dry-cure method showed an increase in tensile strength and extension at break compared to the un-treated fabrics (Table 4-37). This could be expected since chitosan has affinity for cellulose and forms a strong coating which may have contributed to increased tensile strength and extension at break.

Table 4-37 Tensile strength and extension at break of cotton fabrics

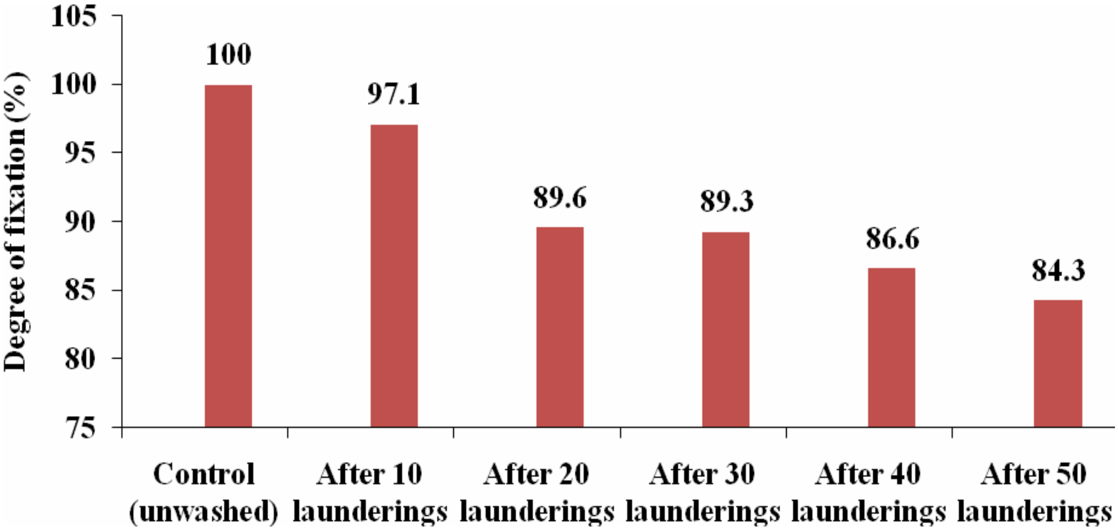
Cotton Fabrics	Sample	Tensile Strength (N)	Increase in Tensile Strength (%)	Extension at Break (%)	Increase in Extension at Break (%)
Light plain (110 g/m^2)	Untreated	439	8.7	6.7	23.9
	Treated*	477		8.3	
Heavy plain (189 g/m^2)	Untreated	571	17.2	10.2	14.7
	Treated*	669		11.7	
Unmercerized twill (276 g/m^2)	Untreated	932	9.4	12.2	11.5
	Treated*	1020		13.6	
Mercerized twill (276 g/m^2)	Untreated	1170	6.0	10.9	11.9
	Treated*	1240		12.2	

*** with 3 g.L^{-1} chitosan**

4.5 Laundering Durability of Chitosan Post-Treatment

Previous studies [176, 307] have indicated poor durability of chitosan treated cotton fabrics. This was attributed to the lack of strong binding between chitosan and cotton fabrics.The laundering durability of ink jet printed cotton fabrics post treated with chitosan is shown in Figure 4-18. After 10 launderings, the degree of fixation of pigments was 97% compared to the unlaundered control sample. After 20 and 30 launderings, the fixation was almost 90%. The loss of the pigments can be attributed to the removal of chitosan loosely fixed on the fabric by van der Waals'forces or hydrogen bonding. Surprisingly, even after 50 launderings, almost 85% of the pigments were fixed on the fabric. If there had been no strong bonding between chitosan and cotton fabric, there would have been severe loss of pigment after 50 laundering cycles. These findings suggested that there exists strong chemical interaction between chitosan and cotton fabric and that chitosan can be used as a durable finish for fixation of pigment based inks.

Figure 4-18 Durability of chitosan post-treatment



N.B. Degree of fixation of cotton fabric without chitosan post treatment after 5 launderings = 23.8%.

The wash fastness of the fabric samples after different laundering cycles was found to be excellent. The rub fastness improved one scale after 30 launderings which might be due to the removal of loosely fixed chitosan and the pigments during laundering cycles (Table 4-38).

Table 4-38 Colour fastness properties after different laundering cycles

Samples	Rubbing Fastness[a]		Wash Fastness						
	Dry	Wet	Colour Change[b]	Staining[a]					
				Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
After 10 launderings	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
After 20 launderings	3-4	2-3	4	4-5	4-5	4-5	4-5	4-5	4-5
After 30 launderings	4	3	4	4-5	4-5	4-5	4-5	4-5	4-5
After 40 launderings	4	3	4	4-5	4-5	4-5	4-5	4-5	4-5
After 50 launderings	4	3	3-4	4-5	4-5	4-5	4-5	4-5	4-5

4.6 Scanning Electron Microscopy of Chitosan Treated Fabrics

The film forming ability of chitosan was examined using scanning electron microscopy. Figures 4-19 (a), (b) and (c) shows micrographs of untreated cotton fibres at magnification 800x, 1600x and 6000x, respectively.

The micrograph at magnification 800x and 1600x shows the arrangement of cotton fibres in the yarns within a woven fabric structure. The fibres are relatively parallel, bent due to the effect of the twist in the yarn and due to the interlacing of the yarns in the fabric structure. All the three micrographs especially the micrograph at 6000x magnification shows the clean fibre surfaces with no evidence of any deposition or material lying on or between the fibres.

Figure 4-19(a) Morphology of untreated cotton (magnification 800x)

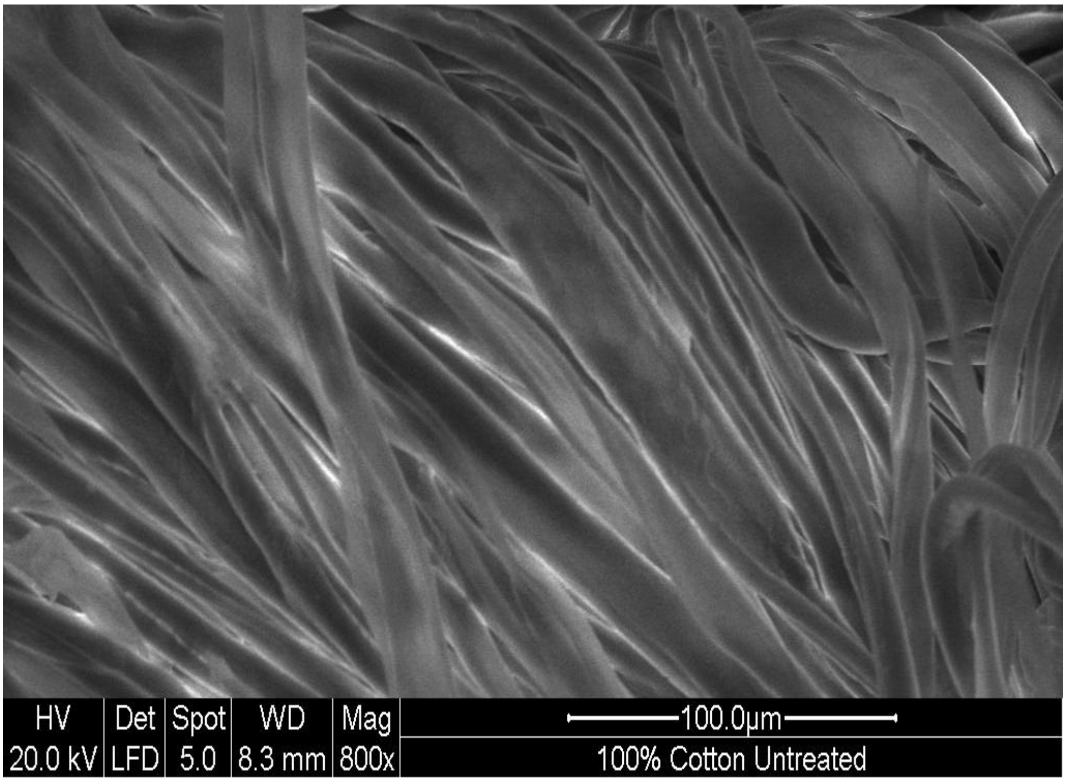


Figure 4-19(b) Morphology of untreated cotton (magnification 1600x)

