Doctoral Dissertation

Supercritical CO_2 technology in resource-effective production of functional and smart textiles

Molla Tadesse Abate

* * * * * *

In partial fulfilment of Erasmus Mundus Joint Doctorate Programme in
Sustainable Management and Design for Textiles

Jointly organised by

University of Borås
Politecnico di Torino
Soochow University

August 2020

Supercritical CO_2 technology in resource-effective production of functional and smart textiles

Department of Textile Material Technology
University of Borås
Skaraborgsvägen 3, 501 90 Borås
Sweden

ISBN 978-91-88838-87-2 (pdf)
ISSN 0280-381X, Skrifter från Högskolan i Borås, nr. 110

I hereby declare that the contents and organisation of this dissertation constitute my original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

…………………………………......
Molla Tadesse Abate
August 2020
Bahir Dar, Ethiopia

Abstract

The demand for functional and smart textiles has risen nowadays due to the lifestyle change of human beings. Along with this, the production of functional and smart textiles is consistently increasing. However, the conventional dyeing and finishing methods used to produce the functional textiles have issues such as the requirement of a large amount of fresh-water, energy, and chemicals and the associated wastewater pollution which poses harmful effect to humans, animals, and the environment. Moreover, due to the stringent environmental legislation on effluent release and hence the necessity of wastewater treatment, it has also become an economic problem for the textile industry. Thus, the textile industry has nowadays focused on alternative green technologies and eco-friendly chemical agents to minimize these problems. In this regard, supercritical carbon dioxide (scCO$_2$) dyeing technique is a promising alternative to conventional aqueous-based methods as it avoids the use of water, uses less energy, and fewer chemicals minimizing the waste generation which is important to improve the ecological footprint and reduced production cost. Owing to these important attributes, scCO$_2$ dyeing has been investigated in the last three decades as an environmentally benign process and now it is commercially successful in an industrial scale for dyeing polyester fibres. Thus, employing this technique to textile functionalization can bring additional economic and environmental benefits for the textile dyeing and finishing industry. Nevertheless, only a few attempts have been made so far in using this technology for textile finishing despite having promising potentials.

This thesis used scCO$_2$ dyeing technology intending to explore its potential to the production of functional and smart textiles. To fulfil this, firstly, different functional dyes and functional finishing agents of interest suitable for scCO$_2$ media were selected based on literature data and some screening experiments. Based on this, chitosan very low molecular weight and lactate derivatives, curcumin natural dye, and two commercial photochromic dyes based on spirooxazine and naphthopyran dye classes were selected. Secondly, these agents were incorporated into the polyester fabric using $scCO_2$ impregnation technique to impart range functionalities such as antimicrobial, antioxidant, UV protecting and smart UV-sensor fabrics. Moreover, the functional and colour performances of these functional textiles and the effects of the processing variables on the functional/colour properties were explored. Besides, the thesis includes the production of pH sensing functional fabric with a halochromic molecule using photo grafting technique as an alternative resource-efficient method.

The results showed that $scCO_2$ is a viable technique for the production of functional polyester fabric in a resource-efficient and eco-friendly way. Dyed polyester fabric with additional functionalities such as antimicrobial, antioxidant, UV protection, and UV sensing properties were realised in a single step. The fabrics developed have demonstrated desirable colour and functional properties without affecting each other confirming compatibility. Moreover, the functional fabrics exhibited the required durability and fastness properties sufficient for various applications. This thesis contributes towards widening the application of supercritical CO_2 dyeing technique further and paves a way for sustainable production of functional and smart textiles in a resource-efficient and eco-friendly way. Moreover, the functionalization of cotton fabric with a pH indicator dye using the photo-grafting technique was successful and exhibited good halochromic property towards different pH environments with potential application in several smart textile areas.

Keywords: Supercritical CO_2, Polyester, Functional textile, Smart textile, Antimicrobial, Antioxidant, UV protection, Textile UV-sensor, Curcumin, Chitosan, Photochromic materials, Photo-grafting, halochromic textile.

Abstrakt

Efterfrågan på funktionella och smarta textilier har under senare tid ökat på grund utav människans förändrade livsstil. I samband med detta ökar ständigt produktionen utav funktionella och smarta textilier kontinuerligt. Dock har de konventionella färgnings- och beredningsmetoder som används för att producera funktionella textilier vissa tillkortakommanden såsom: användandet av stora kvantiteter färskvatten, energi och kemikalier; förorening utav avfallsvattnet vilket påverkar människor, djur och miljön. Vidare medför sträng lagstiftning angående utsläpp och därpå följande nödvändighet av vattenreninsgsåtgärder en ekonomisk börda för textilindustrin. Därför fokuserar textilindustrin i dag på alternativa gröna teknologier och miljövänliga kemikalier för att minimera dessa problem. Ur denna synvinkel är teknologin att färga med superkritiskt koldioxid ($scCO_2$) ett lovande alternativ till konventionella vattenbaserade metoder då den undviker användningen utav vatten, reducerar energiåtgången och använder färre kemikalier vilket minimerar avfallsproduktionen vilket är viktigt för att minska det ekologiska avtrycket samt reducera produktionskostnader. Tack vare dessa aspekter så har $scCO_2$-färgning undersökts under de senaste tre decenierna som en miljövänlig process och numera är den en, i industriell skala, komersiellt framgångsrik metod för att färga in polyester fibrer. Icke desto mindre har endast ett fåtal försök gjorts för att använda denna teknologi som en textil slutberedningsmetod trots sin lovande potential för detta ändamål.

I denna avhandling användes $scCO_2$-färgningsteknologin med intentionen att utforska dess potential för produktion utav funktionella och smarta textilier. För att genomföra detta gjordes för det första ett urval utav olika funktionella färgämnen och funktionella beredningskemikalier med intressanta egenskaper vilka också lämpar sig för $scCO_2$-färgning. Detta urval gjordes på grundval utav litteraturstudier samt preliminära mätningar. Baserat på nyss nämnda kriterier valdes chitosan med väldigt låg molekylvikt och laktatderivat, naturlig kurkumin (gurkmeja) samt två komersiella fotokroma färgämnen baserade på spirooxanin och naphtopyran klasserna som färgämnen. För det andra inkorporerades dessa färgämnen in i ett polyestertyg med hjälp utav impregnerande scCO$_2$-teknik för att förmedla en mängd funktionaliteter såsom: antimikrobiell, antioxidant, UV-skydd samt en smart UV-senorik. Förutom detta innehåller avhandlingen också produktionen utav ett pH-kännande funktionellt tyg med en halokrom molekyl tillverkad med hjälp utav så kallad ”photo-grafting” teknik som ett alternativ resurssål metod.

Resultaten visar på att scCO$_2$-färgningsteknologin är en användningsbar teknik för framställning utav funktionella polyestertyger på ett resurssnålt och miljövänligt vis. Färgade polyestertyger med tillagd funktionalitet såsom: antimikrobiell, antioxidant, UV-skydd samt UV-kännande, kunde tillverkas i ett enda steg. De tillverkade tygerna uppvisar önskvärda färgegenskaper samt funktionella egenskaper utan att dessa egenskaper påverkar varandra vilket indikerar hög kompatibilitet. Vidare uppvisade de funktionella tygerna tillräckligt goda stabilitets och härdighetsresultat för att kunna användas i en rad olika applikationer. Denna avhandling bidrar med att utöka användningsområdet för scCO$_2$-färgningsteknologin och banar väg för en hållbar produktion av funktionella och smarta textilier på ett resurssnålt och miljövänligt sätt. Vidare var funktionaliseringen utav ett bomullstyg med en pH-indikator med hjälp utav ”photo-grafting”-teknik en framgång och uppvisade goda halokroma egenskaper gentemot olika pH-miljöer, tydande på en potentiell användning inom flera smarta textila områden.

Keywords: Supercritical CO$_2$, Polyester, Functional textile, Smart textile, Antimicrobial, Antioxidant, UV protection, Textile UV-sensor, Curcumin, Chitosan, Photochromic materials, Photo-grafting, halochromic textile.

Riassunto

La domanda di tessuti funzionali è significamente aumentata negli ultimi anni a causa del cambiamento di stile di vita degli utilizzatori. Ciò ha fatto si che la produzione di tessuti funzionali sia in costante aumento. Tuttavia, i metodi di tintura e finissaggio convenzionalmente utilizzati per produrre tessuti funzionali presentano alcuni limiti come il grande utilizzo di acqua ed ausiliari chimici. Questi ultimi possono essere causa di un significativo inquinamento delle acque reflue che può causare danni all'ecosistema ed alle popolazioni limitrofe. Inoltre la rigorosa legislazione ambientale in materia di rilascio degli effluenti impone alle aziende tessili il trattamento delle acque reflue, questo processo ha un significativo impatto sul costo del prodotto finito. Pertanto, l'industria tessile si è concentrata su tecnologie ecologiche alternative e agenti chimici ecologici per ridurre al minimo questi problemi.

In questo contesto, la tecnica della tintura in anidride carbonica supercritica ($scCO_2$) è considerata come una promettente alternativa ai metodi convenzionali. Questa tecnica evita l'uso di acqua, utilizza meno energia e meno sostanze chimiche minimizzando la generazione di rifiuti, andando così a migliorare l'impronta ecologica e riducendo i costi di produzione. Grazie a queste importanti caratteristiche, la tintura $scCO_2$ è stata studiata negli ultimi tre decenni come un processo ecologicamente conveniente. Al giorno d'oggi essa è utilizzata a livello industriale per la tintura di fibre di poliestere. Pertanto, l'utilizzo di questa tecnica per la funzionalizzazione dei tessuti può apportare ulteriori vantaggi economici e ambientali all'industria tessile. Tuttavia, finora sono stati fatti solo pochi tentativi nell'uso di questa tecnologia per il finissaggio tessile.

Questa tesi ha utilizzato la tecnologia della tintura in $scCO_2$ allo scopo di esplorare il suo potenziale per la produzione di tessuti funzionali. In primo luogo sono stati selezionati diversi coloranti ed agenti di finissaggio funzionali in base ai dati della letteratura e ad alcuni esperimenti di screening. Da questi studi sono stati selezionati i derivati del lattosio, il chitosano a basso peso molecolare peso molecolare, la curcumina, e dei coloranti fotocromici basati sulla spirooxazina ed il naftopirano. In secondo luogo, queste sostanze sono state incorporate nel tessuto di poliestere usando la tecnica di impregnazione $scCO_2$ per conferire una vasta gamma di funzionalità quali proprietà antimicrobiche, antiossidanti, protezione e sensing dei raggi UV. Inoltre, sono state esplorate le prestazioni funzionali e colorimetriche di questi tessuti andando a studiare l'effetto delle variabili di processo sulle proprietà studiate. Inoltre, la tesi comprende la produzione di tessuto utilizzabile come sensore di pH ottenuto funzionalizzando il substrato tessile con una molecola alocromica. Per la produzione di questo materiale è stato utilizzato un metodo di finissaggio fotochimico.

I risultati hanno mostrato che $scCO_2$ è una tecnica efficiente ed ecologica per la produzione di poliestere funzionale. Infatti, la produzione di tessuti con funzionalità antimicrobiche, antiossidante, rilevamento e protezione dai raggi UV è stata ottenuta mediante una singola operazione unitaria. I tessuti ottenuti hanno riportato le qualità desisderate sia dal punto di vista colorimetrico che da quello funzionale. Inoltra la tintura ha dismostrato di possedere una solidità soddisfacente per le varie applicazioni.

Questa tesi contribuisce ad ampliare ulteriormente l'applicazione della tecnica di tintura in CO_2 supercritica e apre la strada ad una produzione sostenibile di tessuti funzionali. Inoltre, la funzionalizzazione del tessuto di cotone con un colorante sensibile al pH ha dimostrato la possibilità di produrre sensori di pH basati su materiali tessili, impiegando processi fotochimici a basso impatto ambientale.

Parole chiave: CO_2 supercritica, poliestere, tessuto funzionale, tessuti antimicrobici, tessuti antiossidanti, protezione dagli UV, sensori UV, curcumina, chitosano, materiali fotocromatici, tessuti alogenocromici.

摘要

随着生活方式的转变，现如今人们对功能纺织品和智能纺织品的需求与日俱增，伴随需求而来的该类产品的生产研发活动也相应增加。通常用于生产功能纺织品的技术为染整加工技术，传统的染整加工技术往往会消耗大量的新鲜水、能源、化学品并带来水污染，污染的水会对人类、动物以及环境造成有害影响。污水排放严格的环境法规使工厂增加了污水处理成本，因此寻找替代的生态化学品、绿色加工技术成为当下解决上述问题的有效途径。其中，超临界二氧化碳流体染整技术（以下简称scCO$_2$技术）由于其不使用水，耗能低，添加化学品少，从而排污少，生产成本低，有助于提高生态足迹，和传统水介质染色技术相比具有很好的发展前景，过去三十年来引发了研究者们的高度关注，目前在聚酯纤维染色中已有工业应用。如果将此技术应用于纺织品功能化，则可为染整工业带来新的环境效益及经济效益。尽管有较好的潜在应用前，但是目前这方面的研究报导还比较少。

本文主要基于scCO$_2$染整技术来探究其在功能及智能纺织品领域应用的可行性。首先，研究了筛选了不同功能染料和功能整理剂，主要优选出低分子量的壳聚糖及其乳酸衍生物，姜黄染料，以及基于螺噁嗪及萘并吡喃结构的两种光致变色染料；其次，将这些助剂在scCO$_2$中用浸渍法应用于涤纶织物从而获得抗菌性、抗氧化性、抗紫外性能以及获得智能紫外感知织物；本论文还研究了制备功能纺织品的工艺参数、颜色性能以及功能性；此外，本论文还采用加酸显色分子通过光接枝技术制备了一种pH敏感织。

研究结果表明，scCO$_2$染整技术在生产加工功能性涤纶织物来说是一资源效益型和环境友好的切实可行的技术。织物可通过一步法染整加工在获得颜色的同时获得功能性，诸如抗菌性、抗氧化性、抗紫外性能、紫外感知性能，且颜色和功能具有较好的相容性，互不冲突。制备的功能纺织品表现出了较好的耐久性和色牢度。本论文的研究为功能和智能纺织品的可持续生产加工奠定了技术基础。

本论文采用光接枝技术将pH指示染料应用于棉织物经FTIR表征证明反应成功完成。光接枝样品在不同的pH环境下表现出了较好的酸碱变色性能，这为其在智能纺织品领域的应用提供了技术依据。

关键词：超临界二氧化碳流体，聚酯，功能纺织品，智能纺织品，抗菌，抗氧化，紫外防护，纺织品紫外传感器，姜黄，壳聚糖，光致变色材料，光接枝，酸碱变色纺织品

Preface

The work presented in this thesis was conducted in the following laboratories

- Textile Materials Technology, Department of Textile Technology, Faculty of Textiles, Engineering, and Business, University of Borås, 50190 Borås, Sweden
- Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy
- College of Textile and Clothing Engineering, Soochow University, 215006 Suzhou, Jiangsu, China
- Department of Material Engineering, Faculty of Textile Engineering, Technical University of Liberec, 461 17 Liberec, Czech Republic

Acknowledgements

I would like to express my sincere gratitude to my supervisors Prof. dr.ir Vincent Nierstrasz, Prof. Ada Ferri, Prof. Jinping Guan, and Prof. Guoqiang Chen for their unreserved support and useful guidance throughout my study. I would also like to thank my examiner Prof. Satoko Okubayashi for reviewing this thesis and her valuable feedbacks and friendly treatment during the review process.

This study has been funded through the European Commission under the joint doctoral programme - Sustainable Management and Design for Textiles (SMDTex) and China Scholarship Council. I am very grateful for the financial support and opportunity given to me. I would also like to thank Prof. Xianyi Zeng, the coordinator of the programme, for his assistance in many issues during my study.

I am thankful to Prof. Roberta Bongiovanni for her guidance during my stay in Politecnico di Torino. Sincere thanks to Prof. Yan Chen and Dr. Eva Gustafsson for their coordination and support during my stay in Suzhou and Boras. I am also grateful to Prof. Martina Viková, and Prof. Michal Vik at the Technical University of Liberec for their expertise and collaboration. I would also like to thank Jorge A. Ferreira (University of Boras), Roberta Peila (CNR-ISMAC, Biella, Italy), Herlinde De Keersmaecker (Ghent University, Belgium) for their kind assistance during my laboratory work and testing samples.

I am grateful to all friends and colleagues in Borås for their support and kindness, Sina, Junchun, Yuyang, Veronica, Emanuel, Tuser, Felicia, Milad, Katarina, Julia, Haike, Carin, Ulrika, Anders, and Elinor. Thank you to all SMDTex friends, Melkie, Daniele, May, Nett, Mulat, Prisca, Sweta, Tarun, Razieh, Sheenam, Roy, Marzieh, and Sarah for the nice discussions and memorable time we had together. Special thanks to Dr. Sina Seipel for her kind support, friendship, and being a nice teammate at all times. Thank you, Daniele and Emanuel, for your kind help in translating the abstract.

Finally, I would like to thank all my family and friends for their continuous support and encouragement all the time.

Dedication

* * * * * * * * * * *

To my parents who have been doing everything to me and my brothers to see us successful and happy

Molla Tadesse Abate
Bahir Dar/Ethiopia
August 2020

Table of Contents

List of tables

List of figures

Acronyms

API	Active pharmaceutical ingredients
CFCs	chlorofluorocarbons
CFU	Colony forming units
CL	Chitosan Lactate
CLW	Chitosan very low molecular weight
CO_2	Carbon dioxide
cps	Centipoise
DDA	Degree of deacetylation
FTIR	Fourier Transform Infrared
HDI	Hexamethylene diisocyanate
IR	Infrared
LLDPE	Linear low-density polyethylene
MW	Molecular weight
NIST	National Institute of Standards and Technology
PCL	Poly (caprolactone)
PDMS	Poly (dimethyl siloxane)
PET	Poly (ethylene terephthalate) or Polyester
PMMA	Poly (methyl methacrylate)
PTFE	Poly (tetrafluoro ethylene)
PVC	Poly (vinyl chloride)
$scCO_2$	Supercritical carbon dioxide
SCFs	Supercritical Fluid (s)
UPF	Ultraviolet Protection Factor

Symbols

°C	Celsius (centigrade)
CP	Critical point
K	Kelvin
k	Kinetic rate constant
K/S	Colour Strength
kDa	kilo Dalton
Mpa	Mega pascal
P_c	Critical pressure
T	Triple point
T_c	Critical temperature
T_g	Glass transition temperature
T_m	Melting temperature
ΔH_m	Melting enthalpy

Chapter 1

Introduction

1.1 Background and motivation

Functional clothing is a domain of textiles that are designed to deliver specific functions to the users in addition to their usual purposes. Functional textiles encompass areas like protective textiles, medical textiles, industrial textiles, sports textiles, automotive textiles, and packaging textiles. In recent times, functional and smart textiles have emerged as a growth filed. The market for functional clothing is predicted to reach 244.6 billion USD by 2025 and the global smart textile market size is expected to reach 5.5 billion USD by the same year [1]. Among the textile fibres used for smart and functional textile applications, polyester and viscose (rayon) fibres are the basic and most used ones [2]. The worldwide production volume of textile fibres has increased from 23.94 million metric tonnes in the year 1975 to 98.5 million metric tonnes in 2017. Among this, about 53.7 million metric tonnes (54.5%) were polyester (PET) fibres and the volume is estimated to increase in the coming years [3]. These statistics clearly show that smart and functional textiles are one of the most important fields in the textile industry and polyester is the most important textile fibre in the production of functional and smart textiles.

These functional textiles are mainly manufactured by conventional dyeing and/or finishing process or incorporating various functional finishing agents into the textile structure during the fibre production process. However, the conventional wet textile processes; particularly the dyeing and finishing processes consume a huge amount of water, chemicals, and energy. It is estimated that 100 – 150 litres of water are required to produce 1 kg of finished textile, on average [4]. This, in turn, results in a huge amount of wastewater discharge which causes large scale water pollution, one of the global environmental problems. The wastewater discharge of textile wet processing industry lies between 40 and 300 m^3 per ton of finished textiles [5]. This wastewater discharge is contaminated with dyes, finishing agents, salt, alkalis and acids, auxiliary chemicals, and other solvents. A large amount of unfixed dyes and finishing chemicals leaves the process in which the exact amounts depends on the type of dyes or functional agents and the process used. In conventional polyester dyeing, it is estimated that approximately 5-10 % of the dye is lost and ends up in the effluent [6-8]. According to the World Bank estimate, 17 to 20 % of industrial water pollution comes from textile dyeing and finishing operations [9]. This is a huge problem posing a series threat to the flora and fauna and due to this the textile industry is mostly criticized for its role in environmental pollution.

The immediate solution for minimizing wastewater pollution is the treatment of the wastewater before disposal. For this, several effluent treatment techniques such as physicochemical, biological, combined treatments and other technologies have been used to remove pollutant compounds from the wastewater [10, 11]. However, the effluents from the textile processing industry are complex mixtures of many pollutants which are difficult to treat and have been a tough job for the textile industry in meeting wastewater discharge limits. On top of that, many of the techniques used to purify the wastewater are characterized by high process cost and produce another toxic waste that needs to be incinerated or disposed of using other disposal routes [12]. The wastewater treatment could reduce the toxicity of the pollutant stream to some extent, but it cannot avoid the problem from the root. It is also an expensive option which increases the production cost of the textile industry in general. Therefore, replacing water as a dyeing and finishing medium would be an ideal solution which solves the problem from the source.

Nowadays, the textile industries have focused on the use of alternative eco-friendly techniques and agents to minimize waste generation and reduce toxic chemicals. In this regard, more emphasis has been given for the development of cleaner, cost-effective, and value-added textile products to solve the issues related to health and the environment. Not only the product but also the methods of production of the future itself must bring technological innovation and sustainability for possible advancements while keeping the balance of nature. Thus, the textile industries have focused on the use of green technologies as an alternative to conventional textile wet processing to promote sustainable production and reduce waste generation. Some of the important green technologies and renewable natural materials such as biopolymers, enzymes, and natural dyes used for sustainable textile production have been reviewed by [13]. As discussed in the review, some of the green technologies adopted recently include, supercritical CO_2, microwave, plasma, ultrasound, and electrochemical reduction of dyes.

The use of environmentally friendly supercritical CO_2 as a dyeing medium has shown promising results owing to many advantages over the conventional systems [14]. Supercritical CO_2 dyeing has several advantages such as it does not require any water, surfactants, or dispersing agents, and does not involve drying at the end of the procedure. It is non-toxic, non-flammable, inexpensive, chemically inert under many conditions, and easily manageable critical conditions (details about $scCO_2$ will be dealt in the next chapter). It was shown that the $scCO_2$ dyeing process is not only environmentally superior to aqueous dyeing but also economically [15]. Due to these attributes, it has been given considerable attention and the potentials of $scCO_2$ in textile dyeing have been investigated extensively for the past three decades as described in these two review papers [16, 17]. To date, $scCO_2$ dyeing of polyester fibres with disperse dyes is successful at industrial scale [18]. In addition to dyeing, $scCO_2$ technology has also a promising potential to overcome the environmental and technical issues in many other commercial textile applications for example in textile functionalization or finishing industry. However, the use of $scCO_2$ processing technique to produce functional textiles is very limited so far. Therefore, further development and adaptation of this technology to the textile finishing industry is crucial and timely. Some of the motivations which gave a push towards conducting this research are:

- The outstanding environmental and economic advantages compared with conventional water and organic solvent-based functionalization processes.
- The great opportunity for enormous freshwater saving in textile dyeing and finishing processes and its special importance in the areas where water resource is limited.
- The resource efficiency of $scCO_2$ process which can profitably be used to develop high value and high purity products without a trace of solvent.

- The stringent environmental regulations always imposed and the continued consumer demand for high quality and safer products, hence the promising potential that $scCO_2$ has for future development.
- The commercial success of $scCO_2$ dyeing of polyester and the research interest to adopt it for other textile processes such as textile functionalization.

Thus, this thesis explores the possible use of $scCO_2$ dyeing technique for the development of functional and smart textiles in an eco-friendly way as an alternative to the conventional dyeing and finishing methods. Several functionalities of interest have been considered based on literature data and broad screening process and those which have promising potential were selected and investigated in this thesis. Many kinds of functional finishing agents are used to impart various functionalities to textiles. However, most of the agents are based on synthetic compounds in which many of them are not environmentally safe with a harmful effect on humans and animals. Considering this, this thesis also gives due attention to the possibilities of using sustainable and green agents based on natural products such as bioactive functional agents.

1.2 Purpose and contributions

This thesis aims to investigate the potential of supercritical CO_2 dyeing technology for the development of smart and functional textiles to make use of its advantage and expand its application in the textile industry. Specifically, it focuses on a novel approach towards functionalization of polyester fabric in a resource-efficient and water-free $scCO_2$ media. The main goal is first, to explore functionalities and the associated functional finishing agents suitable in $scCO_2$ medium, and second is to develop the functional fabrics and investigate the effects of the production parameters on the colour and functional performances towards determining optimum conditions. For each developed functional fabric, suitable characterization techniques have been used and the results are carefully analysed.

This thesis also includes an investigation towards functionalization of cotton fabric with a modified pH indicator dye, Nitrazine Yellow (GMA-NY) using photo grafting technique as an alternative method. The study was aimed to compare the properties of the functionalized fabrics developed by both methods. Unfortunately, the dyeing of cotton with GMA- NY using

$scCO_2$ was not successful and only experimental results concerning photo grafting technique is presented here.

This thesis mainly contributes towards expanding the application of $scCO_2$ dyeing technology for the development of functional textiles that was insufficiently explored up to now. Investigation of functional finishing agents suitable for $scCO_2$ processing and application of these agents into polyester fabric has been attempted. The main contributions of the thesis are outlined below.

