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A Quest for Better Textile Printed Qualities: from Inkjet Ink Chemistry to Textile Surface Modification

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Abstract

Textile fabric generally possesses porous surface structure that introduces more ink spread and penetration leading to less printing and color qualities. With different textile surfaces, printing ink has to be compatible with both physical and chemical parameters. Among so many printing processes for textile printing, inkjet printing is gradually taking places of the conventional screen printing process. Likewise, ink chemistry plays an important role in governing printing qualities. Textile surface pretreatment both physically and chemically can improve better textile printed qualities, color reproduction and product performances. This article describes briefly the types of textile fabrics, their surface chemistry, their surface modification, inkjet ink requirement and ink-textile fabric interaction to produce an acceptable printed quality. A brief summary of research activities and commercial trend of textile-inkjet printing in Thailand is given and discussed.

Keywords: Textile surface, inkjet ink chemistry, surface treatment, printed qualities.

Introduction

Ink Chemistry

The inkjet industry has seen some very interesting developments in late 2010 and so far in 2011 and made strong surges into the screen printing industry in the last decade and specifically saw dramatic market share in the graphic arts markets. This was especially so in both outdoor and indoor graphics for wide format and super-wide format printing [1].

Textile printing is one of the targeted printing substrate because the printed designed and vivid colors increase more values to the textile fabrics [2]. The colorant used in the printing inks on the textile fabrics can be dyes and pigments. The general ink components compose of colorant (dye or pigment), deionized water and cosolvent, dispersant, base and pH buffer, defoamer, penetrant or wetting agent, humectant, chelating agent, corrosion inhibitor, biocide, binder and viscosity modifier. Not all the mentioned ingredients are normally used. Due to the green house and climate change problems, water-based formulation of coating and printing are of good practice. The general water-based ink formulation contains 60-90% of water as aqueous carrier medium, 5-30% of glycol as viscosity control or humectants, 1-10% of pigment dispersion to provide color, 0.1-10% surfactant for wetting and penetrating of fabric surface, 0.05-1% of biocide to prevent biological growth of microorganisms, 0.1-0.5% buffer to control pH of the inks, and other additives added where needed at not more than 1%.

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Basic requirements of inkjet inks are jettability and printability which are controlled by viscosity and surface tension of the ink. Surface tension controls physical properties for drop formation in that dynamic surface tension of inks governs the time for drop flight during which chemical species migrate to the drop surface. On the other hand, static surface tension prevents ink from weeping out of the print head when not jetting and wetting the medium for good penetration. Viscosity affects jet dynamics by viscous damping of the generated capillary wave. The jet velocity changes the break off length of the jet. Conductivity of the drops should be less than 10 mS, high conductivity indicates salt content which can corrode print head; above a threshold value to allow complete charging of the drops for the uniform deflection. When a proper surface tension and viscosity of the ink are established, a voltage window over which a stable stimulation occurs without satellite formation of ink droplets can be realized. Another main point of the ink is the pigment-to-binder ratio and the type of pigment dispersion which provides the ink color reproduction and the product performance. Actually, both dye and pigment chemistries can promote ink-substrate interaction [3, 4].

There are many types of fiber ranging from natural fiber to man-made fiber. They include silk (amino and carboxylic acid groups), nylon (amide group), wool (amino acid and carboxylic acid groups), polyester (ester group), cotton (hydroxyl group), rayon (regenerated cellulose fiber), and polyblends (a mixture of functional groups). Due to different surface functional groups, a selection of colorants for textile substrates and their modes of interaction with fibers are given in Table 1 [5] which indicates that pigmented ink type can be used with all types of fibers.