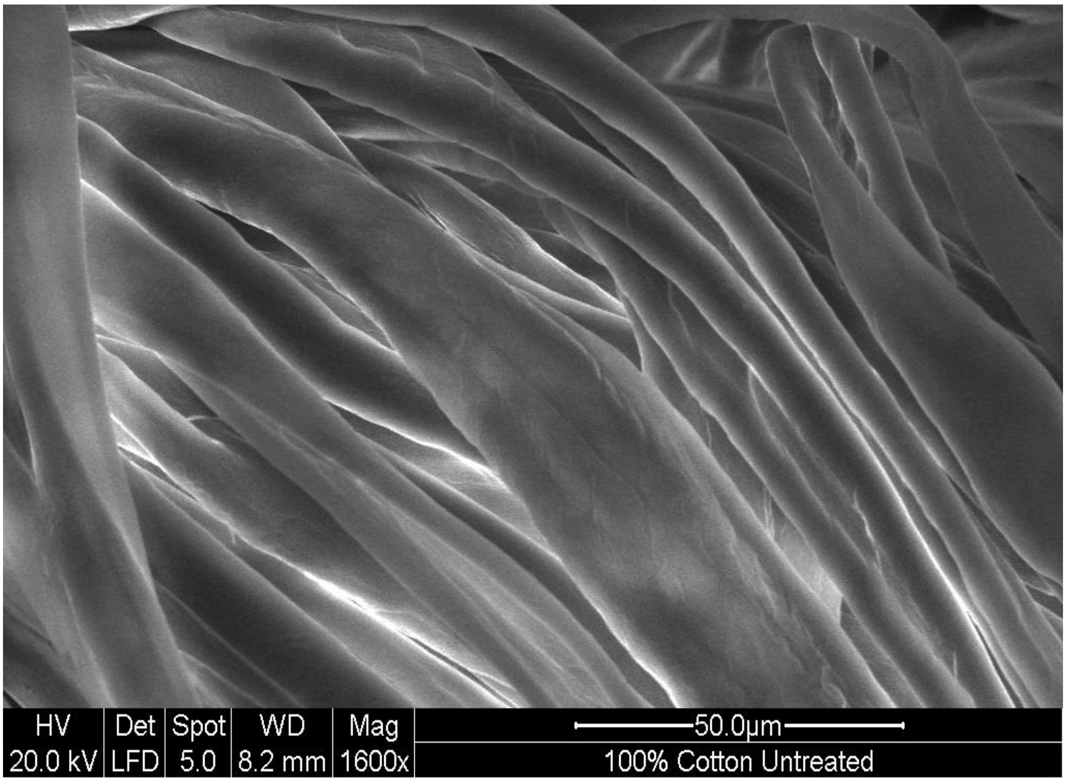


Figure 4-19(c) Morphology of untreated cotton (magnification 6000x)

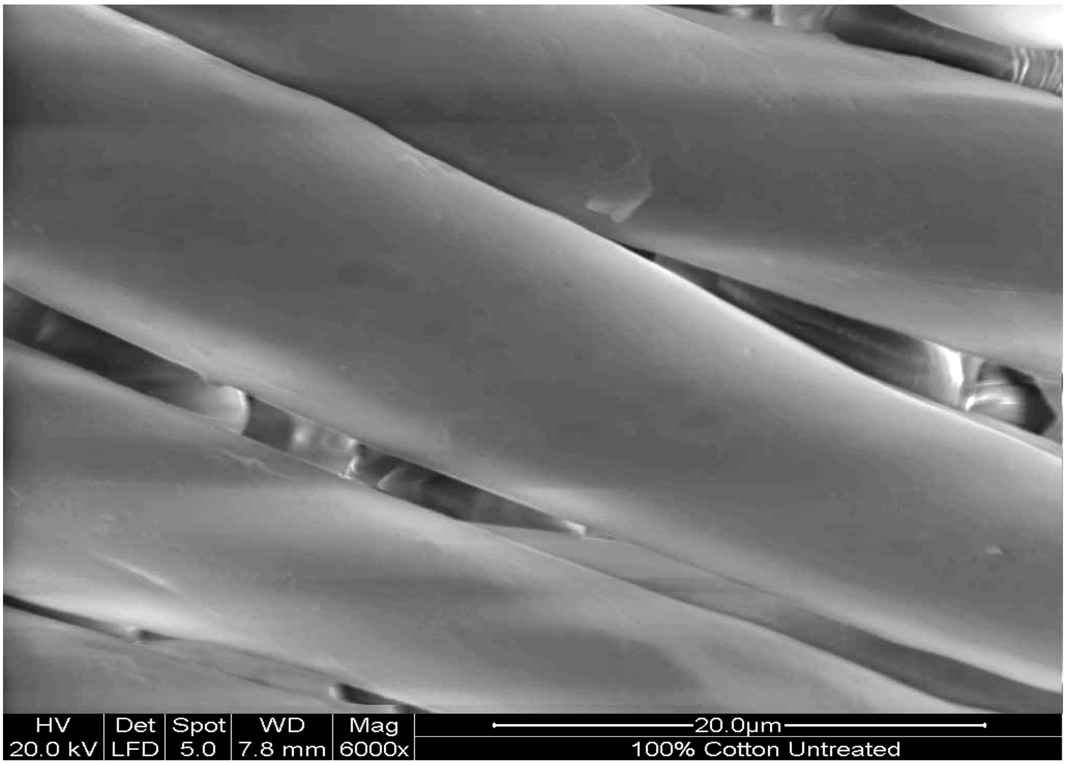
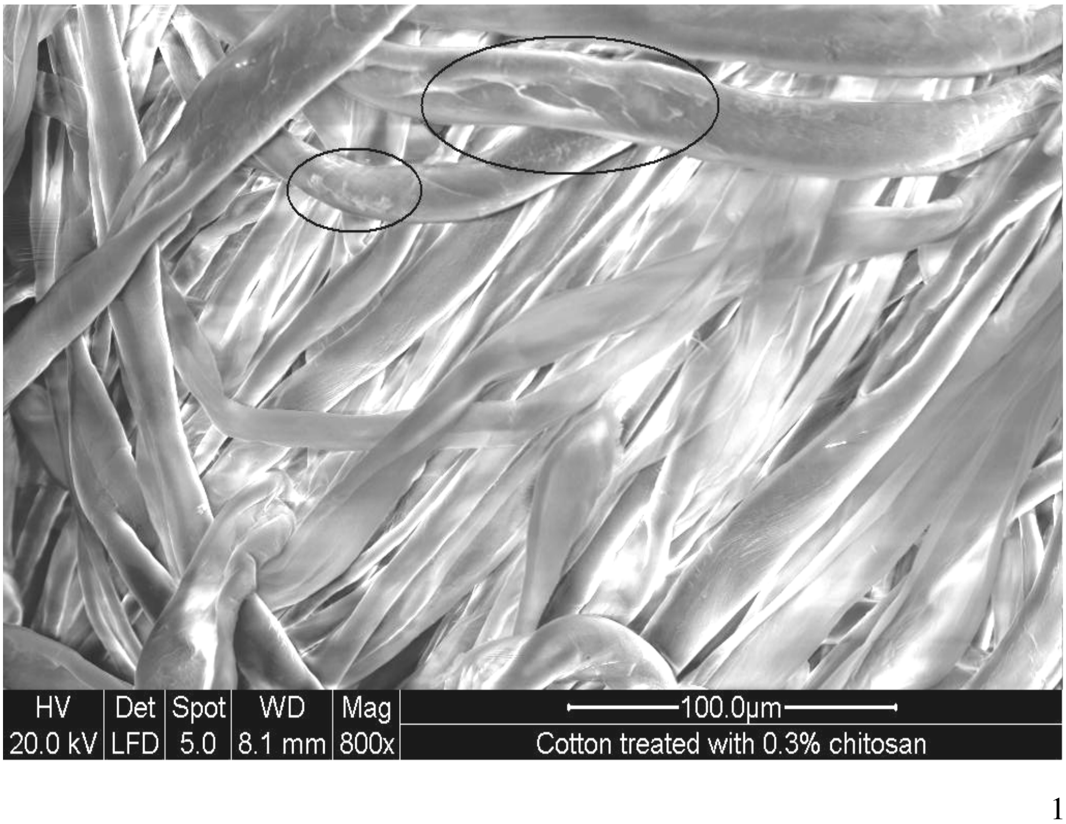


Figure 4-20 (a), (b) and (c) shows micrographs of cotton fibres treated with 3 $g.L^{-1}$ chitosan (MW 156,000) at magnification 800x, 1600x and 6000x, respectively. In Figure 4-20 (a), the circled areas show the deposition of chitosan and the film formed by chitosan on cotton fibres.