- Simultaneous dyeing and antimicrobial functionalization of polyester were achieved by using selected chitosan biopolymers and a disperse dye in $scCO_2$ media. Both the colour and antimicrobial performance were examined and hence their compatibility was assessed (Paper I).
- Mordant free dyeing of polyester fabric with curcumin natural dye has been explored for the first time achieving a dyed polyester fabric with multiple functional properties using $scCO_2$ dyeing method without additional substrate pre/post-treatment. The effects $scCO_2$ dyeing conditions on the colour and functional properties have been studied and optimized processing condition was determined (Paper II and III).
- A novel UV responsive smart textile sensor fabric has been successfully developed with the most important commercial spirooxazine and naphthopyran dyes for the first time using $scCO_2$ dyeing technique. The photochromic behaviours of these photochromic colourants in solution and after incorporated into the polyester fabric have also been investigated (Paper IV and V).
- Surface functionalization of cotton fabric with a modified NY dye has been investigated using photo grafting technique. The halochromic performance of the grafted fabric subjected to acidic and alkaline pH environments both in wet and vapour conditions have been examined (Paper VII).

1.3 Structure of the thesis

The thesis is organized into eight chapters. **Chapter 1** describes the background information, purpose of the thesis and its contributions. **Chapter 2** provides the theoretical aspects of supercritical fluid technology particularly impregnation and dyeing mechanism of polymers in supercritical CO_2. Some studies conducted about the functionalization of textiles and some polymeric films using $scCO_2$ impregnation technique have also been reviewed. In **Chapter 3**, details about the materials, a description of the high-pressure lab dyeing equipment, the dyeing procedures and steps followed, and the characterization techniques and testing methods used in this study are presented. Chapters 4 to 6 present the main research findings of the thesis. **Chapter 4** presents experimental findings based on combined dyeing and functional finishing of polyester fabrics with disperse dye and chitosan biopolymers are discussed. **Chapter 5** presents colouration and bioactivation of polyester with curcumin natural dye. This chapter comprised two parts, the first part discusses the colouration properties, and the second part presents the functional properties. **Chapter 6** presents the investigation carried out to develop photochromic textiles by using photochromic dyes to produce UV sensing polyester fabric in $scCO_2$. In **chapter 7**, the experimental results concerning the production of a smart textile pH sensing fabric with a modified pH indicator dye (GMA-NY) is presented. Finally, the conclusions of the results and recommendations for future research are presented in **chapter 8**.

1.4 List of publications

This thesis is based on the work presented in the following publications:

I. **Abate, M.T.**, Ferri, A., Guan, J., Chen, G., Ferreira, J.A. and Nierstrasz, V., "Single-step disperse dyeing and antimicrobial functionalization of polyester fabric with chitosan and derivative in supercritical carbon dioxide". *The Journal of Supercritical Fluids*, **147** (2019) 231-240.

II. **Abate M.T.**, Ferri A., Guan J., Chen G., Nierstrasz V., "Colouration and bio-activation of polyester fabric with curcumin in supercritical CO_2: Part I - Investigating colouration properties", *The Journal of Supercritical Fluids*, **152** (2019) 104548.

III. **Abate M.T.**, Zhou Y., Guan J., Chen G., Ferri A., Nierstrasz V., "Colouration and bio-activation of polyester fabric with curcumin in supercritical CO_2: Part II – Effect of dye concentration on the colour and functional properties", *The Journal of Supercritical Fluids*, **157** (2020) 104703.

IV. **Abate, M.T.**, Seipel, S., Yu J., Viková, M., Vik, M., Ferri, A., Jinping, G., Chen, G. and Nierstrasz, V.A., "Supercritical CO_2 dyeing of polyester fabric with photochromic dyes to fabricate UV sensing smart textiles", *Dyes and Pigments*, **183** (2020) 108671

V. **Abate, M.T.**, Seipel, S., Viková, M., Vik, M., Ferri, A., Jinping, G., Chen, G. and Nierstrasz, V.A., "Comparison of the photochromic behaviour of dyes in solution and on polyester fabric applied by supercritical carbon dioxide", *IOP Conf. Series: Materials Science and Engineering,* **459** (2019) 012026. *[Conference paper]*

VI. **Abate M.T.**, Ferri A., Guan J., Chen G., Nierstrasz V., "Impregnation of materials in supercritical CO_2 to impart various functionalities", in Advanced Supercritical Fluids Technologies, *IntechOpen*, 2019. *[Book chapter]*

VII. Kianfar P., **Abate M.T**, Trovato V., Rosace G., Ferri A., Bongiovanni R., Vitale A., "Surface Functionalization of Cotton Fabrics by Photo-Grafting for pH Sensing Applications", *Frontiers in Materials*, **7** (2020) 00039

1.4.1 Contribution report

- **Paper I-III** – **Abate M.T**. was responsible for planning, conducting the experiment, and writing the paper. All the co-authors have participated in the planning, refinement of the manuscript, and approval of the final version

- **Paper IV and V** – **Abate M.T**. and **Seipel S.** have an equal contribution on planning, testing/analysis/discussion of the result, and writing the paper. Abate M.T. experimented. All the co-authors have participated in the planning, refinement of the manuscript, and approval of the final version

- **Paper VI** - **Abate M.T**. was responsible for planning, information gathering, reviewing research works, organizing, and writing the chapter. All the co-authors have participated in proof-reading, improvement, and approval of the final version of the chapter

- **Paper VII** - Kianfar P., **Abate M.T.**, Trovato V., and Vitale A. planned and conducted the experiments. Rosace G., Ferri A., Bongiovanni R., and Vitale A. conceived and designed the experiment. All authors contributed to writing the article.

Chapter 2

Supercritical Fluids (SCFs)

This chapter reviews the state-of-the-art technologies about supercritical fluids with a special focus on $scCO_2$ since it is the fluid used in the study. Some applications of $scCO_2$, the impregnation, and dyeing mechanisms and processes, the interaction between $scCO_2$ and polymers, and the factors affecting the $scCO_2$ impregnation process will be discussed. Furthermore, some researches carried out so far to functionalize textile fibres and some polymeric materials through $scCO_2$ assisted impregnation technique will be presented.

2.1 What is a Supercritical Fluid?

When a substance is heated and/or compressed its state changes; the solid melts into a liquid and the liquid vaporizes into a gaseous state and vice versa. To better explain this phenomenon, the phase diagram of a single substance (CO_2 as an example) is illustrated in **Fig. 2.1**. The phase diagram shows the regions corresponding to the different states of CO_2 under different conditions of temperature and pressure. Looking into the phase diagram, the triple point (T) is the point at which the three known phases (solid, liquid, and gas) coexist at equilibrium. If a substance in its gaseous state is compressed, it becomes liquid when it crosses the gas-liquid line. However, once it is heated above its critical temperature, liquefying is almost impossible under any pressure as the thermal energy of the gas molecules become too high. Moving upward along the liquid-gas coexistence curve, both the temperature and pressure increases. During this time, the liquid becomes less dense because of thermal expansion and the gas becomes denser as the pressure rises. Finally, it reaches a point at which the densities of the two phases become identical and at this point, the distinction between the gas and the liquid disappears. This point is called the critical point (CP) of a substance. This critical point is, therefore, the point where the vapour-liquid equilibrium ends. For pure substances, this critical point represents the highest temperature and pressure at which gas and liquid can coexist at equilibrium [19]. Above this point, substances are neither in liquid nor in a vapour state, but they are described as supercritical fluids (SCFs). Therefore, a supercritical fluid (SCF) is defined as a substance for which both its pressure and temperature are above the critical values simultaneously [20]. In the supercritical region, an isobaric temperature increases above the critical temperature or an isothermal pressure increase above the critical pressure maintains the fluid at supercritical state without a phase transition.

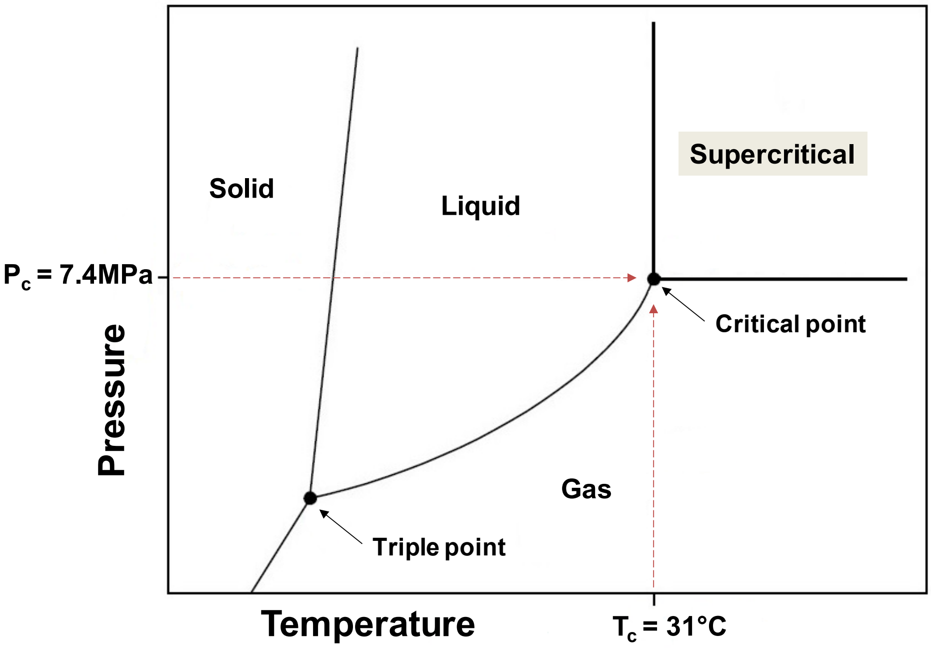


Fig. 2.1 The phase diagram of a pure substance (CO_2 as an example)

For a pure substance, there are particular values of critical temperature (T_c) and critical pressure (P_c). The critical parameters of some typical molecules used as SCF solvents are shown in **Table 2.1**.

Table 2.1 Critical parameters of some fluids [21].

SCF	T_c (°C)	P_c (MPa)
He	-269	0.2
Ar	-122	4.9
CO_2	31	7.4
C_2H_6	32	4.9
N_2O	37	7.3
C_3H_8	97	4.2
NH_3	132	11
H_2O	374	22

The more fundamental interest in SCFs arises because of their unique properties intermediate between gases and liquids. They acquire a special combination of liquid-like density and gas like viscosity and diffusivity properties. **Table 2.2** shows typical values for the density, viscosity, and diffusivity property of SCFs at the gas, SCF, and liquid states, taking CO_2 as an example. Looking into the values in the table, the viscosity and diffusivity values of SCF are much closer to the gas than the liquid. On the other hand, the density is higher in the supercritical state than in a gaseous state, which is closer to the liquid. In general, a higher density of SCFs helps to acquire high solvating power and the low viscosity is important for easy penetration and compressibility. High diffusivity generally results in improved mass transfer [22].

Table 2.2 Comparison of some physical properties of CO_2 at different states [22].

Fluide properties	Gas (313 K, 1 bar)	SCF (313 K, 100 bar)	Liquid (300 K, 500 bar)
Density (Kg m^{-3})	2	632	1029
Viscosity (μPa s)	16	17	133
Diffusion Coeff. (m^2 s^{-1})	$5.1*10^{-6}$	$1.4*10^{-8}$	$8.7*10^{-9}$

Furthermore, the physicochemical properties of the SCFs can be fine-tuned by changing the pressure and temperature. The most familiar property in this regard is the density behaviour as illustrated in **Fig. 2.2.** Near the critical point, a small change in temperature and/or pressure induces a great change in the fluid density. At the lowest temperature (31 °C), near the critical temperature of CO_2, the density increases rapidly when it reaches the critical pressure. As the temperature is increased, the change is less dramatic and moves to higher pressures. As can be seen from the figure, within the pressure range of 74 to 250 bars, and temperature between 31 °C to 180 °C, CO_2 density can be fine-tuned in the range of 116 to 918 Kg m^{-3}. However, controlling the density property especially near the critical point is difficult as many effects are correlated with the density.

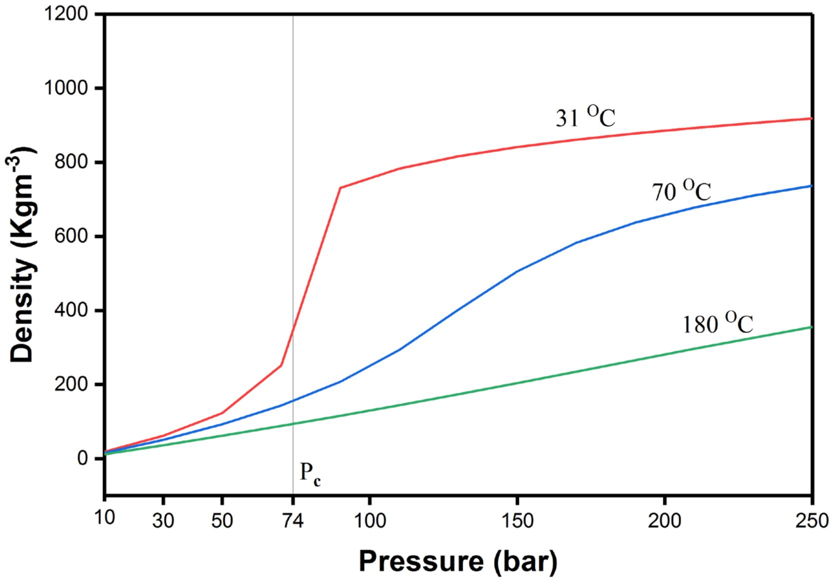


Fig. 2.2 Pressure-density isotherm for CO_2 (the fluid data is obtained from NIST Chemistry web book) [23]

2.2 Supercritical CO_2

Among the fluids listed in **Table 2.1**, CO_2 is the most widely used supercritical fluid primarily due to its attractive environmental and physical properties. CO_2 is non-toxic, non-flammable, relatively cheap, naturally abundant, environmentally friendly, and chemically inert under many conditions. Compared to other pure compounds, CO_2 has a low critical temperature (T_c = 31 °C) and pressure (P_c = 7.4 MPa) which is easily attainable and hence economically feasible. For example, water has a critical point of T_c = 374 °C and P_c = 22.1 MPa [24] which is relatively high. Moreover, CO_2 is abundantly available in the atmosphere and from industrial fermentation and combustion processes, ammonia synthesis, and mineral springs thus do not need an additional CO_2 production facility. Therefore, it can significantly help reduce the CO_2 emissions and reduces the cost and time required to discard the waste CO_2 from these manufacturing industries. Besides, since $scCO_2$ has similar solubility property to organic solvents like chlorofluorocarbons (CFCs), it can be an ideal candidate to replace them in many industrial applications. Generally, $scCO_2$ is considered as a green solvent which can be used as an environmentally friendly alternative to organic solvents. Unlike the materials processed with liquid solvents, which requires washing and drying to remove residual species and solvents, those materials processed by $scCO_2$ do not require solvent removal and drying, as the CO_2 can be released at the end of the procedure.

Looking into the molecular structure, CO_2 is a linear and nonpolar molecule with two symmetrical polar bonds. It has no dipole moment with a polarity near hexane and pentane. However, due to its strong quadrupoles, its properties are different from other nonpolar molecules of similar size and molecular weight, but without strong quadrupoles [25]. Beyond its critical point, CO_2 has unique properties. It exhibits densities and solvating power like liquid solvents and at the same time, it has extremely high diffusivity characteristics and viscosity like gases. Nevertheless, there was no significant difference in polarity between liquid and supercritical CO_2 [26].

2.2.1 Solvent properties of $scCO_2$

Carbon dioxide exhibits both nonpolar tendency (low dielectric constant) and polar properties (Lewis acidity and strong quadrupole moment) at the same time [27]. However, the polarity of CO_2 is generally smaller than most of the polar solvents. Thus, nonpolar and low molecular weight molecules are generally soluble in $scCO_2$, whereas polar and high molecular weight compounds have very low solubilities. The solvent capacity of CO_2 is similar to that of n-hexane [16, 28]. Certain amorphous fluoropolymers and silicones are the two classes of polymeric materials which are soluble in $scCO_2$ at readily accessible temperature and pressure [29, 30]. The solubility of various compounds in $scCO_2$ has been measured extensively and many studies that report the solubility of dyes have been published [21]. The solubility behaviour of $scCO_2$ towards various solutes is highly dependent on its density and the effect is significant at a higher temperature. This is because increasing the fluid density decreases the mean intermolecular distance, increasing the number of interactions between the solvent and the solute [31]. Besides, the functional groups available on the dye structure were reported to affect the solubility of the dye. For example, dyes with nitro or halo groups are more soluble than those with amino, carboxyl, or hydroxyl groups in the same ring positions [32-34]. The solubility of disperse dyes in $scCO_2$ is generally low but it has been demonstrated sufficient for dissolving disperse dyes. The solubility of disperse dyes varies under dyeing conditions of 120–140 °C at 30 MPa between 10^{-4} and 10^{-7} mole fractions [16], which is comparable to disperse dyeing in the aqueous system [35]. To enhance the solvating power of $scCO_2$, a small percentage of co-solvents (also known as entrainer or modifiers) such as acetone, alcohols, water, and other solvents are commonly used [36, 37]. Modification of disperse dyes and synthesis of new dyes has also been reported for improving the solubility and affinity property with the fibre [38-40]. The solubility of various disperse dyes in $scCO_2$ have been widely studied and a large number of solubility data is available in the literature [14]. Concerning this, solubility prediction and correlation of various compounds including dyes in $scCO_2$ have been largely investigated in the literature. Several methods exist for estimating the solubility of compounds in $scCO_2$. Among those, correlation models based on theoretical approach (equation of state and expanded liquid model) [41-43], density-based approach (empirical and semi-empirical model) [44, 45], software methods (regression equations, quantitative structure-property relationship – QSPR, neural networks, theoretical linear solvation energy relationships – TLSER) [46-50] have been widely used. The availability of solubility data of various compounds can be used to assess the compatibility of SCF for a given application and can also be used to determine the best working conditions of a given fluid to optimizing the process.

2.2.2 Some applications of $scCO_2$

The unique properties of $scCO_2$ have resulted in its use in various application areas. In earlier times, SCFs ($scCO_2$ in particular) were mainly used for extraction and chromatography applications. Extraction of compounds from various natural products was the first commercial use of SCFs. A well-known example of SCF extraction is decaffeination of coffee and extraction of hops [51]. It has been successfully used for extraction of relatively nonpolar compounds while the extraction of some polar compounds is still a challenge. SCF chromatography is also another application of SCFs mainly used to separate polar compounds demonstrating faster separation and better resolution of components than the high-performance liquid chromatography (HPLC) used conventionally. Nowadays, applications of $scCO_2$ have widened and increasing interest is shown in many areas. $ScCO_2$ is also an attractive technique in the synthesis and processing of polymer systems particularly for tissue engineering and drug delivery applications [52, 53]. To date, it has been successfully used as a solvent and impregnation media in the processing of various materials for instance in extraction and purification, impregnation (dyeing, drug loading), polymer modification, microcellular foaming, polymerization and reaction medium, catalysis, for techniques such as supercritical fluid chromatography, and so on. The potential applications of $scCO_2$ for a selected industrial process can be found in a review by Ramsey *et al.* [54]. $ScCO_2$ is among the novel green technologies for textile processing as discussed in these reviews [55, 56]. As this thesis focuses on investigating the potential application of $scCO_2$ solvent for dyeing and functionalization of polyester fabric, studies related to impregnation/ dyeing of some polymeric materials, specifically polyester fibre in $scCO_2$ medium is presented here.

2.3 Impregnation of materials in $scCO_2$

Impregnation of polymeric materials using SCF technique is becoming one area of interest in the development of novel functional products. The environmental and economic advantages over the conventional impregnation methods are the motivation behind the use of SCF impregnation. The conventional impregnation techniques have drawbacks such as the use of hazardous solvents, high energy consumption, very long diffusion rates. Due to this, it requires long contact time and the poor efficiency of the process also requires a large number of additives and solvent [57]. The use of $scCO_2$ assisted impregnation can solve these problems because of its unique properties and environmental friendliness. Besides its environmental advantages, this also arises from the opportunity to take advantage of the high diffusivity, solubility, low surface tension, and easy solvent removal of $scCO_2$ process securing high product purity free of residual solvent. The possibility of obtaining a product without any trace of solvent is especially important in the production of functional foods, active food packaging, and pharmaceutical products [58]. This also reduces the cost incurred to remove the residual solvent after the impregnation process. Another advantage of CO_2 which make it suitable for impregnation of polymers is its swelling and plasticizing action towards many polymeric materials which is very essential for solute loading. Due to these advantages, $scCO_2$ assisted impregnation technique has been chosen for the impregnation of several polymeric materials with different additives including dyes, drugs, and functional finishing agents.

Nowadays, $scCO_2$ impregnation process is becoming most important and effective method used to incorporate different active compounds into polymers for various applications such as the development of sustained-release materials, active food packaging materials, drug loading, dye impregnation, and so on. Drug loading to polymers is one of the active research in which the $scCO_2$ impregnation technique has been successfully used to load different drugs to various polymers for a variety of applications [59-61]. Jerome *et al.* reviewed the application of $scCO_2$ assisted impregnation of active pharmaceutical ingredients (API) into various polymeric structures by using $scCO_2$ impregnation technique [62]. The state of the art and the use of $scCO_2$ assisted impregnation process for the preparation of drug-eluting implants were discussed in the review. Wood impregnation with quaternary ammonium compounds (QAC) [63] and fungicide in $scCO_2$ to protect against warping and biological deterioration was reported in which the latter is successful in industrial scale [64]. Recently, analysis of the impregnation process was reported focusing on the unit operations of pressurized CO_2. Some boundary conditions and rules that can be used to generate impregnated materials in $scCO_2$ are suggested [57]. Dyeing of various polymeric materials in $scCO_2$ represents the most important case of $scCO_2$ impregnation, which will be discussed in subsequent sections.

2.3.1 Impregnation process and mechanism in $scCO_2$

The general impregnation process in $scCO_2$ comprises three main steps: (1) dissolution of the solute, (2) the sorption of the mixture ($scCO_2$ and solute) in the polymer matrix, and (3) depressurization of the system. Schematic representation of the impregnation process is illustrated in **Fig. 2.3**. Generally, the dissolution of the solute and sorption of the solute mixture are carried out simultaneously. During dissolution, total or partial dissolution could be possible depending on the property of the additive and/or the processing conditions. The sorption of CO_2 and active compound is dependent on the extent of polymer swelling and plasticization, which is also dependent on the chemical nature of the polymer and the impregnation condition (mainly temperature and pressure) of the system [65]. The final depressurization step removes the CO_2 and it is also one mechanism used to incorporation solute molecules into the polymer matrices specific to SCFs. Fast depressurization could improve the amount of solute incorporated into the polymer due to a rapid decrease in the solvating power of $scCO_2$. However, very rapid depressurization may cause polymer foaming, cracking or could even degrade the polymer [66]. Thus, the rate of depressurization should be carefully selected based on the specific polymer and additive used.

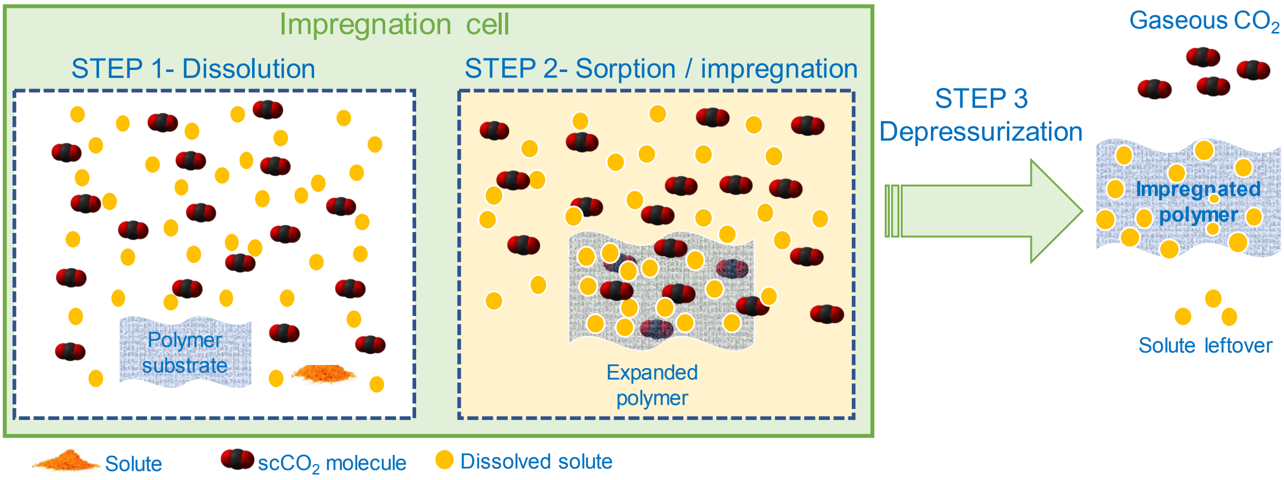


Fig. 2.3 Schematic of the three steps of impregnation process of a polymer substrate

The impregnation mechanism depends on both the solubility and affinity behaviour of the active compounds in the scCO$_2$-polymer system. The impregnation is feasible if the impregnate (solute) is soluble in scCO$_2$, if the polymer is swollen by scCO$_2$, and if the partition coefficient is favourable enough so that enough solute can be charged into the polymer matrix [67]. During the impregnation process, both soluble and insoluble molecules can be found fully or partially dispersed in scCO$_2$ dyeing cell or vessel. Two impregnation mechanisms were suggested based on the solubility and affinity behaviours of the solutes. The first one applies when the additive is readily soluble in scCO$_2$ in which they are transported by the compressed gas (CO$_2$ acts as a carrier) and can penetrate easily into the swollen polymer matrix. In this case, even a solute that has low affinity for the polymer can be trapped within the polymer matrix during depressurization. This approach has been mentioned effective when glassy polymers are used due to improved plasticization effect resulting in enhanced solute infusion [68]. A different mechanism is when the solute is insoluble or has very low solubility in scCO$_2$ but has a high affinity to the polymer. This results in a preferential partition of a solute towards the polymer over the fluid (high partition coefficient of a solute). It has also been demonstrated that, if the partition coefficient for the solute is large enough, a good impregnation can be obtained even though the solubility of the impregnate in scCO$_2$ is low [69]. This is the key mechanism by which scCO$_2$ impregnation of dyes and drug molecules is applied into polymer matrices. In both mechanisms, the active species interact either physically or chemically with the polymer. For solutes having good affinity to the polymer, the chemical interactions such as H-bonding are the main mechanism of incorporation into the polymer matrix. On the other hand, for active compounds with poor affinity to the polymer, incorporation is based on physical entrapment in the polymer matrix known as deposition [70].

