Innovative Technologies for Sustainable Textile Coloration, Patterning, and Surface Effects

Faith Kane, Jinsong Shen, Laura Morgan, Chetna Prajapati, John Tyrer, and Edward Smith

Abstract The environmental impact of textile dyeing and finishing is of paramount concern in the textile industry. Enzyme and laser processing technologies present attractive alternatives to conventional textile coloration and surface patterning methods. Both technologies have the capability to reduce the impact of manufacturing on the environment by reducing the consumption of chemicals, water and energy, and the subsequent generation of waste.

Two emerging textile processing technologies, laser processing and enzyme biotechnology, were investigated as a means of applying surface design and color to materials with a focus on improving the efficiency and sustainability of existing textile design and finishing methods.

Through industrial stakeholder engagement and interdisciplinary research involving textile design, fiber and dye chemistry, biotechnology and optical engineering, this design-led project brought together design practice and science with a commercial focus. Each technology was used to modify targeted material properties, finding and exploiting opportunities for the design and finishing of textiles. The work resulted in a catalog of new coloration and design techniques for both technologies making it possible to achieve: selective surface pattern by differential dyeing, combined three-dimensional and color finishing and novel coloration of textile materials.

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The chapter provides a literature review mapping the use of enzyme biotechnology and laser processing technology within textile design and manufacturing to date, identifying current and future opportunities to reduce environmental impacts through their application. The methodological approach, which was interdisciplinary and design-led, will be introduced and the specific design and scientific methods applied will be detailed. Each of the techniques developed will be discussed and examples of the design effects achieved will be presented. And, an indication of the reductions in chemical effluent, efficiencies in resource use, and design-flexibility in comparison with traditional textile coloration and surface patterning techniques will be given.

Keywords Textile coloration · Laser processing · Enzyme processing · Agile manufacturing · Sustainable design · Material finishing · Textile design

1 Introduction

Color, pattern, and surface effects are fundamental elements of textile design and production, and critical to the functional and expressive role they play in material culture. Dyeing, printing, and finishing processes offer extensive opportunities for creativity and innovation within this area, but in the context of globalized mass production, they have become one of the most environmentally damaging facets of the textile industry. Due to the scale of the industry, the environmental and social impacts are significant and have been identified as one of the key challenges to achieve sustainability within the sector. Traditional methods routinely involve harmful chemicals that can have devastating effects on workers' health and the local environment through exposure and water and air pollution. In addition, vast amounts of water and energy are consumed during processing, leaving large water footprints in the developing economies where much industrial activity currently occurs, adding to the decline of water, reducing sources of clean water, and increasing associated costs [77].

In response to this, advances in technology are emerging that facilitate new methods of textile coloration, pattern, and surface effects with promising signs for more environmentally friendly processing [42]. Methods such as plasma processing, supercritical carbon dioxide dyeing, ultrasonic dyeing, and digital printing have begun to be adopted within various industrial contexts. Plasma treatment, for example, aids more efficient dyeing through facilitating increased dyeing rates, dye-bath exhaustion, and improved dye homogeneity on all fiber types [37]. Supercritical carbon dioxide dyeing, adopted for some product ranges by brands such as Nike and Adidas, claims waterless processing without effluent production, resulting in high dye fixation and good leveling on polyester with potential for application to a wider range of substrates [8, 17]. Within the context of circular design and manufacturing, ultrasonic dyeing has been implemented to enable natural dye solutions for natural and regenerated fiber by IndiDye® [33]. Within this process, ultrasonic pressure waves push the dye into the core of the fiber eliminating the need for chemical fixatives, auxiliaries, and wastewater [26]. And, digital printing methods have enabled more bespoke and on-demand modes of textile coloration, pattern, and surface design through platforms such as Spoonflower, which have the potential to minimize surplus stock and preconsumer waste [84].

Alongside these approaches, enzyme and laser processing technologies present attractive alternatives to conventional methods of producing color, pattern, and surface effects and have the capability to minimize the impact of manufacturing on the environment through increasing efficiency and reducing the consumption of chemicals, water, and energy. This presents opportunities for sustainable innovation through the redesign and modification of existing products and systems. Further, both technologies have the potential to catalyze and facilitate new postindustrial systems of production and consumption through opportunities for open and codesign, agile, and responsive manufacturing.

1.1 Overview

This chapter provides a summary of research undertaken to investigate laser processing and enzyme biotechnology as means of applying color, pattern, and surface effects to textiles with a focus on providing more efficient alternatives to traditional techniques. Through industrial stakeholder engagement and interdisciplinary research involving textile design, fiber and dye chemistry, biotechnology, and optical engineering, this textile-led project brought together design practice and science with a commercial focus. Each technology was used to modify targeted material properties, identifying and exploiting opportunities for the design, and finishing of textiles. The work resulted in a catalog of new coloration and design techniques for both technologies.

This chapter provides overviews of the use of laser processing and enzyme biotechnology within textile design and manufacturing to date, identifying current and future opportunities to reduce environmental impacts through their application. First, the methodological approach, which was interdisciplinary and design-led, will be introduced. Each of the techniques developed during the work will be discussed, and examples of the design effects achieved will be presented. Finally, an indication of the reductions in chemical effluent, efficiencies in resource use, and design flexibility in comparison with traditional textile coloration and surface patterning techniques will be given.

1.2 Methodology

The work undertaken employed a textile-led interdisciplinary methodology, drawing on methods associated with design, craft, science and engineering. These areas find a natural meeting point within textile practice, which tacitly draws on knowledge from each [68]. While it has been noted that engineers and designers rarely meet within commercial settings [52], the need for interdisciplinarity within research and innovation has grown in response to the complexity of current societal challenges [19, 25, 53]. Within this context, textile design research methodologies have evolved over recent decades to construct bridges between concepts of beauty and utility, aesthetics and function, which enable the investigation of the imaginative alongside the technical, and more latterly toward the development of "quantified design" [25].

The research outlined in this chapter is aligned with such thinking, employing methods originating in design practice and craft, alongside scientific experiment in a unified approach. This was underpinned by the establishment of a team of researchers with backgrounds in design, textile chemistry and biotechnology and optical engineering. Distinct but aligned periods of creative exploration and scientific experiment were undertaken and synthesized through design practice [51, 52, 70]. This generated both qualitative and quantitative data, which was analyzed to understand: the creative potential of the techniques established; the properties and qualities of resulting textiles as relevant to industry; and the potential savings in chemical, water, and energy use. The aim was to investigate the creative potential of laser and enzyme processing as more sustainable alternatives to traditional methods of achieving textile coloration, pattern, and surface effects. As such, the work progressed to: establish workshop conditions for textile sampling using both laser and enzyme processing; develop new techniques for coloration, patterning, and surface effects; and create textile design collections for analysis, review, and evaluation. The following text provides further detail relating to the methods employed in regard to both the laser and enzyme investigations, respectively.