Figure 4-20(a) Morphology of chitosan treated cotton (magnification 800x)



In Figure 4-20 (b), the circled areas (1) show small deposits of chitosan on the surface of the fibres. The circled area (2) show large deposits of chitosan forming web like films between parallel fibres and the circled areas (3) show formation of web like films by chitosan between non-parallel fibres at their crossover points. There is also evidence of smaller interfibre bridges (4) where a thin film bridges chitosan deposits on the surface of adjacent fibres.

Figure 4-20(b) Morphology of chitosan treated cotton (magnification 1600x)

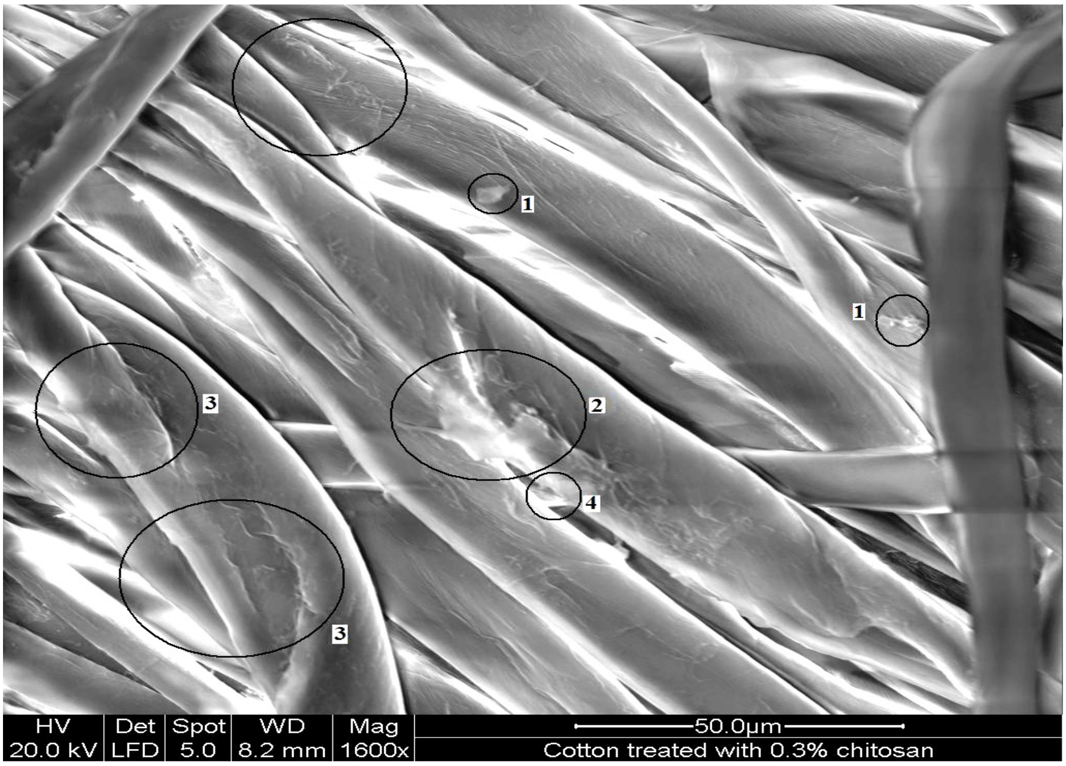
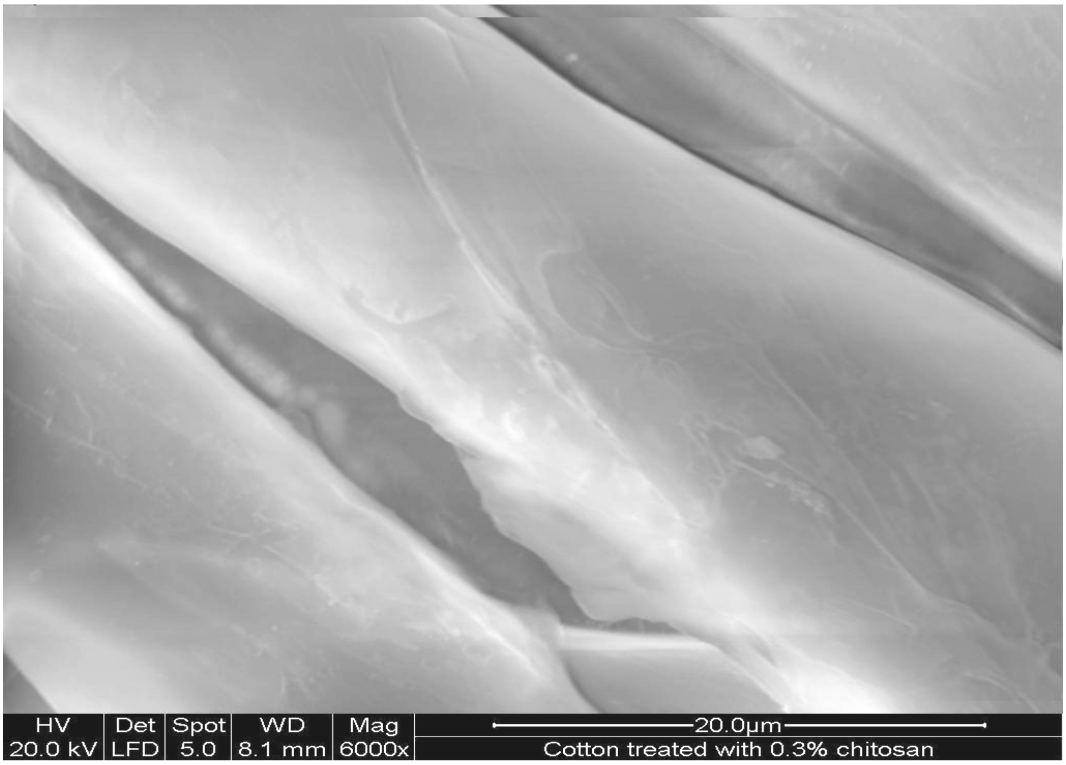


Figure 4-20 (c), the chitosan treated cotton fibres showed slightly rough surface. The roughness was attributed to the surface deposition of the chitosan. It appeared that chitosan coated the individual cotton fibres which can be attributed to its film forming ability.

The deposition of chitosan on the surface of the fibres might be expected to increase the surface friction and affect the overall “feel” of the fabric but not the stiffness. The increase in the stiffness found with chitosan treated fabrics could be the result of the inter-fibre bonding that occurs due to the formation of films and bridges between fibres.

Figure 4-20(c) Morphology of chitosan treated cotton (magnification 6000x)



4.7 Chemical Interaction between Chitosan and Cotton Fabric

The poor laundering durability of chitosan treated cotton fabrics have been attributed to the lack of strong binding between chitosan and cotton fabrics [176, 307]. However, the results of laundering durability of chitosan treated cotton fabrics (see Section 4.3.9) showed that apart from van der Waals' forces or hydrogen bonding, there exists the possibility of a strong chemical interaction between chitosan and cotton fabric. It is well known that the carbonyl groups in cellulose form Schiff base compounds with amino groups of chitosan and carboxyl groups in cellulose form ionic bonds with amino groups of chitosan. After such bonds form, they tend to rearrange through amadori transition and produce more complex bonds [339]. We therefore expected that an increase in number of carbonyl or carboxyl groups in cellulose would result in an increase in the number of bridging bonds between cellulose and chitosan and hence enhance the fixation of pigments.

4.7.1 Determination of Carboxyl Group Content in Cotton

As can be seen from Table 4-39, the methylene blue absorption values (K/S) indicated that the carboxyl group content of heavy cotton (189 g/m^2) was less than that of light cotton (110 g/m^2). If an increase in the carboxyl groups enhances cross-linking between cellulose and chitosan via formation of ionic bonds, then the fixation should be enhanced in case of cotton fabric with more carboxyl group content. But this was not the case as the degree of fixation was more for heavy cotton fabric compared to the light cotton fabric. Also, cotton fabric which was bleached twice showed a low carboxyl group content but higher degree of fixation compared to the cotton which was bleached once. It was therefore clear that the carboxyl group content of the cotton does not affect the cross-linking between chitosan and cotton nor does it enhance pigment fixation.