Textile printing in Thailand has been still using the conventional screen printing for a long time. Around the year of 2000, inkjet printing on textile by inkjet printing was experimented at Chulalongkorn University under the technical cooperation between Chulalongkorn University and Canon Inc (Tokyo) after Canon announced its second inauguration with the launch of the First Global Corporation Plan, which introduced the corporate philosophy of "*kyosei*" to Thailand in 1991. The active researcher groups at the Faculty of Science, Chulalongkorn University started to do a lot of research works; then published many good technical articles and produced many capable graduates who are now working for the printing and its allied industries.

Institutional Research in Textile Inkjet Printing

Due to many different aims of each institution at university levels, there are not so many research and developments carried out effectively. The university levels namely, Chulalongkorn University (CU), King Mongkut's University of Technology Thongburi (KMUTT), and the some campuses of Rajamangala University of Technology group and Rajabhat University group and vocational college altogether nine printing institutions only offer the printing curricula with different purposes. Besides the Rajabhat and Rajamangala

Table 1 Selection of colorants for textile substrates and their mode of interaction with fibers [5]

Ink type	Fiber	Pre-treatment	Post-treatment	Color formation
Reactive dye	Cotton, silk and wool	Alkaline	Steam and wash	Covalent fiber bonding
Acid dye	Silk, wool and nylon	Acid donor	Steam and wash	Electrostatic and hydrogen bonding with fiber
Disperse dye	Polyester	Thickener	High-temperature steam and wash	Hydrophobic-solid state mechanism
Pigment	All fibers	Binder/not required*	Dry/heat	No interaction: complex surface polymer bonding mechanism

*Pretreatment may be needed when color enhancement is desired.

Universities, the printing vocational colleges are very keen at training printers directly for serving the printing industries. Only CU and KMUTT and perhaps some private universities conduct the in-depth research. Very seldom that inkjet printing researches on textile fabrics are experimented. Thanks to the generous support from Canon Inc (Tokyo) who brought in new digital printings to our department since 1992, the professors and students at both bachelor and master degrees joining hands learnt to do the digital printing in toner and inkjet printing on all kinds of substrates. The technical cooperation lasted for about 10 years. During this long duration, we received research equipment and technical guidance along with our own developments until we can set up our research methodologies and evaluations. The Department of Imaging and Printing Technology can develop its academic ability to run its Ph.D. curriculum in Imaging Technology and now an English program in Graphic Communication is progressing and it can accept its first batch of students next year.

The active research group at the Faculty of Science, Chulalongkorn University started the first project to evaluate some strategies to control fading of prints from the dye-based ink jet printing on paper [6, 7]. Then the new direction to print on the textile fabric was suggested. The aim of the textile printing research is to fine tune the existing available technologies or to synthesize new pretreatment chemicals for padding on the textile surface to obtain better inkjet printing qualities. After several investigations on the dye-based ink, the polymer-pigmented jet ink was proposed based on the reasons mentioned in Table 1.

The effects of pigment/resin inks on inkjet printing for fabrics were investigated [8, 9] and later the cotton fabric was selected as a printing substrate for further investigation. Preparation of the pigmented inkjet inks and their characterization regarding print quality of pretreated cotton fabric [10–12] were investigated. In these two researches, the pigmented inkjet inks were prepared in house by many importing pigment dispersion techniques and ink binders from Japan. Good ink jetting could be achieved with medium color saturation.