2 Laser Processing

A laser is a device that emits an intense beam of light composed of electromagnetic waves that are in phase (coherent) and of the same wavelength (monochromatic). Infrared and ultraviolet laser irradiation can be harnessed for photothermal and photochemical properties, respectively. Lasers are used widely in manufacturing for materials processing, including cutting, marking, welding, and drilling, as well as for medical procedures and measurement applications [10]. The use of laser technology for textile processing is less established. However, as research develops and the cost of machinery becomes more affordable for factories and educational institutions, their use has become more widespread [30].

Lasers provide an energy efficient means of material processing and have been shown to have fiber modification capabilities that can enhance and improve dyeability without excessive water or chemicals, therefore offering potential environmental benefits compared to traditional textile dyeing processes. For graphic processing, they enable specificity and control by digital generation of imagery. The effect of laser irradiation on different textile substrates varies depending on the method of application and the material. Laser technology's advantages of digital control for design flexibility and precision capabilities coupled with noncontact processing offer unique benefits not achievable by other means. It is these unique attributes and controllable parameters of the laser that offer potential for novelty and innovation through consideration of new processes and opportunities for textile design.

For the design of textiles, laser processing has been utilized across the fashion, accessory, and home textile market sectors. Couture and high street clothing sectors have embraced laser technology to create fashion-led effects, such as fringing, and as a form of garment embellishment. Offering precision cutwork with heat sealing of fabric edges to prevent fraying, laser cutting technology has become standard equipment in university art and design departments, leading to a growth in creative use within textile design. For example, Hur [32] used the laser to cut individual textile units to build customizable, modular fabrics, while Moriarty's [58] layered laser cut rubber "lace" gave a new aesthetic to the traditional textile process of lace making.

While laser technology excels in providing efficient, noncontact cutting, it can also be harnessed for the purpose of textile surface modification. Lasers have been used to replace chemical and wet processing techniques to recreate conventional textile surface design effects such as devoré and stonewashed denim. Infrared CO_2 laser technology has been adopted successfully for commercial processing of denim in the manufacture of worn or weathered-look jeans. Through precise parameter control, infrared laser irradiation can fade the color of indigo-dyed denim by removing a thin layer of dye from the surface of the cotton, revealing the white undyed fiber underneath [38, 62, 63]. In comparison to traditional stone washing processes, the technique has eliminated the use of chemicals and reduced water use by 85% saving significant wastewater effluent [18]. This has led to the development of garment and textile-specific laser machinery. For example, Jeanologia [34] produced laser processing equipment capable of processing fabric lengths and direct-to-garment (DTG) laser finishing equipment that allows the garment to be processed in three-dimensional form.

Advantages of utilizing infrared laser irradiation as an efficient, dry, and targeted heat source have positive implications for reduction of wastewater and processing time of textile production in comparison to traditional wet finishing methods. These advantages have been beneficial to denim manufacture in creating laser-faded effects on denim [18, 63]. As such, use of CO_2 laser technology has become increasingly commonplace in the textile industry [62]. The use of laser technology on other textile substrates presents numerous further opportunities for sustainability in the field of textile research. This section reviews emerging laser-based techniques for textile coloration and surface patterning by utilizing laser irradiation for fiber modification, dye fixation, or thermal setting.

2.1 Laser Coloration and Surface Patterning: Fiber Modification

Research studies have reported harnessing the photochemical and photothermal energy that laser processing can provide to modify textile material properties. Studies that have examined the effect of laser irradiation on the properties of synthetic fibers and fabrics using ultraviolet (UV) [6, 36, 88] and infrared (IR) [7, 49] irradiation have reported an increase in the dye absorption properties of synthetic polymers, resulting in improved dye performance. Laser-enhanced dye uptake has been identified on PET (polyester) [3, 21, 36], polyamide (nylon) [9, 21], and polypropylene textiles [76]. Enhanced hydrophilic properties of polymer fibers after laser irradiation have been attributed to an increase in the amorphous: crystalline ratio [7, 49] that improves bonds between dyestuffs and polymer due to the creation of more functional groups after laser irradiation [7, 76]. Capacity for enhanced dyeing has also been attributed to morphological changes to polymer fibers [36], with surface roughness providing increased surface area for improved adhesion of dye particles to fiber [5, 6, 21, 76, 87].

Increasing the intensity of laser irradiation increased the color strength of laser pretreated synthetic fabrics after dyeing [40, 49, 76]. Therefore, by controlling the intensity of laser irradiation delivered to the substrate, the uptake of dye on the material could be controlled, allowing varied depth of shade across the textile surface. High-intensity laser irradiation increased the wettability, light, rubbing, and wash fastness of tested fabrics; however, properties such as bending rigidity and tensile strength were negatively affected by an increase in laser intensity [31, 76].

On cotton, unlike synthetic fibers, laser modification was found to reduce the amount of direct dye absorbed, leading to decreased color strength as laser intensity increased [15, 50].

Fewer studies have investigated the effect of laser irradiation on the properties of wool; however, a small number have shown that laser irradiation can reduce felting and shrinkage of woolen textiles [60] and that UV [67, 89] and IR [54] laser irradiation can improve the dyeability of wool. A combination of laser and plasma treatments was shown to increase hydrophilic properties as an all-over treatment on woolen textiles [20]. UV irradiation was found to disrupt the cysteine disulfide bonds on wool fibers and increase surface oxidation leading to a reduced water wetting time [75], suggesting that UV irradiation increased the hydrophilic properties of wool fibers.

The effects of laser irradiation on coloration for textiles have been studied from a design perspective, identifying the potential for surface pattern achieved through tonal dye differentiation after laser pretreatment [1, 3, 9, 51, 67]. Periolattoa et al. [67] suggest potential for design outcomes using stencils to mask UV irradiation on wool, resulting in selective UV exposure on the substrate. Drawing on the digital graphic potential of a CAD controlled laser, Bartlett [9] identified the potential for using an increased dye uptake on synthetic textiles to create imagery, while Akiwowo [3] further developed a laser-based pretreatment for PET textiles by considering improved dye uptake as an alternative patterning method.

Within the study presented Morgan et al. [54] explored CO_2 laser technology, as an effective surface design tool for wool and wool blends by ascertaining the effect of infrared laser irradiation on the surface and dyeing properties of wool substrates, revealing the potential for textile surface design. The laser technique used laser irradiation to modify the surface of woolen textiles, increasing dye affinity. The process removed microscopic scales from the wool fiber surface, resulting in an enhanced dye performance in the laser-treated areas (Fig. 1).

