Journal of Textiles, Coloration and Polymer Science
https://jtcps.journals.ekb.eg/
Egyptian Society for Textile Science and Technology
الجمعية المصرية لعلوم وتكنولوجيا النسيج

Enzymes in Digital Printing of Polyamide Fabric

Ahmed G. Hassabo [a]*, Nehad Z. Gouda [b], Nadeen Khaleed [b], Sohaila Shaker [b] , Neaama A. Abd El-Salam [b], Nourhan A. Mohamed [b], A. M. Ibrahim [c], and Hanan A. Othman [b]

[a] *National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Pretreatment and Finishing of Cellulose-based Textiles Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt*

[b] *Benha University, Faculty of Applied Arts, Printing, Dyeing and Finishing Department, Benha, Egypt*

[c] *Department of Chemistry - College of Pharmacy in Khartoum- of Africa University*

Abstract

The stamping techniques needed by the apparel industry must be more adaptable and environmentally friendly. In this case, digital printing with inkjet and sublimation transfer printing technology offers synthetic textile substrates a workable solution. Because it is light, soft, strong, and durable, polyamide (pa) fibre stands out among synthetic fibres. Absorbing sweat although this fabric has outstanding physical and mechanical qualities, has a low surface energy by nature, which makes it difficult for the enzyme or ink solution to stick to it during the printing process. However, gaseous plasma treatment can activate the pa surface. Non-thermal atmospheric plasma can replace chemical primers based on risky pa surface changes since it is quick, safe, and dry curing.

Keywords: digital printing, inkjet printing, polyamide fabric.

.

Introduction

An ancient art form that has been practised for thousands of years is textile printing. [1]. It is among the most varied and important ways to add colours and patterns to textile fabrics. [2]. It also refers to the process of combining a design idea, one or more colours, and a substrate (often textiles) with a natural or artificial thickener, while using a method to correctly apply the colours. [3]. The primary goal of printing is to produce vibrant patterns with distinct boundaries on textile textiles without any dye leaking outside the confines of the design motif. [4]. Textile printing is characterised as a controlled method of painting cloth with predetermined patterns or motifs using specialised printing methods and equipment. [5].

Classification of printing techniques:

Direct printing and indirect printing are the two categories of traditional textile printing procedures.

1- Direct printing: The most widely used technique for including a colour pattern is direct printing. It is known as over-printing when it is done on white clothing over previously coloured fabric. [6].

Block printing: In India, one such traditional art form that has been passed down through the years is block printing. [7]. The printing paste is applied to the design surface of the block before pressing it onto the cloth and pressing it firmly and continuously on the fabric, making a strong print by skillfully striking it on the back with a wooden mallet. No doubt raised printing blocks were used in the earliest textile printing processes (creating imprints). [8].

Screen printing: is a development of stencilling, where a coloured image is produced by transferring colour (printing paste) through openings in a silk screen placed on a fabric surface. [9].

Digital printing: One of the most intriguing advancements in the manufacturing and textile industries is digital printing. Digital textile printing has outstanding print fastness and can reproduce an unlimited variety of colours and hues. [10].

2 -Indirect printing: Direct printing and indirect printing are distinct from one another. Direct printing techniques include resist and discharge printing. Since the beginning, these methods have been used

*Corresponding author Ahmed G. Hassabo, E-mail: aga.hassabo@hotmail.com, Tel. 01102255513
Receive Date: 12 July 2023, **Accept Date:** 06 August 2023
DOI: 10.21608/JTCPS.2023.222706.1227
©2024 National Information and Documentation Center (NIDOC)

in textile printing. These styles will always be crucial since the outcomes are frequently unique and visually superior, even though contemporary technology has enabled the use of direct printing possible for many more designs and lowered the need to employ them in recent years. [11].

Resist printing: In the process of resist printing, the previously treated fabric is first imprinted with the resist agent before being dyed a different colour. A dye will only colour the portions that are not coated with the resistant paste, creating a pattern on a vibrant background. [4].

discharge printing: The foundation fabric is first printed with a discharge chemical to perform discharge printing. Using a paste containing the discharge agents, colourful textiles are printed. The discharge agent is chemically activated during the fixation process, bleaching away the ground colour to produce the white pattern. [12].

ink-jet printing: A digital printing technique called ink-jet printing enables printing on a range of textile substrates without requiring any physical contact between the substrate and the ink. [10]. Technology for inkjet printing is used in several industries, including the textile industry. because it uses digital control and a noncontact printing approach, which makes the process simple, and rapid, and uses less material. [13]. An inkjet print head is used to apply tiny droplets of dye to the fabric in this type of printing. Cotton, bamboo, and silk fabric sheets that have been carefully prepared are among the fabrics used for inkjet printing. [8].

The quality of printing is significantly impacted by the colour ink used in ink-jet printing technology. As a result, printing inks changed as printer technology advanced. [10]. Colourant (dye or pigment), solvent (water), and additional chemicals (such as surfactant, salt, and pigment ink binder) make up jetting ink. [14]. Yellow, magenta, cyan, and black are the four fundamental colours used in digital printing, which creates new challenges for textile colour mixing. [15].

Ink-jet printing for textile applications has recently attracted more attention. Speed, flexibility, inventiveness, cleanliness, competitiveness, and environmental friendliness are just a few benefits of ink-jet printing. [15]. The two main categories of inks used for fabric printing are dye-based inks and pigment-based inks. Over dye-based ink printing, pigment-based ink printing enhances the fabric's wash and light fastness. In addition to saving energy and water, it is also environmentally friendly. [16].

Inkjet printing of enzymes: Enzymes can be inkjet printed into textile surfaces to help with resource-efficient small- and large-scale product development. [17]. Enzymes are frequently utilised in solution form, making recovery, downstream processing, and associated purification difficult. Enzyme printing on solid support can overcome these difficulties while also providing opportunities for financial gain through catalysis that is more active and stable, resistant to denaturation, and has a longer shelf life. [18].

Tyrosinase: A copper-containing enzyme called tyrosinase (polyphenol oxidase) catalyses the conversion of monophenols like L-tyrosine (4-hydroxyphenylalanine) to o-diphenols like L-dopa (3,4-dihydroxy-L-phenylalanine). It can catalyse the conversion of diphenol to o-quinone, which can then undergo non-enzymatic polymerization to generate colours like melanin. [19].