Table 4-39 Methylene blue absorption and corresponding fixation values by different cotton fabrics

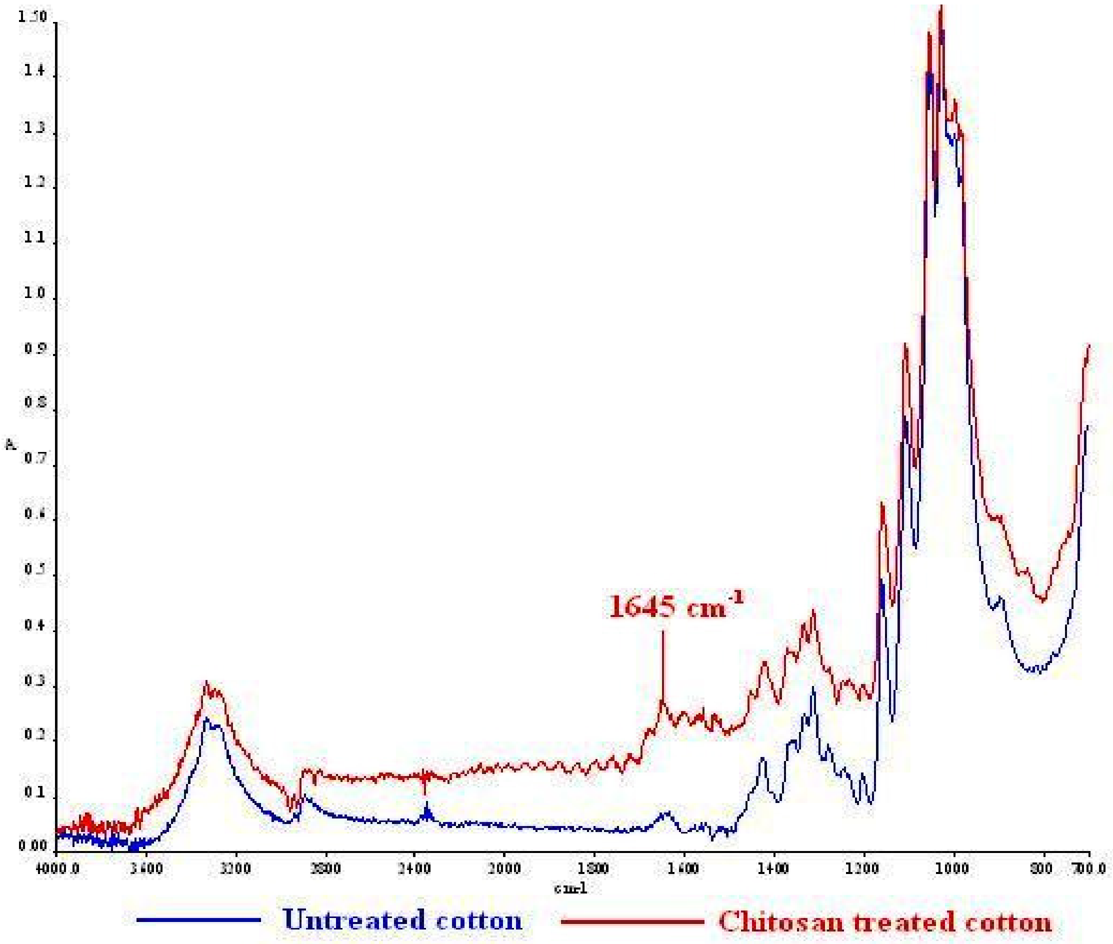
Fabric Samples	K/S at $\lambda_{max} = 670$	Degree of Fixation, %
Heavy cotton (189 g/m^2)	8.50	102.7
Light cotton (110 g/m^2)	9.98	91.7
Cotton (124 g/m^2) bleached once	8.96	85.4
Cotton (124 g/m^2) bleached twice	5.74	88.0

The cotton fabric (124 g/m^2) was bleached twice to increase terminal aldehyde groups. The purpose was to study the effect of the aldehydic carbonyl groups on the cross-linking of chitosan and cotton and on the pigment fixation. It was evident that the decrease in the methylene blue absorption value from 8.96 to 5.74 was due to the reduction in carboxyl group content. This also indicated the formation of more terminal aldehyde groups as a result of second bleaching. Also, the fixation slightly increased for cotton fabric which was bleached twice. This occurred due to increase in the aldehydic carbonyl groups which enhanced cross-linking between chitosan and cotton.

4.7.2 FTIR-ATR Analysis

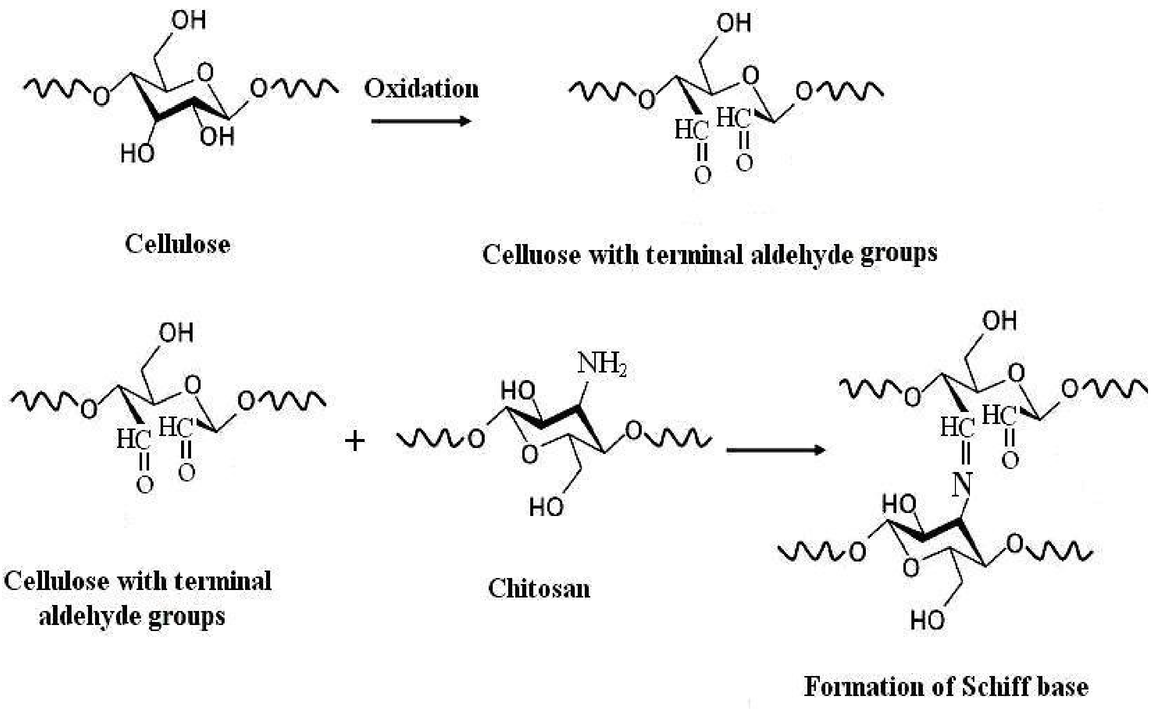
Figure 4-21 shows the FTIR-ATR spectra for untreated and chitosan treated cotton fabrics. A strong absorption peak appeared at 1645 cm^{-1} for chitosan treated cotton fabric which was absent in the untreated cotton. This suggested the formation of Schiff base (C=N double bond) between aldehydic carbonyl group of cotton and amino group of chitosan.

Figure 4-21 FTIR-ATR spectra for untreated and chitosan treated cotton fabrics



This supports the argument that the fixation of pigments on cotton fabric is due to film formation of chitosan on the fibre surface and is accompanied by cross-linking between cellulose and chitosan. The methylene blue test and FTIR-ATR analysis suggested that the cross-linking reaction between cellulose and chitosan during film formation arises by Schiff base formation between carbonyl groups of cellulose and primary amino groups of chitosan (Figure 4-22). Though only trace amounts of carbonyl groups exist in cellulose, it appears evident they play an important role in cross-linking to chitosan. It was also found that increase in the carbonyl groups of cellulose enhanced cross-linking and in turn, enhanced the pigment fixation which was not the case with carboxyl groups in cellulose.

Figure 4-22 Possible chemical reaction between cellulose and chitosan



4.8 Chitosan Post-Treatment of Different Ink Jet Printed Textile Fabrics

The degree of fixation of HP pigment based black ink on different textile fabrics post treated with chitosan is summarized in Table 4-40. The wet pick up (%) of chitosan varied from fabric to fabric.