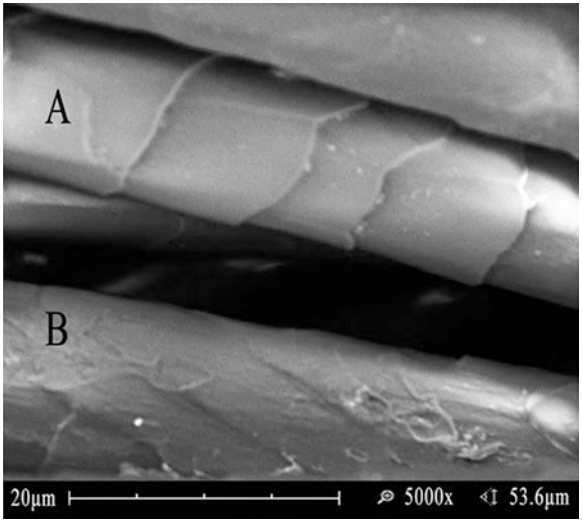


Fig. 1 Effect of selective laser irradiation on wool fibers. Wool fiber A: wool scales intact. Wool fiber B: scales have been removed by laser irradiation [54]

Fig. 2 Laser-enhanced dyed and engraved wool samples [51]

Targeted designs were laser marked on the surface of the cloth making use of differential dye uptake to achieve multitonal surface design on wool. Laser engraving was found to be effective in removal of the felted or brushed surface fibers of milled wool, to reveal the underlying woven structure. Used in parallel to the dyeing procedures, laser pretreatment combined three-dimensional relief surfaces with the multitonal design effects (Fig. 2).

Infrared laser irradiation as a pretreatment to dyeing PET/wool-blended textiles with reactive and disperse dyes facilitated a novel method of generating multicolored textile surface design [51]. Dye exhaustion and color difference values were calculated, revealing laser irradiation to have a positive effect on the uptake of disperse dye. Microscopic analysis of the laser-irradiated fabric showed an increased PET surface area on the blended textile, causing PET properties to dominate the laser irradiated area. When cross-dyed in a mixed dye bath, the disperse dye was the

Fig. 3 Laser patterned PET/wool blend (55/45) design samples dyed with contrasting disperse and reactive dye colors [51]

predominant color on the laser irradiated areas, while untreated areas retained the reactive dye color (Fig. 3).

It was demonstrated that the laser pretreated wool or blended textiles could be dyed at a reduced temperature and time, saving water and energy while combining coloration and patterning in one process. During coloration, the potential for an estimated 54% reduction of energy was displayed compared to immersion dyeing procedures. Textile performance tests showed that high fastness to washing and rubbing was achieved to meet current industry and consumer standards.

2.2 Laser Coloration and Surface Patterning: Dye Fixation

Existing research studies that utilize laser irradiation for textile coloration and patterning predominantly employ the laser as a pretreatment to dyeing textiles to enhance the substrate's affinity for dye [3, 9, 21, 36, 49, 54, 76]. However, mechanical tests have shown that the thermal stress of laser irradiation applied to the substrate is ultimately a damaging action [7, 15]; therefore, achieving a high depth of shade was detrimental to the tensile strength of the material, revealing scope for improved performance of existing laser dye techniques. In addition, laser pretreatment techniques used in the creation of surface designs had limitations; only tonal design effects could be achieved. Textile dyeing is an energy-dependent process; therefore, the photothermal properties of infrared laser irradiation present potential to activate a dye reaction on a textile substrate in a targeted manner suitable for the design and patterning of textiles [51]. Attempts toward a laser dye-fixation approach to surface design of textiles can be recognized in a small number of studies. Some success has been reported in introducing dye at the point of laser irradiation [9, 22, 39, 51].

Kearney and Maki reported a system for fixing reactive dye to cotton by way of an argon-ion laser [39] after screen-printing dye onto fabric in the form of a paste. The study provided a feasible low-heat dye-fixation method; however, at a maximum speed of 0.6 mm/s, the process was slow and the screen-printing stage of the process negated the advantage of noncontact laser processing. Textile dyeing company, Zaitex, and Textile equipment company, Tonello, developed a "Garment Flash Printing" system for adding pattern to cotton textile garments using a laser [11] involving a laser, pigments, and a polymeric binder to add color to cotton fabrics [22]. The process involved the use of a laser to fix the pigment, applied as a resin as an all-over treatment on cotton fabric. Tonello developed the method from a commercial perspective, specifically focusing on application for denim garment finishing.

Bartlett [9] considered the effects of laser irradiating a fabric wet with dye, identifying a slight increase in uptake within the dye bath. In this research, Morgan [51] further explored the potential of a dye reaction that takes place at the point of laser interaction providing technical refinement of a laser dye-fixation technique and exploration of its creative potential. A laser dye-fixation approach to textile coloration led to the development of the "*peri-dyeing*" technique. The prefix *peri* denotes around or adjacent [64]. The peri-dyeing technique considers the laser as a targeted energy source for "on-the-spot" fixation. It involved applying dye locally to the surface of a textile substrate followed by laser irradiation: Therefore, the dye reaction takes place at the point of (or adjacent to) laser interaction with the dye liquor and textile material.

The laser-based peri-dyeing technique [51] allowed intricate, targeted surface design of textile substrates. Photographic quality graphics and multicolored surface design effects were achieved on natural wool and synthetic PET and polyamide fabrics. The noncontact laser apparatus allowed precision detail to be achieved on highly textured fabrics or finished three-dimensional garments, providing an advantage over digital printing methods. The permanence and durability of the coloration process were assessed through material performance testing procedures, including fastness to washing, rubbing, and tensile strength, which met with commercial standards across all conducted tests [56]. Peri-dyeing enabled digital design innovation, direct-to-garment processing, and potential for customization in the manufacture of finished textile goods with sustainability benefits through reduced energy, water, and chemical consumption [57] (Figs. 4, 5, 6, and 7).

2.3 Laser Surface Texturing: Thermal Setting

Adding surface texture and three-dimensional effects to textiles can provide enhanced functional properties, such as insulation, absorption, compression, or strength in addition to adding shape, movement, and design aesthetics. Three-dimensional surface effects can be added during textile construction, stitching, or via wet techniques such as devoré, flocking, felting, and shibori. Lasers have been

Fig. 4 Laser peri-dyed wool textiles [51]

Fig. 5 Laser peri-dyeing on textured and brushed wool fabrics [51]

Fig. 6 Peri-dyed PET textiles: Multicolor and photographic designs [51]

Fig. 7 Direct to garment peri-dyed PET sportswear prototypes [56]

used to create design-led three-dimensional forms, such as laser-assisted origami textiles [47], laser-bonded synthetics [24], and laser-molded textiles by using IR laser irradiation to heat-set predetermined shapes in synthetic textiles [55].

Laser welding has been used to bond seams in garment construction and in fashion. In the case of thermoplastic fiber fabrics, such as PET, lasers can be used to create stitch-less, water-resistant seams. As reported by The Welding Institute (TWI), this technique often requires an additive that is applied to the seam interface and reacts under the laser energy, melting and bonding the two surfaces together [16]. Current uses of this technology include Airbags, medical and protective clothing, and footwear with sealed seams. Goldsworthy [24] explored the design potential of laser welding technology to bond synthetics producing three-dimensional and relief qualities. By harnessing the laser for bonding and lamination of the fabrics to produce multilayered materials, Goldsworthy was able to develop a range of surface finishing methods while keeping the fabric 100% recyclable. Furthering this technique, Paine et al. [65] used laser welding technology to create targeted compressive effect on garments.