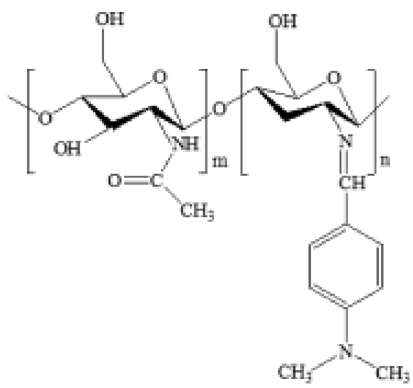
Since we have demonstrated that the inkjet printing on textile fabrics can be a better candidate and can replace the conventional screen printing [13]. Sapchokul et al. [12] found that the surface-modified pigments had a low viscosity and high surface tension because of low dispersant content. The inks formulated on surfactant dispersion showed a good compatibility, good printability and good textile properties. Therefore, one more research needed to revisit these points and the use of a lot of surfactant is not so environmentally friendly. Thus, Leelajariyakul et al. [14] used two sets of pigment dispersions: surface-modified pigments and the microencapsulated pigments to prepare the inkjet inks for silk fabric printing. The surface-modified pigments contained the sulfonated groups whereas the microencapsulated pigments had the carboxylic group with an additional polymer shell surrounding the pigments. In this work, the fabric surface pretreatment was introduced to improve the printing properties and enhancing color saturation. The cationic type reagent treated surface and the untreated surface were both printed with the two sets of in-house made inks. Both inks had their own properties because of the different ink chemistries but all had the good ink storage stability which is suitable for the piezo-type print head. When evaluating the printed fabrics, the surface-modified pigmented inks gave a better color reproduction, color gamut on both the treated and untreated fabrics. However, light fastness and wash fastness of the microencapsulated inks printed fabrics were better. Therefore, it was thought that a proper textile surface pretreatment may improve the relatively low light and wash fastnesses by a suitable pretreatment chemical.

Phattanarudee et al. [15] studied pretreatments of silk fabric with amino compounds for ink jet printing. The pretreatment solutions were serine, glycine, aspartic acid, sericin, chitosan, and a commercial pre-treating chemical called Sanfix 555. Both the untreated and treated fabrics were printed with in-house formulated pigmented inks and later steamed to fix the ink on the fabric surface. The pretreatments containing the amino compounds improved hydrophilicity of the silk fabric with the exception of chitosan. The color gamut from sericin, chitosan, and Sanfix 555 pretreatments was wider than that from the amino acid pretreatments. The chroma of the cyan color was most improved. The fabric, after the pretreatment with sericin, showed a significant improvement in dry crock fastness while wet crock fastness was improved by serine and glycine. The chitosan slightly improved both dry and wet crock fastness. Wash fastness of all the pretreated and printed fabrics including the untreated and the printed fabrics was excellent because the pigmented ink was formulated with pigment and binder. Bending stiffness of the silk fabrics after the chitosan pretreatment was significantly higher than those with other pretreatments. The ink penetration in sericin and chitosan padded layers was shallower than those for amino acids, enhancing ink deposition on the fabric surface. The amino compound pretreatments held and fixed additional ink on the fabric surfaces resulting in a wider color gamut of the inks. Although the amino group containing compound such as chitosan can interact with the anionically surface-modified pigment/binder jet inks to increase color saturation and increase color gamut, chitosan introduced stiffness to the treated fabrics [15, 16]. We tried several mentioned amino compounds and new compounds used as the fabric surface pretreatment in order to decrease stiffness of the fabrics as well as reduced concentration in the treating solution.