Table 4-40 Effect of chitosan post-treatment on pigment fixation on different textile fabrics

Fabric Samples	K/S		Degree of Fixation (DF %)	Colour Difference, ΔE	WPU (%)
	Before washing	After washing			
Heavy cotton (189 g/m^2)	4.8	5.3	110.0	1.4	80
Light cotton (110 g/m^2)	4.8	4.4	91.7	1.8	90
Desized cotton (124 g/m^2)	8.1	5.8	71.6	4.8	92
Scoured cotton (124 g/m^2)	7.1	5.8	81.7	2.9	98
50/50% PET/CO (110 g/m^2)	5.3	4.2	79.3	3.2	80
100% Polyester (50 g/m^2)	6.4	1.8	28.1	16.9	45
Wool (230 g/m^2)	7.5	6.4	85.3	3.0	94
Silk (25 g/m^2)	9.2	9.1	98.9	0.4	78
Viscose (62 g/m^2)	9.7	8.7	89.7	2.3	67

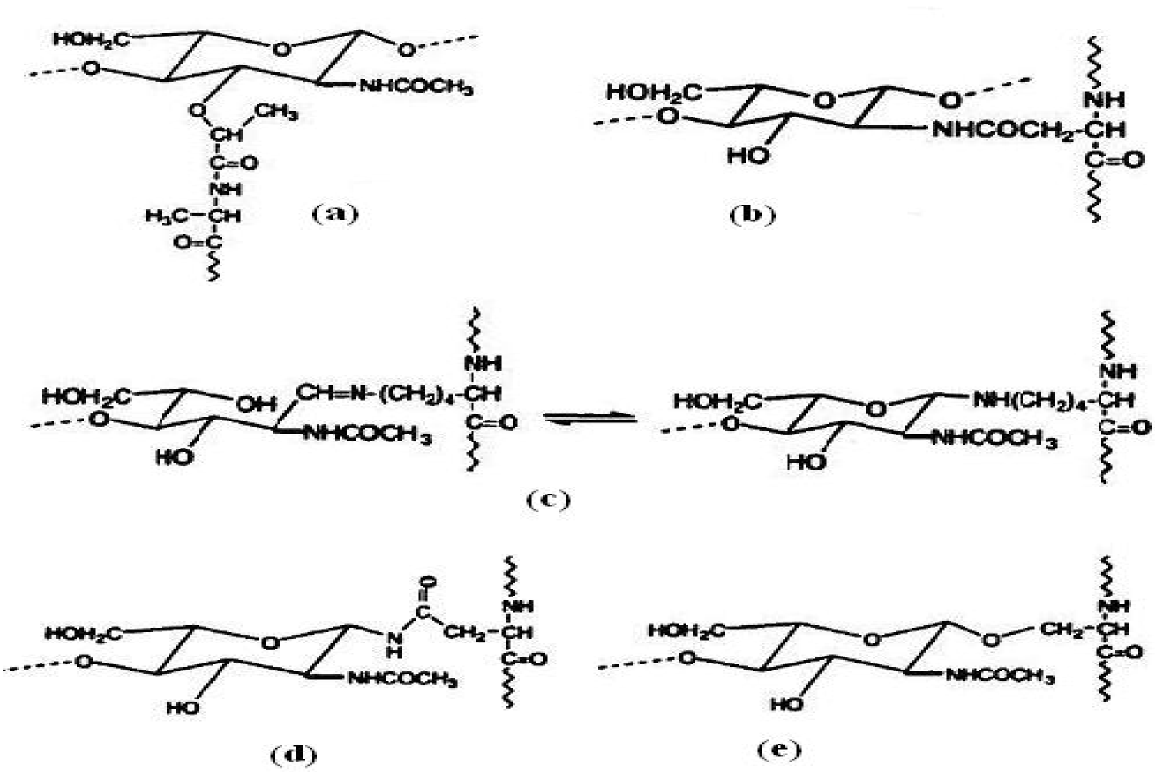
The heavy cotton showed higher fixation than the light cotton which might be due to the high amount of carbonyl groups present in the heavy cotton for cross-linking compared to light cotton. The presence of more carbonyl groups in heavy cotton seems to be obvious due to its weight (mass per unit area) almost twice than that of light cotton. The desized cotton showed decreased fixation of around 70%. This suggested that the presence of residual size and/or fats and waxes which are normally not removed during desizing might have hindered cross-linking of chitosan with cotton fabric. Hence preparation prior to printing is important. Compared to desized cotton, scoured cotton showed increase in fixation of up to 10% indicating enhanced cross-linking due to removal of fats and waxes and other impurities in cotton during scouring process. Hence, adequate preparation of fabric prior to ink jet printing and chitosan post-treatment is important.

Fixation of almost 80% was observed in case of 50/50% polyester/cotton blend fabric. The fixation in polyester/cotton blends would further improve if the ratio of cotton were increased. The 100% polyester fabric showed lowest fixation value of around 30% compared to other fabrics. This poor fixation might be attributed to the inert nature of polyester fabric and lack of reactive groups for cross-linking with chitosan. The polyester fabric also had only half the amount of chitosan due to low wet pick up (45%). Surface treatment of polyester fabric that can generate reactive groups for cross-linking with chitosan might improve fixation. Slight spreading of ink was observed on the edges of the solid image printed on polyester fabric which was due to lack of absorbency. Apart from polyester, all other fabrics did not show any spreading whatsoever when observed visually.

The application of chitosan to wool and silk fabric ink jet printed with black pigment resulted in 85% fixation on wool and close to 100% fixation for silk (Table 4-39). Both of these fibres are proteinaceous.

Various researchers have proposed number of possible bonding between chitosan and protein chains (Figure 4-23) such as (a) bonding through the carboxylic acid groups of a small number of N-acetylmuramic acid units in the chain and the amine group of a terminal alanyl residue [145]; (b) amide group formation between an unacetylated amine group of chitosan and a carboxylic group in the protein chain [340], the latter being either the C-terminal carboxylic acid group or the side group of an acidic amino acid; (c) bonding through formation of a Schiff base [341]; (d) bonding through an N-glycosidic structure involving the amide group of asparagines [342] and (e) bonding through an O-glycosidic structure involving serine [342].

Figure 4-23 Possible bonds involved in chitosan-protein complexes



This suggests that chitosan has strong affinity towards protein and that it can be used for fixation of pigments on protein fibres such as wool and silk. The lower fixation of pigments on wool fabric compared to silk fabric might be attributed to the presence of covalently bound lipids in wool which imparts hydrophobic nature to wool [343]. The bound lipids might have restricted the adhesion of chitosan on wool thereby lowering the fixation of pigments. The lower fixation of pigments on wool compared to silk could also be due to different degrees of fabric preparation, the difference in the fibre diameter and in weight per square unit area. Viscose, which is a regenerated cellulosic fibre showed almost 90% fixation of pigments after chitosan post-treatment.

In general, chitosan post-treatment worked well for all the fibres included in the present study except polyester.

4.9 Fixation of Epson CMYK Paper Inks with Chitosan (MW 156,000) Post-Treatment

From Section 4.2.6, it was seen that 10 $g.L^{-1}$ chitosan (CH82), a medium molecular weight chitosan, could fix the Epson four colour CMYK paper inks. This experiment examines whether the lower molecular weight chitosan (MW 156,000) can also fix the Epson four colour CMYK inks at a concentration as low as 3 $g.L^{-1}$.

Table 4-41 Effect of chitosan (MW 156,000) post-treatment on fixation of Epson inks

Epson Inks	Degree of Fixation (%)		
	Cured only (without chitosan post-treatment)	Post treated with medium MW chitosan (CH82) at 10 g.L^{-1} concentration	Post treated with low MW chitosan (156,000) at 3 g.L^{-1} concentration
Cyan	6.4	98.5	90.8
Magenta	43.1	99.0	93.7
Yellow	14.3	99.7	95.2
Black	80.8	99.4	96.6

Post-treatment with low molecular weight chitosan at 3 g.L^{-1} concentration gave fixations above 90% in all the four colour inks. Compared to medium molecular weight chitosan, the fixation slightly decreased in case of all the inks which might be not only due to low molecular weight but also due to lower concentration (3 g.L^{-1}) used. The degree of fixation increased in the order of CMYK. The reasons for the different fixation values of the four inks are not known (Table 4-41). The wash fastness was found to be excellent while the dry and wet rub fastness values were acceptable (Table 4-42).

Table 4-42 Effect of chitosan (MW 156,000, 3 g.L^{-1} concentration) on colour fastness of samples printed with Epson inks

Epson Inks	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Cyan	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Magenta	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Yellow	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Black	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.10 Antimicrobial Activity of Ink Jet Printed and Chitosan Post-Treated Cotton Fabric

In recent years there has been an increase in the market demand for antimicrobial textile products. Two major requirements of an antimicrobial agent used for textiles are that it should be safe for the human body and be durable to launderings. Leaching and non-leaching are the two types of antimicrobial finishes used for textiles. The leaching type finish kills the bacteria by releasing the active substances from the treated fabrics. Such a finish not only loses its antimicrobial property after repeated launderings but also kills useful organisms. It may also cause allergic reactions and rashes onto the human skin. Moreover, the micro-organisms can adapt and become resistant to such finish [344]. The non-leaching type finish is highly durable against launderings as it is bound to the fabric through chemical reactions. Hence, such finish is free from most of the drawbacks of leaching type antimicrobial finishes.