Resulting from the study presented, Morgan et al. [55] report on a technique for three-dimensional molding of synthetic textiles using the photothermal properties of infrared laser irradiation. They describe a system to apply and control the three-dimensional effects through controlled tension and targeted laser irradiation. The molding technique was used to design accurate surface architectures, engineered surface effects, and three-dimensional design features on knitted PET and polyamide textiles (Fig. 8). Combining three-dimensional laser molding with laser dyeing processes attained an effect akin to shibori dyeing. However, the laser-based technique provided unique design aesthetics, offering control, with a level of precision and repeatability that cannot be achieved with existing shibori processes or textile production techniques.

The use of laser technology to create three-dimensional textile forms presents efficient processing advantages over traditional methods: Unlike regular textile embossing equipment, for each new design, the dry laser process does not require physical molds or plates to be cast, stitching, or complicated loom set-up, instead,

Fig. 8 Laser-molded PET and polyamide textiles [51]

offering ease of pattern change through digital generation of designs. The use of purely synthetic materials may provide additional sustainability benefits for ease of material recovery, redesign, and recycling at end of primary use.

3 Enzymatic Processing

Enzymes are biocatalysts that catalyze specific chemical reactions within the cells of all living organisms, resulting in the growth and maintenance of the cell. The majority of commercial enzymes are sourced and obtained from a variety of different microorganisms such as bacteria, fungi, and yeast. However, these naturally occurring enzymes are often not found in nature in large quantities and, therefore, require isolating and fermenting for industrial use [61].

Enzymes differ from chemical catalysts in several distinct ways and bring a wide range of processing benefits. Reactions catalyzed by enzymes are generally very fast and highly specific, typically performing one type of reaction effectively. Enzymes are capable of catalyzing reactions under comparatively mild reaction conditions, such as at temperatures below 80 °C, under atmospheric pressure, and at around neutral pH. In contrast, chemical catalysts often require high temperatures, high pressures, and use of extreme pH. Therefore, enzymes can dramatically reduce energy and chemical consumption and production costs. Enzymes are biodegradable which can help reduce the impact of manufacturing on the environment. Enzymes rarely get involved in side-chain reactions, which eliminate the production of by-products making them extremely efficient during processing unlike typical chemical catalysts which are less specific and often produce unwanted by-products which can prove difficult and costly to dispose of. Furthermore, enzymes are not consumed in reactions and remain unchanged, offering the possibility of repeated and continuous reuse, therefore leading to potentially new sustainable industrial processes such as closed loop [2, 35].

Advances in biotechnology have led to the development and manufacture of new commercial enzymes. These enzymes may have improved properties such as stability under certain conditions, higher activity at lower temperatures, and reduced dependency on additional chemicals (cofactors) being present [61, 66].

Consequently, enzymatic approaches have found a wide range of applications in the textile industry [4, 14, 27, 28, 43], ranging from replacing conventional production methods to novel fabric finishing treatments. Enzymatic desizing is one of the earliest examples of enzymes being implemented on an industrial scale. The enzyme amylase is used in the enzymatic desizing process to break down and remove "size" (starch), a protective lubricant which is commonly applied to yarns during the weaving of fabrics. Since its adoption during the early part of the twentieth century, it has proved to be a valuable method replacing conventional processes which required the use of harsh chemicals such as oxidizing agents [29]. Another group of enzymes called cellulases has found acceptance within textile wet processing. Cellulases are used to bio-polish cotton fabrics, and enzymatic removal of surface microfibers enables fabrics to maintain a new look for longer. Cellulases and another enzyme group known as laccases are also used in the production of denim fabrics and garments to produce stonewashed looks and/or alter the color and shade of dyed denim by fading. Stonewashed effects on indigo dyed cotton denim are used to be created by pumice stones, however, the use of pumice stones caused damage to both fibers and machines. Other well established enzyme-based textile processes include bio-scouring and bleach clean-up, both processes are described in more detail in Shen and Smith [80]. Although the value of enzymes in textile processing has long been evident in terms of environmentally friendly, energy and water savings, improved product quality and process integration, and cost reduction, enzymes to date have not been investigated for their creative potential in textile design.

3.1 Protease and Laccase

Research presented within this section demonstrates the ability of two specific enzymes, protease and laccase, as creative tools to achieve, through controlled application, innovative coloration and/or decorative surface pattern on textiles.

Protease (EC.3.4.21.62) belongs to a class of enzymes called hydrolases, which are capable of breaking down large molecules into smaller fragments. To date, there has been considerable interest in the application of protease to achieve a variety of functional finishing effects on wool through modification of the wool cuticle scale by catalyzing the hydrolysis of peptide bonds in wool protein molecules. Studies have investigated the reduction in wool prickle, improved fiber softness, and anti-shrinkage treatments [78, 79]. However, if not carefully controlled, this group of enzymes can cause significant damage to the wool fiber due to the enzyme penetrating into and attacking the wool fiber core [59, 81], resulting in strength and weight loss [12]. Thus, no commercial treatments have been developed so far, mainly because the use of protease can result in unpredictable, difficult to control reactions leading to unacceptable fiber damage. However, surface modification or controlled degradation of wool fibers through enzymatic treatment presents clear opportunities that could be exploited for aesthetic design purposes.

Laccase (EC.1.10.3.2), belonging to a class of enzymes called oxidoreductase, can catalyze redox reactions, which reduce molecular oxygen to water and simultaneously perform one-electron oxidation of various substrates such as diphenols and aromatic amines with or without a mediator [74, 79].

Laccase products such as DeniLite™ (Novozyme) and PrimaGreen® EcoFade LT100 (Dupont Genencor) based on laccase-mediator systems have found much success as enzymatic processes for decolorizing predyed denim, offering alternatives to traditional abrasive stonewashing processes, where dye is removed from fabrics or garments using pumice stones to achieve color fading and/or worn effects.

In contrast, laccases are also capable of oxidizing an extensive range of basic aromatic compounds, transforming them into colored polymeric products via oxidative coupling reactions [46, 74]. The reaction mechanism of laccase catalyzation is one electron oxidation of aromatic compounds to form free radicals while reducing molecular oxygen into water. These free radicals are very reactive and then undertake further reactions themselves or with the initial aromatic compound and polymerize in a nonenzymatic pathway to form colored products. These colored products are capable of being adsorbed onto or reacting with numerous textile fibers enabling coloration [23, 69, 79]. The potential for laccases to be used within the area of textile coloration, specifically for the generation of decorative surface pattern design, remain relatively unexplored.