2.3.2 Interaction of $scCO_2$ with polymers

To fully exploit the use of $scCO_2$ for various new applications, it is important to understand how it interacts with various polymeric materials. Several investigations that focused on the interaction between $scCO_2$ and polymers have been reported. There are three most important effects to explain the interaction of $scCO_2$ and polymers. These are sorption of CO_2 molecules, swelling, and plasticization of the polymer (T_g reduction). The sorption of the small CO_2 molecules into polymers leads to swelling of the polymer and consequently changes the physical and mechanical properties of the polymer. A sorption amount up to 20 wt. % was reported causing about the same percentage of swelling [67]. A swelling study on poly (methyl methacrylate) (PMMA) with $scCO_2$ resulted in 9 - 25% volume expansion [71]. The swelling of polymers is the most important effect by the $scCO_2$ when considering impregnation of a polymer matrix with active compounds such as dyes and drug molecules. When the polymer swells, large pores are formed (free volume increases) creating favourable condition for the additives to diffuse into the polymer matrix easily. When pressure is released after a definite impregnation time, the CO_2 molecules are rapidly desorbed from the polymer matrix leaving the solute molecules trapped inside the polymer matrix.

Another important consequence of $scCO_2$ sorption is the strong plasticization effect on a variety of polymers. For common glassy polymers with T_g in the range from 80 to 100 °C, a reduction in T_g to below room temperature could be observed due to 8-10 wt. % CO_2 sorption [72]. Plasticization generally causes changes in the polymer system that result in a decrease in rigidity, increase the elongation and flexibility of individual chains within the polymer, reduction in T_g, and increase in toughness [73]. The CO_2 is used as a carrier for the solute and acts like a lubricant resulting polymer softening thereby decrease the T_g of the polymer. A reduction in T_g of up to 30 °C was observed in the case of PET [74]. The drop in T_g depends on the degree of crystallinity of the specific polymer in which higher T_g reduction was observed on amorphous polymers. This phenomenon facilitates the diffusion of the dyes and other solute molecules inside the polymer matrix during $scCO_2$ impregnation. Also, changes in properties such as an increase in melting temperature (T_m) due to crystallization effect and increase in melting enthalpy (ΔH_m) was observed leading to changes in mechanical properties of several polymers [75]. An increase in yield strength and modulus and a decrease in ultimate elongation were also observed after $scCO_2$ impregnation of several polymers. This suggested that the degree of crystallinity had been increased due to $scCO_2$ treatment [76]. More details about changes in physical and mechanical properties of PET fibres during $scCO_2$ impregnation are presented in section **2.4.1.4.**

2.3.3 Variables affecting the $scCO_2$ impregnation process

The impregnation process depends on several factors such as temperature, pressure, the molecular structure of the polymer, depressurization condition, the phase behaviour and so on. Generally, increasing the pressure and temperature leads to a faster impregnation of the polymer matrix. Amorphous polymers are much easier to impregnate than semi-crystalline or cross-linked ones as the latter are more difficult to swell. A higher solute concentration leads to a higher substrate loading at equilibrium [67]. Some of the variables and their effects on the impregnation process are described below.

2.3.3.1 Effect of pressure

Generally, increasing the pressure at isothermal condition increases the density of the fluid resulting increase in the specific interaction between the solute and CO_2 molecules thereby enhancing solubility of the solute [25]. The pressure increase may also promote the impregnation of solutes by generating a greater concentration gradient of the solute between the CO_2 phase and the polymer. Moreover, polymer swelling increases with the system pressure, which facilitates the diffusion of more amount of solute into the polymer matrix. Generally, an increase in the impregnation yield was consistently reported when higher pressures are used, but once the material is saturated with the solute, no further increase in impregnation yield was observed by increasing the pressure [70]. Therefore, determination of the optimum pressure for the maximum impregnation yield is crucial for a specific solute and polymer system. The effect of pressure is further dependent on the concentration and affinity behaviour of the solutes used. When additives that have high affinity to the polymer are used, the substrate gets saturated relatively fast and easily at lower pressures and a further increase in pressure may not bring about additional solute loading. In the case when the solute has a poor affinity towards the polymer, the partitioning becomes more favourable for the CO_2 phase leading to a reduced solute loading. In this case, working at lower pressure was reported preferable to improve the partitioning of the solute in favour of the polymer phase. Nevertheless, the consequent low level of CO_2 sorption and hence polymer swelling were not well explained when lower pressure is used [62]. When less additive concentration is used, increasing the pressure results in complete dilution in CO_2 phase (i.e. non-saturated CO_2 phase). This creates a lower concentration gradient of the solute between the CO_2 phase and the polymer leading to lower solute loading into the polymer [70].

2.3.3.2 Effect of temperature

Temperature is another important variable that could affect the impregnation of solutes into polymer matrices. Generally, near the critical point of CO_2, a small increase in temperature causes a large density reduction and hence decreases the solvating power. However, the solubility behaviour of CO_2 is further complicated by the presence of cross-over (retrograde) region in the fluid phase. Chimowitz *et al.* [77] studied retrograde behaviour and the cross-over effect of several solute molecules in SCF. The cross-over pressure is the pressure at which the high temperature - solubility isotherm and low temperature - solubility isotherm intersects, and this point is assumed to be distinct for different solutes. For two solutes with different crossover pressures, a temperature change affects ideally in an opposite way within the same pressure and temperature region. Below the crossover point, the solubility of a given solute generally decreases with increasing temperature under isobaric condition while the reverse is true above this crossover point [77]. This decrease in the solubility of the active compound in the CO_2 phase under isobaric condition has a positive effect on the incorporation of solutes into the polymer. Due to the poor solubility, the affinity between the solute and the CO_2 phase decreases which improves the solute loading into the polymer. The same phenomena but a reverse effect was observed by Yu *et al.* during drug loading of poly (*l*-lactic acid) film with supercritical impregnation. At pressures above 120 bar, the drug loading increased with temperature under isobaric conditions, whereas below 120 bar the drug loading decreased [78]. According to Rojas *et al.,* the effect of temperature is further dependent on the amount of the solute used, whether excess solute (operate without complete miscibility) or a smaller amount of solute being completely dissolved in CO_2 phase is used as explained in detail [70].

The same phenomenon was also observed for disperse dyes as explained by Montero and his co-workers [25]. Generally, increasing the system temperature under isobaric condition increases the sublimation pressure of the dyes but at the same time, the solvent density decreases. At lower pressure (assume below the crossover pressure), the decrease in solvent density is dominant and dye solubility decreases with increasing temperature. However, at higher pressures, the increase in sublimation pressure with temperature overcomes the decrease in solvent density and dye solubility increases with rising temperature. According to them, the dyes were further identified as temperature controllable and density controllable displaying different crossover pressures. The relative location of the cross over point of the disperse dyes was determined based on the observed change in solubility with temperature and pressure. In the case of temperature controllable dyes, a controlled reduction in dye solubility could be achieved by carefully reducing the system temperature, which leads to a dye to partition favourably towards the fibre (positive effect on dye impregnation). On the other hand, density controllable dyes are those in which a controlled reduction in pressure at constant temperature (reduction in density) could result in a controlled reduction in solubility of the dye.

Furthermore, as explained earlier, a higher temperature can change the structure of the polymer due to the decrease in the T_g (plasticization effect). Thus, the mobility of the polymer chains increases with temperature which further facilitates the diffusion of more CO_2 molecules leading to enhanced swelling and subsequent solute deposition. Moreover, for semi-crystalline polymers, if the temperature increases above the melting temperature, the crystallites melt, and consequently more CO_2 can be absorbed enhancing the swelling which favours higher solute impregnation [60]. Nevertheless, the temperature effect on solute impregnation is not consistent in which both positive and negative effects were reported [62].

2.3.3.3 Effect of impregnation time

The $scCO_2$ dyeing process generally needs shorter dyeing time compared to the conventional aqueous or solvent dyeing methods due to its gas like low viscosities and diffusion properties. The kinetics of the impregnation process in $scCO_2$ is mainly dependent on the diffusion phenomena (affinity or diffusion coefficient) of solutes especially in the amorphous region of the polymer. Generally, rapid penetration of materials into polymers by $scCO_2$ is consistently reported compared with conventional liquid solvents. Increasing the impregnation time generally improves the solute mass transfer due to better swelling and plasticization effect which also is more pronounced when higher pressure and temperature is used. Long impregnation times enhanced the impregnation yield of cinnamaldehyde and thymol into cassava starch films and cotton gauze, respectively [79, 80]. However, a very long time of impregnation may cause thermal degradation of both the active compound and polymer. It was also mentioned that mixture compounds need a relatively shorter time of impregnation because of their greater diffusion coefficient as compared with pure compounds [70]. In the case of dyeing polyester with disperse dye, diffusion is much faster in $scCO_2$ due to the swelling and plasticization effect leading to increasing polymer free volume favouring faster dye uptake.

2.3.3.4 Effect of solute concentration, molecular size, and state of the polymer

Solute concentration and molecular size could also affect the $scCO_2$ impregnation process. Generally, higher concentration has a positive effect on solute incorporation, but it is only until the saturation uptake is reached. Above the equilibrium or saturation point, increasing the concentration could not improve the solute loading. When lower concentration is used, a lower concentration gradient of the solute between the CO_2 phase and the polymer is established leading to lower solute loading into the polymer [70]. Moreover, the molecular size of solutes has also a significant effect on the solubility and hence the amount of solute loading in $scCO_2$ impregnation process. Solutes with bigger molecular size have generally poor solubility in $scCO_2$ which could affect the amount of impregnation. Micronization of the dye particles has shown to increase both the dissolution and dye uptake of disperse dyes in $scCO_2$ dyeing of polyester. For this purpose, reducing the dye particle size using supercritical anti-solvent process has been widely practised [81]. Finally, compared with amorphous and crystalline polymers, the swelling of amorphous polymers is more pronounced and so does the diffusion of solute molecules into and within the polymer matrix resulting in higher solute incorporation.

2.3.3.5 Depressurization condition

Depressurization is the final step of $scCO_2$ impregnation which is essential to control the final solute loading as well as to recover the CO_2 and unused solutes. The effect of the rate of depressurization is dependent on the solubility and affinity behaviours of the solutes. If the solute has a higher affinity to the polymer and remains dissolved in the fluid phase during the depressurization phase (high solubility), a lower pressurization rate could improve the solute deposition [82]. However, if the solute is close to its solubility limit in the fluid phase, its deposition is weakly dependent on the rate of depressurization. On the other hand, if the solute has higher affinity towards the CO_2 phase (poor affinity to the polymer), a slow depressurization generally disfavoured higher solute loading because the solute prefers to stay dissolved in the fluid phase instead of the polymer phase. In this case, fast depressurization favours enhanced solute incorporation irrespective of the solubility behaviour of the solute. However, very rapid depressurization may cause polymer foaming, cracking or could even degrade the polymer [62].

2.4 Dyeing of textile fibres in $scCO_2$

The first patent describing the dyeing of textile substrates in the $scCO_2$ medium was applied in 1988 by Professor Schollmeyer and his research group in Deutsches Textilforschungszentrum Nord-West (DTNW), Krefeld, Germany [83]. From that time, several other patents and many research outcomes about the dyeing of various textiles in $scCO_2$ have been reported. Many studies focusing on process development for various fibres and fabrics, dyeing process optimization, the solubility of dyes, the mechanisms, and equipment development have been undertaken. As a result, $scCO_2$ dyeing of polyester fibres has now achieved the necessary commercial requirements and $scCO_2$ dyeing polyester fibres with disperse dyes is available at industrial scale. Currently, the Netherlands based company, DyeCoo Textiles Systems B.V., is building $scCO_2$ dyeing machines and few of its dyeing machines installed in Thailand and Taiwan are fully operational [84].

The principles behind dyeing and impregnations processes in $scCO_2$ are almost the same. The general process scheme for the dyeing of textiles in $scCO_2$ is presented in **Fig. 2.4.** Briefly, dyestuff in powder form is placed inside a high-pressure dyeing vessel, the sample to be dyed is wrapped in a perforated beam or mesh and suspended inside the reaction vessel, and then the vessel is sealed, purged with gaseous CO_2, and preheated. When the working temperature is reached CO_2 is compressed isothermally to the chosen working pressure and kept at this pressure until the pre-set dyeing time reaches and released afterwards. Generally, a dyeing time of 10 to 60 min is enough depending on the temperature and pressure, the fibre type, and the required depth of shade. After dyeing, the unused dye and CO_2 is separated and can be reused. Though the dyeing principle remains the same, several laboratory-scale, and pilot-scale $scCO_2$ dyeing equipment have been designed with only a few technical and operational differences [85-88]. To date, however, there is only one fully operational industrial-scale $scCO_2$ dyeing machine built by DyeCoo. DyeCoo's industrial-scale $scCO_2$ dyeing machine called DyeOx which consists of three dyeing vessels with a loading capacity up to 200 kg. In the DyeOx, the fabric to be dyed is wrapped in a beam and the dyestuff is placed in separate cartilage. The cartilage containing the dyestuff is connected to the beam and introduced into the vessel for dyeing. The dyeing steps involve loading, pressurization, dyeing/levelling, rinsing, depressurization, and unloading which takes around 2 hours of process time. During dyeing, higher circulation of the dye is performed for better solubility and uniform dye uptake [84].

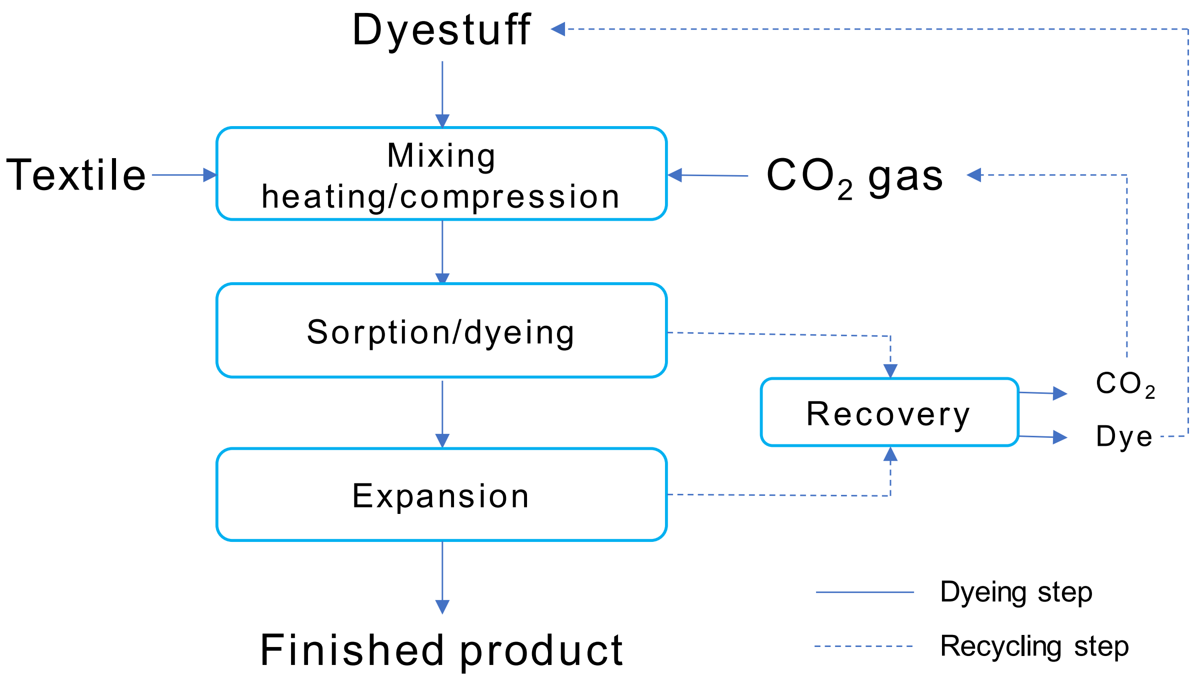


Fig. 2.4 A simplified scheme of the dyeing process of textiles in $scCO_2$. Adopted from [57]

Dyeing of textiles in supercritical CO_2 has many advantages over the conventional aqueous dyeing. First and foremost, it avoids the use of freshwater and the associated wastewater generation. This significantly reduces the cost incurred for freshwater usage and wastewater treatment. Besides, the process has simpler dye formulations with significantly less dyestuff compared with water-based dyeing methods. It also avoids the use of auxiliary chemicals (e.g. dispersing agents, surfactants, and others) which otherwise should be used in aqueous dyeing to improve the disperse dye solubility in water. The dyeing process in $scCO_2$ is relatively fast due to the higher diffusivity of the CO_2 which makes the dye molecules to diffuse more rapidly into the fibre free volumes. A comparison of conventional aqueous dyeing and $scCO_2$ of polyester is shown in **Fig. 2.5**.

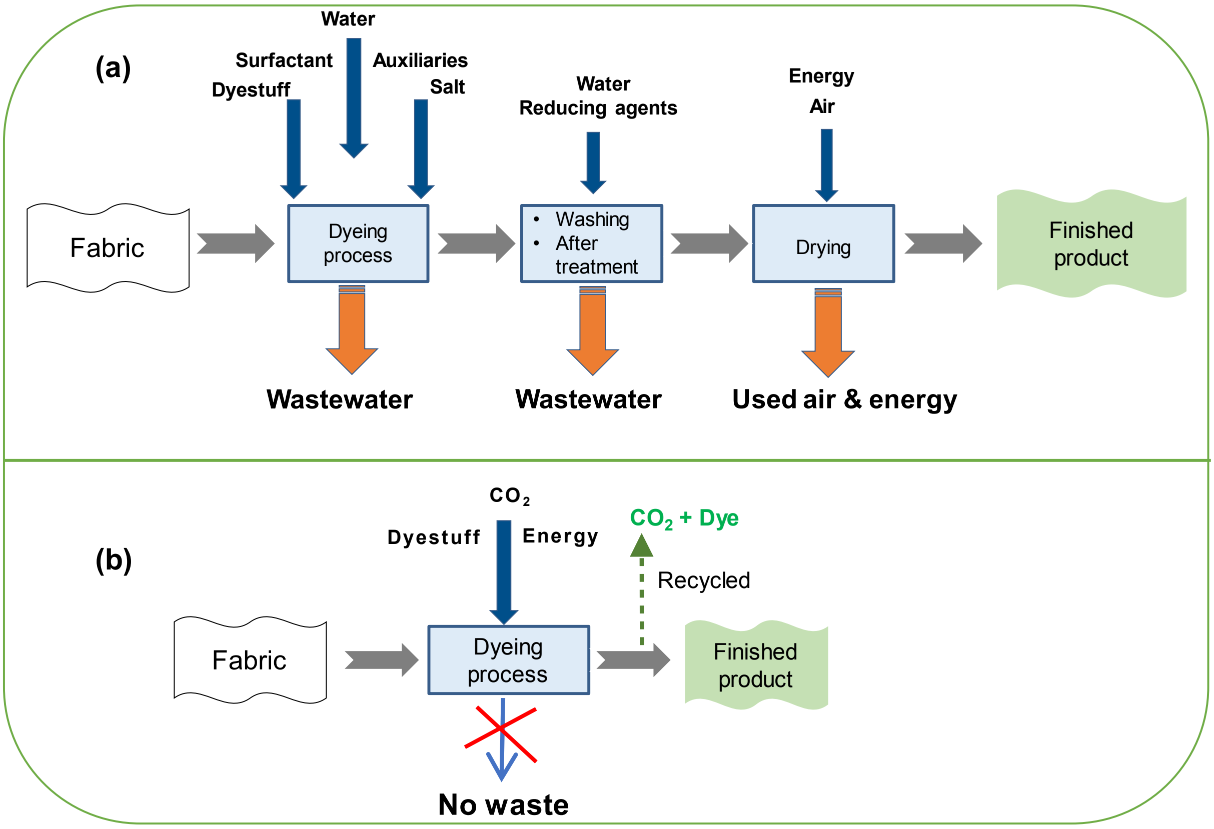


Fig. 2.5 Schematic of (a) conventional aqueous-based dyeing of polyester and (b) $scCO_2$ dyeing of polyester

Moreover, dye utilization in $scCO_2$ is generally high reaching up to 99% without dye hydrolyzation problem and even the small amount of unused dyes and the CO_2 can be easily separated by simple depressurization and can be recycled leaving no waste generated. Furthermore, in $scCO_2$ dyeing, no drying is required saving a huge amount of energy and minimizes the associated air emissions, while drying is one of the standard procedures in aqueous dyeing processes. Economic wise, though the initial investment cost of supercritical dyeing machine is higher than that of the aqueous ones, the operating cost is lower than the conventional aqueous dyeing processes. In this regard, $scCO_2$ dyeing process has a 50% lower overall cost due to its short process time, recyclable CO_2 gas and dyes, elimination water and wastewater, auxiliary chemicals, and drying [15]. Therefore, the advantages of using $scCO_2$ dyeing are both environmental and economic.

Various kinds of textile fibres such as poly (ethylene terephthalate) (PET), nylon, polypropylene, polyethylene, cotton, silk, and wool have been investigated for their suitability in the $scCO_2$ dyeing process. Based on the evaluation of previous publications, most of the research and development activity has been directed towards dyeing of polyester fibres. On the other hand, the dyeing of natural fibres in $scCO_2$ has still challenges. Despite its advantage in polyester dyeing, the low polarity of $scCO_2$ is the main problem hindering the polar hydrophilic fibres to be dyed in the $scCO_2$ medium. Moreover, these natural fibres have no physical attraction towards disperse dyes and the reactive dyes that are normally used to dye natural fibres in water media are polar, which are not soluble in $scCO_2$. To solve this problem, different techniques such as using polar modifiers, reactive disperse dyes, reverse micelle systems, and others have been proposed by researchers to adopt $scCO_2$ dyeing process for the colouration of natural fibres. Some studies about $scCO_2$ dyeing of natural fibres can be referred here [89-93]. Since the scope of this thesis is limited to dyeing and functionalization of polyester fibres, it will only focus on studies related to polyester.

2.4.1 Dyeing of PET in $scCO_2$

To date, the main technological development and optimizations related to $scCO_2$ dyeing were focused on PET even though some reports are available on other synthetic and natural fibres. PET is the most successful fibre and disperse dyestuffs are almost exclusively used to dye polyester fibres in $scCO_2$ dyeing. Therefore, some background about PET fibre, disperse dyes, the dyeing mechanism of polyester with disperse dyes in $scCO_2$, and some common effects of $scCO_2$ dyeing process on PET properties are presented in this section.

2.4.1.1 PET fibre

PET was invented by Winfield and Dickson in 1941 and commercialised by DuPont in 1950 [94, 95]. Since then it has become the most important and dominant manmade fibre in terms of volume and product value on the market due to its important properties and versatility in various applications. Generally, synthetic fibres account for the majority of textile fibres produced worldwide. Among the synthetic fibres, polyester fibre has the highest share of the global fibre production making it the world's most widely produced fibre [96]. This is due to its several useful properties such as high strength, durability, stable, abrasion resistance, and resistance to acid, alkali, and bleaches suitable for various applications. PET is a relatively hydrophobic (non-polar) and semi-crystalline fibre with 65-85% crystallinity consisting of tightly packed, highly ordered polymer molecules. PET has a glass transition temperature (T_g) in the range from 68 to 120 °C, and a melting temperature from 252 to 265 °C depending on the orientation of polymer chains and crystallinity [97, 98]. Polyester is the most versatile fibre extensively used in various apparels and technical textile applications. It's the most used textile fibre in the functional textile domain and the most investigated fibre as far as $scCO_2$ dyeing is concerned. However, some drawbacks of polyester include the difficulty of dyeing, hydrophobic nature, and less breathable. Therefore, improving the hydrophilicity and dyeability of polyester are becoming increasingly important.

2.4.1.2 Disperse dyes

Disperse dyes are a class of non-ionic dyes with relatively low molecular weight and low water solubility. Due to the low water solubility, the molecules can exist in a highly dispersed state in water with the help of dispersing agent added in the formulation during the dye synthesis or during the dyeing processes. Most disperse dyes are based on simple azo structure (which accounts for more than 50%) because of the diverse diazonium ion and coupling components possible for easy substitution. The next importance to the azo structure is anthraquinones which accounts for about 25 % and the rest are based on nitro, methine, and other structures [99]. Most commonly, disperse dyes are used to dye polyester, cellulose acetate and triacetate, polyamide, and acrylic fibres due to their substantivity towards these hydrophobic fibres [100]. Usually, the solubility of the dyes in $scCO_2$ is the main criteria used to choose dyes appropriate for $scCO_2$ processing. A lot of data is available concerning the solubility of disperse dyes based on different structures such as azo, anthraquinone, benzothiazole, and mordant in $scCO_2$ as described previously. Generally, the solubility of the disperse dyes in $scCO_2$ corresponds to that of water and their dissolving kinetics seem to be dependent on the particle size, molecular weight, and the dye structure [101]. Dyes with lower molecular weight and smaller particle size have better solubility in $scCO_2$ but this does not seem to be a general rule. For many disperse dyes, however, the dye structure consistently correlates with the solubility in $scCO_2$. For example, the introduction of highly polar groups such as hydroxyethyl, amino, carboxy, cyano, and acetylamino into the dye structure decreases the solubility. The polar groups can enable hydrogen bonding between different molecules which can associate and interact with each other forming high molecular weight dye aggregates resulting decrease the solubility [32, 33]. On the other hand, nitro and halogen groups have shown a positive effect on the solubility of dyes in $scCO_2$. Therefore, this factor should be carefully considered during dye synthesis as well as selection of disperse dyes for $scCO_2$ dyeing.