The antimicrobial activities of the ink jet printed and chitosan post-treated cotton fabrics after different numbers of launderings were evaluated as described in Section 3.3.4 and are listed in Table 4-43.

Table 4-43 Antimicrobial activity of ink jet printed and chitosan post-treated cotton fabrics against *Klebsiella Pneumoniae* after launderings[a]

Number of Launderings[a]	Number of Surviving Colonies or Cells (CFU/ml)	Reduction (%)
0 (control)	238	---
2	0	100
4	0	100
6	0	100
8	19	92
10	33	86

a. One laundering by ISO 105-C06:1994 (E) method with C1M test conditions is approximately equal to five domestic or commercial launderings at temperatures not exceeding 60 ºC.

The chitosan post-treated fabrics maintained 100% bacterial reduction for up to 6 launderings. After 8 launderings, the bacterial reduction decreased to around 90% and after 10 launderings, the bacterial reduction further decreased to 86%. The loss in the antimicrobial activity after 8 and 10 launderings is believed to be due to the loss of chitosan during laundering.

In a study carried out by Lim [176], the antimicrobial activity of chitosan treated cotton fabric against *Staphylococcus aureus* considerably decreased to 31% after only 2 launderings. This was attributed to the poor durability of chitosan treated cotton fabric due to lack of strong binding between chitosan and cotton fabrics. It was concluded that the chitosan treatment on cotton fabric cannot be used as a durable antimicrobial finishing, because the fabric needs at least 80% bacterial reduction against *Staphylococcus aureus* to be considered as an antimicrobial product. From the results obtained in the present study, the explanation of poor durability of chitosan and the conclusion drawn in Lim's study seems to be unsatisfactory. The reason for the different conclusions may be explained by the fact that the molecular weight of chitosan used in Lim's study was much lower (28,100) than the molecular weight (156,000) of chitosan used in the present study. Another, but less probable reason could be that the test organism used in the Lim's study was *Staphylococcus aureus* (Gram positive bacteria) and that used in the present study was *Klebsiella Pneumoniae* (Gram negative bacteria).

In our view, we conclude that a chitosan post-treatment can be used to provide durable antimicrobial finishing provided the MW of the chitosan is such that it can provide a durable film on the fibre surface. This study has shown that a MW of 156,000 achieves a desirable outcome. The durability of lower MW chitosans has yet to be assessed.

PART II: FORMULATION OF CHITOSAN BASED INK JET INKS

Gore [354] invented ink-set for ink jet printing which contains a polymer system which reacts with chitosan salt such as chitosan acetate (MW 5000) to produce a gel precipitate on a substrate. These ink-set provided benefits such as increased drying time, smudge fastness, smear fastness and water fastness. The present work differs from the aforementioned invention in that although it was suggested that the invention can be used on various substrates including textiles, it was specifically demonstrated on the paper rather than on textile substrate. In the above invention, the theory behind the interaction of chitosan and polymer system was not explained. It was suggested in the invention that chitosan and its derivatives can be included in the inks but no attempt was made to formulate inks containing chitosan. In the invention, the chitosan acetate was included in a separate fixer fluid rather than in an ink. In the present work, parent chitosan (MW 156,000) was used rather than the salt derivative of chitosan as mentioned in the above invention. Furthermore, no reactive polymer system was included in the inks formulated in the present work.

The work carried out so far in the present study has shown that the chitosan can be used as a textile binder for post-treatment of ink jet printed fabrics. Therefore, chitosan was selected to be used as binder in the formulations of ink jet inks to be printed on cotton fabric.

4.11 Direct Incorporation of Chitosan to Formulate Pigment Based Ink Jet Inks

The ink jet inks were formulated, evaluated, printed and cured as described in Section 3.3.11.1. Table 4-44 shows the particle size distribution of the four ink jet ink formulations prepared using chitosan. As chitosan is cationic in nature and the surface modified pigments used for ink formulations carry anionic charge on their surface, it was expected that the ionic interaction between chitosan and surface modified pigments would result in aggregation of pigments thereby causing increase in the particle size distribution. However, as seen from Table 4-44 the particle size of all the four ink formulations remained stable over period of one month. This suggested that there was no interaction between chitosan and surface modified pigments. The reason could be the low concentration of chitosan (0.16 mg/ml) and pigments (0.04 mg/ml) used for preparation of ink formulations. In addition, the polarity of solvents such as glycerol and isopropyl alcohol has been shown to affect the solubility of chitosan [347]. It is quite possible that these solvents used in ink formulations might have hindered the interaction between opposite charges of chitosan and surface modified pigments.

Table 4-44 Particle size distribution of ink formulations containing chitosan

Ink Jet Ink Formulations	Mean Particle Size Diameter (nm)	
	As prepared	After one month
Cyan 250C	100.9	100.2
Magenta 260M	120.5	120.5
Black 200	130.6	130.5
Black 300	130.3	130.2

Table 4-45 shows the effect of freeze/thaw cycling on the particle size distribution of ink formulations. Compared to storage of inks for one month, cycling between 20 & 60°C showed considerable increase in the particle size. This might have occurred due to the aggregation of pigment particles caused by the sudden change in temperature. The cycling may also have influenced the interaction between chitosan and pigment particles causing the increase in the particle size. Nevertheless, the particle size distribution of all the formulations remained well below 200 nm and within the acceptable range for ink jet printing.

Table 4-45 Effect of freeze/thaw cycling on particle size distribution

Ink Jet Ink Formulations	Mean Particle Size Diameter (nm)	
	As prepared	After 4 cycles
Cyan 250C	100.9	159.7
Magenta 260M	120.5	151.3
Black 200	130.6	151.2
Black 300	130.3	169.8

Table 4-46 shows the viscosity of the ink formulations over a period of one month and after 4 freeze/thaw cycles. The viscosity remained stable over a period of one month and after 4 freeze/thaw cycles indicating good stability of ink formulations for ink jet printing.

Table 4-46 Effect of storage period and freeze/thaw cycling on ink viscosity

Ink Jet Ink Formulations	Viscosity (centipoise) at 25°C		
	As prepared	After storage for one month	After 4 freeze/thaw cycles
Cyan 250C	2	2	3
Magenta 260M	2	2	4
Black 200	4	4	4
Black 300	3	3	3

All the ink formulations prepared were found to be quite stable in terms of particle size distribution. The viscosity, despite increasing after freeze/thaw cycling remained suitable for ink jet printing of cotton fabric. Table 4-47 shows the degree of fixation of magenta ink formulations with and without chitosan after ink jet printing on cotton fabric and curing. The magenta ink containing chitosan showed almost 97% fixation compared to the fixation (52.6%) of magenta ink without chitosan. It was clear that chitosan can enhance the fixation of the pigments on the ink jet printed cotton. Hence, it is possible to formulate inks containing chitosan for ink jet printing of cotton fabric.

Table 4-47 Degree of fixation of magenta ink formulations

Samples	K/S at λ_{max} = 530 nm before washing	K/S at λ_{max} = 530 nm after washing	Degree of Fixation (%)
Cotton fabric printed with magenta ink without chitosan	0.050	0.026	52.60
Cotton fabric printed with magenta ink containing chitosan	0.090	0.087	96.67

The colour characteristics of the ink jet printed and cured cotton fabrics are shown in Table 4-48. The colour difference (ΔE^*) was acceptable for fabric printed with chitosan containing magenta ink. The colour difference and hue difference (ΔH^*) for fabric printed with magenta ink without chitosan were high confirming marked shade difference. The ink containing chitosan showed higher chroma compared to the one without chitosan. The prints appeared lighter, less saturated and bluer for ink containing chitosan than the prints for ink without chitosan.

Table 4-48 Colour characteristics of ink formulations printed on cotton

Samples	L^*	a^*	b^*	C^*	ΔE^*	ΔH^*
Cotton fabric printed with magenta ink without chitosan	2.2	-3.3	1.5	-3.4	4.18	1.2
Cotton fabric printed with magenta ink containing chitosan	0.0	-0.6	-0.1	-0.6	0.64	-0.3

Table 4-49 shows the fastness properties of fabric ink jet printed with magenta ink formulations. The wash fastness in terms of staining was excellent in case of both inks, with and without chitosan which could be due to very low concentration of pigments used in the formulations. Wash fastness in terms of colour change was excellent in case of ink containing chitosan while it was poor in case of ink without chitosan. This again shows excellent fixation ability of chitosan resulting in production of wash fast prints. The dry rub fastness was good and the wet rub fastness was acceptable in case of ink containing chitosan. The rub fastness was poor in case of ink without chitosan due to lack of binding of pigments to the cotton fabric.