3.2 Coloration and Surface Patterning by Enzymatic Degradation

In this study, the enzyme protease was employed to selectively modify a wool/polyester blended fabric to impart decorative surface patterning [73]. A series of controlled experiments for studying the interaction between enzyme and substrate (a compound on which an enzyme exerts its catalytic effect) were undertaken to achieve either partial or complete removal of the dyed wool fiber component with a view to reveal undyed polyester yarns which formed part of the fabric blend, resulting in novel fading and differential fabric relief (Table 1). Longer treatment times resulted in greater weight loss and lighter shades being produced, as reflected by *K*/*S* values. The activity of protease is highly specific, therefore, it caused neither

Table 1 The effect of protease processing at different durations of time on wool degradation from wool/polyester samples dyed using reactive dye Lanasol Blue CE

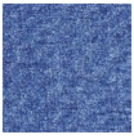
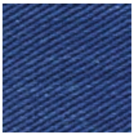
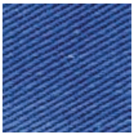
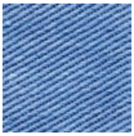
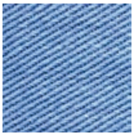
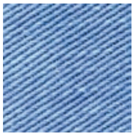
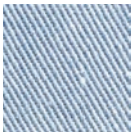
Wool/polyester fabric samples	Duration of enzymatic treatment with protease (h)				
	Untreated	0.5	1	2	4
Predyed at 2% owf					
K/*S* (620 nm)	5.89	3.88	2.93	1.40	0.47
Weight loss (%)	–	10.0	16.5	30.0	40.5

Table 2 The effect on dye decolorization by processing with a laccase-mediator system for different durations of time on cotton (100%) samples ring-dyed with indigo dye (C.I. Vat Blue 1)

Cotton fabric samples	Duration of enzymatic treatment with laccase-mediator system (h)				
	Untreated	0.5	1	2	4
Indigo dyed with 6-dip and 6-nip					
K/*S* (640 nm)	19.67	9.40	5.74	5.94	4.11
Indigo dyed with 1-dip and 1-nip					
K/*S* (640 nm)	6.77	1.92	1.27	0.88	0.61

modification nor damage to the polyester fibers. Investigations concluded that significant subtraction of the dyed wool component from the blend could be achieved if the correct combination of enzyme concentration, agitation, and treatment times were applied.

In a different study, a laccase-mediator system was explored to generate surface pattern design through selectively decolorizing indigo-dyed cotton fabric [70]. A series of controlled experiments were undertaken, which consisted of enzymatic treatments with different processing parameters using 100% cotton fabric ring-dyed with indigo dye (C.I. Vat Blue 1). Experiments were designed to gain a clear understanding of the interaction between the laccase-mediator system and indigo dye and to achieve partial or complete removal of indigo dye from dyed cotton fibers with a view to reveal undyed cotton fibers and yarns which formed the underlying layers of the fabric. Investigations led to the development of an optimized enzymatic process which enabled indigo-dyed cotton fabrics to be processed to achieve various levels of fading by simply altering processing conditions, as shown in Table 2. Longer treatment times resulted in lighter colored shades being produced.

To explore the decorative pattern design potential of protease and laccase-mediator systems, surface-patterning design techniques inspired from traditional Shibori-resist dyeing methods [85] were selected for design trials. Patterns consisting of simple repeats of design elements [86] such as lines or geometric shapes were chosen for exploration to create an all-over repeat pattern across the length of fabric.

Dyed wool/polyester and cotton fabrics comprising different degrees of compression and accessibility were manipulated and prepared using stitching, or folding, pleating, and clamping (as illustrated in Figs. 9, 10, and 11) to achieve surface patterning through enzyme processing. Fabrics were treated in a liquor bath containing the enzymes. In principal, the enzymes would be restricted to selected areas made accessible, therefore, as a result, the enzymes would only be able to degrade or decolorize by fading selected areas of the fabric. This in theory would facilitate the generation of decorative surface patterning through contrast in color and/or texture through the use of localized enzyme treatment.

Results successfully demonstrated a diverse range of highly individual patterns could be generated with the use of varying resist techniques trialed with enzyme processing [70, 73]. The resulting visual aesthetic qualities achieved were heavily governed by the techniques used, which controlled the degree of liquor accessibility and penetration, and consequently the level of wool degradation or decolorization.

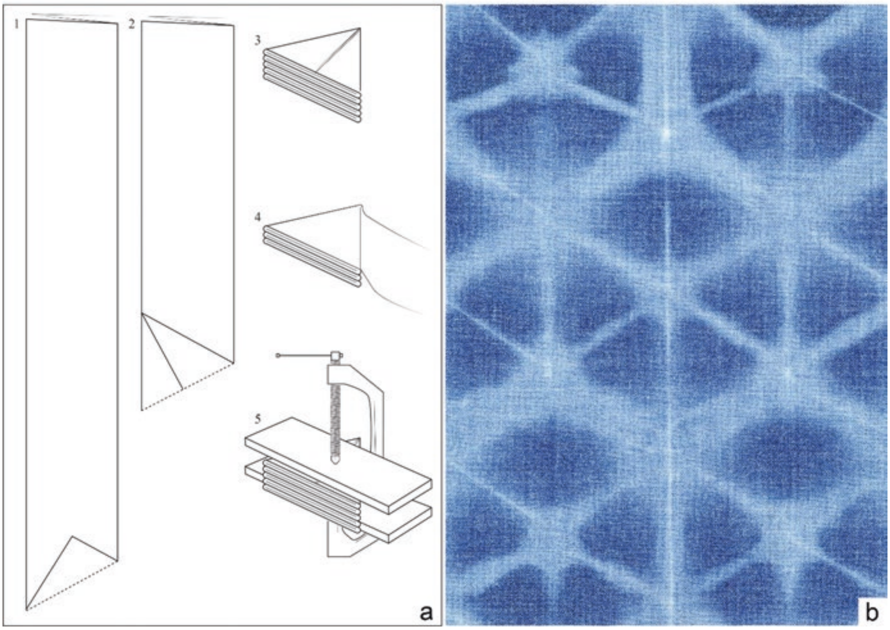


Fig. 9 Illustrated diagram showing Shibori technique using pleat, fold, and clamp-resist method (**a**) to generate a colored pattern design using protease processing on wool/polyester blended fabric (**b**) [73]