2.4.1.3 Dyeing mechanism in $scCO_2$

In principle, the dyeing mechanism in the $scCO_2$ medium is similar to the water-based system. Generally, high temperature in the range of 120-130 °C is required in both $scCO_2$ and aqueous based systems to dye polyester. The CO_2 in its supercritical state performs two key actions during dyeing. The first is to solubilize the dye and transport it into the fibre surface and the second is to transfer heat to the fibre [102]. As illustrated in the schematic (**Fig. 2.6**), the dyeing steps are as follows: (i) dissolution of the dye, (ii) transfer of dye to the fibre, (iii) adsorption of dye on the fibre surface, and (iv) penetration and diffusion of the dye molecules into the fibre. When a semi-crystalline polymer such as PET is in contact with the $scCO_2$ fluid, the small CO_2 molecules can penetrate to the free volume of the amorphous region and swells the fibre creating additional free volumes. This also increases the mobility of the polymer chains resulting in the increased degree of plasticization due to decrease in glass transition temperature (T_g) [103]. The swelling and plasticization effects allow the small dye molecules which are dissolved and transported to the fibre surface by the CO_2, to penetrate and diffuse into the polymer system in the amorphous region of the fibre. During the diffusion process, the dye molecules are believed to be bound physically to the polyester molecules via dispersion forces. When the system is depressurized at the end of the dyeing process, and the CO_2 molecules are removed by the shrinking fibres and the dye molecules are trapped inside the polymer matrices [102]. This mechanism was first suggested by Saus *et al.* [101] and later confirmed by Tabata *et al.* [35].

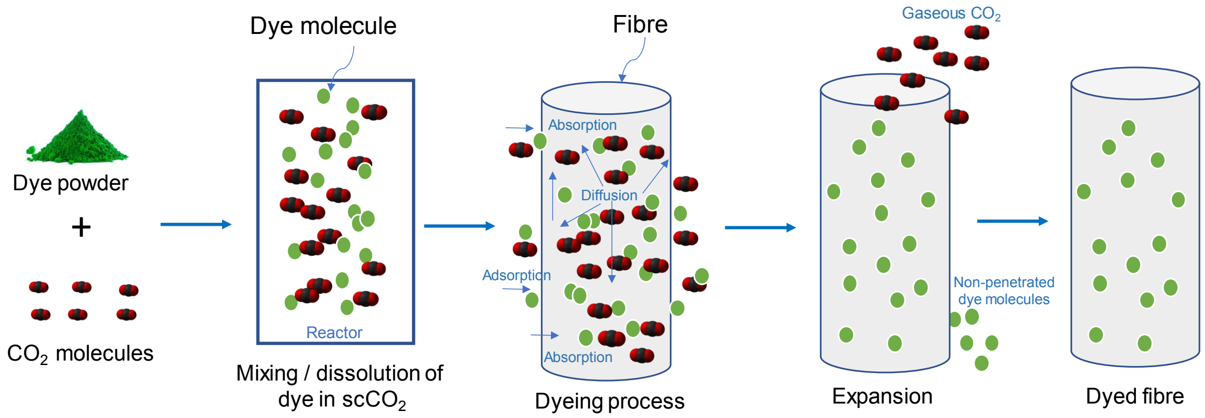


Fig. 2.6 Schematic of dyeing mechanism of PET fibre in $scCO_2$

2.4.1.4 The effect of $scCO_2$ process on PET properties

Knowledge about the influence of the $scCO_2$ dyeing medium on the fibre properties and characteristics is important because it could affect the quality and the reproducibility of the dyeing and consequently, its industrial applicability in the future is decided based on the observed effects. Based on this, several researchers investigated the changes in the physical, mechanical, and morphological properties of polyester fibre induced by $scCO_2$ treatment. Batch *et al.* reviewed the effects of $scCO_2$ on the physical properties and morphology of PET [16]. Generally, the results reported to date indicate that no significant effect on the fibre properties could be detected due to $scCO_2$ treatment of polyester materials. The process does not alter the thermal stability of the polymer and no fibre damage was observed [104]. Also, the absence of chemical change and insignificant change in crystal size but a slight increase in the melting temperature and melting enthalpy was reported [76, 98, 105]. However, some physical, mechanical, and morphological changes were detected. The commonly observed changes due to $scCO_2$ treatment were a decrease in T_g value (reduction of about 20-30 °C) due to the plasticization effect of CO_2 [106]; an increase in crystallinity due to the rearrangement of molecular chains into more ordered configurations promoted by the chain mobility [107]; and some changes in surface morphology due to migration of oligomers to the surface of the fibre forming new micro-voids at their previous sites [108, 109]. Furthermore, a small increase in shrinkage and elongation was also observed after $scCO_2$ treatment of PET and the extent of increase for both the shrinkage and elongation is more pronounced when non-heat set material is used [110]. Therefore, $scCO_2$ is a suitable medium for the treatment of PET without causing any problem if heat-set material is used. Moreover, $scCO_2$ treatment may result in fabric stiffness and harsh hand presumably due to the absence of mechanical action and an increase in crystallinity of the polymer structure. One study showed that CO_2 cleaning process of woollen fabrics caused a decrease in fabric flexibility and elastic recovery from bending [111]. Overall, no adverse effect was observed so far when PET is treated in the $scCO_2$ medium under optimum dyeing conditions and those changes on the morphology and crystallinity are less significant and do not differ from those caused by the conventional methods. In this regard, further studies might be necessary to adequately define all the effects, if any more.

2.5 Functionalization of materials in $scCO_2$

Modification of polymeric materials via $scCO_2$ impregnation techniques to impart various functionalities has also been reported. A wide range of polymeric materials such as poly (methyl methacrylate) (PMMA), polyethylene, poly (vinyl chloride) (PVC), poly(caprolactone) (PCL), polyamide, polycarbonate, poly(tetrafluoroethylene) (PTFE), linear low-density polyethylene (LLDPE), polyester, and so on have been impregnated with various functional compounds using $scCO_2$. A range of functional agents from metal carbonyl complex to organic dyes have been employed for the impregnation of these polymeric materials [68]. Textile materials have also been treated with different functional agents using $scCO_2$ impregnation technique. The most common active chemical species that have been used functionalize textiles using $scCO_2$ impregnation technique are based on functional dyes (natural and synthetic origin), silicon and fluoropolymer, natural extracts, and organometallic-based agents [112]. Special emphasis has been given for functionalities such as antimicrobial, antioxidant, flame retardant, water/oil repellent, and so on. Some of the studies and the strategies used to modify polymer materials in the form of fibre, fabric, and films are presented in this section.

2.5.1 Functional dyes

One strategy to functionalize textiles is through dyeing with dyes having additional functional property. In this approach, either dyestuff having inherent functional property are used or functional properties are manifested into the dyes through molecular design. To modify the dyes, the functional units can be integrated into a dye molecule via covalent bonding or crosslinking during synthesis. As far as $scCO_2$ dyeing is concerned, most of the times disperse dyes are modified to possess certain functional groups based on the needed functionality. Incorporation of a quaternary ammonium structure into mono, diazo, and anthraquinone was reported to prepare dyes with antimicrobial functionality [113]. Therefore, simultaneous dyeing and functionalization of textiles can be achieved by choosing these specific dyes with additional functionality. Abou Elmaaty *et al.* synthesized antibacterial hydrazonopropanenitrile dyes and applied to polyester fabric using $scCO_2$ achieving excellent colour and antibacterial activity [114]. The same research group also prepared a series of disperse azo dyes with a potential antimicrobial activity and applied to Nylon 6 using $scCO_2$ impregnation technique [115]. Higher antibacterial efficiency and better colour fastness property were obtained compared with the conventional exhaust dyed samples. Xiaoqing *et* *al.* reported fluorescent dyeing of polyester using disperse fluorescent yellow 82. The obtained dyed polyester fabric exhibited the required warning clothing function with good photostability and fastness properties [116]. Furthermore, many natural dyes such as curcumin, berberine, and henna have been investigated as functional dyes. Curcumin is widely used as a food colourant possessing several medical properties like anti-inflammatory, antitumor, antifungal, and antibacterial activities. Curcumin has been used to impregnate polyester films and poly(hydroxybutyrate) (PHB) granules in $scCO_2$ dyeing media [104]. Some photochromic dyes were also used as disperse dyes applied to various polymers to develop textile-based UV sensor materials [117, 118] in $scCO_2$.

2.5.2 Silicon and fluoropolymer-based compounds

Silicon and fluoropolymer based functional agents among the most common agents that have been used to functionalize textiles. Prorokova *et al.* used low molecular weight polytetrafluoroethylene to modify polyester in $scCO_2$ for the fabrication of water/oil repellent fabric [119, 120]. They were able to achieve an ultra-thin fluoropolymer film with extremely low water absorption and an additional increase in hydrophobicity was observed when the fabric was pre-treated with weak alkali forming oxygen-containing groups. Xu *et al.* [121] also prepared water and oil repellent polyester fabric using organic fluorine in a $scCO_2$ medium. In both cases, the treated fabrics gained good water/oil repellent property with improved mechanical property without affecting the air permeability of the fabric. A modified dimethyl siloxane terminated with silanol group (PDMS) was applied to a cotton fabric with the help of crosslinking agents in $scCO_2$ to functionalize cotton [122]. The use of the crosslinking agent demonstrated better silicon deposition. The deposition of silanol compound was on the surface of the fabric, while for $scCO_2$ deposition was possible about 1 μm under the fabric surface. Chen *et al.* synthesized CO_2-philic biocidal fluorinated pyridinium silicon and quaternary ammonium salt (QAS) and applied to cotton in $scCO_2$ medium [123, 124]. They also prepared silicon-containing 2,2,6,6-tetramethyl-4-piperidinol (TMP)-based N-chloramine and N-halamine polysiloxane and impregnated them in polyethylene (PE) and polypropylene (PP) fibres, respectively using $scCO_2$ solvent [125, 126]. In all cases, antibacterial activity was achieved with good durability properties. Recently, Zefirov *et al.* [127] applied perfluoroalkyl methacrylate/hydroxyalkyl methacrylate to Nylon fabric with the aid of diisocyanate crosslinking agent in $scCO_2$ and they obtained a durable coating with good oil/water repellent properties.

2.5.3 Organometallic compounds

SCF impregnation of organometallic compounds into polymer matrices has also been studied by many researchers. Silver in different forms has been widely applied to different fibres and polymeric films to develop various functionalities. Silver nanoparticles were used to modify wool fabric in $scCO_2$ and the treated fabric demonstrated excellent catalytic, antistatic, and antibacterial activities [128]. Two different silver precursor materials, Ag (hepta) and Ag (cod) (hfac) were applied to cotton fabric using pressurized CO_2 and subsequent reduction of the impregnated precursor using hydrogen gas was investigated. Cotton fabrics modified with these silver precursor exhibited good antibacterial inhibition [129]. A silver-containing additive [1-5cyclooctadien silver (I)-1,1,1,5,5,5-hexafluoroacetylacetonate] was applied into polyimide substrate using $scCO_2$ and a highly reflective polyimide film was obtained for possible aerospace application [130]. Silver nitrate was successfully impregnated into injection moulded polycarbonate parts via $scCO_2$ impregnation technique to impart antibacterial properties. The impregnated samples acquired a bacterial reduction of up to 99.99% after one hour of contact time. Furthermore, $scCO_2$ has been also used to impregnate other metallic materials into various substrates. Chiu *et al.* impregnated silk fabric with platinum (Pt) [131] and Ni-P and TiO_2 [132]. Iwai *et al*. fabricate conductive cotton fabric with palladium (II) hexafluoroacetylacetonate using $scCO_2$ impregnation and subsequent reduction with sodium borohydride ($NaBH_4$) in aqueous solution [133]. Xu *et al.* used hematite nanoparticle to fabricate water repellent cellulosic fibre using $scCO_2$ impregnation [134]. Belmas *et al.* widely investigated impregnation of p-aramid fibres with organometallic complexes in $scCO_2$ before electroless metal plating to improve the adhesion between the fibre and metal layer [135, 136].

2.5.4 Natural active compounds

Several natural-based agents such as thymol, carvacrol, eugenol, pyrethrum extract, and others have been used to impregnate different polymers to modify the material properties and develop different functionalities. Zizovic *et al.* widely investigated impregnation of thymol into various substrates using $scCO_2$ impregnation technique. In this research group, Milovanovic *et al.* impregnated cotton gauze and cellulose acetate [80, 137, 138], Markovic *et al.* treated corona modified polypropylene [139], and Ivanovic *et al.* impregnated PCL and PCL-HA (PCL-Hydroxyapatite) with thymol in $scCO_2$ medium. Thymol has also been used to impregnate PLA and LLDPE polymers in $scCO_2$ [140, 141]. Furthermore, $scCO_2$ was successfully used to impregnate carvacrol into cellulose acetate beads [142], Eugenol into LLDPE film and polyamide fibres [143, 144], and pyrethrum extras into polypropylene and polyamide fabrics as well as cellulose acetate beads and films [145]. Other natural extracts such as mango and olive leaf extracts were also applied to PET and PET-PP films, respectively [146, 147] in $scCO_2$. Flame retardant PET was also developed with sensitizer in $scCO_2$ [148]. Chitin and chitosan were applied to polyester using $scCO_2$ and results showed that chitosan lactate could be impregnated but no chitin could be impregnated [149]. In most of the cases, the impregnation of natural compounds has probably occurred due to their high affinity towards the polymers as their solubility in $scCO_2$ is relatively low. The affinity between the active compounds and the polymer creates some chemical interaction between the active compound and the polymer favouring a preferential partitioning of the solute within the polymer phase. However, thymol and some other natural active compounds have a low affinity towards polyolefins in general. In such cases, the impregnation is possibly happened due to physical entrapment or deposition of the active substances into the polymer matrix during the depressurization step of CO_2 [70].

Chapter 3

Materials and Methods

In this chapter, detailed specifications of the materials and equipment used, the dyeing and impregnation procedures, and the characterization techniques employed to evaluate the properties of developed samples along with the recommended test standards will be described in detail.

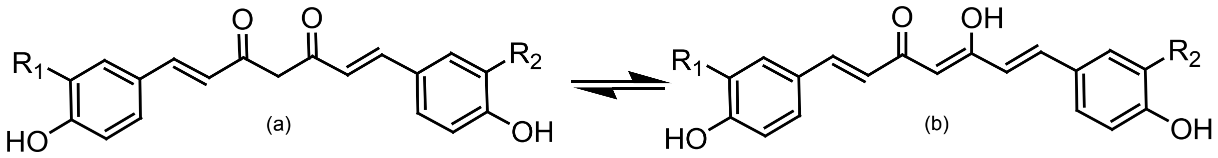
3.1 Materials

3.1.1 Substrates

Two kinds of polyester fabrics, pique-knitted (123 g/m^2) and plain-woven (147 g/m^2) supplied by DyeCoo (Weesp, Netherlands) and FOV Fabrics (Sweden), respectively were used for scCO_2 dyeing experiment. The fabrics were washed at 60 °C for 30 minutes with a standard detergent using domestic laundry washing machine before use to remove spin oil and other contaminants. They were used after drying in ambient condition. For UV grafting experiment, a scoured and bleached plain-woven cotton fabric with a mass of 331 g/m^2 was used. Before use, the fabric was washed using 2% non-ionic detergent at 40 °C for 20 min at neutral pH condition.

3.1.2 Dyestuffs

High performance disperse dyes (TERASIL®SC) tailored for scCO_2 dyeing received from DyeCoo (Weesp, Netherlands) were used. Two kinds of curcumin natural dye (**Fig. 3.1**), having the same molecular weight 368.38 g/mol but with different purity were used in this study. One is low purity curcumin from turmeric (*Curcuma longa*) with ≥ 65 % purity (HPLC) indexed under product number no. c1386, CAS-No 458-37-7 and the other is curcumin with high purity (≥ 80 % curcumin) indexed under product number no. c7727, CAS-No 458-37-7, acquired from Sigma-Aldrich Sweden AB (Stockholm, Sweden). The low purity curcumin was used during the investigation of the colour properties and the higher purity curcumin was used in the investigation of the functional properties.



Curcumin = (R_1=R_2=OCH_3)
Demethoxy derivative = (R_1=H and R_2=OCH_3)
Bisdemethoxy derivative = (R_1=R_2=H)

Fig. 3.1 Chemical structure of curcumin; a) Keto and b) Enol forms

3.1.3 Functional finishing agents

- Chitosan and its derivatives having different molecular weight and viscosity **(Table 3.1**) were acquired from Sigma-Aldrich AB, Sweden. The generalised structure of chitosan and chitosan lactate used in the main experimental section are shown in **Fig. 3.2.**

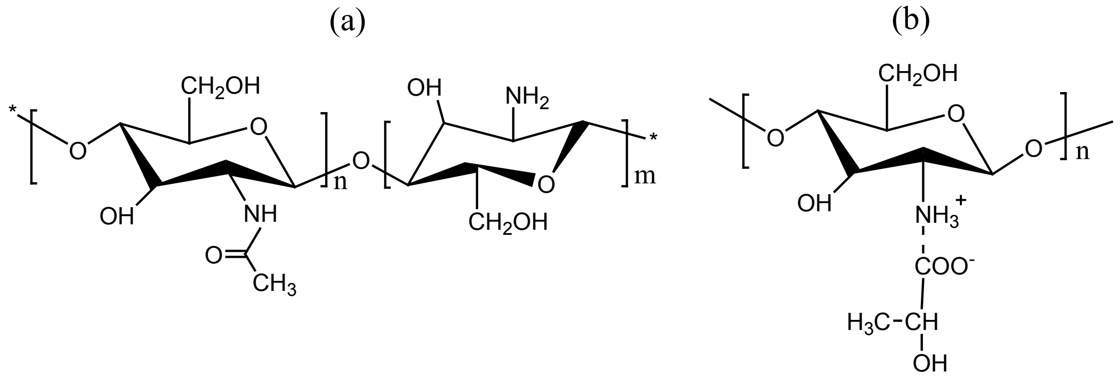


Fig. 3.2 The molecular structure of chitosan (a) and chitosan lactate (b) used in the study

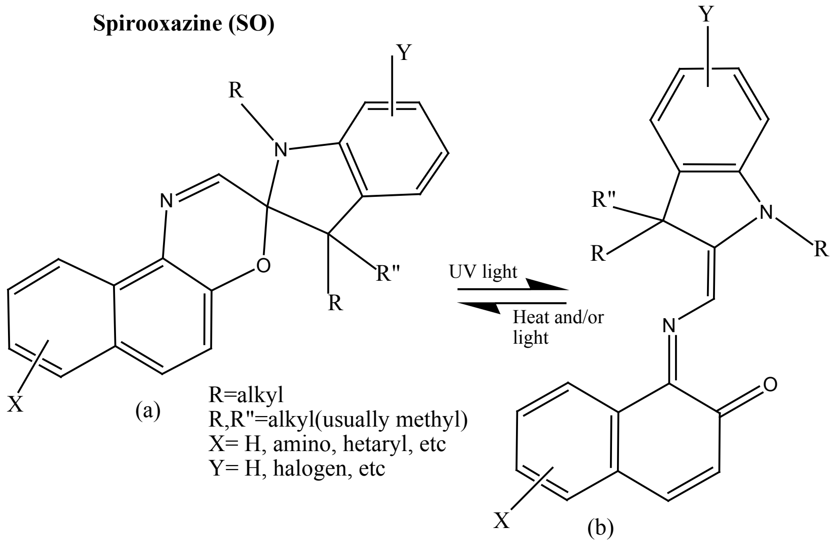
- Curcumin natural dye was used both as a colourant and as a finishing agent since it possesses multiple functional properties in addition to imparting colour. Among the two kinds of curcumin presented above, the one with higher purity (≥ 80 %) was used for the investigation of functional properties.

Table 3.1 Chitosan and derivative used and their properties as indicated in the product data-sheet

Chitosan type	DDA (%)	MW (kDa)
Chitosan low Mw	75-85	50-190
Chitosan from shrimp shells	≥75	-
Chitosan lactate	>80	5
Chitosan oligosaccharide lactate	>90	5
Chitosan oligosaccharide	>72	≤5
Chitosan (10 cps), very low Mw	≥90	30

MW- Molecular weight, kDa-kilo Dalton, cps-centipoise

- Two commercial photochromic dyes; Sea Green from Spirooxazine (SO) and Ruby Red from Naphthopyran (NP) dye classes (Vivimed Labs, UK) **(Fig. 3.3)** were used for the development of photochromic polyester fabric.



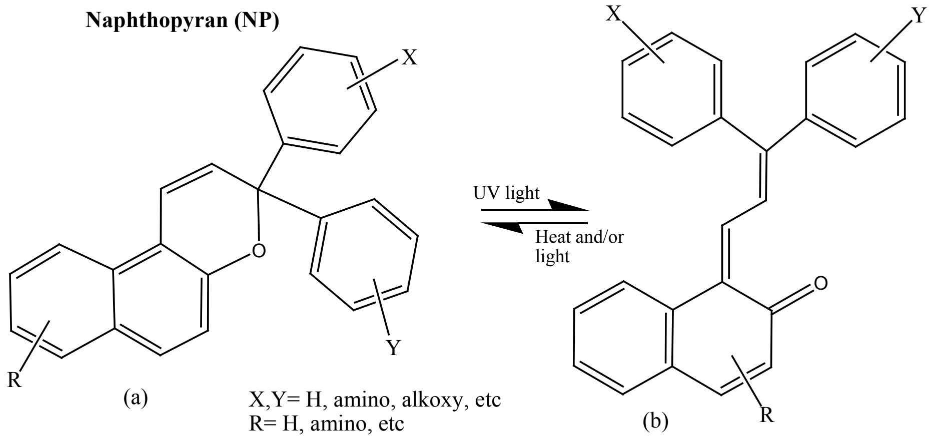


Fig. 3.3 Generalized structures of Spirooxazine (sea green) and Naphthopyran (ruby red) dye classes and their photochromic transformation from (a) ring closed to (b) ring open forms.

- For the photo grafting experiment, Nitrazine Yellow indicator dye (NY) modified with glycidyl methacrylate group (GMA-NY) was synthesized as described in previous work [150]. Briefly, the GMA molecule is linked to the NY dye through epoxy ring-opening of GMA in an acidic condition in the presence of boron trifluoride diethyl etherate (BF_3OEt_2) as a catalyst (**Fig. 3.4 a**). The GMA-NY dye solution was diluted to 0.06 M aqueous solution before use. The colour change mechanism of azo pH indicator dye is based on azo-hydrazone tautomerism through proton donation as shown in **Fig. 3.4 b.**

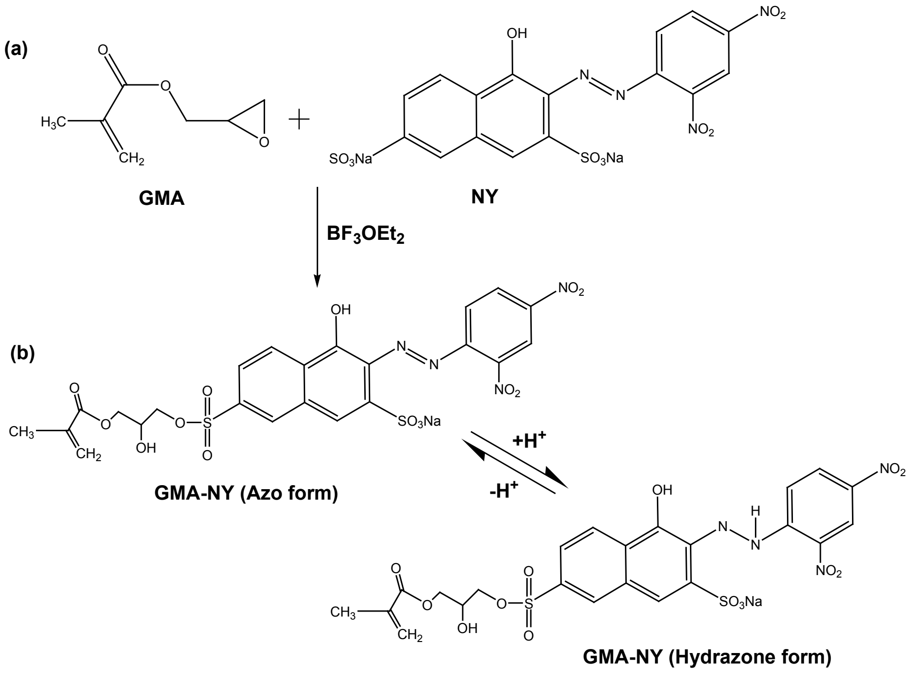


Fig. 3.4 Schematic representation of (a) synthetic reaction between GMA and NY in acidic condition (BF_3OEt_2) and (b) tautomeric azo - hydrazine forms GMA-NY dye

3.1.4 Other reagents and products

- Agar (select agar), Nutrient broth, Hexamethylene diisocyanate (HDI), Isopropanol, and dodecylamine were purchased from Sigma-Aldrich (Stockholm, Sweden). The Nutrient agar and nutrient broth used for the analysis of curcumin dyed samples were obtained from Sinopharm chemical reagent Co.Ltd., China and Shanghai Sincere Biotech Co.Ltd., China, respectively.
- 2, 2’-Azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS) used to assess the antioxidant activity was obtained from Shanghai D & B chemicals technology Co.Ltd., China. Potassium persulphate, disodium hydrogen phosphate, and potassium dihydrogen phosphate were of analytical reagent grade. Nutrient agar and nutrient broth were obtained from Sinopharm chemical reagent Co.Ltd., China and Shanghai Sincere Biotech Co.Ltd., China, respectively.
- The CO_2 used was purchased from AGA Industrial gases (Lidingo, Sweden) with 99.5 % purity.
- Benzophenone (≥99%) and ethanol (≥99.8%) and other chemicals were purchased from Sigma Aldrich, Italy and were used as received.

3.2 Equipment and dyeing procedure

3.2.1 Equipment

All the experiments presented in this thesis using $scCO_2$ were carried out using a high-pressure reactor (cylindrical shaped stainless steel vessel) shown in **Fig. 3.5.** The dyeing vessel has an internal volume of 290 mL and maximum pressure and temperature of 30 MPa and 130 °C, respectively. The vessel is equipped with a needle valve used to fill and remove CO_2 and a safety valve to vent CO_2 when the pressure exceeds the maximum limit to protect overpressure. It has also a tight closure with a Teflon seal.

Fig. 3.5 The high-pressure dyeing vessel and its parts used in this work

The laboratory dyeing machine used to heat the dyeing vessels under constant rotation is shown in **Fig. 3.6**. It is equipped with high-temperature oil (glycerine) bath, a rotary wheel where the vessels are mounted, a motor, a controller (time and temperature), a heater, and a cooling element.