Printing polyamide fabric

Polyamide: Polyamide fabric: High tensile strength, high flexibility, and outstanding chemical resistance are just a few of the excellent mechanical qualities of nylon, a polymeric fibre. The polyamide's high toughness is also due to the flexibility of the aliphatic segments in the amorphous regions. [20]. They have outstanding mechanical qualities at high temperatures as a result of the low friction coefficient (self-lubricating), high melting temperature, and glass transition temperature, giving them excellent endurance. [21].

One of the most significant synthetic fabrics is polyamides, also referred to as nylons. Atoms of carbon, hydrogen, oxygen, and nitrogen must be present in any nylon. The names of the various nylons are determined by the percentage of carbon atoms in the initial materials' molecules. Thus, nylon66 is produced from hexamethylene diamine (which has six carbon atoms per molecule) and adipic acid (which also has six carbon atoms per molecule). Nylon 6 is produced by amino caproic acid, which contains a six-carbon atom molecule. [15].

Polyamide Structure:

The two most widely used and produced polyamides are nylon 6 and nylon 66. The scheme illustrates the key structural similarities and differences between nylon 6 and 66. [22].

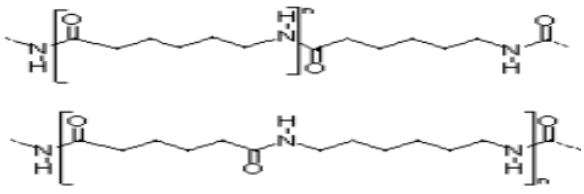


Fig. 1. Comparison between nylon 6 (above) and nylon 66 (below)

The polymer known as PA6.6 is made up of structural units connected by amide groups (-CONH-). Hexamethylenediamine (H2N(CH2) 6NH2) linear

polycondensation yields PA6.6. The first six in polyamide 6.6 stand for the number of carbons in the diacid, whereas the second six stand for the number of carbons in the diamine. [23].

Polyamide properties: Since polyamide has a lower specific gravity than the majority of other fabrics, it can be used to create extremely light, sheer fabrics with good strength. Because of nylon's high strength, it is used for many different industrial products in addition to records. Its higher abrasion resistance is four to five times more than that of wool. [22].

Dyes used in polyamide printing

1 -Acid dyes

Acid dyes are mostly used to colour P.A. fibres. It links the sulfonic group content of the dye with the amino-terminal content groups of the fibres in a process that takes place in an organic acid solution with a pH range of 4.5 to 5.5. The dye sublimation technique used in knitted PA6.6 materials has a low washing strength because the chemical linkages do not provide the essential conditions for dying. [24].

2 -reactive dyes

As they have an electrophilic group capable of forming covalent bonds with amine groups in polyamides, reactive dyes are also used to dye polyamide. The azo and anthraquinone functions, chromophoric groups, chlorotriazine, and sulfatoethylsulfonyl groups are the primary groups of reactive dyes. [25].

3 -disperse dye

Low wash fastness is achieved by dispersing colour within PA6.6 fibres. Many of the shades of the PA6.6 substrate are altered as a result of the interaction of the amine groups with the chromophores, and the colours are generally vivid, except for red shades. [25].

Digital Printing on Polyamide 6.6 Fabric Treated with Non-Thermal Plasma :

Plasma functionalization is the process of altering the traits and qualities of polymers as well as the chemistry on their surface. [26].

The change of state is the underlying physical principle of plasma technology. When given energy, a substance can transform from its solid state into a liquid and ultimately into a gas. When gaseous matter receives energy, ionisation takes place, causing it to ionise and transition into the plasma state, where electrons are released from atoms or molecules. The plasma's electrons pick up energy in the region of 0.1 to 10 eV. Without offering a situation of thermodynamic equilibrium, without which neutral ions and molecules disintegrate, the ions and molecules achieve energies in the region of 0.025 eV. [27].

Since the majority of textile materials are heat-sensitive polymers, non-thermal plasma or cold plasma, which can be used at atmospheric pressure or low pressure, is the type of plasma used in textile processes. [28].

These plasma types—plasma jet (PJ), glow discharge (GD), corona discharge (CD), and dielectric barrier discharge—can be applied to textile substrates and atmospheric pressure. [24].

the nonthermal plasma surface modification of the PA6.6 substrate under air pressure to receive dye utilising the sublimation process with dispersed dye.

Preparation of Samples and Plasma Treatment:

The knitted PA6.6 cloth was divided into samples of 25 x 60 cm and submitted for plasma application. The Model AS400 Atmospheric PressurePlasma System from Plasma Treat GmbH (Steinhagen, Germany) was installed in the Beneficiation Laboratory of SENAI CETIQT and used for plasma treatment.

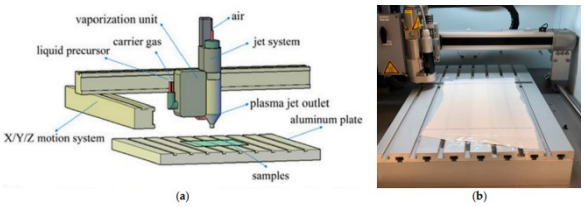


Fig. 2. (a) Schematic drawing of the experimental apparatus and (b) Sample of PA 6.6 textile substrate submitted to plasma treatment. [29].

The material was heated to 180° and sublimated for 15 seconds in a 38 cm flat press with a LIVE brand drawer and an alligator opening.

Results

1 -test for colour fastness: The sublimated fabric's colour shift and transfer in the washing were rated as acceptable or very good (4-5.5). A colour shift occurred between 4 and 4-5. The improvement in the transfer of the colour red can be seen in Table, which shows that there was no discernible difference in the transfer of samples between polyamide treated with plasma and polyamide without treatment.

2 -Colourimetry and Colouristic Strength: It was clear to see that the colours of the fabrics that

had plasma treatment were more vibrant than the hues of the untreated fabric.

3 -Lysozyme and Tyrosinase Sequential Inkjet Printing on Polyamide Fabric:

Tyrosinase: A copper-containing enzyme called tyrosinase (polyphenol oxidase) can catalyse the oxidation of tyrosine residues on some proteins, turning them into o-quinone, which can then non-enzymatically react and crosslink with amino groups. [30]. Tyrosinase has been researched for potential protein modification, including sericin, casein, and gelatin. [31].