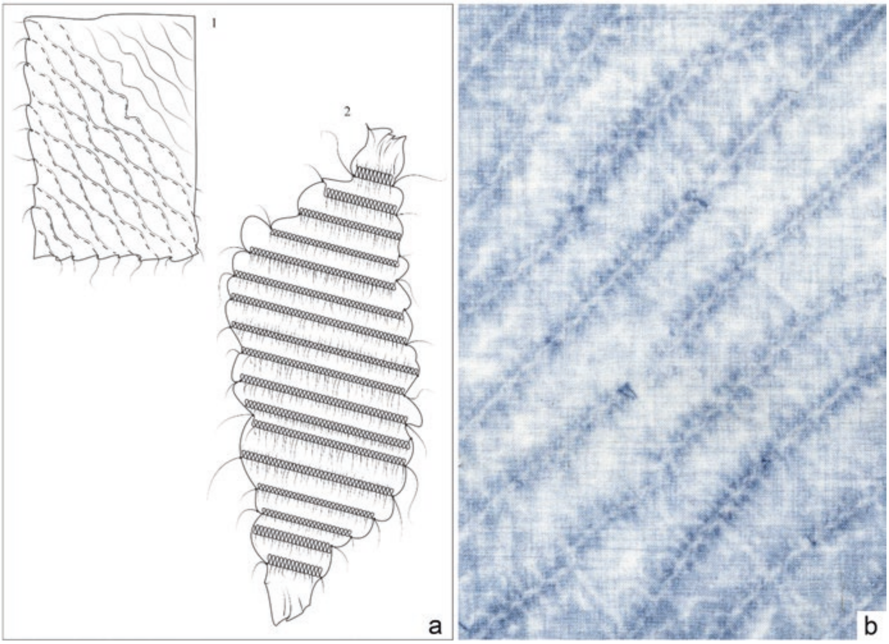


Fig. 10 Illustrated diagram showing Shibori technique using stitch-resist method (**a**) to generate a colored pattern design using protease processing on wool/polyester blended fabric (**b**) [73]

Irregular surface modification resulted in subtle pattern variations and irregularities, and design elements displayed distinctive soft edges. In general, stitch techniques employed (Fig. 10) enabled greater access to the enzyme containing liquor, resulting in lighter and softer colored patterning. In contrast, pleat, fold and clamp techniques allowed a different style of patterning, designs with greater color contrasts and stronger depths of shade resulted from an increased level of pressure and compression applied with the use of a G-clamp, completely restricting enzyme access to some areas of the fabric (Figs. 9 and 11).

3.3 Enzymatic Surface Modification for Subsequent Coloration and Surface Patterning

Certain chemicals such as the cationic surfactant cetyltrimethylammonium bromide (CTAB) present on wool fiber can decrease the activity of protease [82, 83]. Therefore, the application of CTAB as a pre-treatment was explored as a chemical resist method to selectively inhibit the activity of protease towards wool fibers to impart decorative patterning. Preliminary studies found that a pre-treatment with CTAB followed by enzyme processing was capable of altering wool fiber characteristics enabling differential coloration (dye uptake) and felting properties during subsequent dyeing and post-processing (Table 3). Fibers treated

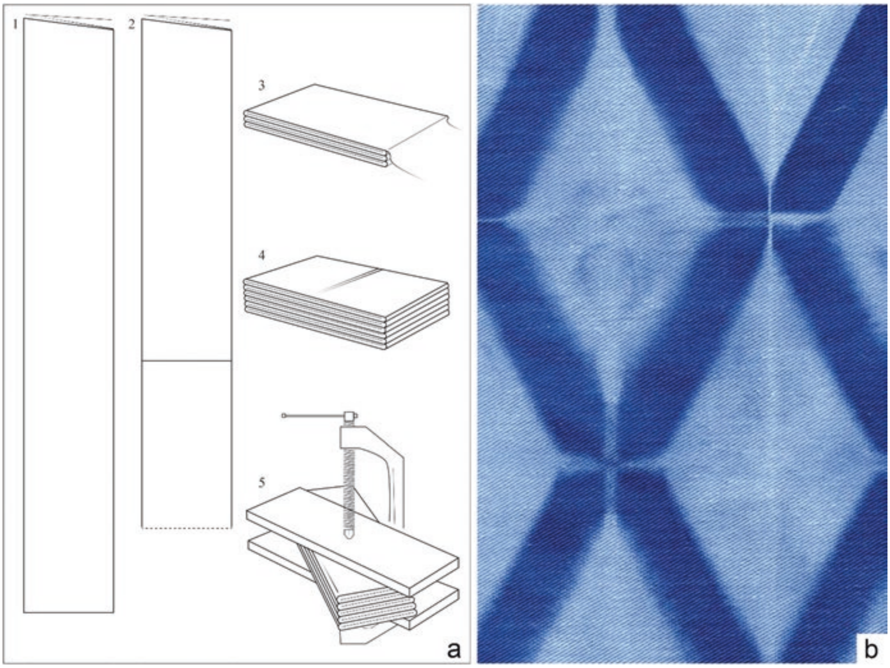
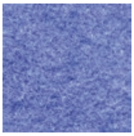
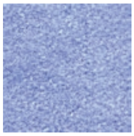
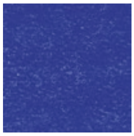


Fig. 11 Illustrated diagram showing Shibori technique using pleat, fold, and clamp-resist method (**a**) to generate a colored pattern design using laccase-mediator system on 100% cotton fabric (**b**) [70]

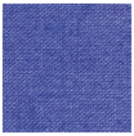
Table 3 The effect on dye uptake of CTAB pre-treated 100% wool fabrics followed by protease treatment and post-competitive dyeing using acid dye

C.I. Acid Blue 140	CTAB followed by protease treatment	Protease treatment
Competitively dyed at 0.5% owf		
Competitively dyed at 5% owf		

with CTAB and protease altered the dye uptake and anti-shrinkage properties. These contrasting properties present opportunities that could be exploited for textile design, however, further work would need to be undertaken to explore its creative potential.

Another enzyme pre-treatment method explored the application of protease within a printing paste to selectively modify wool fiber cuticle scales to generate

Table 4 The effect on dye uptake of protease pre-treated 100% wool fabrics followed by competitive low temperature dyeing using acid dye

Dye	Non-protease treated sample	Protease pre-treated sample
C.I. Acid Blue 140		
C.I. Acid Blue 45		

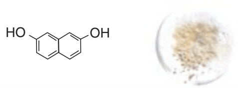
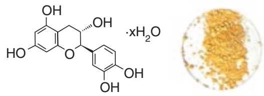
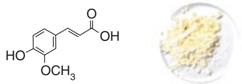
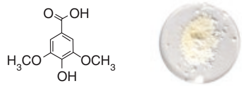
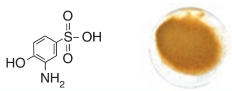
surface pattern. The enzyme was restricted to the surface of the fiber using textile screen printing methods. Protease applied within an Indulca (a polysaccharide product of gum guar) printing paste led to wool fiber modification through the disruption and removal of wool cuticle scales resulting in greater fiber hydrophilicity, leading to easier dye diffusion especially when dyed at lower temperatures (Table 4). The effects of differential dye uptake in terms of shade depth were explored to produce surface patterning, however, further study is required to produce well-defined surface pattern with this method [70].