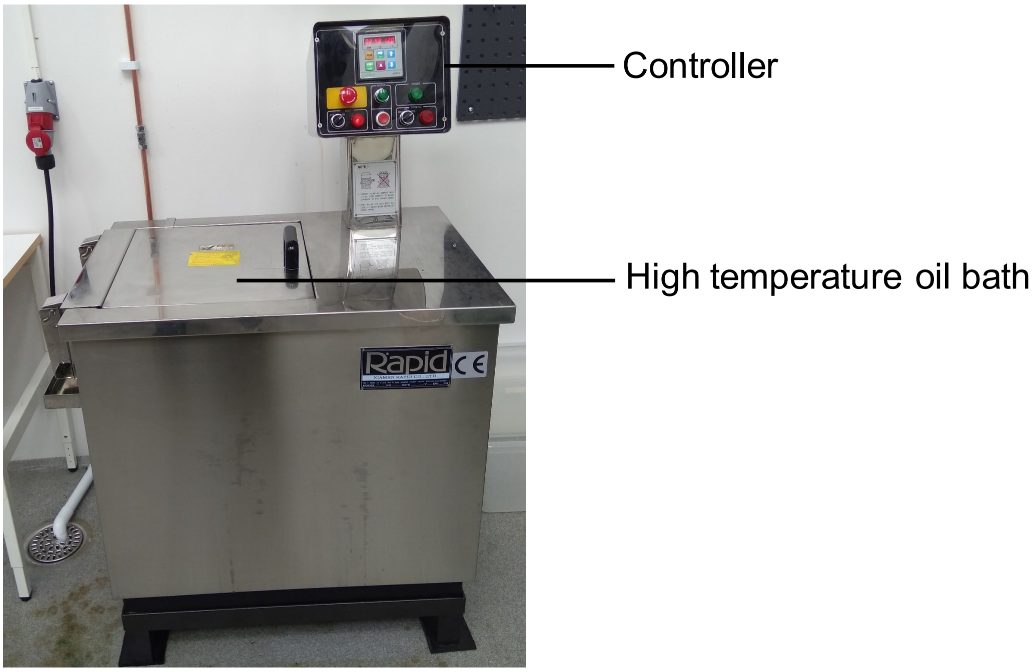


Fig. 3.6 Rapid colour CF/SF LA2002 laboratory dyeing machine used

3.2.2 Lab dyeing procedures

The lab dyeing procedure contains three main actions namely preparation of the substrate and impregnates (dye, functional finishing agent, and others), CO_2 filling, and dyeing/impregnation process as described below.

3.2.2.1 Preparation

The pictures showing the preparation steps before starting the dyeing/impregnation process is presented in **Fig. 3.7**. In this step first, the substrate (polyester fabric) was cut to A4 size and weighted using a precision balance (a) and the fabric is rolled up around the Teflon mesh or beam (b). Then, the required amount of dye is calculated based on the weight of the fabric (the weight of the fabric sample was around 10 g), measured and made ready (c). Next, the required number of steel balls decided based on the type of fabric (see **Table 3.2**) were introduced into the vessel (d). The steel balls are used to provide stirring action for a better flow of CO_2 during dyeing. Afterwards, the dye/functional agent is placed at the bottom of the vessel (e) and the rolled fabric is suspended inside the vessel (f). For the first experiment in which the disperse dye and chitosan biopolymers were used together, a small bag (pouch) made from bleached cotton fabric was used to keep the dye to avoid direct contact between chitosan and the dye before the dyeing process. Finally, the vessel is tightly closed using a torque wrench at 70 Nm, the weight was recorded, and ready to fill the CO_2 (h).

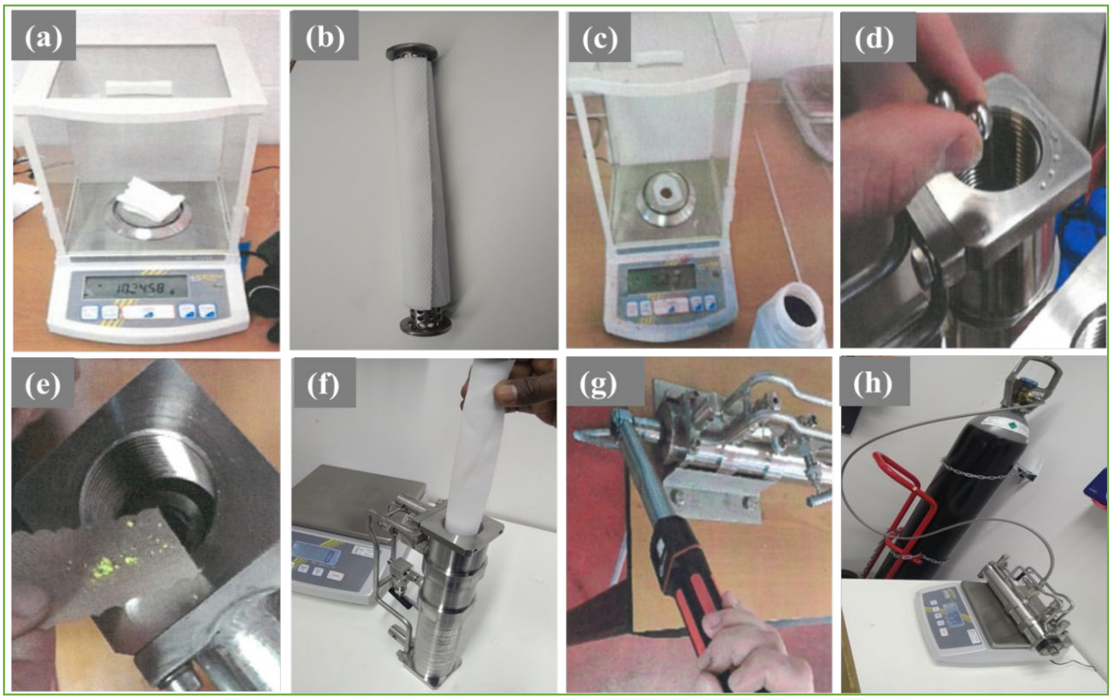


Fig. 3.7 Preparation of fabric sample, dye/impregnate and making the vessel ready for CO_2 filling before the dyeing experiment

3.2.2.2 Determination of the amount of CO_2

The exact amount of CO_2 for each temperature and pressure combinations was decided considering the density (known from working pressure and temperature of CO_2), the type of fabric, the number of steel balls, and whether beam or mesh is used. For this, a reference standard prepared by DyeCoo was used to determine the number of steel balls based on the fabric type and whether mesh or beam used as shown in **Table 3.2.** The density of CO_2 for each temperature and pressure combinations was taken from a standard table of NIST chemistry webbook [23]. The densities of CO_2 for some temperature and pressure combinations used in this study are presented in **Table 3.3** as an example. Using the density and the volume of the cylinder, the amount of CO_2 required for each experimental conditions was calculated using **Equation (3.1).**

$$\text{Mass of } CO_2 = \text{Density of } CO_2 * \text{Volume of cylinder} \qquad (3.1)$$

Note that, the volume of fabric and mesh (5 mL) and steel ball (1.25 mL each) was deducted from vessel's volume and this effective volume was used in the calculation. For example, for 8 steel balls, for a non-rigid and non-delicate fabric, and using mesh the effective volume of the cylinder is, 290 mL – (5 mL + 8×1.25 mL) = 275 mL. Therefore, 275 mL is the volume used to calculate the exact amount of CO_2 used for this specific condition.

Table 3.2 A reference standard used to decide the required amount of CO_2 based on the type of the fabric (weighing 5 to 10 g) and the number of steel balls used for dyeing at 25 MPa and 120 °C as an example.

Option	Fabric type	Mesh	Beam	No. of steel balls			Amount of CO_2 (g)
				0	2	8	
1	Rigid and delicate			X			147
2	Rigid and delicate				X		145
3	Rigid and not delicate					X	142
4	Not rigid but delicate	X		X			144
5	Not rigid but delicate	X			X		143
6	Not rigid and not delicate	X				X	139
7	Not rigid but delicate		X	X			131
8	Not rigid but delicate		X		X		130
9	Not rigid but delicate		X			X	126

Table 3.3 shows the amount of CO_2 used for each pressure and temperature combinations using the same type of fabric (non-rigid and non-delicate), 8 steel balls, and with mesh. For example, to run an experiment at 250 MPa and 120 °C using 5 to 10 g non-rigid and non-delicate fabric sample, using mesh, and 8 steel balls (marked red in the table), 139 g of CO_2 (i. e. 505.6 *0.275 = 139 g) is required. The value of 505.6 in Kg m^{-3} is the density of CO_2 at 250 MPa and 120 °C.

Table 3.3 Amount of CO_2 required for different pressure and temperature combinations for polyester fabric (non-rigid and non-delicate) having a weight range of 5 to 10 g.

Temperature (°C)	Pressure (MPa)	Density (Kg m^{-3})	Amount of CO_2 (g)
80	15	427.2	118
100	15	332.4	91
120	15	280.4	77
80	20	593.9	163
100	20	480.5	132
120	20	401.2	110
80	25	686.2	189
100	25	588.5	162
120	25	505.6	139

3.2.2.3 CO_2 filling procedure

After the cylinder is ready, the next step is filling the required amount of CO_2 to the vessel. The high-pressure equipment used in this work is not equipped with pumping and automatic compression system, thus CO_2 was filled manually according to the following procedure. Before filling with CO_2, the vessels were pre-cooled in a separate freezer to approximately 0 °C to get enough amount of CO_2 in the cylinder. Because at room temperature (e.g. 20 °C), the density of CO_2 is around 140.65 Kg m^{-3} considering a pressure of 50 bar during filling (see **Fig. 3.8**). Thus, the theoretical maximum amount of CO_2 that can be compressed at this temperature is 140.65 * 0.29 = 40.8 g, which is not enough. By cooling the vessel, enough amount of CO_2 can be attained because at 0 °C, the density of CO_2 is 940.52 Kg m^{-3} (see **Fig. 3.8**) considering the same pressure of 50 bars during filling. Thus, at 0 °C, the maximum theoretical amount of CO_2 will be 940.52 * 0.29 = 272.7 g, which is enough to work within the critical density region of CO_2. After cooling the vessels, the mass of the cylinder without CO_2 is recorded (weight of the vessel, fabric, dye/impregnate, and steel balls), the vessel was kept on the scale, connected to the CO_2 bottle, tarred, and the required amount of CO_2 was precisely filled. The exact amount of CO_2 determined based on the working pressure and temperature as presented in the previous section was used for each experiment. After filling, the vessels are mounted on the shaft rotating inside the pre-heated oil bath and the dyeing/impregnation steps continue.

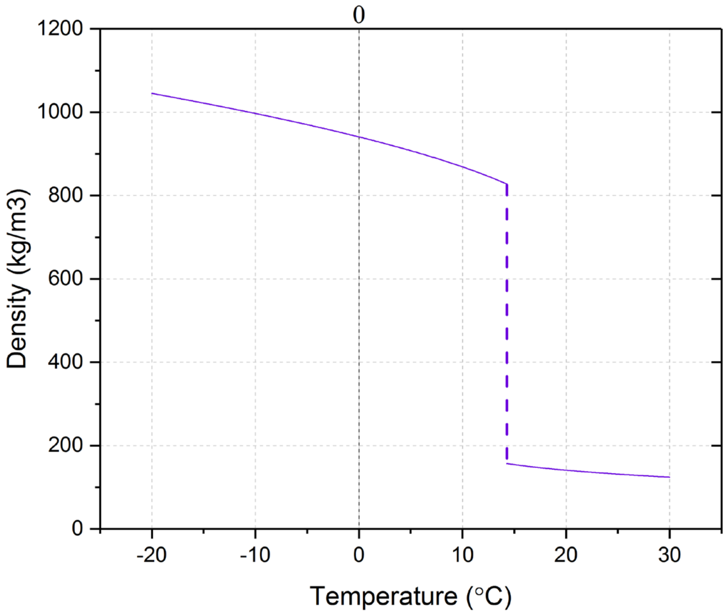


Fig. 3.8 Density profile of CO_2 at 50 bars (pressure at room temperature) as a function of temperature [23].

3.2.2.4 Dyeing steps and process

After mounting the vessels into the high-temperature oil bath, a dyeing program was set based on the temperature and time of the process. The pressure and temperature profile during dyeing are shown in **Fig. 3.9**. The figure shows the dyeing steps for running an experiment at 120 °C, 25 MPa for 60 min of dyeing time as an example. In all the experiments, the oil bath is pre-heated at least to about 60 °C before the introduction of the vessels. After the vessels are introduced into the oil bath, the temperature rose at a rate of 3 °C per minute until the required dyeing temperature reaches. Initially, when the vessels are introduced into the oil bath, the temperature of the bath is around 60 °C and the pressure is around 50 bars. During the pressurization step [P], the temperature rose to 120 °C causing the pressure to increase to

250 bars. Once the required temperature is reached, the dyeing and levelling step [D/L] continues for the desired time (60 min in this case). After the desired dyeing time is reached, depressurization step [DP] continues by reducing the temperature until about 60 °C at a rate of 2-3 °C per minute and dyeing is completed.

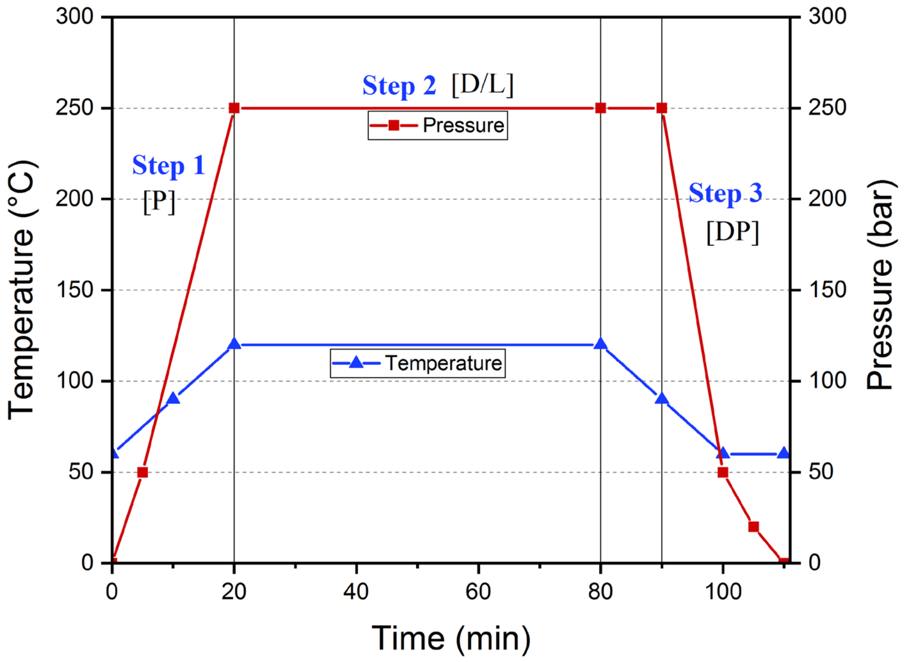


Fig. 3.9 Dyeing step showing the temperature and pressure profile of the dyeing vessel. [P] Pressurization, [D/L] – Dyeing and Levelling, and [DP] – Depressurization.

As illustrated in the schematic of **Fig. 3.10**, the overall lab dyeing procedure is briefly described as follows. The dyeing vessel (3) was pre-cooled in a separate freezer (2) and subsequently filled with the required amount of CO_2 determined as presented in the previous section. Then, the vessels were mounted on the shaft rotating inside the pre-heated oil bath (4) and the temperature rose at a rate of 3 °C per minute to the working temperature. In this thesis, the dyeing and impregnation experiments were carried out in the temperature range of 80 to 120 °C, a pressure range of 15 to 25 MPa, dyeing time of 30 to 90 min, and different concentrations. After a definite dyeing time, the temperature was reduced slowly to about 60 °C at a rate of 3 to 2 °C min^{-1}. After depressurization step, the vessels are taken out and weighted again to check if the CO_2 was escaped or not during the dyeing process. Those experiments which showed leakage of CO_2 were discarded. Then, the CO_2 is vented slowly by gently opening the needle valves until the pressure reaches atmospheric pressure. Finally, the samples were retrieved from the vessels and ready for characterizations without reduction cleaning. During the initial screening, few samples were also rinsed in acetone to check the level of unfixed dyes which was negligible and was not used afterwards.

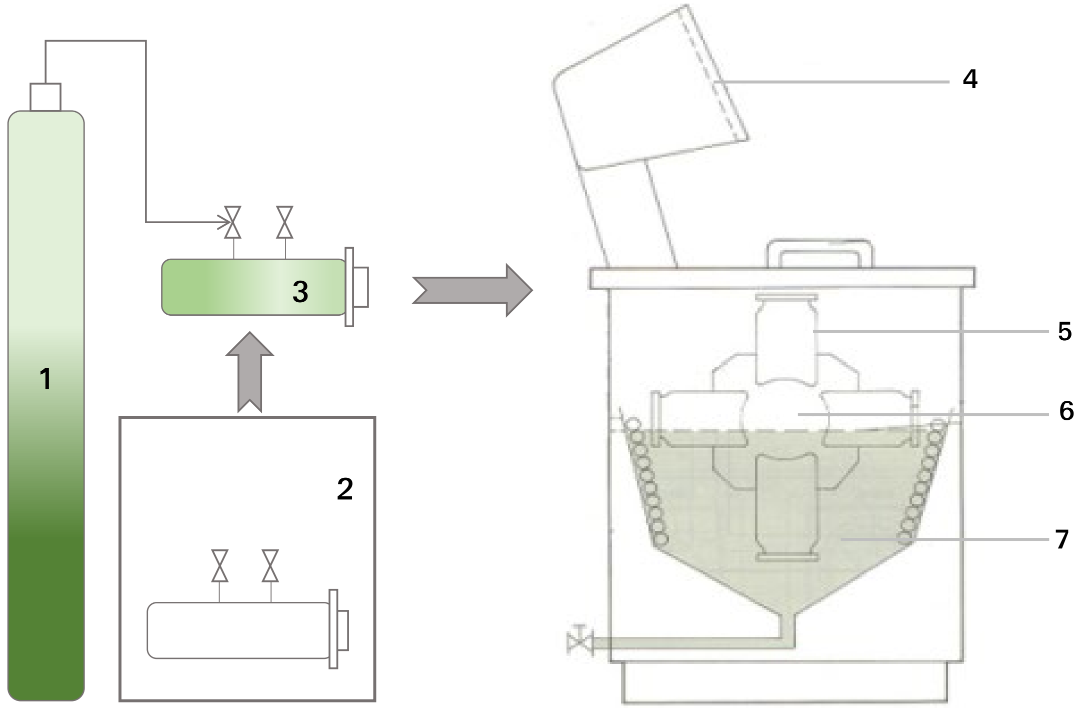


Fig. 3.10 Schematic of $scCO_2$ lab dyeing procedure (1) CO_2 tank, (2) Freezer, (3) Dyeing vessel, (4) Control board, (5) Dyeing vessel mounted on the shaft, (6) Shaft, (7) High-temperature oil bath

3.2.3 Photo-grafting process

For the photo grafting experiment, the cotton fabric substrate was cut into 8 cm x 8 cm and immersed into a dye solution containing 2 wt. % (weight percentage or on the weight of the fabric – owf) benzophenone photoinitiator and 0.06 M diluted solution of GMA-NY for a given time (10-60 s). After immersion, the excess liquid was removed by a soft tissue paper and subjected to UV irradiation using Dymax ECE 5000 flood metal halide lamp (**Fig. 3.11**). The intensity of the UV lamp used was 110 mW/cm^2 for 2 min each side. The photo grafting process was carried out under inert atmosphere using constant nitrogen flow. After UV grafting, samples were then rinsed in distilled water for 2 h and rinsed again for 24 h after changing the water bath to remove the unreacted species and GMA-NY homopolymer. Finally, the rinsed samples were dried in an oven for 30 min at 70 °C and ready for characterization.

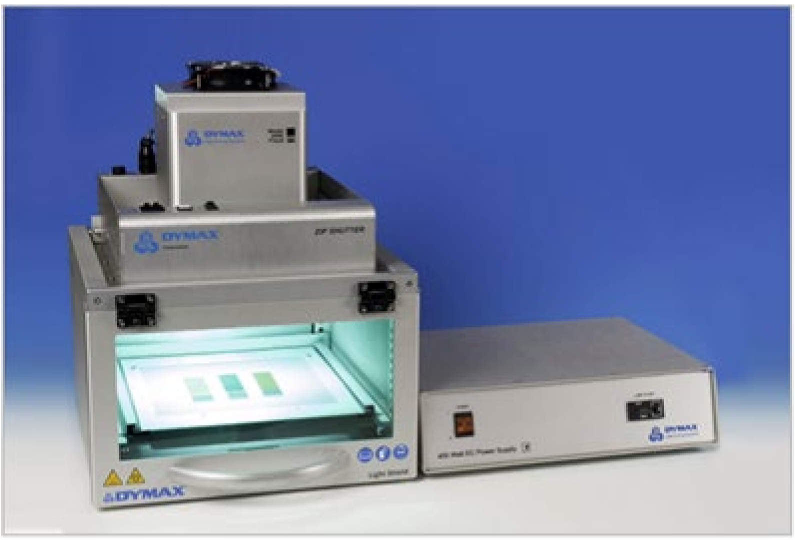


Fig. 3.11 Dymax ECE 5000 flood UV lamp setup

3.3 Characterizations

The characterization techniques and test protocols used in the study are presented in this section categorized as surface properties, colour properties including UV-vis, and functional properties.

3.3.1 Surface properties

3.3.1.1 FTIR-ATR measurement

FTIR-ATR measurements were performed to determine the chemical modification of polyester after dyeing and impregnation with chitosan and derivatives. For this, the infrared spectra of samples were acquired using the Nexus 510 spectrometer (Thermo Nicolat). The spectrometer has 0.32 cm/s mirror velocity, 35 mm aperture, and an ATR accessory (Specac Ltd.) equipped with ZnSe crystal with 45° angle of incidence. The spectra of the samples were collected in the attenuated total reflectance mode (ATR) in ambient condition. The collect specifications were from 4000-400 cm^{-1} wavenumber range, 50 scans at 4.0 cm^{-1} resolution. For photo grafted cotton fabric samples, FTIR-ATR spectroscopy analysis was performed using Nicolat ^{TM} iS50 FTIR spectrometer (Thermo Scientific) equipped with a diamond crystal. The spectrum was collected using a resolution of 4 cm^{-1} and 32 scans.

3.3.1.2 Zeta (ζ) potential

The streaming potential method has been used to determine the ζ potential of samples using surPASS electrokinetic analyser (Anton Paar GmbH, Austria). The instrument is equipped with VisioLab data analysis software and has been used to analyse the result. The fabric sample (10×20 mm) in a rectangular shape was attached to both sides of the adjustable gap cell and the two samples are kept face to face within a 0.1 mm gap. A 0.001 M KCl was used as an electrolyte solution and 0.1 M HCl solution was used to adjust the pH to about 3–3.5 immediately before running the test. Then, the instrument automatically adjusts the pH from about 3 to 10 with an automatic titration system achieved through the addition of 0.01M NaOH from a bottle connected to the instrument in the course of the measurement. All measurements were performed at room temperature.

3.3.1.3 Water contact angle (θ_{H2O})

Water Contact Angle (θ) measurement was performed to assess the wettability of the samples. The instrument used was the Theta optical tensiometer instrument (Biolin Scientific, Sweden) equipped with OneAttension analysis software. During measurement, the sample was kept on top of a sample holder and a drop of distilled water (3 µL) is dispensed from above. After the droplet is placed, continuous measurement of the contact angle of a drop was recorded for 10 s and the mean values were recorded. The sessile drop and Young Laplace analysis mode were used during the analysis. For each sample, three independent measurements were performed at different places and the average values are reported. This measurement was conducted for combined dyed and chitosan impregnated samples.

3.3.1.4 Scanning Electron Microscopy (SEM)

SEM measurements were conducted to observe the changes in surface morphology of the samples after $scCO_2$ processing and chitosan impregnation. Scanning electron microscope (Cambridge S240, UK) was used at 16 mm working distance and 15 kV acceleration voltages. Before the analysis, samples were sputter-coated with gold in rarefied Argon atmosphere at 0.1 – 0.2 mbar using Emitech K 550 sputter coater with a deposition current of 20 mA for 180 s. Then, samples were mounted to scanning electron microscope and images were recorded at different magnifications.

3.3.2 Colour properties

3.3.2.1 Colour strength

To determine the colour strength (*K/S*), the reflectance values of dyed samples were first measured using Datacolour CHEK Pro TM spectrophotometer (USA). The samples were folded twice (four layers) and reflectance measurements were carried out in the wavelength range of 400 to 700 nm under the condition of D65 illuminant and 10° standard observer. Then, the *K/S* values are calculated from the measured reflectance values using the Kubelka – Munk function (**Equation (3.2)**). Three readings were recorded at different sites of the same sample and the average *K/S* values at the maximum absorption (or minimum reflectance) were reported.

$$\frac{K}{S}=\frac{(1-R)^2}{2R} \tag{3.2}$$

where: ***K*** and ***S*** are spectral absorptions and scattering coefficients, respectively; ***R*** is the minimum spectral reflectance ratio.

The total colour difference (*ΔE*) indicates the colour difference between the dyed and non-dyed polyester fabric as can be calculated according to **Equation (3.3).** This colour difference was used to evaluate the background colour of photochromic dyed fabric samples. The colour difference was also used to evaluate the colour change of UV grafted samples when introduced into different pH conditions. For UV-grafted cotton fabric, the value of *Δb* was also monitored due to the characteristic colour change of the pH indicator dye (GMA-NY), mainly takes place in the blue-yellow colour region. The photo-grafted cotton fabric before exposure to different pH conditions was used as a control sample to calculate the *ΔE* and *Δb* values.

$$\Delta E = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \tag{3.3}$$

where: *L, a,* and *b* are colour space coordinates. *ΔL** is the lightness difference, *Δa** is the red/green difference, and *Δb** is the yellow blue difference between the standard and sample colours.