Lysozyme: A well-researched tiny globular protein called lysozyme (1,4-N-acetylmuramidase) is used as an antibacterial, antifungal, and antiviral agent. [32]. Wool, cotton, polyester (PET), polyamide-6,6, and other fibrous materials have all had lysozyme covalently attached to them. However, most of the time, harsh surface-binding agents like glutaraldehyde were used. [33]. Three tyrosine residues in lysozyme can be catalysed by tyrosinase to covalently bond to an amino group-containing fibrous surface.

Enzymes can be printed using digital inkjet technology on textile surfaces for a variety of purposes, including bacterial suppression and controlled drug delivery. [34]. In addition to a flexible, lightweight, and sturdy support medium, textile surfaces can offer more surface area for tolerating higher numbers of enzymes.

Ink formulation and printing: For enzyme-containing inks to print well, the ionic, rheological, and printhead parameters must be adjusted properly.

The goal is to preserve adequate enzymatic activity during printing procedures, as well as acceptable ink flow, drop generation, and subsequent ink spreading on fabric.

For each combination of enzymatic ink and printed, these parameters must be changed. As a result, the viscosity, surface tension, ionic profiles, and printing temperature of the two produced inks (lysozyme and tyrosinase) were each individually optimized for the corresponding enzyme concentrations. Both enzymes were evenly distributed throughout the ink solution and had a semi-transparent appearance, which indicated a low likelihood of printed nozzle clogging. [35].

Surface modification of fabrics: Through plasma treatment, PA surfaces can be altered to introduce functional groups and improve surface energy.

This affects the fabric's physical characteristics and wetting behaviour. As a result, PA's surface wettability was increased following plasma treatment, with a reduction in water contact angle of roughly 25° compared to untreated cloth. A minor (1%) decrease in cloth tensile strength was also brought on by plasma treatment. Results showed that after plasma treatment, the atomic percentages of oxygen (6%) and nitrogen (1.8%) on the PA surface rose. At binding energy of 288 eV, the peak intensity of amido carbonyls rose (by about 13%), indicating the production of carboxylic species in the hydrocarbon or carbonyl groups of plasma-treated PA textiles. [19]. Additionally, the data analysis revealed that the increase in polar species caused the IEP of the plasma-treated tissue to move to a lower pH value (3.3) than the untreated tissue (4.3).

These altered surface characteristics may improve enzyme adhesion and other binding capacities. Due to potential electrostatic interactions, the plasma-modified PA surface might encourage improved adherence with enzymes. [36].

On-Fabric Enzyme Binding and Catalytic Activity: Tyrosinase and lysozyme-containing ink had activity levels of 654 20 and 481 21 units mL-1 against their respective substrates, respectively. As anticipated, none of the enzymes displayed any discernible action against the other enzyme's substrate. All samples were properly washed in buffer solution once the printing sequence was finished to get rid of any unbound enzymes on the PA surface.

Surprisingly, there was no discernible action against L-tyrosine in any of the printed samples. It showed that lysozyme was covalently attached to the PA surface by printed tyrosinase through the formation of irreversible complexes. [37]. Three tyrosine residues—Tyr20, Tyr23, and Tyr53—make up the structure of the lysozyme protein and can be catalysed by tyrosinase to produce o-quinones when oxygen is present.

The plasma-stimulated amino groups on the PA surface may have further non-enzymatically interacted with these o-quinones to crosslink lysozyme through an addition process. [38]. Shear stress is used in a piezoelectric printer to expel ink drops, and it has been discovered that this stress has a detrimental effect on lysozyme activity. An activity drop of 10–20% may still occur even after ink and printed parameter optimisation because of printing mechanics. The interaction between the substrate and immobilised lysozyme on PA fabric would then shift from a macro to a microenvironment, which would have an impact on activity. The anticipated covalent interaction of printed enzymes with fabric surfaces may result in steric obstruction and diffusion restriction.

Out of the three tyrosine residues on the lysozyme structure, Tyr53's proximity to the aspartic acid residue (Asp52) on the active site may also have an impact on the enzyme's ability to function. In addition, enzymes in ink solutions reacted with the

substrates in a homogenous condition, as opposed to printed enzymes, which reacted with the substrates in a heterogeneous state and could therefore exhibit lower activity. [39].

These findings suggest that the pretreatment that enzymes get and the order in which they are printed affect their capacity to actively bind with PA surfaces. Tyrosinase printed before lysozyme resulted in overall increased activity and stronger enzyme binding. The ability of plasma-treated samples to bind enzymes was superior to that of the corresponding untreated samples. comparable plasma therapies. [19]. Because of their increased roughness, hydrophilicity, and electrostatic interactions, the materials utilised in this work have been shown to improve enzyme adsorption on PA surfaces. [40].

By being exposed to oxygen and nitrogen gas by plasma treatment rather than untreated PA, tyrosinase could have obtained appropriate adsorption on the PA surface with greater access to the oxygen content required for catalysis. Even though the sample (pLT) received plasma treatment, there was less chance of such adsorption and accessibility to surface oxygen when lysozyme was printed before tyrosinase, which led to poor catalysis and surface binding. The favourable protein conformation required for the conversion of tyrosine residues to o-quinones may have also been detected by the high adsorption of lysozyme from the first print sequence to the plasma-treated surface. Thus, tyrosinase was printed on plasma-treated fabric (pTL) before lysozyme, which resulted in the maximum enzyme cross-linking capacity and overall activity. [39].

The measurement of surface -potential at various pHs of streaming liquid further proved the presence of properly cross-linked enzymes on printed PA. Comparing printed sample (pTL) to plasma-treated and untreated samples, the IEP of the printed sample (pTL) considerably changed into the alkaline zone (pH 7). The surface charge of the amino acid groups found in printed enzymes contributed to this shift. Tyrosinase and lysozyme have IEPs between pH 4.7 and pH 5.0, respectively. [39].

Antimicrobial Activity and Storage: By keeping the printed fabrics at 4 °C for 30 days, it was determined whether they had a good chance of being used. The most consistent lytic activity against the lysozyme substrate was demonstrated by sample pTL. Therefore, the identical printed sample's lytic activity was assessed against an ink solution containing lysozyme (Figure 4). As anticipated, both ink and fabric activity steadily decreased over time. When compared to ink activity on day one, fabric and ink lost over half of their activity after 30 and 20 days, respectively. Ink solution experienced this decline at a faster rate than printed cloth, though. After 30 days, the lytic activity of fabric was 63% while that of ink was 48%.whenever similar beginning activity levels are contrasted. The structure of an enzyme's protein typically undergoes irreversible changes over time, which causes a steady decline in activity. Better activity performance by printed fabric for a longer period compared to ink solution may be brought on by the protein lysozyme's conformational stabilisation brought on by cross-linking with the fabric surface. [39].