3.4 Coloration and Surface Patterning by Enzymatic Polymerization

In this study, the potential for laccase to be used within the area of textile coloration, specifically for the generation of decorative surface pattern design, was investigated. A selection of natural phenolic compounds and non-phenolic compounds consisting of naphthalene and benzene derivatives (Table 5) were carefully selected as laccase substrates to synthesize dyes in-situ on either nylon 6,6 or wool fabrics.

Laccase catalysis of the selected aromatic compounds resulted in a variety of colors being produced in aqueous solutions and on both wool and nylon fibers after enzymatic treatment [70]. Each aromatic compound was catalyzed by laccase to form characteristic color shades, predominately ranging from yellows, oranges, and browns as seen in Table 5. It is believed that the coloration created on both fiber types was a result of colored dimeric, oligomeric, and polymeric products formed by laccase oxidation of aromatic substrates, which are capable of reacting non-enzymatically in a nucleophilic manner forming covalent bonds with amino groups found on the surface of nylon and wool fibers [69], to result in reasonably good color fastness to wash. In general, wool fabric samples were darker in comparison to nylon samples which were lighter and/or brighter. The differences in coloration observed between nylon and wool were due to differences in dyeability characteris-

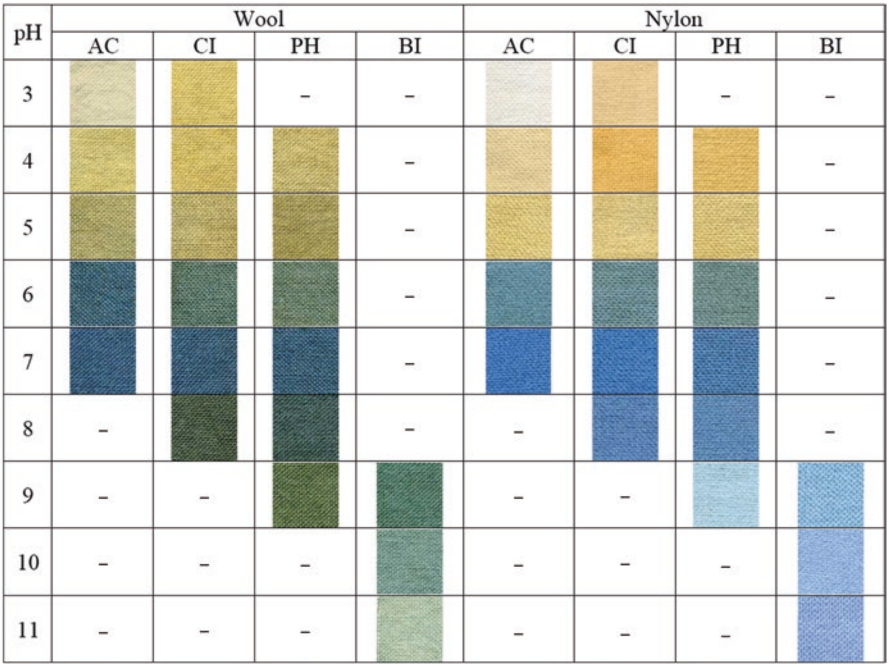
Table 5 Chemical structures of aromatic compounds selected for study and their corresponding laccase-catalyzed colored solutions and coloration of nylon and wool fabrics [71]

Group	Aromatic compound	Chemical structure and form	Coloured product	Coloration on nylon and wool
1	1,2-Dihydroxybenzene			
	1,4-Dihydroxybenzene			
2	2,7-Dihydroxynaphthalene			
3	Catechin			
4	Ferulic acid			
	Gallic acid			
	Syringic acid			
5	2,5-Diaminobenzenesulfonic acid			
	3-Amino-4-hydroxybenzenesulfonic acid			

tics arising from different types and quantities of functional groups present in each fiber (especially amounts of primary amine groups) and aromatic compound structures affecting the various types of molecular interactions occurring between fiber and laccase-synthesized products, in addition to different levels of affinity, rate of uptake, and final saturation values [72].

Prajapati et al. [72] found that a diverse color palette could be produced with the use of three different aromatic compounds as laccase substrates: 1,4-dihydroxybenzene, 2,7-dihydroxynapthalene, and 2,5-diaminobenzenesulphonic acid.

Table 6 Color range achieved on wool and nylon when treated with 2,7-dihydroxynapthalene in the presence of laccase using different pH and buffer systems



pH	Wool				Nylon			
	AC	CI	PH	BI	AC	CI	PH	BI
3			–	–			–	–
4				–				–
5				–				–
6				–				–
7				–				–
8	–			–	–			–
9	–	–			–	–		
10	–	–	–		–	–	–	
11	–	–	–		–	–	–	

Source: Prajapati, C
AC acetate buffer, *CI* citrate buffer, *PH* phosphate buffer, *BI* bicarbonate/carbonate buffer

Various reaction processing parameters such as buffer systems and pH values, laccase and aromatic compound concentrations, and reaction times were investigated to establish the range of achievable colors, all in the absence of additional chemical auxiliaries. Previously, unreported colors such as blues, greens, and pinks were achieved. The use of varied buffer systems, pH values, and aromatic compound concentrations proved most beneficial for extending the ranges of possible hues. For example, the use of the compound 2,7-dihydroxynapthalene in the presence of laccase resulted in a variety of hues, ranging from yellow, green, and blue across both fiber types simply through pH control (Table 6).

To determine the coloration and design potential by laccase catalyzation of the selected aromatic compounds, fabrics were specially constructed using a combination of undyed nylon, wool, and polyester yarns. Basic plain, twill, satin, and sateen structures in addition to simple jacquard weaves were used to generate a selection of woven fabric designs. Weaves were then dyed using the one-step laccase-catalyzed coloration process. As shown in Fig. 12, the use of different fiber types and weave structures enabled simple color variations to be produced. Shadow, reserve, and contrasting effects are achievable with the newly developed laccase-catalyzed dyeing process.

Fig. 12 Examples of one-step laccase-catalyzed coloration on nylon, wool, wool/polyester, and specially constructed woven jacquard designs, using different dye bath conditions. (Source: Prajapati, C)

4 Summary and Conclusions

An overview of the alternative techniques for producing color, pattern, and surface effects on a range of textiles using laser and enzyme processing are shown in Table 7.

This chapter shows how two different novel approaches, the biological and the digital, can disrupt conventional textile processing each offering potential sustainability benefits within the context of current textile design and manufacture and within emergent and future postindustrial systems of production and consumption.