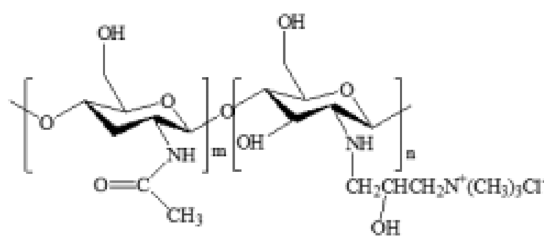
New Types of Pretreatment Chemicals

To make the treated fabrics being soft to touches after the treatment and printing, the softener-like structures such as cationic chitosan by modifying chitosan structure perhaps can be used as a fabric surface treating solution. The past research dealing with the use of pretreatment solutions of chitosan (CS), *N*- [(4-dimethyl aminobenzyl) imino] chitosan (DBIC), *N*- [(2-hydroxy-3-trimethyl ammonium) propyl] chitosan chloride (HTACC), glycine (Gly), and a mixture of CS and Gly, for padding polyester fabrics prior to printing with a set of seven-color pigmented water-based ink jet inks had been experimented. After padding the fabrics with the above cationic pretreatments, they were printed with a piezo-electric drop-on-demand jet printer. CS, DBIC and HTACC were characterized by IR and NMR spectroscopy. The zeta potentials of the pretreatment solutions, the inks and the fabrics were measured. The K/S values, color gamut, tone reproduction, outline sharpness, and the surface appearance of the fabrics were characterized. Statistical evaluation of the significance of the results was performed. Among the pretreatments, the HTACC at 0.1% (w/v) yielded fabrics with the highest K/S values, widest color gamut and gamut volume, more color saturation with good tonal reproduction, and the sharpest and smoothest outline of printed character, and a smooth fabric surface with less stiffness. Additionally, HTACC inheriting the antibacterial property is beneficial for textile application. The proposed ionic interactions between the protonated amino groups of CS and the anionic portion of the encapsulated ink pigments, and van der Waals and hydrophobic interactions between the polyester and the pigments are the likely reasons for these enhanced properties of the printed fabrics [17]. The structures of (a) DBIC and (b) HTACC both synthesized in our laboratory are shown in **Fig.1**. HTACC provides the better color performance and less stiffness at the same loading in the padding solution than does the DBIC.

Further, the effects of pretreatment solutions of chitosan (CS) and glycine (Gly) on polyester fabric and



(a)



(b)

Fig.1 Chemical structure of Chitosan derivatives:
(a): N-[(4-dimethyl aminobenzyl) imino] chitosan (DBIC)
(b): N- [(2-hydroxy-3-trimethyl ammonium) propy1] chitosan chloride (HTACC)

their printing results were in-depth investigated. The polyester fabrics were padded with CS (4% w/v) or Gly (5% w/v) solution prior to printing with a set of seven-color pigmented water-based jet inks from a piezo-electric jet printer. Hydrophobicity/hydrophilicity of the untreated and treated polyester fabrics was measured by wicking test. K/S values and color difference of the polyester printed fabrics were investigated. The printed fabric with Gly pretreatment had the higher K/S values and color difference than those with CS pretreatment due to its interaction with color inks. Gly increased hydrophilicity of the treated polyester fabric, while CS markedly decreased the hydrophilicity. Gly pretreatment solution gave the higher K/S values and color difference of the printed polyester fabric. The absorption of upper portion solution of each pretreatment solution mixed with any individual color ink was measured. It was found that the mixed solution of Gly pretreatment solution with all color inks had the significantly lower absorbance than the CS pretreatment solution. Gly, a small amino acid molecule, has an isoelectric point (PI) at 5.97. At a pH of less than 5.97 Gly is in a form of the protonated amino group ($-NH_3^+$) and can interact with the negative charge of polymer encapsulated pigment in ink leading to precipitation of Gly-pigment product. Thus, the upper portion solution had clearer solution, whereas CS a long chain polymer, was also in a form of the protonated amino groups with some hindrance due to its molecular size resulting in a lower interaction with the encapsulated pigment even though it had a relatively high absorbance because of the less pigment remained in the positive charges. This confirms that Gly rendered a higher interaction with the encapsulated pigment in the color inks [18]. The above finding indicates that by choosing the right cationic surface pretreatment chemicals padded on the fabric surface, the padded chemicals could reduce the jet ink penetration and less spreading, a higher color gamut of the printed fabric can be realized. Electronic interaction and polymer-pigment agglomeration on the fabric surface can also help increase color saturation and wider color gamut. Some new research has been reported at ICIPT 2011 [19].