Bacterial colony formation allowed researchers to observe the antibacterial activity of lysozyme in more detail. For this, Micrococcus lysodeikticus was the bacteria of choice. Lysozyme can change some of its gram-positive, cell wall-maintaining structure. [41].

The same quantity of these bacteria was cultured on both the enzyme-printed (pTL) blank and blank cloth. A red dot in the Figure depicts a bacterial colony, and there were noticeably fewer of these colonies in the printed sample. Enzymes have a solid rectangle design printed on them. On the blank sample, colonies grew both inside and outside the cloth region in an identical pattern. On an enzyme-printed sample, however, bacterial growth was prevented in a pattern that resembled a semicircle inside the fabric. This was accomplished by using lysozyme that was printed on fabric to catalyse the formation of -(1-4) glycoside linkages between N-acetylglucosamine and N-acetylmuramic acid in the bacteria's cell wall. The printed fabric's antibacterial effectiveness was thus amply demonstrated. [42].

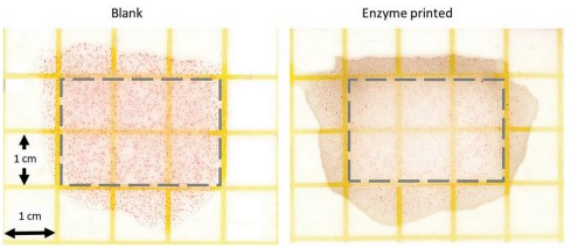


Fig. 3. Antimicrobial effect of enzyme printed polyamide-6,6 fabric. Fabrics were placed inside the grey dashed area

Ph: Tyrosinase-containing ink and cloth had an ideal pH (6) that was comparable to its activity in buffer solution. Instead of printing close to pH 9, lysozyme-containing ink was preferred to print close to pH 6. Prior to printing, lysozyme was most active around pH 9. However, compared to pH 6, the activity for pH 9 dramatically decreased after printing. The lysozyme protein structure's susceptibility to inkjet printing force at pH 9 at the ink's optimal ionic strength was the primary cause of this behaviour. [39].

Disperse UV-Absorber-Enhanced Ink-Jet Inks to Polyamide Fibres for Digital Printing:

UV absorbers have been employed to shield polymeric materials from photodegradation brought on by natural or artificial light sources rich in ultraviolet rays. Recently, there has been an increase in interest in using UV absorbers when dyeing and printing textile fabrics to prevent colour fading. Particularly for automotive coloured upholstery, which can be exposed to direct sunshine and temperatures exceeding 50oC, high light fastness of dyed/printed materials is required. [43].

Tinuvin 477-DW and Tinuvin 5333-DW were employed as the active ingredients. An aqueous UV-absorber dispersion called Tinuvin 477-DW was created for waterborne coatings. Based on a hydroxyphenyl-s-triazine chromophore that has been redshifted, it is appropriate for coatings and substrates that need robust UVA range wavelength protection. It fully satisfies the requirements of high-performance industrial, ornamental, and wood coatings thanks to its high heat stability and outstanding photo-permanence, which also give superior UV stabilisation. It is advised to use Tinuvin 477-DW for clear and light-pigmented coatings in products for caring for wood, waxes, coatings on plastics (films, bottles, containers), panels, and glasses, UV-blocking varnishes on printed materials (paper, board, and wood), glass coatings (architectural glazing, packaging), and adhesives and bonding layers, among other applications. For the protection of UVA range-sensitive substrates, prints, or contents, Tinuvin 477-DW is especially well suited. It provides highly long-lasting protection to coatings and coated substrates thanks to its extremely high thermo-, photo-, and water-leaching resilience. The colour and aesthetic of unfinished and stained wood are effectively protected by Tinuvin 477-DW. Additionally, it works particularly well for UV-blocking varnishes on coloured or printed materials to stop the prints from fading. [44].

Tinuvin 5333-DW: For use in coatings, adhesives, sealants, and printing inks, Tinuvin 5333-DW is an aqueous dispersion containing a combination of UV absorbers (UVA) and a hindered amine light stabiliser. It was created to satisfy the high performance and long-lasting demands of radiation-curable (UV, electron beam) exterior water-based industrial and architectural coatings. High thermal stability, full preservation of dry-film properties including inherent colour, transparency, gloss, and other coating film properties including water impermeability and blocking resistance, hardness and scratch resistance are not affected by Tinuvin 5333- DW's high-performance UV absorbers and low-alkaline amino ether HALS blend. Stir-in product that mixes easily with water-based systems without applying high heat. Tinuvin 5333-DW is appropriate for coatings on glass (architectural glazing, packaging materials), wood (joinery coatings, stains, deck finishes), vinyl (displays, PVC liners, tarpaulins, floor tiles), plastic (coatings), metal (overprint varnishes), board, paper, laminates, and adhesives and sealants. [44].

Ink formulation: The water-based ink formulations contain 2% w/v dye, 75% v/v water, a miscible solvent made of a 20/5 v/v mixture of 2-propanol (IPA) and ethylene glycol (EG), 0.05% w/v dispersion agent, and varying amounts of aqueous solution. The two UV absorbers each receive 10%. Included is the reference formulation sans the active ingredient. A Sonicator UP100H homogenizer was used to blend the mixture of materials for 10 minutes at room temperature. [44].

Ink-jet printing: A Canon iP7250 printer was used to print on paper, then transfer the image on paper, followed by thermostabilizing polyamide fabric for 30 seconds. Following a cold water washing, the printed samples were reduced-cleared for 20 minutes at 60° C using a solution containing 2g/l sodium dithionite and 1.5g/l sodium carbonate. After being rinsed in cold water, the samples that had cleared the reduction process were left to air dry.