3.3.2.2 Colour levelness

To evaluate the colour uniformity, an objective method using levelness parameters (*L*) and visual observation were used. The *L* value is derived from the standard deviation of the *K/S* values at different places of the fabric with consideration of the photopic spectral luminous efficiency function. The luminous efficiency function, *V(λ),* is a dimensionless function established to describe the change of relative spectral sensitivity with wavelength by adjusting the maximum luminous efficiency to 1.0 as illustrated in **Fig. 3.12**. The larger the L value, the better the colour uniformity [151].

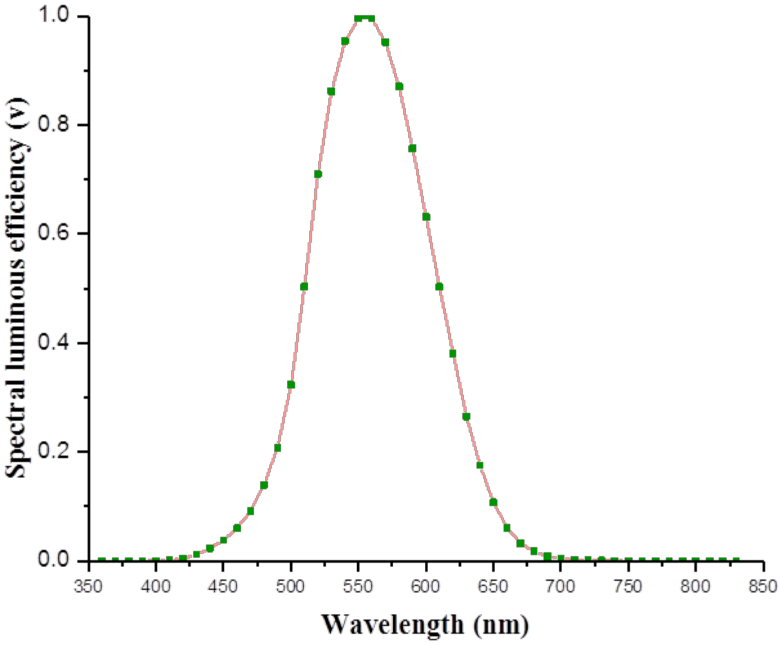


Fig. 3.12 The relative luminous efficiency of the photopic vision

Levelness parameters

The differences between *K/S* values obtained from different areas of a dyed fabric sample is generally used to evaluate the colour levelness. These differences can be obtained using the standard deviation *S(λ)* of a *K/S* value at a certain wavelength (*λ*) according to **Equation (3.4).**

$$S(\lambda) = \sqrt{\frac{\sum_{i=1}^{n}\left[(K/S)_{i,\lambda} - \left(\overline{K/S}\right)_{\lambda}\right]^2}{n-1}} \tag{3.4}$$

where *λ* is the wavelength of the measurement; ***i*** refers to the different sites measured on an individual fabric; ***n*** is the total number of spots measured (n = 16 used in this work); $(K/S)_{i,\lambda}$ is *K/S* value of ith measurement at a specific wavelength, λ; and $\left(\overline{K/S}\right)_{\lambda}$ is the arithmetic mean of the K/S values of the sixteen measurements of the individual sample as defined in **Equation (3.5)**.

$$\left(\overline{K/S}\right)_{\lambda} = \frac{1}{n} \times \sum_{i=1}^{n} (K/S)_{i,\lambda} \tag{3.5}$$

The mean *K/S* value at the maximum absorption wavelength (λ_{max}) is considered as the colour strength of the individual sample.

However, the magnitude of the standard deviation is not only a function of the difference of *K/S* values from different places of the fabric but also a function of the average *K/S* value of that fabric. This means, with the same percentage difference between $(K/S)_{i,\lambda}$ and $\left(\overline{K/S}\right)\lambda$, the absolute difference is bigger with larger average colour strength. Therefore, a relative value of sample standard deviation, $S_r(\lambda)$ is necessary (**Equation (3.6)**) to compare the evenness of two pieces of fabrics having different average colour strengths. This minimizes the influence of $\left(\overline{K/S}\right)$ λ on the standard deviation [152].

$$S_r(\lambda) = \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(K/S)_{i,\lambda}}{\left(\overline{K/S}\right)_{\lambda}} - 1\right]^2}{n-1}} \tag{3.6}$$

To relate with the visual observation, $S_r(\lambda)$ should be adjusted by the spectral luminous efficiency function, $V(\lambda)$, since the human sensitivity to different wavelength is different compared with the instrumental measurement [151]. The un-levelness parameter $u(\lambda)$ can be calculated using this function, according to **Equation (3.7)**.

$$u(\lambda) = S_r(\lambda)V(\lambda) \tag{3.7}$$

Besides, as *K/S* value is a function of wavelength, at a different wavelength, the *K/S* value and the change of the *K/S* value with the colour strength are not consistent. Hence the overall $S(\lambda)$

in the whole spectrum is considered using **Equation** (3.8). Intervals of 10 nm are used in the summation. The larger the *U* value, the inferior the levelness of the dyed fabrics.

$$U = \sum_{\lambda=400}^{700} S_r(\lambda)V(\lambda) \tag{3.8}$$

Although the *U* value can be used directly to evaluate the colour levelness (*L*) of dyed fabrics with different colour and *K/S* values, its magnitude is not equally sensitive to the materials with high colour levelness as it is to that with low colour levelness. For this a levelness parameter, *L* which can give better proportional agreement with the actual levelness increments was suggested by [152] and calculated according to **Equation** (3.9)**.**

$$L = 1.20\left[2.00 - \ln \sum_{n=400}^{700} S_r(\lambda)V(\lambda)\right] \tag{3.9}$$

where: 1.20 and 2.00 are empirical constants used to adjust the value to be between 1 and 5. According to these values, the larger the *L* value, the better the levelness of the colouration

3.3.2.3 Dynamic colour measurement

The colouration and fading properties of $scCO_2$ dyed photochromic polyester samples were measured using an LCAM Photochrom 2 spectrophotometer (Technical University of Liberec, Czech Republic). This specially designed photochrom can measure the colour build-up and fading behaviour of photochromic textile samples continuously over several cycles of UV-irradiation and relaxation. The LCAM Photochrom 2 is equipped with LED Engine LZ1-00UV00 LED as an activation light source with 1680 mW radiometric power and 365 nm emission peak of wavelengths. It has a dual system measuring light source with combined high-power white LEDs with CCTs of 4000, 5000, and 7000 K. During measurement, samples are illuminated with 60 klx, an illuminance between brightest sunlight intensity (120 klx) and daylight intensity without direct sunlight at noon (20 klx). Besides, the temperature of the samples was regulated to around 21 °C and reflectance values were recorded in 2 seconds intervals during continuous UV irradiation and shutdown.

The obtained reflectance values were converted to *K/S* values using the Kubelka-Mulk function and the *K/S-time* datasets were fitted to an extension of the first-order kinetic model,

Equation (3.10). This model has been commonly used to describe the behaviour of photochromic dyes incorporated into the textile matrix during colouration and fading [153].

$$\Delta\frac{K}{S} = \left(\frac{K}{S_0} - \frac{K}{S_\infty}\right)e^{-kt} + \frac{K}{S_\infty} \tag{3.10}$$

where: ***K/S₀*** and ***K/S∞*** are the initial and final (saturated) colour intensity values respectively attained upon exposure or relaxation of UV light, ***k*** is the rate constant, and ***t*** is the time of exposure. The subscripts define the time relationships: (0) is the time on the beginning and (∞) indicates the time in infinity (saturation).

The half-life of colour change ($t_{1/2}$) is a measure of the rate of photochromic colour change and is calculated using **Equation (3.11)** [154]. The half-life of colouration ($t_{1/2\text{colouration}}$) is the time required for absorption to reach half of its maximum level upon UV irradiation and similarly, the half-life of fading ($t_{1/2\text{decolouration}}$) is the time taken to reach one-half of the initial absorbance (K/S_∞) when the UV light is removed [155].

$$t_{1/2} = \frac{\ln 2}{k}[s] \tag{3.11}$$

Accordingly, the colourability and fading behaviour of $scCO_2$ dyed photochromic polyester fabrics were assessed in terms of the colour yield (ΔK/S) during activation with UV-light, rate constants of colour development ($k_{\text{colouration}}$) to achieve maximum colouration (K/S_∞), and rate constant of colour fading ($k_{\text{decolouration}}$) to revert to the ring-closed colourless state (K/S_0), and half-lives ($t_{1/2}$) of colouration and decolouration.

3.3.2.4 Colour fastness tests

The colour fastness to laundering was evaluated according to the ISO standards like the previous experiment. For curcumin dyeing experiment, washing was performed according to the test number B1S (ISO 105-C06) at 50 °C, 50 RPM for 30 minutes using Gyrowash washing and dry-cleaning colour fastness tester (James H. Heal Co. Ltd, Halifax England). For combined chitosan/disperse dyeing experiments, the fastness to washing was tested according to ISO 6330:2012 domestic washing and drying procedure. The samples were washed at 40±3 ◦C, using 20 ±1 g reference detergent for 30 min using a domestic laundry machine. 100 % polyester ballast fabric was added to achieve the specified weight of the reference washing machine and washing was carried out once (1W). The grayscales complying with ISO 105-A02 and ISO 105-A03 were used to rate the colour change and staining of each type of fibre in the multi-fibre adjacent fabric.

The colour fastness to rubbing was performed according to ISO 105-X12:2016 test standard using crock meter (Roaches crock meter). Samples were rubbed with a dry and wet rubbing cloth (bleached white cotton fabric) sliding back and forth on the test fabric 20 times. The staining on the white cotton rubbing cloth was assessed according to ISO 105-A03 grey scale rating. The lightfastness test was carried out with Xenotest alpha light fastness tester (Atlas Co, UK) according to ISO 105- B02: 2014 test procedure. Fabric samples were exposed xenon arc lamp for 20 h in a standard testing condition. The blue wool scale was used to grade the lightfastness. This test was performed for the samples dyed with high purity curcumin.

For photochromic dyed samples, the fastness to washing was tested according to ISO 6330:2012 domestic washing and drying procedure presented above but here washing was carried out once (1W) and ten (10W) times. To assess the fastness to washing, a comparative study on the photochromic properties of samples was made before and after washing. The reduction of colour yield (*K/S*) after laundry can be used to express the durability of the photochromic effect. The durability was evaluated according to relative terms using **Equation (3.12)**. The fastness percentage is the magnitude of the residual photochromic performance after washing.

$$\text{Fastness (\%)} = \frac{K/S_{(2)}}{K/S_{(1)}} \times 100 \qquad (3.12)$$

where: $K/S_{(1)}$ and $K/S_{(2)}$ are the colour yield upon UV exposure of the photochromic fabric before and after the standard repeat washing, respectively.

For photochromic dyed samples, their durability against abrasion was also investigated. The abrasion resistance of samples was tested using Martindale 2000 abrasion tester (Cromocol Scandinavia AB). Before testing, samples were conditioned for 24 h at 65 ± 2% relative humidity and 20 ± 2°C temperature and then rubbed for 20000 cycles with a load of 12 kPa using a Wool abradant cloth. Then, the photochromic performance of samples before and after abrasion was compared.

3.3.2.5 UV-Vis spectroscopy

To measure the halochromic property of the GMA-NY dye solution in alkaline and acidic conditions, UV-Vis spectroscopy analysis was used. For this, absorbance spectra were collected using a 6850 Janeway UV-Vis spectrophotometer in the range of 300-800 nm and resolution of 0.5 nm using cuvettes having 1 cm path length.

3.3.3 Functional properties

3.3.3.1 Antibacterial activity of chitosan powder

The antimicrobial activity of six chitosan powder samples was evaluated using ISO 20645:2004 E agar diffusion plate standard test method. Gram-negative bacteria *E. coli ATCC 25922* was used as per the test standard. Agar plates were prepared by mixing 12.5 g nutrient broth and 7.5 g select agar in 500 mL distilled water based on the manufacturer's direction. This media was sterilized and carefully poured into the sterile circular plates and allowed to solidify. A previously grown bacteria solution with a concentration of 1.54×10^9 colony forming units (CFU/mL) was diluted 100 times and 100 µL of this bacteria solution was uniformly spread on each agar plate. Five millimetres diameter sterile filter paper discs were impregnated with chitosan/derivative solutions of two different concentrations (0.5% and 1% dissolved in 1 % (w/v) acetic acid) and carefully placed on top of the inoculated agar plates. Then, the plates were incubated for 24 h at 30 ˚C and the antimicrobial activity was determined through measuring the zone of inhibition around the discs. The width of the inhibition zone is calculated according to **Equation (3.13)**.

$$H = \frac{D - d}{2} \tag{3.13}$$

where: **H** is inhibition zone in mm, **D** is the total diameter of the disc and inhibition zone in mm, **d** is the diameter of the disc in mm.

3.3.3.2 Antimicrobial activity of fabric samples

To evaluate the antimicrobial activity of developed samples, ASTM E2149-10 standard test method was used. This test method is a quantitative standard antimicrobial test procedure for textiles under dynamic contact condition. A representative test strain, gram-negative bacteria *E. coli* ATCC 25922 was used according to the requirement of the test standard. A liquid working bacteria solution ($1.5\text{-}3.0\times10^5$ CFU/mL) was prepared using a 50 mL sterile nutrient broth solution in 250 mL Erlenmeyer flask. Fabric sample (*ca.* 1 g) was cut into small pieces and transferred to the Erlenmeyer flask containing 50 mL working bacteria solution. Then, the flasks containing the control and test samples were shaken for 1 h at 30 ˚C using a wrist action incubator shaker. After 1 h, the bacteria solution was diluted 1000 times and 100 µL of the diluted bacteria solution was inoculated onto agar plates and incubated at 35 °C for 24 h and viable cells were counted. The average values of duplicate bacteria counts were converted to CFU/mL and the antimicrobial efficiency was estimated by calculating the percentage of bacteria reduction according to **Equation (3.14).**

$$\text{Reduction } \% \text{ (CFU/mL)} = \frac{\text{B} - \text{A}}{\text{B}} \times 100 \qquad (3.14)$$

where: **A** and **B** are the surviving cells (CFU/mL) for the flask containing the treated samples (chitosan treated and dyed) and the control (untreated fabric), respectively, after 1-hour contact time under shaking.

3.3.3.3 UV protection property

The UV protection of developed bioactive polyester fabric samples was assessed in terms of ultraviolet protection factor (UPF) and UV transmittance in the UV region (UV-A and UV-B) relative to un-dyed polyester fabric. The UPF and the level of UV transmittance through the fabric samples were measured using Labsphere UV-1000F ultraviolet transmittance analyser (Labsphere Inc., USA) at the critical wavelength (390 nm). For each sample, four measurements were read at different positions and mean values were used. The ratings of UV protection properties were according to Australia/New Zealand Standard AS/NZS4399:2017 [156]

3.3.3.4 Antioxidant property

Antioxidant properties of fabric samples were determined in terms of % inhibition of peroxidation by ABTS radical scavenging activity. The spectrophotometric measurement used to analyse the ABTS radical scavenging activity according to the method reported in [157]. ABTS radical cation ($\text{ABTS}^{\cdot+}$) was prepared by mixing a previously prepared ABTS stock solution (7 mmol) with 2.45 mmol potassium persulfate solution and stored in a dark room for 12 to16 h at room temperature. The absorbance of $\text{ABTS}^{\cdot+}$ was adjusted to 0.700±0.025 at 734 nm by diluting it with phosphate buffer solution (0.1 M, pH 7.4) before use. Then,10 mg of the sample was added to 10 mL of $ABTS^{\cdot +}$ solution and allowed for 30 min. Finally, the scavenging capability of $ABTS^{\cdot +}$ at 734 nm was calculated according to **Equation (3.15).**

$$\text{Antioxidant activity (\%)} = \frac{A_c - A_s}{A_c} \times 100 \qquad (3.15)$$

where: A_c is the initial absorbance of $ABTS^{\cdot +}$ and A_s is the absorbance of the remaining $ABTS^{\cdot +}$ in the presence of the fabric sample.

3.3.3.5 Halochromic property

The change in colour of photo grafted cotton fabrics when introduced to acidic and basic environments was assessed through data colour measurements. Datacolor Check II plus spectrophotometer in reflectance mode under the condition of D65 illuminant and 10 ° standard observer was used. The colour change of the samples was evaluated after introduced into acidic (≈3.5) and alkaline (≈8.5) media (both in wet and vapour environments). For the wet condition, fabric samples were introduced into aqueous pH media for 2 min and the colour change was measured immediately in wet condition. In the case of vapour condition, the colour change was measured after the samples were kept in a closed chamber to acidic and alkaline vapour for 24 h. For each sample, at least three measurements were repeated and average values were reported. The pristine untreated cotton fabric was used as a reference sample and the photo-grafted cotton fabric without exposure to different pH conditions was instead used as a control sample. The reflectance values acquired by the spectrophotometric measurement were then used to calculate the colour strength in terms of *K/S* values using the Kubelka – Munk function (**Equation (3.2)**)

3.4 Functionalization approaches used in this work

3.4.1 Choice of functional finishing agents

Due to their toxicity and environmental issues related to most of the synthetic functional finishing agents, there has been an increasing motivation towards the used of agents based on non-toxic and environmentally friendly materials. Recently, more attention has been given to sustainable and eco-friendly antimicrobial agents based on natural products such as chitosan and its derivatives, curcumin, and other natural based materials. Many different bioactive natural products have also been explored for various functional textile applications. Due to this, this thesis gave due attention to natural agents suitable for $scCO_2$ processing. The dyes and functional finishing agents used in this study were selected based on broad screenings according to literature data and using some screening experiments by taking their suitability for $scCO_2$ condition into consideration. Accordingly, three kinds of functional finishing agents namely chitosan (very low molecular weight chitosan and chitosan lactate), curcumin natural dye, and photochromic dyes were chosen and investigated in detail in this work.

3.4.2 Dyeing and impregnation conditions

Before the main experiment, preliminary experiments were carried out to demine the optimum dyeing and impregnation conditions. Based on this, the condition of 120 °C, 25 MPs for 1 h was determined as an optimum condition and used for the dyeing/impregnation experiments in this work. For the simultaneous dyeing antimicrobial functionalization experiment, a fixed amount of dye (0.4 wt. %), chitosan (3 wt. %), a crosslinking agent (5 wt. %) was used for comparison purposes. For the colouration and bio-activation experiment of polyester fabric using curcumin natural dye, an orthogonal array design presented in **Table 3.4** was used to study the effects of the dyeing variables on the colour properties.

Table 3.4 Dyeing conditions used for the dyeing of polyester fabric using curcumin

Sample code	Dyeing conditions			
	Pressure (MPa)	Temperature (°C)	Time (min)	Concentration (wt.%)
S1	15	120	60	0.1
S2	20	120	60	0.1
S3	25	120	60	0.1
S4	25	80	60	0.1
S5	25	100	60	0.1
S6	25	120	30	0.1
S7	25	120	90	0.1
S8	25	120	60	0.5
S9	25	120	60	1

To study the functional properties of curcumin-treated samples, higher purity curcumin was used and four different concentrations (0.25, 0.5, 0.75, and 1 wt. %) were selected to study the effect of dye concentration on the functional property. For the photochromic dyeing experiment, a small amount of photochromic dye powder (0.027 wt. % ≈ 2.56 mg) was used. In both cases, the same dyeing condition (120 °C, 25 MP, for 1 h) was used.

3.4.3 Impregnation strategies

In this thesis, two approaches were followed to functionalize polyester fabric using $scCO_2$ dyeing and impregnation route. In the first approach, a combined process was followed in which the dye and functional agent (i.e. disperse dye and selected chitosan biopolymers) were used in a single bath to dye and functionalize polyester in a single step. In the second approach, selected dyestuffs which can offer additional functionalities to the textile were chosen and directly applied to polyester fabric in $scCO_2$ bath. In the latter case, the curcumin dye powder and photochromic colourants were directly applied into the $scCO_2$ dyeing vessel along with the polyester fabric without fabric modification and any auxiliary agent as schematized in **Fig. 3.13**,

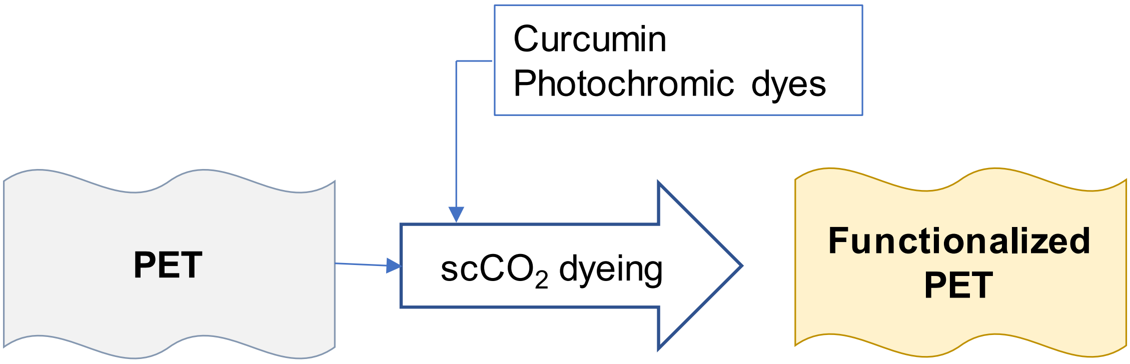


Fig. 3.13 Schematic of the impregnation of PET with curcumin and photochromic dyes in $scCO_2$ dyeing medium

In the first approach that used disperse dye and chitosan biopolymers in a single step, two strategies were followed. In the first one, a washed pristine polyester fabric was used without modification and in the second strategy; the polyester fabric was modified before $scCO_2$ treatment and a crosslinking agent was applied to link chitosan molecules with the amine groups of modified polyester. Surface modification of polyester fabric surface was carried out according to the procedure previously used by Knittel *et al.* [158]. Briefly, the polyester fabric was treated with alkylamine (5 g/l dodecylamine) in isopropanol: water (1:1) using the conventional disperse dyeing technique to acquire amino functional groups on the fabric surface to enhance the adhesion between the fabric and chitosan/derivative through chemical bonding. We have strictly followed the same procedure and conditions to modify polyester fabric surface as there was a material limitation for quantification of the surface amino groups. The finishing strategy for modification followed by dyeing in $scCO_2$ is illustrated in **Fig. 3.14.** Subsequently, the modified polyester fabric was treated with a formulation containing disperse dye, chitosan biopolymer, a crosslinking agent (5 wt. % HDI) in $scCO_2$ based on the dyeing procedure and conditions presented in the method section.

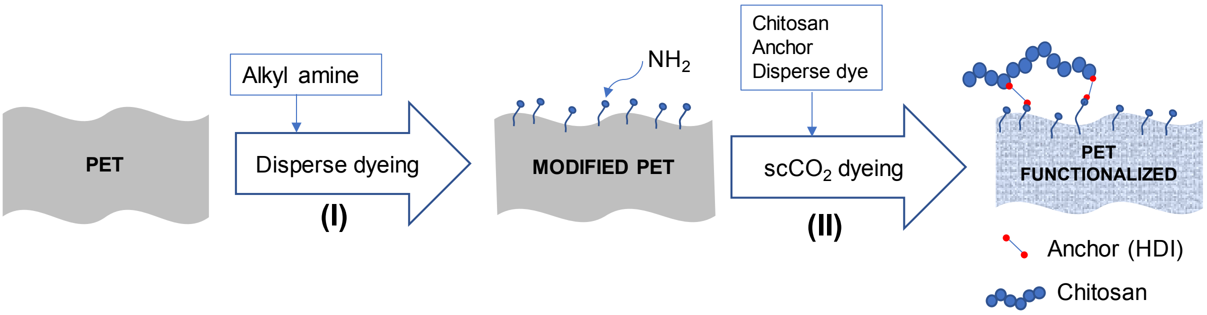


Fig. 3.14 Finishing strategy of polyester fabric via fibre surface modification (I) followed by chemical bonding with chitosan biopolymer in $scCO_2$ dyeing medium (II)

3.4.3.1 Impregnation yield

For the single step dyeing antimicrobial functionalization experiment, the weight gain of each sample after the impregnation procedure was determined gravimetrically to estimate the actual amount of dye and chitosan impregnated to the fabric expressed as a percentage of weight gain according to **Equation (3.16)**

$$\text{Weight gain (\%)} = \frac{W_f - W_i}{W_i} \times 100 \qquad (3.16)$$

where: W_i is the weight of the fabric before dyeing and W_f is the weight of the fabric after dyeing.

Alongside, a blank treatment was carried out considering the possible extraction of oligomers and contaminants from polyester during $scCO_2$ treatment. Then, the weight gain percentage of the blank polyester (calculated in the same way) was deducted from the weight gain of chitosan impregnated sample to estimate accurate chitosan amount impregnated into the polyester. Similarly, for samples developed using a crosslinking agent, the weight of crosslinking agent initially added was deducted from the final weight of the substrate after impregnation and before calculating the impregnation yield to accurately estimate the amount of chitosan impregnation. Here we assumed that the crosslinking agent added is fully participated in the reaction to avoid overestimation of the impregnated amount. Hence, the actual weight gain could be higher than what is reported here. On the other hand, since the amount of dye used was negligible (less than one order of magnitude), the weight of the dye used was not considered during weight gain calculation. Finally, the chitosan types which exhibited higher weight gain were chosen and used in this study.

3.5 Sample notations

The notations of samples used in chapter 4 and 6 are presented in **Table 3.5.**

Table 3.5 Samples notation

Sample	Description
U	Untreated PET fabric
D	PET only dyed (without a functional agent)
CLW	Very low molecular weight chitosan
CL	Chitosan lactate
CLW+D	PET treated with dye and very low molecular weight chitosan
CL+D	PET treated with dye and chitosan lactate
CLW+HDI+D	Modified PET treated with low molecular weight chitosan and dye in the presence of anchoring agent
CL+HDI+D	Modified PET treated with chitosan lactate and dye in the presence of anchoring agent
B	Bacteria only sample (flask)
SO-SG	Samples dyed with a sea-green photochromic dye
NP-RR	Samples dyed with a ruby-red photochromic dye

Chapter 4

One-step disperse dyeing and antimicrobial functionalization of polyester fabric with chitosan biopolymers

In this chapter, the results of the study concerning the combined dyeing and antimicrobial functionalization of polyester with disperse dye and selected chitosan biopolymers in $scCO_2$ solvent medium will be presented. The study aimed to investigate the suitability of $scCO_2$ technique for dyeing and impregnation of polyester fabric with disperse dye and chitosan biopolymers to produce coloured and functional polyester in a single step. Introduction about the related studies followed by results and discussions will be described. The content of this chapter has been published as part of the paper I.