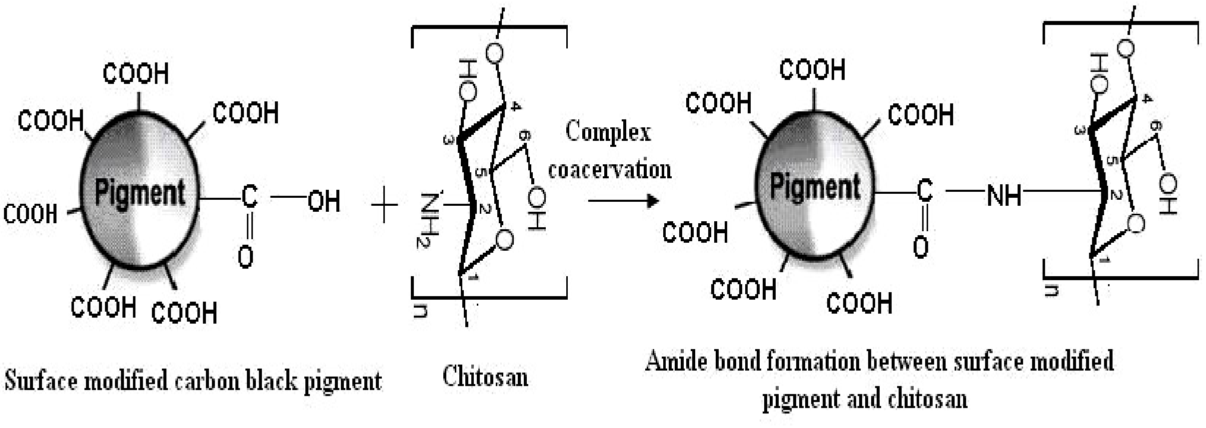
Table 4-49 Fastness properties of fabric ink jet printed with magenta inks

Ink Jet Ink Formulations	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Magenta ink without chitosan	2-3	1-2	1-2	4-5	4-5	4-5	4-5	4-5	4-5
Magenta ink with chitosan	4	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

4.12 Formulation of Ink Jet Ink using Chitosan Encapsulated Pigment Nanoparticles

In the present study, complex coacervation process was used as described in Section 3.3.11.2.1 to produce novel chitosan encapsulated pigment nanoparticles. Nanoparticles are formed by coacervation (a spontaneous phase separation process) that results from electrostatic interactions when oppositely charged species are mixed together [348]. The success of this process is mainly dependent on the intermolecular linkages created between the positively charged amino groups of chitosan and the negatively charged carboxylated groups of surface modified pigments. To the author's best knowledge, the present study is the first attempt reported to use chitosan and surface modified pigments to prepare nanoparticles and to use these nanoparticles to formulate ink jet inks for printing on cotton fabric. The proposed mechanism for the formation of chitosan encapsulated pigment nanoparticles arising from electrostatic interaction via amide linkage is shown in Figure 4-24.

Figure 4-24 Formation of amide linkage between surface modified carbon black pigment and chitosan



4.12.1 Preparation of Chitosan/Pigment Nanoparticles with Desirable Particle Size

For ink jet printing, the particle size of pigment should be at least lower than 1000 nm. Therefore, experiments were carried out to determine the ratio of chitosan and pigment at which the particle size of the chitosan/pigment nanoparticles formed was less than 1000 nm. The initial mean particle size of the Cabojet 300 carbon black pigment as measured by the ALV particle analyser was 130.30 nm. From Table 4-50, 4-51, 4-52 and 4-53, it can be seen that the particle size of the nanoparticles formed was well above 1000 nm in all cases with two exceptions. First, a particle size of 880 nm was found when 5 ml of 0.1% w/v pigment was mixed with 2 ml 0.1% w/v chitosan. Secondly, the particle size of 740 nm was obtained when 5 ml of 0.1% w/v pigment was mixed with 3 ml 0.1% w/v chitosan (Table 4-53).

It can be noted that the formation of nanoparticles with desirable particle size (i.e. less than 1000 nm) is possible only at very dilute solutions of pigment (initial concentration of 0.1% w/v) and chitosan (initial concentration of 0.1% w/v). In general, the particle size of the nanoparticles was found to be dependent on both the concentration and the ratio of the two oppositely charged species (pigment and chitosan). In the study carried out by Mohanraj (348), the particle size of the nanoparticles showed a direct correlation to the concentration of chitosan i.e. with the decrease in the final concentration of the chitosan, there was a decrease in the particle size of the nanoparticles. In the present study, no such correlation was noted.

Table 4-50 Effect of different ratios of 1% w/v pigment black to 1%w/v chitosan on the size of the nanoparticles formed

Pigment/chitosan ratio	Final concentration of pigment black (mg/ml)	Final concentration of chitosan (mg/ml)	Mean particle size (nm) (rounded)
5 ml : 0.5 ml (10:1)	9.1	0.9	3020
5 ml : 1 ml (5:1)	8.3	1.7	3630
5 ml : 2 ml (2.5:1)	7.1	2.9	1770
5 ml : 3 ml (1.67:1)	6.3	3.8	2900
5 ml : 4 ml (1.25:1)	5.6	4.5	2880
5 ml : 5 ml (1:1)	5.0	5.0	3170

Table 4-51 Effect of different ratios of 0.5% w/v pigment black to 0.5% w/v chitosan on the size of the nanoparticles formed

Pigment/chitosan ratio	Final concentration of pigment black (mg/ml)	Final concentration of chitosan (mg/ml)	Mean particle size (nm) (rounded)
5 ml : 0.5 ml (10:1)	4.5	0.5	4580
5 ml : 1 ml (5:1)	4.2	0.8	2590
5 ml : 2 ml (2.5:1)	3.6	1.4	1770
5 ml : 3 ml (1.67:1)	3.1	1.9	1490
5 ml : 4 ml (1.25:1)	2.8	2.2	1590
5 ml : 5 ml (1:1)	2.5	2.5	1350

Table 4-52 Effect of different ratios of 0.3% w/v pigment black to 0.3% w/v chitosan on the size of the nanoparticles formed

Pigment/chitosan ratio	Final concentration of pigment black (mg/ml)	Final concentration of chitosan (mg/ml)	Mean particle size (nm) (rounded)
5 ml : 0.5 ml (10:1)	2.7	0.3	3000
5 ml : 1 ml (5:1)	2.5	0.5	5050
5 ml : 2 ml (2.5:1)	2.1	0.9	1000
5 ml : 3 ml (1.67:1)	1.9	1.1	1710
5 ml : 4 ml (1.25:1)	1.7	1.3	1750
5 ml : 5 ml (1:1)	1.5	1.5	4450

Table 4-53 Effect of different ratios of 0.1% w/v pigment black to 0.1%w/v chitosan on the size of the nanoparticles formed

Pigment/chitosan ratio	Final concentration of pigment black (mg/ml)	Final concentration of chitosan (mg/ml)	Mean particle size (nm) (rounded)
5 ml : 0.5 ml (10:1)	0.9	0.1	7450
5 ml : 1 ml (5:1)	0.8	0.2	7130
5 ml : 2 ml (2.5:1)	0.7	0.3	880
5 ml : 3 ml (1.67:1)	0.6	0.4	740
5 ml : 4 ml (1.25:1)	0.6	0.4	5260
5 ml : 5 ml (1:1)	0.5	0.5	4820

In all the cases (Table 4-50, 51, 52 and 53), some sedimentation was observed due to the settling of larger particles formed during the coacervation process.

4.12.2 Formulation of Ink Jet Ink containing Chitosan/Pigment Nanoparticles

The ink jet ink containing chitosan/pigment nanoparticles was formulated as described in Section 3.3.11.2.2 and was ink jet printed on cotton as described in Section 3.3.11.2.3. The ink was visually observed for any sedimentation or settling over a period of one week. No settling or sedimentation was observed indicating the suitability of the ink to be used for ink jet printing. The amount of pigment and chitosan in the formulated ink was calculated to be approximately 0.15 mg/ml and 0.09 mg/ml, respectively. An ink without chitosan and in which the amount of pigment was adjusted to approximately 0.15 mg/ml was used as reference or blank ink.