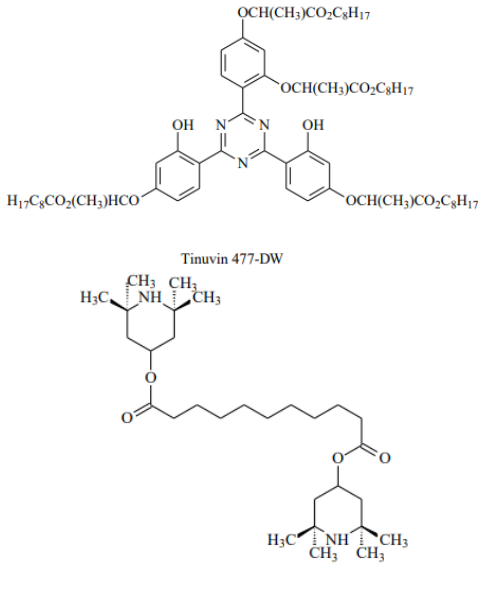


Fig. 4. Structure the UV-absorbers used.

Results

Physical Properties of the Inks: the pH levels of the inks made with Disperse Blue 60 vs storage duration. It is clear from the aforementioned numbers that the pH of the blue formulation without active ingredient 1.1 is slightly acidic. This is because the blue dye was processed and milled in an acidic atmosphere. In comparison to the reference formulation 1.1 (without an active agent), the pH values of the formulations 1.2 to 1.5 significantly

increase when the UV-absorbers Tinuvin 477-DW and Tinuvin 5333-DW are added. However, throughout the course of storage, the pH values gradually fall. This can be explained by the amino groups that both active drugs have in their structures, which give their pH values an alkaline. [45].

the effect of storage time on viscosity: Although it is not so odd for such inks to have a viscosity up to 3cP, it is usually accepted that ink-jet inks should have a viscosity lower than 2cP to be suitable for digital printing applications. [45]. During the storage period, the viscosity of all inks, including those that included and those that lacked active ingredients, first increased sharply. Alcosperse LFD, a sodium salt of a polysulphones derivative that fully dissociates to form additional anionic repulsions and causes an increase in viscosity as a function of storage time, is the dispersion agent found in all inks and is responsible for this rapid increase. Another factor contributing to the inks' high viscosity values is the high density of the active ingredients (1,05g/cm3) and their high viscosity (10–50cP). [46].

Colour measurements of digitally printed samples: As seen by the increased K/S values of the polyamide prints containing Tinuvin 477-DW and Tinuvin 5333-DW in comparison to the reference (1.1), the presence of two active ingredients in the digital ink formulation has led to a considerable dye rise.

The active ingredients may be able to form hydrogen bonds between their hydroxy groups and the amine groups or the N-heteroatom of the disperse blue dye, thereby increasing the solubility of the sparingly soluble disperse dye in the aqueous face and possibly acting as a "carrier" and encouraging higher dye uptake by polyamide fibre compared to the reference digital printing ink. [44].

Disperse Azo Dyes to be Applied as Nano-Inks in Printing polyamide fabric

Azo dyes: are organic substances that are created when two organic groups are chemically coupled together to create coloured molecules. One or more azo groups may be present in azo dyes. They make up more than half of the dyes now in use. Depending on how many azo groups there are as well as how many and what kind of oxochrome groups are present, they vary in terms of how complicated they are. [47].

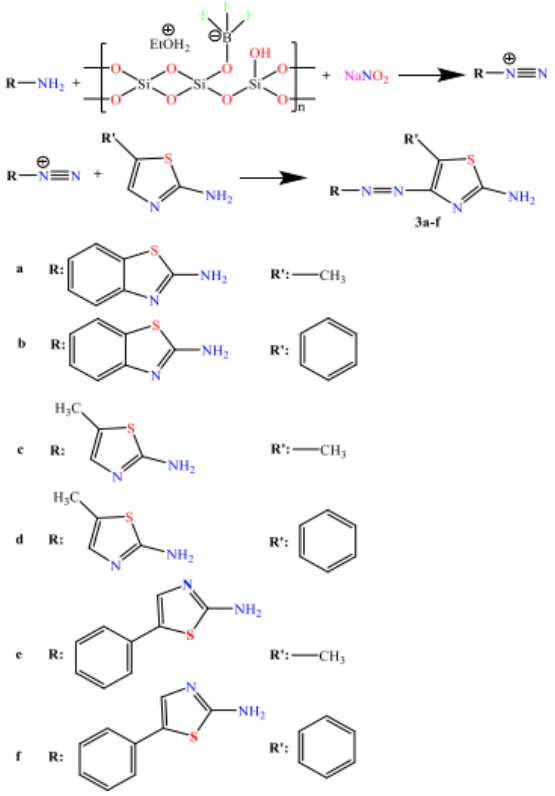
Synthesis of dyes: To create the new dyes, the free grinding diazotization technique was used. Three minutes at room temperature were spent grinding a combination of a heterocyclic amine (0.01 mol), silica-supported boron tri-fluoride (BF3.SiO2; 0.15 mol), and sodium nitrite (0.01 mol). After that, 1 ml of deionized water was added, and 2 minutes were spent stirring. To create the dye, a heterocyclic coupler (0.01 mol) was added to the mixture and stirred for 2 minutes. To isolate the catalyst, the produced dyes are dissolved in 20 cc of chloroform and filtered. Recrystallization of the products from 20 to 50 ml of ethanol. Utilizing IR spectra, the diazotization's conclusion was confirmed. [48].

Preparation of inks: The process of creating inks using the prepared dyes is known as microencapsulation. For six inks, a dye to-polymer ratio of 2:1 was created. The following formula was used to prepare the ink: 8% dye dispersion, 10% propane-1,2,3-triol, 10% 2,2'-oxydiethanol, 5% urea, 4% polyvinyl alcohol (PVA), and 63% deionized distilled water. The shell core of the dye particle is surrounded by the polymer that has the COOH group. The dispersion is dominated by the attraction between the dye molecule and the polymer; the stability of the particles is achieved by the repulsion between the particles in the water and the polymer's entropic influence. For 30 minutes, the ink's parts were ultrasonically blended at 100 rpm to create a homogeneous mixture. The ink's pH was then adjusted to a range of 7-9 by adding sodium hydroxide (10% by weight). Later, an 8 m pore-size filtering sieve was used to remove the inks. After being prepared, the inks were kept in glass containers with lids and put in a desiccator to prevent them from absorbing moisture from the air. The inks were then loaded into the inkjet printer's inking unit. [49].