4.1 Introduction

The demand for antimicrobial textiles has risen over the years due to the growing human awareness about personal hygiene and healthy lifestyle. To fulfil this demand, antimicrobial textile production has increased over the years and it became one of the fastest-growing fields in the textile industry. To impart antimicrobial functionality to the textile, many different synthetic functional agents such as quaternary ammonium compounds, triclosan, N-halamines, silver-based compounds, metal salts, polybiguanides, and natural compounds have been used [159-161]. However, most of these synthetic antimicrobial agents are toxic both for the user and the environment. This leads to consumers to demand safer products and governments and regulatory bodies are also imposing more stringent regulations to minimize the risks associated with it and the negative environmental impacts [162]. Due to this, there has been an increasing motivation towards the development of antimicrobial textiles based on non-toxic and environmentally friendly materials. In this regards, more attention has been given to sustainable and eco-friendly antimicrobial agents based on natural products such as chitosan and its derivatives, curcumin, and other natural based materials [163, 164]. Many different bioactive natural products have been explored for various functional textile applications. Among these biomaterials, chitosan is one of the most abundant, renewable, and biodegradable biopolymers available in nature with proven antimicrobial activity, non-toxicity, and biocompatibility [165]. Chitosan is a linear polysaccharide composed of randomly distributed β-(1, 4) linked deacetylated unit (D-glucosamine) and the residual acetylated unit from chitin (N-acetyl, D- glucosamine) (see **Fig. 3.2**). It is the deacetylated derivative of chitin produced by treating shrimps and other crustacean shells with sodium hydroxide. According to studies reported, chitosan and its derivatives have demonstrated to possess a broad range of antimicrobial activity when applied to various textile substrates [113, 161, 166-170]. Chitosan can also provide hydrophilicity and support the biocompatibility of polyester which is highly relevant in the development of innovative materials.

Application of chitosan to the textiles is generally carried out by the conventional padding or exhaust methods which are environmentally less attractive. Moreover, these methods of application generally require higher chitosan concentrations for effective antimicrobial activity. However, when high concentrations of chitosan are used, it forms a film on the surface of the fabric which decreases air permeability and increases the stiffness of the fabric [162]. There are also some important limitations related to efficiency and durability of the finish. Due to these shortcomings, there is a need for alternative scientific techniques to apply chitosan to textiles in a more environmentally friendly and efficient way. In response to this, the textile processing industry has nowadays focused on using some green technologies as an alternative to conventional wet processing to promote sustainable production and consumption of textiles. Some latest reports aimed to overcome these problems include plasma technology [171], UV grafting [172], impregnation in supercritical CO_2 [149].

This study attempts to extend the knowledge about the application of $scCO_2$ dyeing technique to functionalize and dye polyester fabric simultaneously with chitosan biopolymers and disperse dye. In addition to its eco-friendliness and effective antimicrobial activity, the presence of some properties suitable for $scCO_2$ media is the motivation behind selecting chitosan biopolymers. According to some reports, chitosan types with low molecular weight and a high degree of deacetylation (DDA) have shown some solubility in $scCO_2$ [149, 173]. Some correlation between the solubility and the number of amino and acetamide groups in the structure of chitosan was discussed showing some potentialities [174]. Chattopadhyaya *et al.* reported that low molecular weight chitosan with low viscosity have shown better penetrate ability into polyester structure compared with high molecular weight chitosan [175]. Therefore, chitosan types with very low molecular weight and viscosity could penetrate fully and/or partially into the swollen polymer matrix in supercritical CO_2 medium and consequently locked inside the fibre matrix during the expansion step of the CO_2. Thus, this study aims at investigating the feasibility of combined disperse dyeing and antimicrobial finishing of polyester fabric with chitosan biopolymers in $scCO_2$ media. Combining the dyeing and finishing process can help to improve economics as well as environmental issues related to the conventional textile dyeing and finishing processes. The study will give an insight into the behaviours of chitosan biopolymers and their compatibility with the disperse dyes applied to the polyester fabric from $scCO_2$ media.

4.2 Results and discussion

4.2.1 Impregnation yield

Initially, a broad screening was carried out on the antimicrobial activity and impregnation yield of several chitosan materials. The antimicrobial activity was assessed by measuring the inhibition zone as presented in the method section. To evaluate the amount of chitosan impregnated into polyester, the same amount of chitosan powder and substrate size was used for all samples and the weight gains were calculated after impregnation experiment according to **Equation (3.16).** Among the chitosan types investigated during the screening experiment, two chitosan biopolymers which exhibited better bacteria inhibition and weight gains, namely, chitosan (10 cps) with very low molecular weight (CLW) and chitosan lactate (CL) were selected for subsequent experiments. According to the result of the broad screening, CLW was impregnated in large amounts (1.22 %) followed by chitosan lactate (0.95 %) presumably due to their better solubility in $scCO_2$ and lower molecular size compared with others. Then, these selected chitosans were applied to polyester fabric based on the impregnation strategies described in **section 3.4.3** and the results of the weight gain are presented in **Table 4.1.**

According to the results of the impregnation yield (weight gains), a similar trend but with improved weight gains were achieved in this set of experiments compared with the results obtained during the screening experiment. Also, some improvement in impregnation amount was observed for modified polyester using a crosslinking agent compared with the non-modified polyester without a crosslinking agent. However, it could be observed that chitosan was hardly impregnated into the polyester fabric as displayed by lower weight gains and it has also been noticed that a considerable amount of chitosan powder remained inside the vessels during the impregnation experiments.

Table 4.1 Weight gain percentage of samples impregnated with chitosan in $scCO_2$

Fabric samples	Weight gain (%)
D	-
CLW+D	1.02±0.14
CL+D	1.48±0.12
CLW+HDI+D	1.66±0.26
CL+HDI+D	1.86±0.18

Moreover, as the weight gains were less reproducible, those samples that have similar impregnation yields were chosen for further characterization and comparisons. Even though weight gains were small, the amount impregnated was enough to evaluate the behaviour of chitosan incorporated into the polyester fabric using $scCO_2$ impregnation method. In this set of experiments, chitosan lactate was impregnated in large amounts in which the relatively higher number of carboxylic and amino reactive groups available in CL could interact with HDI and improved the amount of chitosan add-on when using the second approach.

4.2.2 FTIR-ATR analysis

The available functional groups before and after chitosan impregnation were assessed through FIIR measurements to confirm the incorporation of chitosan molecules into the polyester fabric. **Fig. 4.1** shows the FTIR spectra of non-treated fabric, CLW and CL powders, and modified polyester fabric samples treated with CLW and CL using HDI crosslinking agent. Typical peaks of untreated polyester are 1711 cm^{-1} (C=O asymmetric stretching of carbonyl group), 1241cm^{-1} (stretching vibrations of C─O bonds), 1093 and 1014 (O=C─O─C, or secondary alcohol), 2969/67 cm^{-1} and 718 cm^{-1} corresponds to C − H stretching and bending vibrations of the benzene ring, respectively [176-178]. The broad bands exhibited in the range from 3300 to 3500 cm^{-1} on both chitosan powders and chitosan treated fabrics corresponds to a combined peak of N−H stretching vibration and O−H stretching of chitosan [179]. The peaks at 2932, 2856, and 2858 cm^{-1} can be attributed to C−H asymmetric and symmetric stretching vibrations of methylene group of chitosan and chitosan lactate [180]. Methylene group of isocyanates could also be overlapped in the same region. Furthermore, the peak at 1556 cm^{-1} is typical of chitosan acid salts corresponding to the carboxylate band ($-COO^{-}$) of chitosan lactate [179].

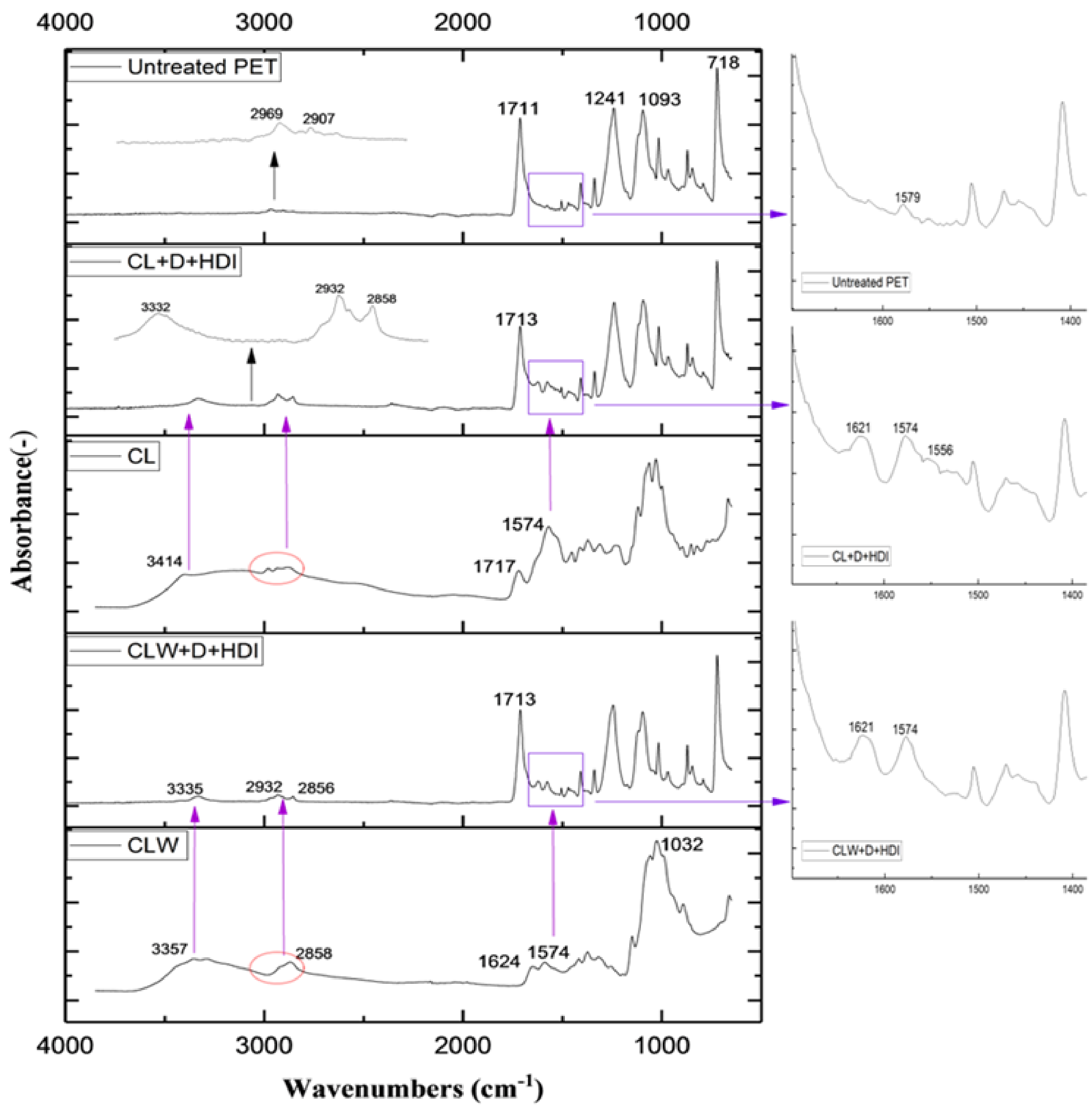


Fig. 4.1 Comparison of FTIR spectra of chitosan powders, polyester fabrics treated with these powders, and untreated polyester fabric samples.

The absence of the characteristic isocyanate peak (2250-2274 cm^{-1}) indicates that all isocyanate groups have been reacted or those unreacted are left out in the reactor [64]. The peaks at 1621 cm^{-1} and 1574 cm^{-1} is assigned to the C=O group and N-H group (bending) of the urethane linkage, respectively. This confirms the formation of urethane linkage between the free –NCO- group and OH group of chitosan [180]. Therefore, the FTIR spectra showed that polyester has undergone changes in surface functional groups suggesting crosslinking reaction between polyester and CLW/CL happened with the help of HDI as an anchoring agent using $scCO_2$ dyeing technique.

4.2.3 Zeta (ζ) potential

Zeta potential is an important indicator of surface charge properties of solid materials such as textiles [181]. The surface charge properties of samples before and after treatment were measured and compared to evaluate the incorporation of chitosan molecules into the fabric. As presented in **Fig. 4.2**, untreated polyester fabric exhibited the lowest ζ potential throughout the entire pH range in agreement with previous studies [182, 183]. The ζ potential of dyed only sample lays between the chitosan treated and untreated samples displaying the intermediate effect of the dye on the surface charge property. On the other hand, all chitosan treated samples exhibited higher positive ζ potential at acidic pH and higher negative ζ potential at basic pH regions. This suggested there is a change in surface charge properties after the treatments due to the absorption of the dye and chitosan molecules.

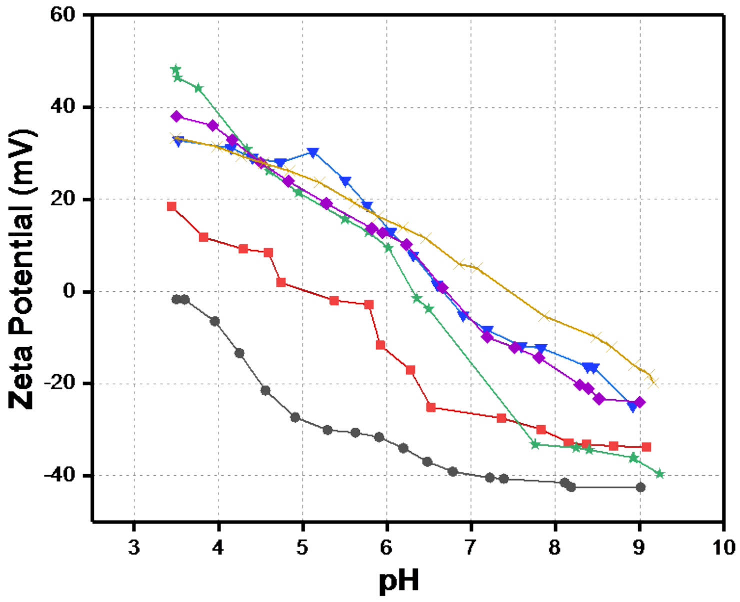


Fig. 4.2 Zeta potential of polyester fabric samples investigated (●) U, (■) D, (▼) CLW + D, (*) CL + D, (♦) CLW + HDI + D, (×) CL + HDI +D

As seen in **Table 4.2**, the shift in the isoelectric point (IEP) to a higher pH region is also an indication of chitosan adsorption suggesting the amino groups of chitosan introduced are protonated when in contact with the electrolyte solution lowering the negative ζ potential [183]. Therefore, the results of ζ potential confirm the presence of protonated amino groups integrated on the fabric surface.

Table 4.2 ζ potential values (in mV) of samples at acidic and alkaline pH and their antibacterial activity (reduction %)

Fabric samples	pH		IEP	Bacteria reduction (%)
	3.5	9		
U	−1.7	−42.5	<3.5	-
D	+18.5	−33.8	4.9	24±9
CLW+D	+32.8	−26.2	6.6	88±3
CL+D	+48.2	−36.1	6.3	93±2
CLW+HDI+D	+38.0	−24.0	6.7	88±1
CL+HDI+D	+33.4	−19.8	7.5	75±2

Isoelectric point (IEP) is the pH at which ζ potential is zero

The pKa value of chitosan varies from 6.1 to 7 depending on differences in the degree of deacetylation, molecular weight, and various environmental parameters [184]. Below its pKa (the acidic region in this case), the NH_2 groups of chitosan are converted to the soluble protonated form (NH_3^+) [185] and the fabric acquires positive surface charge property. However, when the pH exceeds the pKa (i.e. basic pH region), the NH_3^+ groups deprotonate back to their original state. In this case, the negative surface charge property displayed at the basic pH region could be due to the inherent negative ζ potential of the polyester fabric itself. Furthermore, the higher negative ζ potential next to the untreated polyester displayed by CL at the higher pH regions could be due to the presence of carboxyl groups in CL backbone, resulting in a more negative net charge. The higher the carboxyl density at the fibre surface, the more negative the ζ potential is [186]. However, when CL was used in modified fabric using the crosslinking procedure, a decrease in ζ potential values (at both ends) was observed. This suggests that both $-NH_3^+$ and $-COO^-$ functional groups have participated in the crosslinking reaction that leads to a reduction in the density of both groups. Overall, the ζ potential results confirmed that modification of polyester fabric with chitosan in both approaches using $scCO_2$ dyeing technique has been effective.

4.2.4 Wettability property

The hydrophilic/hydrophobic behaviour of the samples before and after treatment was analysed using water contact angle (θ_{H2O}) measurements. As presented in **Fig. 4.3**, the mean contact angle values of dyed only and non-dyed samples exhibited almost similar wettability property which suggests that the dye had less or no effect on the hydrophilic/hydrophobic behaviour of the polyester fabric.

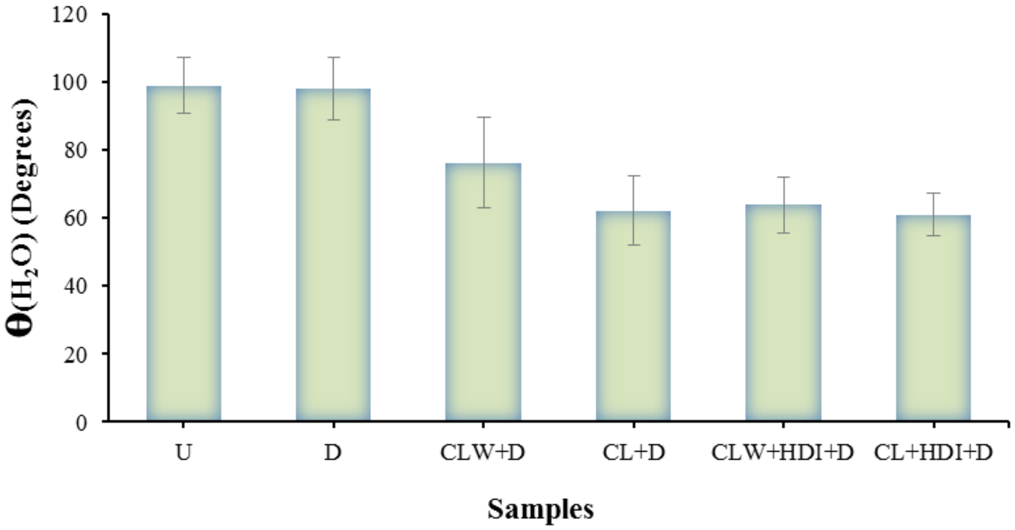


Fig. 4.3 Water contact angle values (in degrees) of the samples investigated

On the other hand, all chitosan treated samples demonstrated an apparent decrease in contact angle, which shows the improvement in the hydrophilicity after chitosan treatment to a certain extent. The increase in wettability is possibly attributed to the introduction of hydrophilic groups (OH, NH_2, NH_3^+ and $-COO^-$) of chitosan and chitosan lactate into the fabric. These new polar groups induce an increase in surface free energy and fibre water interaction, resulting in faster water absorption [187]. Among the chitosan treated samples, those treated with CL displayed slightly lower WCA compared with others. This implies that more polar groups are introduced possibly due to the presence of additional hydrophilic carboxyl groups within the polymer backbone of CL. In conclusion, an improvement in hydrophilicity of chitosan treated samples was observed indicative of incorporation of chitosan molecules onto the polyester fabric.

4.2.5 Surface morphology (SEM)

The changes in the surface morphology of polyester fabric after dyeing and chitosan treatment was analysed through SEM measurements. The SEM images of untreated and treated polyester samples are shown in **Fig. 4.4.** As can be seen in **Fig. 4.4 (a)** (untreated fabric), its surface looks relatively smooth and clean compared with the dyed and chitosan treated ones. On the other hand, on the dyed only sample, oligomer crystals are detected on the surface (**Fig. 4.4 (b)**). Generally, migration of oligomers from the inner part of the fibre to the surface during high temperature and pressure $scCO_2$ treatment has been consistently reported [98, 109]. During the $scCO_2$ dyeing process, the CO_2 penetrates the fibre interior and some oligomers are pushed by the elevated pressure to the fibre surface and form new microvoids at their previous places [109]. Furthermore, a combination of oligomers and chitosan molecules can be seen on the surface CLW and CL treated samples (**Fig. 4.4 (c)** and **(d)**) with few aggregated polymeric structure locked inside. Moreover, both samples treated with the crosslinking agent (**Fig. 4.4 (e)** and **(f)** forms a thin film on the surface of the fibre with some mild grooves possibly due to the higher amount of HDI used, which might make the surface somewhat rougher. Therefore, the SEM images show the presence of chitosan molecules on the fabric surface.

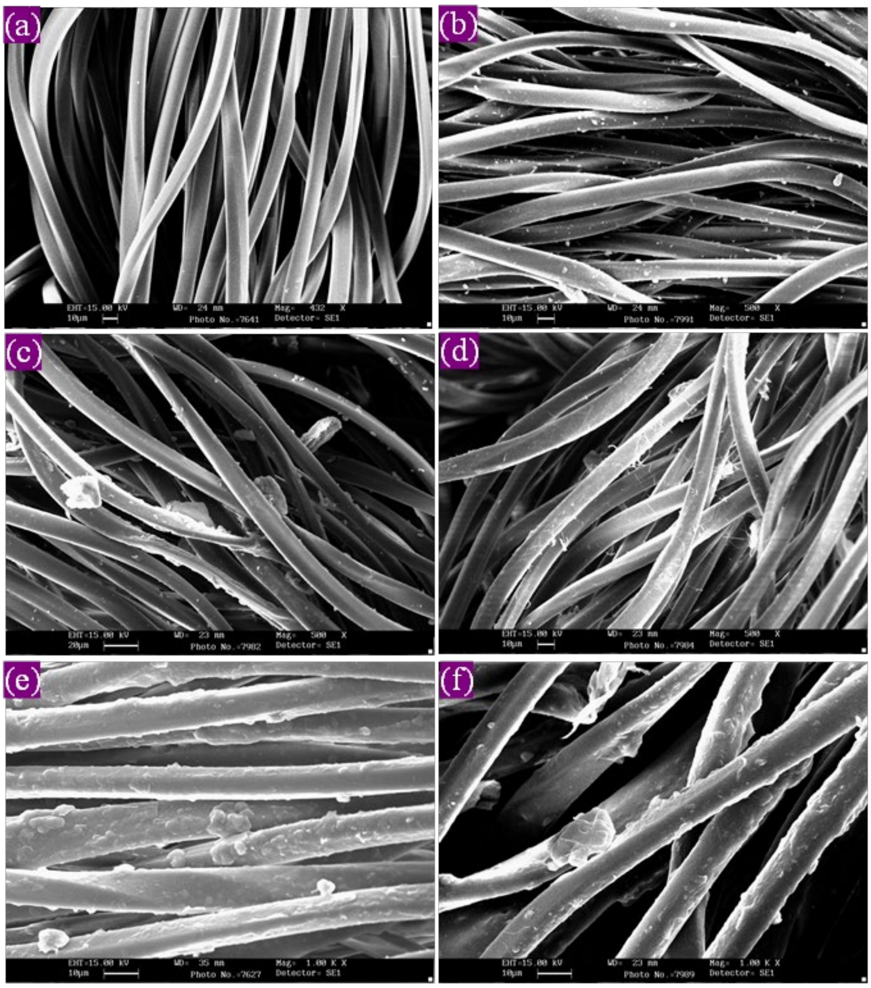


Fig. 4.4 SEM images of some representative samples (a) Undyed polyester, (b) Dyed polyester (c) CLW+D, (d) CL+D, (e) CLW+HDI+D, and (f) CL+HDI+D

4.2.6 Antimicrobial activity and durability

The antimicrobial performance of samples was evaluated based ASTM E2149-10 standard test method. The dyed only sample was used as a control and the evaluation was performed in terms of percentage reduction of CFU of bacteria (*E. coli*). According to the results (**Fig. 4.5),** all the chitosan treated samples exhibited higher antibacterial reduction compared with the dyed only sample. Chitosan treated samples are expected to have higher antibacterial activity as chitosan and its derivatives have proven to have antimicrobial activity against a wide range of bacteria [185]. The antibacterial property of chitosan is believed to originate from its polycationic nature. The cationic group (positively charged amino groups) of chitosan can interact with negatively charged residues of macromolecules at the cell surface of bacteria, which causes extensive cell surface modifications and alters cell permeability and subsequently inhibit the growth of bacteria [162, 166, 188]. Among the treated samples, samples treated with CL exhibited the highest antimicrobial activity (93% reduction) compared with the other samples. This could be due to the highest positive charge density as established from the ζ potential results.

As presented in **Table 4.2**, the positive charge density (as established from ζ potential) and antimicrobial activity correlate well for all samples. For CL treated samples, the higher positive charge density is possibly acquired through the presence of permanent positive charge (NH_3^+), resulting in a polyelectrolyte characteristic independent of the pH of the media. On the other hand, for other chitosan types, the cationic nature can no longer explain its antimicrobial activity at neutral and alkaline media [189]. In this case, the strong coordination capability of the NH_2 group in chitosan might be one possible mechanism of antimicrobial activity, as suggested by [185]. Also, it should be mentioned that the antimicrobial activity of chitosan is also dependent on other factors such as molecular weight or viscosity, degree of deacetylation, concentration, and the type of bacterium [190, 191].