4.1 Key Sustainability Benefits of Laser Processing for Textile Design

The laser-based coloration and design techniques offer innovation with potential sustainability and economic benefits for the field of textiles via eco-efficient manufacture. For example, laser-enhanced dyeing offers potential reductions in energy and wastewater effluent through reduced dyeing temperatures and improved dye performance. Low-temperature processing reduces overall dyeing time and temperature from standard practice, displaying potential for an estimated 54% reduction of energy during dye production in the case of the laser pretreated and dyed wool [54]. The ability to reduce energy used in dyeing by over half would offer exceptional savings with both economic and environmental benefits. Some loss in tensile strength was apparent after laser irradiation, and despite enhancing the affinity for dye, the process did not altogether omit immersion dyeing procedures. These issues were addressed via the laser peri-dyeing technique [51], which added additional water, energy, and chemical saving benefits, further reducing the water and dye required for coloration of wool and synthetic substrates by elimination of dye baths used in conventional exhaust dyeing procedures, while retaining permanence and durability. Laser molding [55] described a dry and efficient process that does not require additional materials, such as thread for stitching. Therefore, using the

Table 7 Overview of alternative techniques for textile coloration, patterning, and surface effects

Selective surface pattern by differential dyeing	Laser coloration and surface patterning: fiber modification Enzymatic surface modification for subsequent coloration and surface patterning
Combined three-dimensional and color finishing	Laser surface texturing: thermal setting Laser coloration and surface patterning: fiber modification Coloration and surface patterning by enzymatic degradation
Novel coloration of textile materials	Laser coloration and surface patterning: dye fixation Coloration and surface patterning by enzymatic polymerization

technique for surface design effects could eliminate the need for additional wet finishing or embellishment for decorative and functional textiles.

Combining the functionality of the laser to perform multiple production tasks at once, such as pattern cutting or laser engraving milled wool as well as the laser dyeing techniques, would allow additional environmentally sustainable benefits to the process compared to outsourcing each individual stage of the production process in addition to storage and transport between phases. Combining techniques in one stage has potential to offer fast response in today's fast changing market, with easily changed CAD files allowing smaller product runs than financially permitted by exposing individual screens for screen printing or die cutters for product pattern cutting. Therefore, as well offering sustainability through reduced temperatures and improved dye performance, laser technology could offer additional advantages through a potential change in production systems.

The flexibility and immediacy of digital processing benefit short-run production, textile sampling, and garment prototyping compared to conventional textile processing techniques that are aimed to be cost-effective for bulk manufacture. Processing limitations of laser techniques may include restrictions in size of the laser bed area, or processing speed for bulk and large volume manufacture. Similar to digital textile printing, turn-around times may be slower than that of rotary or screen-printing methods when volumes increase. However, garment and textile-specific multihead laser machinery capable of direct-to-garment (DTG) finishing and processing of continuous fabric lengths have already been commercialized for the denim industry [34], showing that application-specific laser machinery can be engineered to overcome size and speed constraints for emerging laser textile processing techniques.

The laser-based design techniques discussed in this chapter are capable of digital design generation and targeted, direct-to-garment processing on textile or garment "blanks," postconstruction. Further research involving partners from four sectors of the textile industry [56] identified commercial viability and the opportunity for these digital laser processes to move the design stage further down the production cycle to allow for late-stage decisions and design flexibility, providing a responsive approach to design and distributed manufacture. Providing the textile industry with responsive or agile manufacturing opportunities such as these may offer reduced lead times and smaller minimum orders to reduce surplus stock and minimize or eliminate the creation of excess waste of textile goods; in addition, they may facilitate bespoke or customized production opportunities.

4.2 Key Sustainability Benefits of Enzymatic Processing for Textile Design

Studies discussed in Sect. 3.2 demonstrated the ability of protease and laccase as creative design tools for coloration and surface patterning by enzymatic degradation. With both studies, effects similar to those achieved with conventional surface design processes such as devoré ("burnt out") and discharge printing were achieved. Both patterning styles have remained popular and significant since first introduced because the effects obtained from these processes are often different and aesthetically superior to direct screen-printing styles [48] and digital textile printing. Although both processes are simple and inexpensive methods for producing patterned fabrics through the application of a chemical paste, the processing pastes require the use of either strong alkalis such as sodium hydroxide or reducing agents, in addition to chemical auxiliaries [73]. The heavy use of these compounds can be toxic and hazardous to handle and generate effluents that are difficult to treat and damaging toward the environment [41, 45].

In contrast, surface patterning through enzymatic hydrolysis with protease or decolorization with laccase-mediator system offers simpler, cleaner, and safer alternative processing methods, which principally eliminate or reduce the use of conventional reducing and/or oxidizing agents, chemical auxiliaries, and elevated temperatures for processing. The precise reaction specificity of enzymatic processes facilitates specific and targeted textile finishing without causing undesirable effects such as deteriorating fabric qualities and causing damage to other components. In addition, both enzymatic processes offer new unique design aesthetics which enable the production of individual non- identical, but corresponding surface design patterns with subtle variations, irregularities, and unique characteristics which would be difficult to reproduce and replicate by the means of conventional textile processes. Currently, there is considerable interest within the textile industry to create fabrics with artisan aesthetics, and these qualities are understood to be positive in the current industry where consumers regularly seek individual and unique pieces.

Conventional dyeing processes generally involve the use of different chemicals and dyeing auxiliaries in addition to high temperatures to assist the dyeing process. The coloration of wool and nylon can be achieved with the use of several dye classes, the most important of which are acid, mordant, and premetallized dyes, all of which are applied under acidic conditions with the use of high temperatures, generally at the boil [13, 44]. Coloration and surface patterning by enzymatic polymerization discussed in Sect. 3.4 present advantages over conventional dyeing methods, principally the elimination of premanufactured dyes and chemical auxiliaries, and dyeing at ambient temperatures, therefore reducing energy use, the complexity of the dyeing process, and downstream processing, leading to possible economic and environmental advantages. Although the study shows that a good range of colors is achievable by this method, it is not known yet whether a full gamut of color shades can be achievable. The enzymatic dyeing process offers opportunities for multiple colors and shading to be achieved through simple alterations in processing conditions, which is currently not possible with conventional dyes and methods. The results also demonstrate the ability of laccase as a novel creative tool, which permits effective surface patterning through controlled application for shadow and contrast colored effects.

The opportunities discussed could provide the textile industry with realistic and viable options to use enzyme-based coloration and surface patterning processes, however, further study is required to examine whether the enzymatic processes have the potential to be scaled up to a viable industrial process which can be reproducible and meet commercial standards.

Note This work was undertaken through the *LEBIOTEX* project (Laser Enhanced Biotechnology for Textile Design) – a collaborative research venture between De Montfort University and Loughborough University in the UK. The project was led by Professor Jinsong Shen (De Montfort University) and Dr. Faith Kane (now at Massey University, NZ) with consultation from Professor John Tyrer (Loughborough University, UK) and Dr. Edward Smith (De Montfort University, UK), and research work undertaken by Dr. Laura Morgan (now at University of the West of England) and Dr. Chetna Prajapati (now at Loughborough University). The initial project ran from 2012 to 2015 and explored new opportunities for sustainable textile coloration and surface design using enzyme and laser technologies. The project was funded by the Arts and Humanities Research Council (AH/J002666/1) and was supported by industrial project partners Camira Fabrics, Speedo, and Teresa Green Design.

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