Results

Synthesis of azo dyes: Normally, the diazotization process takes place below 0°C, and when it does, diazonium salts with decreased thermal stability are produced. Utilising nano BF3.SiO2, and heteroaryl diazonium salts were created. It was found to be sufficiently stable to be kept in the dry grinding technique at a comfortable temperature. In the presence of NaNO2 and BF3, amines (benzo[d]thiazole-2- amine, 5-methyl thiazole-2-amine, and 5-phenylthiazole-2-amine) quickly interacted with heterocyclic couplers to form the azo dyes.SiO2.

the fastness properties: utilising the recently created inks, depict the fastness characteristics of inkjet-printed samples. The data demonstrate that the inks' superior fastness is related to their lower particle size. [48]



Scheme 1. The suggested mechanism for azo dyes synthesis. [48]

optimum circumstances for Bacillus sp. protease enzyme modification of polyamide fabric

Proteases, cutinases, and polyamides are three enzymes that can hydrolyze PA. These enzymes have been employed successfully to hydrolyze PA on its surface, causing it to become hydrophilic. Increased polar groups (free amino and carboxylate end groups) are produced on the surface of PA as a result of surface hydrolysis. [50].

Production of Protease Enzyme: Utilizing 6% wheat germ meal and 10% moisture for 7 days, solid-state fermentation was used to create the protease enzyme of Bacillus isolate 16P. Water was used to extract the enzyme, which was then centrifuged at 6000 rpm. The filtrate was employed as a source of enzymes. [51].

Textile Enzymatic Treatments: The materials were rinsed numerous times with tap water after being washed with 10 g/l at 65°C for one hour. The fabrics were then washed for 1 hour at 65°C in an aqueous solution containing 2 g/L sodium carbonate before being repeatedly rinsed with tap water. The materials were then air-dried after being lightly strained. Under continuous orbital shaking at 150 rpm, one gramme of the fabric was incubated in a glass beaker containing a solution of 0.05 M sodium phosphate buffer (pH 8), at a liquor ratio of 50:1. All samples were rinsed with tap water numerous times, 2 g/L sodium carbonate for 1 h at 65°C, and then distilled water for 1 h at 65°C after the enzymatic treatments. The samples were then left to dry in the open air after being rinsed with running tap water for 5 minutes. [51].

Fabric Discoloration: Under the glass temperature (Tg) of PA at 50°C for 90 minutes, the staining was done. Following enzymatic processing, the fabric samples were stained simultaneously in a 500 mL sealed glass jar on a shaking water bath at the correct pH (4.5 for Basic Violet14 and 9.5 for Methylene Blue). The dyeing process used a 0.5% shade, a 50:1 liquor ratio, and 200 rpm of agitation. Following the dying process, samples were washed in an aqueous solution containing 2 g/L non-ionic detergent at 60°C for 1 hour, rinsed numerous times in tap water, and dried in an oven at 50°C for 6 hours. [51].

Printing of PA Fabrics: A manual heat transfer press with a (40* 40 cm) flatbed press at 190 C for 30 s was used to transfer print on enzymatically treated cloth samples (20* 20 cm).

Results

Effect of Treatment Time: At a temperature of around 30°C and an enzyme concentration of 0.05 mg/mL, the effect of treatment duration is examined. In comparison to untreated fabric, the protease-treated PA fabric's wettability time is reduced by around 45% after 30 minutes of treatment. By increasing the relative colour intensity of dyed PA after treatment for 30 minutes, this result is further supported. The wettability and relative colour strength are not improved by extending the response time beyond 30 minutes. [52].

Effect of Enzymatic Treatment Temperature: The importance of temperature in achieving the highest level of enzyme activity is well established. Since protease actively hydrolyzes the amide linkages in polyamide fabrics at this crucial temperature and the number of carboxylic groups rises, the hydrophilicity and the staining with basic dyes are at their highest at this temperature. This increase in carboxylic groups also increases the relative colour strength. Enzymatically treated fabrics lose some of their hydrophilicity and relative colour strength when the treatment temperature is raised by more than 30°C. [52].

Physical Properties: The enzyme treatment modifies the fibre surface visibly. Both positive (hydrophilic qualities) and partially negative (mechanical properties) alterations may occur.

The removal of a thin surface layer could only slightly decrease the fabric's thickness, with no discernible impact on the fibre strength. [53].

Summary: Synthetic textile substrates can now benefit from digital printing using inkjet and sublimation transfer printing technology. In contrast to other synthetic fibres, polyamide (PA) fibre is light, soft, strong, and long-lasting. soaking up sweat Despite the exceptional physical and mechanical properties of this fabric, it has a low surface energy by nature, which makes it challenging for the enzyme or ink solution to adhere to it during the printing process. A gaseous plasma treatment, however, can make the PA surface active. Since non-thermal atmospheric plasma is a speedy, environmentally friendly, and dry curing process, it can substitute chemical primers based on dangerous PA surface changes. The findings revealed a reduction in the textile surface's contact angle, 4-5 grayscale results for colour transfer and change during washing, and an increase in colour intensity. These circumstances permitted sublimation in the knitted PA6.6 fabric, which displayed improved colour strength and washability.

Conflicts of interest

There are no conflicts to declare

Funding sources

There is no fund to declare

Acknowledgments

The authors are gratefully-grateful to acknowledge the Faculty of Applied Arts, Benha University. Furthermore, the authors are gratefully grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

References

[1]. Yen, M.-S. and Chen, C.-W. Effect of chitosan on resist printing of cotton fabrics with reactive dyes, *African Journal of Biotechnology*, 10(8) 1421-1427 (2011).

[2]. Sarkodie, B., Tawiah, B., Agbo, C. and Wizi, J. Status and development of transfer printing in textiles—a review, *AATCC Journal of Research*, 5(2) 1-18 (2018).

[3]. Bae, J. and May-Plumlee, T. Customer focused textile and apparel manufacturing systems: Toward an effective e-commerce model, *Journal of textile and apparel, technology and management*, 4(4) 1-19 (2005).

[4]. Klaichoi, C., Mongkholrattanasit, R. and Rungruangkitkrai, N. Printing of silk fabric with reactive dye using flour of wild taro corm as a resist printing paste, Trans Tech Publ, pp. 503-506.

[5]. Chapman, R. Applications of nonwovens in technical textiles, Elsevier, (2010).

[6]. Haggag, K., Ragheb, A.A., Abd El-Thalouth, I., Nassar, S.H. and El-Sayed, H. A review article on enzymes and their role in resist and discharge printing styles, *Life Science Journal*, 10(1) 1646-54 (2013).