Table 4-54 Degree of fixation of ink containing chitosan/pigment nanoparticles

Ink Jet Formulation	K/S at λ_{max} = 410 nm before washing	K/S at λ_{max} = 410 nm after washing	Degree of Fixation (%)
Cotton printed with blank carbon black pigment ink	0.100	0.044	44.00
Cotton printed with ink containing chitosan/pigment nanoparticles	0.143	0.140	97.90

From Table 4-54, the cotton fabric ink jet printed with ink containing chitosan/pigment nanoparticles showed almost 98% fixation compared to fabric printed with blank ink (44% fixation). The results showed that chitosan/pigment nanoparticles can be used to formulate ink jet inks for ink jet printing of cotton fabric.

Table 4-55 Fastness properties of fabric ink jet printed with ink containing chitosan/pigment nanoparticles

Ink Jet Ink Formulations	Rubbing Fastness[a]		Wash Fastness						
				Staining[a]					
	Dry	Wet	Colour Change[b]	Cellulose Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Carbon black pigment ink (Blank)	2	1-2	1-2	4-5	4-5	4-5	4-5	4-5	4-5
Ink containing chitosan/pigment nanoparticles	4	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5

From Table 4-55, the wash fastness in terms of staining was good in case of both the inks. Wash fastness in terms of colour change was good in case of ink containing chitosan/pigment nanoparticles it was poor in case of the blank ink without chitosan. In case of blank ink, due to absence of chitosan there was pigment loss as illustrated by poor colour change, whereas ink containing chitosan/pigment nanoparticles produced wash fast prints illustrating the chitosan capability to bind pigment to the cotton fabric. The dry and wet rub fastness were acceptable in case of ink containing chitosan/pigment nanoparticles while in case of blank ink without chitosan, both dry and wet rub fastness were found to be poor. This showed that chitosan markedly influenced the rub fastness of the ink jet printed cotton fabric.

Thus, inks containing chitosan as a binder can be formulated for ink jet printing of cotton and provide acceptable colour fastness properties. However, in both the approaches taken to formulate inks containing chitosan, the pigment concentration was very low. To achieve commercial colour strengths, the concentration of the pigment will have to be increased.

Also, the cotton samples ink jet printed with the chitosan inks were heat-cured. However, it should be possible to eliminate the curing step as chitosan has shown to form strong films when batched for at least 3 hours. In this way a simple one-step print and batch process should be feasible. This would be very commercially attractive compared to currently available technologies.

CHAPTER V CONCLUSION

A two-step method, ink jet printing with pigment based inks followed by chitosan based post-treatment was successfully proposed and developed, for the fixation of pigment based inks when ink jet printed on cotton fabrics. Both pad-dry-cure and pad-batch methods were evaluated for application of chitosan as a post-treatment. Both the methods were found suitable for chitosan application. Preliminary experiments showed that a medium molecular weight chitosan (CH82) successfully fixed the commercial pigment based ink jet inks on cotton fabric. The degree of fixation achieved with chitosan (CH82) was better than the commercial textile binders. The water soluble chitosan derivative (NCMCH82) showed low degree of fixation compared to chitosan (CH82) and commercial textile binders. This was due to the water solubility of NCMCH82.

Various factors affecting the degree of fixation of pigment based inks on cotton were explored. The effect of molecular weights of different chitosan samples on the degree of fixation of pigments was evaluated. Chitosan sample with MW <5000 showed poor fixation while chitosan sample with MW of 156,000 gave desired fixation at 3 g.L^{-1} concentration. The degree of fixation decreased in the alkaline pH range due to deprotonation of amino groups of chitosan. Depolymerisation of chitosan revealed that chitosan with MW lower than 156,000 can also be used for fixation of pigments. Addition of plasticizer such as glycerol to chitosan neither affected the degree of fixation nor improved the rub fastness of ink jet printed cotton. Among the textile softeners added to chitosan, the ester based PCE softener decreased the fixation significantly. Silicone based softener did not affect the fixation at 10% on the weight of chitosan concentration but decreased the fixation as the concentration was further increased. Tubigal WAF softener did not affect the fixation at all three concentrations. Also, the addition of softeners did not improve the rub fastness of the cotton fabrics.

The handle of the chitosan treated cotton fabrics in terms of stiffness was evaluated. The depolymerised chitosan gave acceptable hand at 1 g.L^{-1} concentration. Among the three commercial textile softeners, incorporation of Tubisoft PCE ester based softener into chitosan solution showed the most favourable effect on the stiffness of the fabric. The performance properties such as tensile strength and extension at break increased for chitosan (MW 156,000) treated cotton fabrics.

Almost 85% fixation of pigments was observed for chitosan post-treated cotton fabrics even after 50 launderings. This indicated that the chitosan post-treatment can be used as a durable finish and that there exists a strong chemical interaction between chitosan and cotton. The SEM analysis revealed the film forming ability of chitosan on the treated cotton fabric.

Methylene blue absorption test showed that the carboxyl group content of the cotton does not affect the cross-linking between chitosan and cotton nor does it enhance pigment fixation. FTIR-ATR analysis revealed that the cross-linking reaction between cellulose and chitosan during film formation arises by Schiff base formation between carbonyl groups of cellulose and primary amino groups of chitosan.

Post-treatment of different textile fabrics with chitosan (MW 156,000) showed that chitosan could successfully fix the pigment based inks on 50/50% polyester/cotton blend, wool, silk and viscose with degree of fixation ≥ almost 80%. However, the fixation achieved on 100% polyester fabric was only 28%. This could be due to low wet pick up by polyester owing to its hydrophobic nature and due to lack of reactive groups for cross-linking with chitosan. More than 90% fixation was achieved in case of the Epson CMYK inks printed on cotton, when post treated with chitosan (MW 156,000) at 3 $g.L^{-1}$ concentration.

The antimicrobial activity of ink jet printed cotton fabrics post treated with 3 $g.L^{-1}$ chitosan (MW 156,000) was quantitatively evaluated against *Klebsiella Pneumoniae.* The chitosan post treated cotton fabric showed almost 86% bacterial reduction even after the equivalent of 50 domestic or commercial launderings as carried out by ISO 105-C06: 1994 (E) method.

Inks containing chitosan were formulated and were stable in terms of particle size and viscosity over a period of one month and for four freeze/thaw cycles. A magenta ink containing chitosan was ink jet printed on cotton and showed 97% fixation in comparison to 53% fixation of magenta ink without chitosan. Chitosan encapsulated pigment nanoparticles were prepared using complex coacervation technique. Surface modified carbon black pigment with carboxylated (COO^-) surface functionality was selected for preparation of nanoparticles. Nanoparticles with mean particle size of 740 nm and 880 nm were obtained when 5 ml of 0.1% w/v pigment was mixed with 2 ml and 3 ml of 0.1% w/v chitosan, respectively. There was no correlation between the concentration of chitosan and the particle size of the nanoparticles formed. Inks were formulated using these nanoparticles and ink jet printed on cotton fabric. 98% fixation was achieved with ink containing chitosan encapsulated pigment nanoparticles while the blank ink with only surface modified carbon black pigment (without chitosan) showed 44% fixation.

In conclusion, chitosan (with DD > 90% and MW of 156,000) can be successfully utilised as a pigment binding agent and as a durable antimicrobial finish for the post treatment of ink jet printed cotton fabrics. Chitosan can also be used as a pigment binding agent to formulate inks for ink jet printing of cotton fabrics. However, further research is needed to increase the pigment concentration to achieve desirable colour strength.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE RESEARCH

1) Exploration of chitosan with MW in the range of 50,000 to 150,000 for fixation of pigment based inks on cotton and other textile fabrics.
2) Investigation of effect of degree of deacetylation on pigment fixation via chitosan post-treatment of ink jet printed fabrics.
3) Investigation of water soluble chitosan and its derivatives apart from N-carboxymethyl chitosan for post-treatment of pigment ink jet printed fabrics.
4) Fixation of insoluble dyes such as vat dyes and disperse dyes using the chitosan based post-treatment developed in the present study.
5) Formulation of inks containing chitosan with high pigment loading to achieve desirable colour strength.
6) Preparation of pigment dispersions by incorporating chitosan, with or without a suitable dispersant during milling or pigment manufacturing processes.
7) Formulation of pigment based inks using a fibre reactive chitosan derivative as a binder in order to achieve high fastness properties.
8) Exploration of the use of chitosan to develop new toners especially pigment based toners for xerographic printing.
9) Surface modification of polyester to improve degree of fixation when post treated with chitosan.
10) Commercial trials for garment printing may be conducted using a two-step process which comprises ink jet printing followed by spraying the print with chitosan and batch.
11) Commercial trials for garment printing may be conducted using a single step process, viz., ink jet printing of the garment with pigment based ink containing chitosan.

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