Surface Modification of Textile Fabrics by Physical Method

Conventional techniques for modifying textile fabric and polyester surfaces, such as, dip-coating and padding with chemicals usually involve toxic chemical substances and large amount of waste water and, therefore, considered environmentally unfriendly. Compared with conventional techniques, plasma treatment has many advantages. Aspect of plasma-based surface treatment depends largely on the different effects which could be imparted to the fabric when using different gases to produce the plasma. In general, the treatment would only modify the outermost thin layer from nanometer up to micrometer of fabric surface while the fabric bulk properties could be kept unchanged. As a result, the plasma technique has gained more popularity as a preprocessing solution for polymer and textile materials over the past decade. At present, researches using plasma to modify the surface of textile materials have been focusing on textile preprocessing, improving dyeing property and textile functional finishing while the plasma process to enhance the quality of direct printing on fabric surface purpose has received much less attention. Nonetheless, this is an important issue since inkjet printing onto fabric has been shown to be far more superior to conventional textile printing means such as screen printing, roller printing, or transfer printing. We had demonstrated that enhanced pigment adhesion on PET fabrics could be obtained through treatments with various plasma gases. All plasma gas treatments result in increased degree of roughness as evidenced by SEM and AFM. Contact angle measurements reveal that among tested plasma gases, O_2 plasma give the highest hydrophilic properties of PET fabric while SF6 plasma treatment results in the highest hydrophobicity. Incorporation of argon, nitrogen, and oxygen elements is observed in the case of Ar, N_2, and O_2 plasma-treated fabrics, respectively, although unambiguous evidence for polar groups derived from neither nitrogen nor oxygen is not observed. When all parameters are taken into consideration, it is concluded here that improved pigment color printing efficiency is mainly ascribed to an increase in surface roughness [20-22].

Inkjet Printing Technology in Thailand

The majority of inkjet printing today in Thailand is in the drop-on-demand type. Depending on the mechanism used in the drop formation process, the technology can be categorized into two major methods: thermal and piezoelectric principles. The former is the most successful one on the market. Based on its configuration, the thermal ink-jet can be a roof-shooter with an orifice located on top of the heater, or a side-shooter with an orifice on a side located near the heater. The roof-shooter design is used in the print heads from Hewlett-Packard, Lexmark, and Olivetti. The side-shooter design is incorporated in the Canon and Xerox print heads. In the piezoelectric drop-on-demand ink-jet, the deformation of the piezo- ceramic material causes the ink volume change in the pressure chamber to generate a pressure wave that propagates toward the nozzle. This acoustic pressure wave overcomes the viscous pressure loss in a small nozzle and the surface tension force from ink meniscus so that an ink drop can begin to form at the nozzle. When the drop is formed, the pressure must be sufficient to expel the droplet toward a substrate [19].

Because smaller ink droplet volumes are required to achieve higher resolution printing, the nozzle diameter of print heads has become increasingly small. For jetting the ink droplets of 10-14 pl, nozzle diameters in the range of 20-30 μm are found in commercial printers. With the trends towards smaller diameters and lower cost, the laser ablation method has become popular for making ink-jet nozzles.

According to the Software Industry Promotion Agency (SIPA), Thailand's overall printer market in 2010 amounted to about 1.4 million units worth Bt3.98 billion. This represented a growth from 2009 of about 2.3%. Among these, about 1,045,000 inkjet printers were sold in 2010, including 350,000 single inkjet units and 695,000 all-in-one inkjet models. While the market for laser printers reached only 293,000 units, including 225,000 single laser units and 68,000 all-in-one units [23]. Thai Electronic Publishing Club reported in Table 2 about the applications of inkjet printing and estimated growth rate during the years of 2010 to 2015 in Thailand. They also predicted that inkjet printers will be 80% dominated in Thai IT market among other printers by the year 2016. Not only publishing and transpromo-prints, but also other emerging markets, such as textile printing, seem to be the most promising printing target.