[7]. Kašiković, N., Vladić, G. and Novaković, D. Textile printing–past, present, future, *Gazette of Chemists, Technologists & Environmentalists of Republic of Srpska/Glasnik Hemicara, Tehnologa i Ekologa Republike Srpske*, 35-46 (2016).

[8]. Purushothama, B. Handbook of value addition processes for fabrics, Woodhead Publishing India PVT. Limited, (2019).

[9]. Bakr, M., Taha, M.A., Osman, H. and Ibrahim, H.M. Novel green printing of cotton, wool and polyester fabrics with natural safflower dye nanoparticles, *Egy. J. Chem.*, 64(11) 6221-6230 (2021).

[10]. Javoršek, D. and Javoršek, A. Colour management in digital textile printing, *Coloration Technology*, 127(4) 235-239 (2011).

[11]. Kaimouz, A.W., Wardman, R.H. and Christie, R.M. The inkjet printing process for lyocell and cotton fibres. Part 1: The significance of pre-treatment chemicals and their relationship with colour strength, absorbed dye fixation and ink penetration, *Dyes and Pigments*, 84(1) 79-87 (2010).

[12]. Hossain, M., Raman, M. and Islam, M. Overview of piece printing process in textile industry, *Journal of polymer and Textile Engineering*, 12 (2015).

[13]. Shah, M.A., Lee, D.-G., Lee, B.-Y. and Hur, S. Classifications and applications of inkjet printing technology: A review, *IEEE Access*, 9 140079-140102 (2021).

[14]. Majumdar, A., Das, A., Alagirusamy, R. and Kothari, V.K. Process control in textile manufacturing, Elsevier, (2012).

[15]. El-Kashouti, M., Elhadad, S. and Abdel-Zaher, K. Printing technology on textile fibers, *Journal of Textiles, Coloration and Polymer Science*, 16(2) 129-138 (2019).

[16]. El-Hennawi, H.M., Shahin, A.A., Rekaby, M. and Ragheb, A.A. Ink jet printing of bio-treated linen, polyester fabrics and their blend, *Carbohydrate Polymers*, 118 235-241 (2015).

[17]. Fletcher, K. Sustainable fashion and textiles: Design journeys, Routledge, (2013).

[18]. Beletskaya, I.P. and Ananikov, V.P. Transition-metal-catalyzed c–s, c–se, and c–te bond formations via cross-coupling and atom-economic addition reactions. Achievements and challenges, *Chemical Reviews*, 122(21) 16110-16293 (2022).

[19]. Biswas, T.T., Yu, J. and Nierstrasz, V.A. Piezoelectric inkjet printing of tyrosinase (polyphenol oxidase) enzyme on atmospheric plasma treated polyamide fabric, *Scientific Reports*, 12(1) 6828 (2022).

[20]. Louzi, V.C. and de Carvalho Campos, J.S. Corona treatment applied to synthetic polymeric monofilaments (pp, pet, and pa-6), *Surfaces and Interfaces*, 14 98-107 (2019).

[21]. Nascimento, L., Gasi, F., Landers, R., da Silva Sobrinho, A., Aragão, E., Fraga, M., Petraconi, G., Chiappim, W. and Pessoa, R. Physicochemical studies on the surface of polyamide 6.6 fabrics functionalized by dbd plasmas operated at atmospheric and sub-atmospheric pressures, *Polymers*, 12(9) 2128 (2020).

[22]. Wingate, I.B. and Mohler, J.F. Textile fabrics and their selection, Prentice-Hall, (1984).

[23]. Starczak, R. and Wąs-Gubała, J. Uv–vis microspectrophotometric study of wool and polyamide fibres dyed with analogous gryfalan dyes, *Dyes and Pigments*, 132 58-63 (2016).

[24]. Saleem, M.A., Pei, L., Saleem, M.F., Shahid, S. and Wang, J. Sustainable dyeing of nylon fabric with acid dyes in decamethylcyclopentasiloxane (d5) solvent for improving dye uptake and reducing raw material consumption, *Journal of Cleaner Production*, 279 123480 (2021).

[25]. Hunger, K. Industrial dyes: Chemistry, properties, applications, John Wiley & Sons, (2007).

[26]. Iqbal, M., Dinh, D.K., Abbas, Q., Imran, M., Sattar, H. and Ul Ahmad, A. Controlled surface wettability by plasma polymer surface modification, *Surfaces*, 2(2) 349-371 (2019).

[27]. Dave, H., Ledwani, L. and Nema, S.K. Nonthermal plasma: A promising green technology to improve environmental performance of textile industries, The impact and prospects of green chemistry for textile technology, Elsevierpp. 199-249, (2019).

[28]. Amara, I., Miled, W., Slama, R.B., Chevallier, P., Mantovani, D. and Ladhari, N. Surface modifications by plasma treatment, chemical grafting and over dyeing of polyamide nets to improve the antifouling performance in the aquaculture field, *Dyes and Pigments*, 166 107-113 (2019).

[29]. Yan, X., Liu, G.-S., Yang, J., Pu, Y., Chen, S., He, H.-W., Wang, C., Long, Y.-Z. and Jiang, S. In situ surface modification of paper-based relics with atmospheric pressure plasma treatment for preservation purposes, *Polymers*, 11(5) 786 (2019).

[30]. Lantto, R., Heine, E., Freddi, G., Lappalainen, A., Miettinen-Oinonen, A., Niku-Paavola, M.-L. and Buchert, J. Enzymatic modification of wool with tyrosinase and peroxidase, *Journal of the Textile Institute*, 96(2) 109-116 (2005).

[31]. Fu, J., Su, J., Wang, P., Yu, Y., Wang, Q. and Cavaco-Paulo, A. Enzymatic processing of protein-based fibers, *Applied microbiology and biotechnology*, 99 10387-10397 (2015).

[32]. Smolelis, A.N. and Hartsell, S.E. Factors affecting the lytic activity of lysozyme, *Journal of bacteriology*, 63(5) 665-674 (1952).

[33]. Edwards, J.V., Prevost, N.T., Condon, B. and French, A. Covalent attachment of lysozyme to cotton/cellulose materials: Protein verses solid support activation, *Cellulose*, 18 1239-1249 (2011).

[34]. Nierstrasz, V. and Cavaco-Paulo, A. Advances in textile biotechnology, Elsevier, (2010).

[35]. Revathi, R., Rameshkumar, A. and Sivasudha, T. Spectroscopic investigations on the interactions of agtio2 nanoparticles with lysozyme and its influence on the binding of lysozyme with drug molecule, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 152 192-198 (2016).

[36]. Duckworth, H.W. and Coleman, J.E. Physicochemical and kinetic properties of mushroom tyrosinase, *Journal of Biological Chemistry*, 245(7) 1613-1625 (1970).

[37]. Cieńska, M., Labus, K., Lewańczuk, M., Koźlecki, T., Liesiene, J. and Bryjak, J. Effective l-tyrosine hydroxylation by native and immobilized tyrosinase, *PLoS One*, 11(10) e0164213 (2016).

[38]. Kang, G.D., Lee, K.H., Ki, C.S., Nahm, J.H. and Park, Y.H. Silk fibroin/chitosan conjugate crosslinked by tyrosinase, *Macromolecular research*, 12 534-539 (2004).

[39]. Biswas, T.T., Yu, J. and Nierstrasz, V.A. Sequential inkjet printing of lysozyme and tyrosinase on polyamide fabric: Sustainable enzyme binding on textile surface, *Advanced Materials Interfaces*, 9(22) 2200723 (2022).

[40]. Kubiak-Ossowska, K., Jachimska, B., Al Qaraghuli, M. and Mulheran, P.A. Protein interactions with negatively charged inorganic

surfaces, *Current opinion in colloid & interface science*, 41 104-117 (2019).

[41]. Salton, M.R.J. Cell wall of micrococcus lysodeikticus as the substrate of lysozyme, *Nature*, 170 746-747 (1952).

[42]. Jolles, P. Recent developments in the study of lysozymes, *Angewandte Chemie International Edition in English*, 3(1) 28-36 (1964).

[43]. Kehayoglou, A. and Tsatsaroni, E. Dyeing of polyester fabrics with disperse dyes in the presence of a uv-absorber, *Dyes & Pigments*, 23(IKEEART-2019-1929) 53-63 (1993).

[44]. Ek, K. and Nikolaidis, N.F. Disperse ink-jet inks with uv-absorbers as active agents for digital printing to polyester and polyamide fibres.

[45]. Karanikas, E.K. and Nikolaidis, N.F. Preparation of ink-jet inks with quinizarin as "antifraud marker" for textile digital printing, *East African Scholars Journal of Engineering and Computer Sciences*, 3(IKEEART-2020-3901) (2020).

[46]. Lozowski, D. Basf plans to build dispersions plant in huizhou, china, *Chemical Engineering*, 117(9) 63-64 (2010).

[47]. Carmen, Z. and Daniela, S. Textile organic dyes-characteristics, polluting effects and separation/elimination procedures from industrial effluents-a critical overview, IntechOpen Rijeka, (2012).

[48]. Ahmed, K., Shahin, A., Ragheb, A. and El-Hennawi, H. A facile synthesis with one step of disperse azo dyes to be applied as nano-inks in textile printing, *Biointerface Research in Applied Chemistry*, 11(4) 11713-11723 (2020).

[49]. Leelajariyakul, S., Noguchi, H. and Kiatkamjornwong, S. Surface-modified and micro-encapsulated pigmented inks for ink jet printing on textile fabrics, *Progress in Organic Coatings*, 62(2) 145-161 (2008).

[50]. Miettinen-Oinonen, A., Puolakka, A. and Buchert, J. Method for modifying polyamide, *E P2005751935*, (2007).

[51]. O'Neill, A., Araújo, R., Casal, M., Guebitz, G. and Cavaco-Paulo, A. Effect of the agitation on the adsorption and hydrolytic efficiency of cutinases on polyethylene terephthalate fibres, *Enzyme and Microbial Technology*, 40(7) 1801-1805 (2007).

[52]. El-Ola, S.M.A., Moharam, M.E., Eladwi, M.M. and El-Bendary, M.A. Optimum conditions for polyamide fabric modification by protease enzyme produced by bacillus sp, (2014).

[53]. El-Ola, S.M.A., Moharam, M.E. and El-Bendary, M.A. Optimum conditions for surface modification of pet by lipase enzymes produced by egyptian bacilli in comparison with standard one, (2013).

الانزيمات في الطباعة الرقمية لأقمشة البولي أميد

أحمد جمعه حسبو [1] * ، نهاد جودة [2]، نادين خالد [2]، سهيلة شاكر [2]، نعمة عبد السلام [2]، نورهان محمد [2]، أ. م. إبراهيم[3] و حنان علي عثمان [2]

[1] المركز القومي للبحوث (60014618 ID Scopus) ، معهد بحوث وتكنولوجيا النسيج ، قسم التحضيرات والتجهيزات للألياف السليلوزية -الجيزة - مصر

[2] جامعة بنها - كلية الفنون التطبيقية - قسم طباعة المنسوجات والصباغة والتجهيز - بنها - مصر

[3] قسم الكيمياء - كلية الصيدلة بالخرطوم - جامعة أفريقيا

المؤلف المراسل: البريد الإلكتروني: aga.hassabo@hotmail.com

الملخص

يجب أن تكون تقنيات الختم التي تحتاجها صناعة الملابس أكثر قابلية للتكيف وصديقة للبيئة. في هذه الحالة ، توفر الطباعة الرقمية باستخدام تقنية الطباعة النافثة للحبر وطباعة نقل التسامي ركائز النسيج الصناعي حلا عمليا. نظرا لأنها خفيفة وناعمة وقوية ومتينة ، تبرز ألياف البولي أميد (pa) بين الألياف الاصطناعية. يمتص العرق على الرغم من أن هذا النسيج يتمتع بصفات فيزيائية وميكانيكية رائعة ، إلا أنه يتمتع بطاقة سطح منخفضة بطبيعته ، مما يجعل من الصعب على محلول الإنزيم أو الحبر الالتصاق به أثناء عملية الطباعة. ومع ذلك ، يمكن أن يؤدي علاج البلازما الغازية إلى تنشيط سطح السلطة الفلسطينية. يمكن أن تحل البلازما الجوية غير الحرارية محل الاشعال الكيميائية بناء على التغيرات السطحية المحفوفة بالمخاطر لأنها معالجة سريعة وآمنة وجافة.

الكلمات المفتاحية: الطباعة الرقمية ، الطباعة النافثة للحبر ، نسيج البولي أميد.