Activities of Inkjet Printing in Private Sectors and Ink Industry on Textile

Most of the private sectors seldom do their own researches. The sectors usually import the finished products and equipment ready for sale or use. The companies varied from ink traders as many assembled in big malls or their premises. Authentic ink and cartridges are distributed by dealers as well as refilled inks by

Table 2 Applications in inkjet printing and their growth rate

Item	Market/Application	Growth Rate (%) During Year 2010-2015
Current Markets and Applications	Small home /small office	3
	Graphic arts	3
	Industrial/postal marking	no growth
	Large format	1
Emerging Markets and Applications	Home photo/Color copier	6
	Publishing/Transpromo	14
	Textile	9
	Medical imaging	7
	3-D printing	4
	Computer-to-plate	2

Source: Thai Electronic Publishing Club, 2010 smaller shops. The qualities varied depending on prices whoever can afford. Some research units in universities also doing inkjet ink formulations for paper printing and they did their business by setting up incubators which are legally accepted by university regulations and trade laws. Thai Inkjet Club was set up in 2004 by the advertized group of companies who print digitally and other related businesses. The purposes of the club are the venue that people in this business can meet to share their problems, experiences and providing solutions. The Club aims to upgrade and follow up the changing trends of the technologies to the member companies. Members must not be involved in politics and other illegal issues. The club has good governance and is a non-profit organization. The most frequent activities are training courses for use of the inkjet printers and the involved inks and substrates. Organizations of group tours at the related overseas trade exhibitions or conferences in digital printing are some of the secondary activity.

One of the important things of the group research is to develop the stable ink and this should be a starting point for the small business sector. Refilling of jet inks from the importing ink fluids is widely available in the market place. To develop the ink with good jettablity and long storage stability is the beginning point of research to support the local inkjet ink industry.

Several commercial research projects were requested through the SMEs incubators of some private universities. Many projects were investigated in Silaporn University for four months experimental duration in 2009. Two-thirds of the funding was provided by the Board of Investment and one-third from the requesting private company. Some of the successful projects are given here as examples of inkjet ink development and printing:

1. Developments in Production Process, Reduced Production Time and Low Capital Cost of Silk Fabric Inkjet Printing for Hand-Made Craftsmanship of House Decorations, Gifts and Promotional Products. The requested private SME is Dash International Co., Ltd., and Thai Gifts Premium and Home Decorative Items Association.

2. Research and Development of Inkjet Ink for Printing on Poly(vinyl Alcohol) Film and Activator Liquid Used for Water Transfer Printing Process. The requested private SME is Thai Cubic Technology Co., Ltd.

These two projects involved the formulations of inkjet inks used for each particular application. Testing of the finished products, both inks and the printed silk or PVA film is very crucial because of the time of service varied from products to products. Very successful outcomes and outputs were achieved from the projects.

In addition, upon surveying from the import division of the Customs Department, inkjet printers were imported and have been used in inkjet printing on special ordered textile fabrics with some of our investigated padding solutions as a pretreatment process. A small business printing house located in Nakhonpathom Province [24] is one of the successful companies from which premium products ordered specially from the high-end customers are produced. The company uses inkjet printing to create specially designs on textile fabrics, for examples, sportswear, as ordered by its customers. Modern inkjet printing machines, padding machine and necessary characterization instruments have been installed in the company for quality control.

Conclusion

Inkjet is a convenient and low cost printing process that every small office and home can afford to have becuase its printing process is very simple. Research and development of the inks suited particularly each printing substrate, a difficult task, are needed to be finely tuned all involved parameters. Currently, inkjet ink printing materials on cellulosic paper have reached the premium quality and a variety of products are available in market place. Printing on textile fabrics is being targeted with an aim to replace the conventional textile printing processes because of its more environmentally friendly process especially the water-based inkjet inks. Ink chemistry development for vivid and stable ink colors, stable color performance, and usage performance is underway to harmonize with the textile fabric modification for better ink reception by either chemically or physically pretreatment. Development of pretreatment agents has been researched at the Faculty of Science, Chulalongkorn University, as a major research problem for the quest to obtain the better printed fabric qualities. Some successful research outcome has been achieved.

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