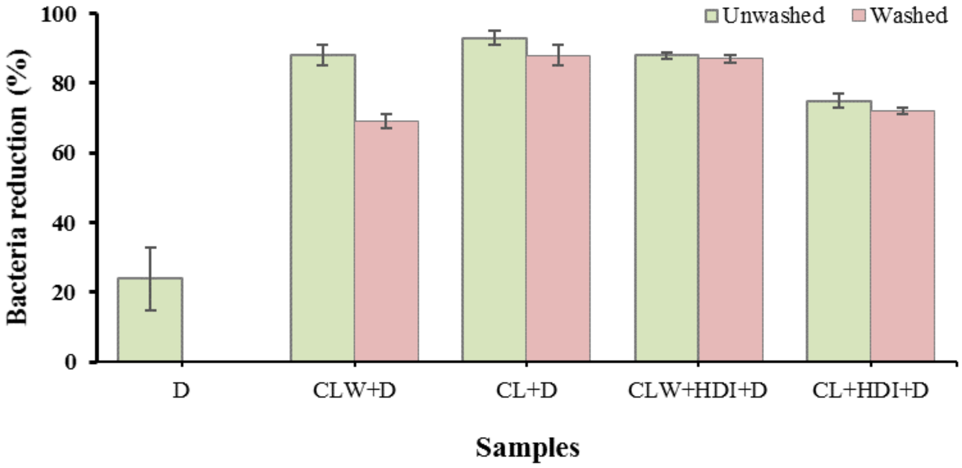


Fig. 4.5 Comparison of bacteria reduction of samples against *E. coli* after 1 hour; before and after washing

The proposed surface modification and crosslinking mechanism of polyester increased the chitosan add-on to some extent, but the antimicrobial activity was not improved as anticipated. This could be due to the undesirable crosslinking of amino groups of chitosan, which are responsible for the antimicrobial activity, with HDI leaving a smaller number of amino groups to interact with the bacteria. Controlling –NCO/chitosan ratios, a preferably lower amount of HDI, during the dyeing process may assist to have a higher number of free amino groups that could enhance the antimicrobial activity.

Furthermore, the antimicrobial activity of samples was measured after washing to evaluate the durability against laundry. After washing, the samples developed with the modified polyester and crosslinking procedure exhibited better durability suggesting the effective crosslinking of chitosan molecules with the fabric. The commercial crosslinking agent, 1,6 hexamethylene diisocyanate (HDI) possesses two reactive groups (-N=C=O) and it has been commonly used as a strong linker of $-NH_2$ and -OH groups [180]. Having two reactive sites, HDI is believed to react both with the $-NH_2$ and -OH groups of chitosan and $-NH_2$ groups of modified polyester giving strong linkage between chitosan and polyester. This has been confirmed during FTIR measurements. On the other hand, the samples produced without surface modification and crosslinking showed inferior wash durability with a significant reduction in antimicrobial activity after washing. This indicates that the chitosan molecules did not fully penetrate the polymer matrix suggesting the adsorption was dominated by physical interactions instead. This could be due to the inadequate solubility of chitosan in $scCO_2$ solvent as demonstrated from weight gain results. However, though the antimicrobial activity was not improved as expected, a marginal enhancement in the durability was possible after fabric surface modification and crosslinking mechanism (**Fig. 4.5**). Overall, though promising results were obtained, the antimicrobial activity should be improved further to be applied as a true antimicrobial fabric especially in medical and hygienic conditions.

4.2.7 Colour strength and fastness

The colour strength (*K/S* value) and the colour fastness ratings using a standard washing and rubbing procedures have been used to assess the colour performance of the samples. According to spectrophotometric measurements and visual observation, all samples exhibited excellent colour intensity and levelness properties **(Fig. 4.6**). Different samples were developed to study the effect of the agents when applied separately and in combination on the colour and antimicrobial performances to assess the compatibility. According to the results, there was no significant difference in the colour performance between the samples dyed separately and in combination with chitosan confirming compatibility. Only a slightly higher colour strength properties were observed when the dyeing was performed in the presence of chitosan compared with the dyed only samples. This could be attributed to the positive effect of chitosan molecules towards improving the hydrophilicity and increased localized amorphous domains of the fibre which promotes the sorption and diffusion of the dyes into the fibre. For CL (having a slightly higher colour strength), the additional amino functionality present in their structure could enhance the crosslinking density (increased amount of CL molecules) resulting in a relatively higher dye uptake.

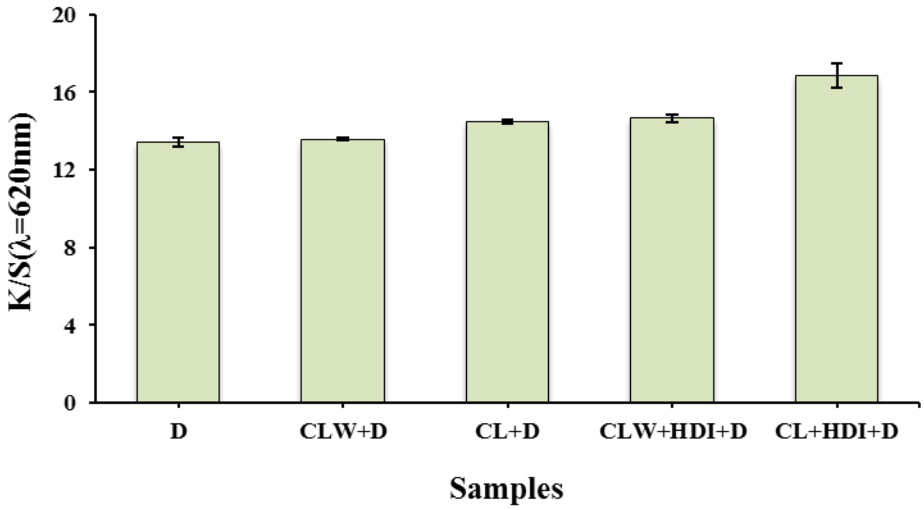


Fig. 4.6 The average K/S value of samples produced under the same dyeing condition

Furthermore, all the samples exhibited excellent colour fastness to washing and rubbing with a rating between 4/5 to 5 for both fade and stain fastness on an adjacent fabric of SDC Multi-fibre DW (wool, acrylic, polyester, polyamide 66, cotton, and acetate). As seen from **ulation** proving compatibility.

Table 4.3, all the dyed samples, with and without chitosan treatment exhibited satisfactory fastness, except for a slightly lower fastness rating for CL treated samples in washing and wet rubbing. Generally, deeper shades have lower fastness properties when subjected to washing and wet rubbing than the lighter ones, because in the case of deep shades, the dye molecules are more saturated and are susceptible to move out easily from the interior of the fibre during washing. Still, this property can be improved industrially as the industrial $scCO_2$ dyeing involves a short rinsing time with a supercritical fluid to remove unfixed dyes to improve this quality [192], something which is absent in our lab-dyeing facility. This is an interesting result which indicates that the colour quality is not affected by the inclusion of chitosan in the dyeing formulation proving compatibility.

Table 4.3 Colour fastness values of samples against washing and rubbing according to greyscale rating

Fabric samples	Washing (colour change)	Rubbing (staining)	
		Wet	Dry
D	5	5	5
CLW+D	5	5	5
CL+D	4/5	5	5
CLW+HDI+D	4/5	4/5	5
CL+HDI+D	4/5	4/5	5

4.3 Conclusion

The study has proved that combined dyeing and antimicrobial functionalization of polyester fabric with chitosan and its derivatives is feasible using $scCO_2$ dyeing technique. To the best of our knowledge, this is the first study which combines the dyeing and functionalization of polyester in $scCO_2$ without affecting the colour and functional properties. Among several tested chitosan materials, chitosan very low molecular weight and chitosan lactate have shown better results in terms of impregnation yield and antimicrobial activity. Excellent colour strength and fastness properties were also achieved and the incorporation of chitosan on the formulation had no significant effect on the colour property confirming the compatibility. Antimicrobial activity with a bacteria reduction rate of 75-93 % was obtained under the condition considered suitable for both dyeing and impregnation processes. Though it is promising, the obtained level of antimicrobial activity is not enough from the hygiene and medical point of view. This could be because chitosan was hardly impregnated into the polyester fabric as displayed by lower weight gains presumably due to their poor solubility in $scCO_2$. Thus, from the viewpoint of possible application, additional studies are yet required to improve the solubility of chitosan and hence impregnation amount. Process wise, however, the combined dyeing and functionalization of polyester fabric used in this study had no compatibility issue which can reduce the cost of production, save the time and energy, increase the production and efficiency, and reduce the load of the effluent with a potential application in cleaner textile production.

Chapter 5

Colouration and bio-activation of polyester fabric with curcumin in $scCO_2$

In this chapter, the experimental findings obtained during impregnation of polyester fabric with curcumin natural dye will be presented. The study aimed to develop coloured and functionalized polyester fabric with curcumin by using $scCO_2$ dyeing technique. In this section, some introduction about curcumin properties and studies related to curcumin and $scCO_2$ will be presented. The evaluation of the colour and functional properties of curcumin dyed samples will be presented and discussed in detail. The content of this chapter has been published as part of paper II and III.

5.1 Introduction

Since the last few decades, it has been reported that synthetic compounds (such as synthetic dyes and functional finishing agents) cause some serious health hazards and environmental problems and becomes an issue all over the world. Dyestuff and textile industries have also become increasingly subjected to several regulations to improve health, safety, and environment. Due to this, there has been a growing interest to use natural colourants for dyeing and finishing of textiles to minimize the negative effects posed by the synthetic dyes and finishing agents [193]. Natural colourants have been regarded as a suitable alternative to synthetic dyes in that it is abundant in nature, biodegradable, and environmentally viable [194]. Curcumin, also known as diferuloylmethane is among the most important natural colourant extracted from turmeric (*Curcuma Longa*). The extract from *Curcuma Longa*, called oleoresin, contains three known components such as curcumin, dimethoxy, and bisdemethoxy derivatives of curcumin in which curcumin is a major component. It exists in two tautomeric forms (keto and enol) with equilibrium strongly favouring an enol form (**Fig. 3.1)** [195, 196]. Curcumin is regarded as a green and sustainable colourant with low toxicity, biodegradability, biocompatibility, and eco-friendliness. Previous studies proved that curcumin was able to impart not only colour but also outstanding multifunctional properties such as antimicrobial, antioxidant, UV protection applied to various textiles [197, 198].

One important challenge in applying curcumin to textiles in the conventional aqueous process is the poor water solubility due to its hydrophobic character [199]. This causes insufficient solubility and limited penetration resulting in uneven dyeing and poor fastness properties in aqueous media. Some efforts such as the addition of surfactants, polymers, lipids, and proteins [200] and modification of curcumin to possess some reactive groups such as vinyl sulfone groups were reported to improve the solubility and fastness properties [201]. Furthermore, fabric pre and/or post-treatments, mordanting, washing, and drying are generally required to improve the dyeing performance of curcumin in conventional processes [202]. However, the mordants used are based on heavy metals which generate contaminated wastewater with residual toxic metal ions harming the environment and public health [203]. Because of these lengthy process steps and the associated environmental issues, the environmental prospect of curcumin as a potential alternative for synthetic dyes is largely hindered. The requirement of these long process steps is also less attractive from the cost of production and environmental impact viewpoint. Therefore, appropriate and improved scientific methods are highly required to gain the advantages from curcumin and to achieve colouration and bio-activation of polyester more safely and efficiently.

The motivation behind choosing curcumin was the presence of comparable properties with the disperse dyes with the possibility to be a safer alternative for polyester dyeing in $scCO_2$ media. Being lipophilic, curcumin is believed to be soluble in non-polar solvents such as hexane and $scCO_2$. Despite the poor water solubility, curcumin has been reported suitable for dyeing of polyester fabric in aqueous media with a high degree of exhaustion and strong dye fibre interaction between curcumin and polyester [204-206]. In these studies, the dyeing behaviour of polyester with curcumin has been demonstrated similar to the typical disperse dye behaviour. Furthermore, curcumin showed sufficient solubility in $scCO_2$ medium with solubilities in the range between 1.82×10^{-8} to 1.97×10^{-6} mole fractions [207], which is comparable to the solubility of disperse dyes (10^{-4} and 10^{-7} mole fractions) in $scCO_2$ [16]. Impregnation of curcumin into poly (lactic-co-glycolic acid) (PGLA) in $scCO_2$ was reported feasible [208]. One report also showed that $scCO_2$ has been used to impregnate PET films and poly(hydroxybutyrate) (PHB) granules with curcumin in $scCO_2$ obtaining promising results [104]. These reports suggest that curcumin could be a suitable colourant to impart colour and functionalize polyester fabric. However, any systematic investigation and application of curcumin natural dye to polyester fibres in $scCO_2$ is very limited despite the suitability of both polyester and curcumin in $scCO_2$ medium.

This study has dealt with colouration and bioactivation of polyester with curcumin using $scCO_2$ impregnation technique. To the best of our knowledge, this is the first study applying curcumin to dye and functionalize polyester fabric using $scCO_2$. Curcumin powder dye was directly applied to polyester fabric without the use of any mordant and substrate pre or post-treatment in $scCO_2$ media. The effects of the processing conditions such as the temperature, pressure, time, and dye concentration on the colour properties and functional efficiency were thoroughly examined. The colour and functional performances of developed samples have been assessed using proper characterization techniques. This study followed a novel approach for realizing multifunctional finishing (colouration, antimicrobial, antioxidant, and UV protection property) of polyester fabric with curcumin natural dye in a single step and in an eco-friendly way. This would address the environmental issues associated with synthetic dyeing of polyester and other challenges associated with the conventional applications of curcumin natural dye to textiles.

5.2 Colour properties

In this section, the results obtained about the effect of dyeing conditions such as system pressure, temperature, time, and dye concentration on the colour strength, levelness, and fastness properties will be discussed.

5.2.1 Effect of pressure

The effect of pressure on the colour strength and levelling properties were investigated in the pressure range of 15-25 MPa at a constant temperature of 120 °C, dyeing time of 60 min, and 0.1 wt. % dye concentration. Results of the colour strength (**Fig. 5.1**) showed that the average *K/S* value increased with the system pressure up to 20 MPa and becomes almost constant afterwards. The samples developed at lower pressure exhibited significantly lower colour strength and levelness compared with those developed at a higher pressure which shows the strong influence of the system pressure on the colour strength and levelness properties. From the literature, the same significant effect of pressure was also reported when PET films were impregnated with curcumin in $scCO_2$ [104] in agreement with the current observation.

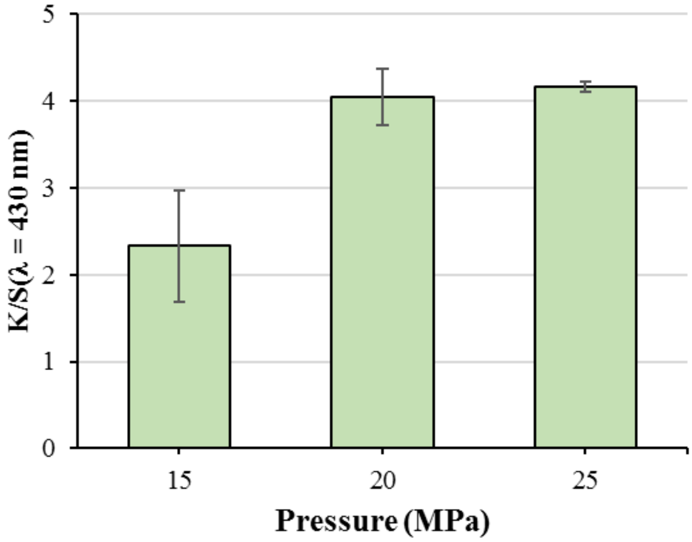


Fig. 5.1 Effect of pressure on the colour strength at a constant temperature of 120 °C, dyeing time 60 min, and 0.1 wt. % dye concentration

The strong influence of system pressure is presumably due to an increase in the density of the fluid when pressure increases resulting in enhanced solvating power and dye supply towards the fibre. Generally, an increase in the density of $scCO_2$ solvent decreases the intermolecular distance between the dye and CO_2 molecules and the interaction increases leading to an increase in solubility [25]. Increasing the pressure also increases the amount of CO_2 molecules penetrating the fibre interior which consequently increases the free volume of the polymer (swelling). This phenomenon promotes the diffusion of the dye molecules within the polymer matrix resulting in improved dye uptake and levelling properties [209]. The results showed that a commercially acceptable dyeing quality could be achieved using pressure exceeding 20 MPa at 120 °C within one hour of dyeing.

Table 5.1 Effect of pressure on the colour levelness at a constant temperature of 120 °C, dyeing time 60 min, and 0.1 wt. % dye concentration

Pressure (MPa)	$\sum_{\lambda=400}^{700} S_r(\lambda)$	U	L	Visual observation[*]
15	18.73	4.32	0.655	××
20	7.44	2.20	1.456	○
25	4.15	1.91	1.621	♦

[*] ♦ Excellent, ○ good, Δ fair, × poor, ×× bad

Furthermore, an increase in colour levelness (L) or a decrease in un-levelness value (U) was observed when the pressure increased (see **Table 5.1**). Excellent colour uniformity was achieved using the maximum pressure used (25MPa). The same and consistent result which supports the results of the levelness parameters was also obtained according to visual observation and relative standard deviation.

5.2.2 Effect of temperature

The effect of dyeing temperature on the colour strength and levelling properties was studied in the temperature ranging from 80 °C to 120 °C with a constant pressure of 25 MPa, a dyeing time of 60 min, and a dye concentration of 0.1 wt. %. As shown in **Fig. 5.2** and **Table 5.2**, both the *K/S* value and colour levelness increased with the dyeing temperature attaining higher colour intensity and uniformity at 120 °C. The obtained un-levelness value and visual observation rating were also consistent with the levelness parameter. A previous study reported a decrease in colour strength when polyester was dyed with disperse dye above 120 ºC when other parameters are fixed [192]. In the present study, however, the dyeing equipment did not allow temperature above 120 °C. According to the results, acceptable colour strength and levelness could be achieved using a dyeing temperature of at least 100 °C.

When the dyeing temperature increase, considering the higher constant dyeing pressure used (i.e. 25 MPa), the polymer flexibility (chain mobility) and free volume increase and this, in turn, leads to decrease in the T_g of the polymer [69, 209]. This facilitates the penetration and diffusion of dye molecules into the fibre structure enhancing the dye uptake and levelling properties.

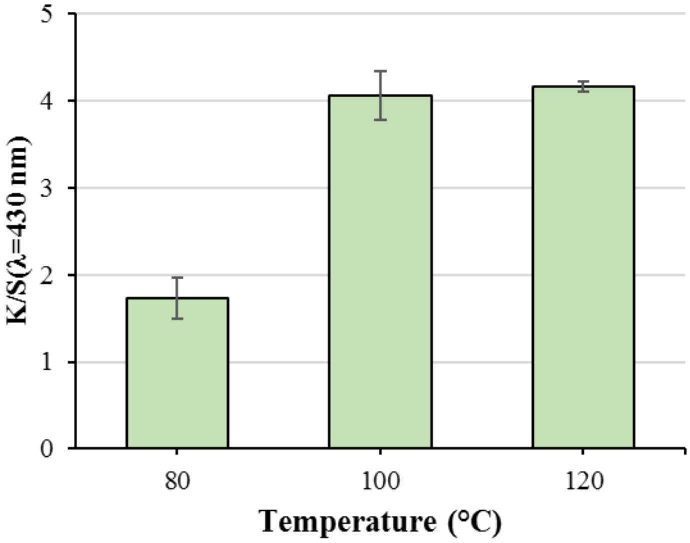


Fig. 5.2 Effect of dyeing temperature on the colour strength at a constant pressure of 25MPa, dyeing time 60 min, and 0.1wt. % dye concentration

In general, when the temperature increases keeping the pressure constant, the sublimation pressure of disperse dyes increases, but the solvent density decreases at the same time. At lower constant pressures, the decrease in solvent density dominates and the solubility of dyes decreases with increasing temperature. However, at higher constant pressures (25 MPa in this experiment), the increase of sublimation pressure of the dyes with temperature overcompensates the decreases in solvent density enhancing the solubility and hence the dye uptake [25]. Therefore, a proper increase in the dyeing temperature at higher constant pressure could improve the colour strength and levelness properties.

Table 5.2 Effect of dyeing temperature on the colour levelness at a constant pressure of 25MPa, dyeing time 60 min, and 0.1 wt. % dye concentration

Temperature (°C)	$\sum_{\lambda=400}^{700} S_r(\lambda)$	U	L	Visual observation*
80	11.47	3.34	0.951	×
100	7.13	2.36	1.369	Δ
120	4.15	1.91	1.621	♦

[*] ♦ Excellent, ○ good, Δ fair, × poor, ×× bad

5.2.3 Effect of dyeing time

To study the effect of dyeing time, samples were developed under the same dyeing condition (120 °C, 25MPa, 0.1 wt. % dye) by varying the time of dyeing from 30 min to 90 min. As can be seen from the result in **Fig. 5.3**, the dyeing time had a less significant effect on the colour strength resulting in almost similar *K/S* values at all dyeing times. According to the *K/S* values, higher dye uptake was attained within 30 min of dyeing and a slight reduction was observed when the dyeing proceeds until 60 min and becoming almost constant afterwards. This suggests that 30 min of dyeing was enough for the small amount of dye used in this study (0.1 wt. %) to be completely taken up by the fibre. This phenomenon could be related to the fast rate of dyeing in the $scCO_2$ medium.

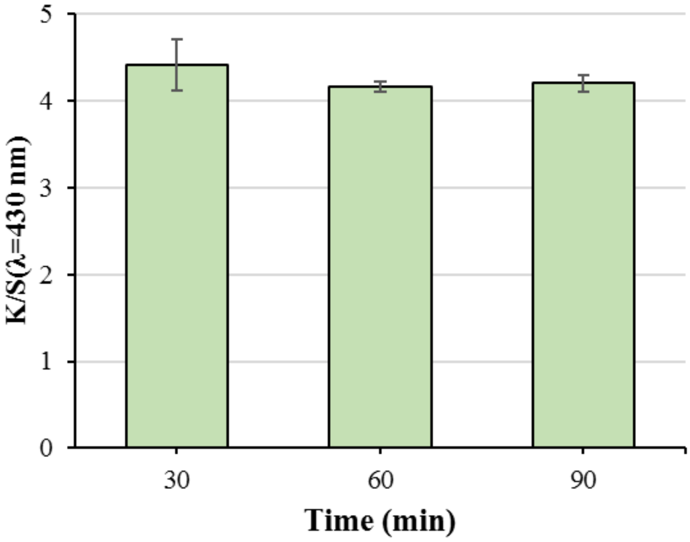


Fig. 5.3 Effect of dyeing time on the colour strength at a constant pressure of 25MPa, a temperature of 120 °C, and 0.1 wt. % dye concentration.

Generally, the rate of dyeing in $scCO_2$ is relatively faster than the conventional dyeing of polyester. The swelling and lubrication effect of CO_2 towards the polymer and its low viscosity and high diffusivity property are the key factors for fast and easy diffusion of the dye molecules into the polymer matrix [35]. The higher dyeing temperature (120 °C) also favours rapid diffusion of dye molecules with the advantage of shortening the dyeing time [210, 211]. Thus, it could be assumed that the small amounts of dye molecules used in this study are absorbed in a short time due to the fast rate of dyeing by $scCO_2$. Though it is less significant, the observed reduction in colour strength with time may be attributed to desorption of the dye molecules due to the extended dyeing time [212] while levelling itself.

Table 5.3 Effect of dyeing time on the colour levelness at a constant pressure of 25MPa, a temperature of 120 °C, and 0.1 wt. % dye concentration.

Time (min)	$\sum_{\lambda=400}^{700} S_r(\lambda)$	U	L	Visual observation*
30	8.78	3.11	1.04	×
60	4.15	1.91	1.621	♦
90	4.06	1.85	1.66	♦

*♦ Excellent, ○ good, Δ fair, × poor, ×× bad

On the other hand, the colour levelness (see **Table 5.3**) showed improvement with the dyeing time until 60 min and it became almost similar afterwards with no difference according to visual observation. Generally, a favourable prolonged dyeing time allows dye molecules to migrate inside the polymer matrix according to the concentration gradient to level itself [16, 209]. It can be observed that, even though higher dye uptake (*K/S* value) was obtained within 30 min of dyeing time, the levelness value obtained at this dyeing time was not enough (see **Table 5.3**). Thus, some additional time (at least 60 min) was required for the diffusion of dye molecules within the fibre interior to obtain uniform shade.

5.2.4 Effect of dye concentration

Three different dye concentrations under the same dyeing condition (120 °C, 25MPa, and 60 min) were developed to study the effect of dye concentration on the colour quality properties. **Fig. 5.4** shows the average colour strength of curcumin dyed samples at its minimum reflectance wavelength (430 nm). According to the results, a significant increase in colour strength was obtained when the dye concentration increase. This suggests an improvement in the dye uptake by the fibre because the *K/S* value is directly proportional to the dye content of the fibre especially at lower dye concentration [213]. The increase in *K/S* value with the dye concentration was expected because a greater number of dye molecules are likely to be transported by the CO_2 and absorbed by the fibre when the input dye concentration is higher. An increase in colour yield with the dye concentration has also been consistently reported in the literature in line with the current observation.

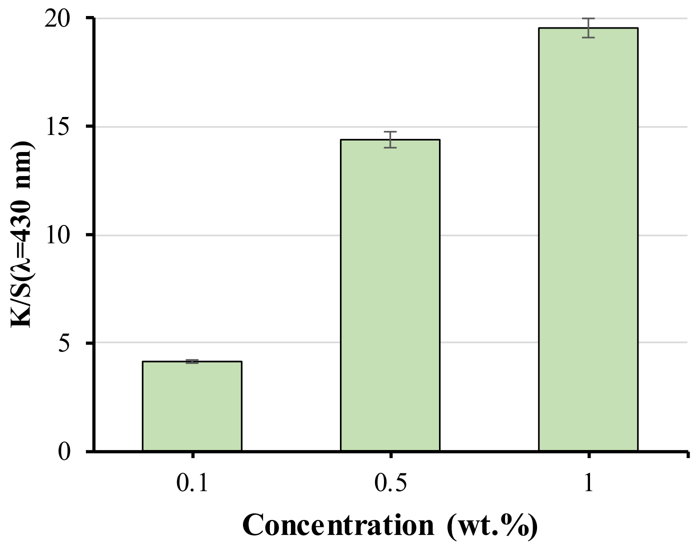


Fig. 5.4 Effect of dye concentration on the colour strength at a constant pressure of 25MPa, temperature of 120 °C, and 60 min dyeing time

In contrast, the increase in dye concentration resulted in a slight reduction in colour levelness as can be seen in **Table 5.4**. Similar results were also obtained according to the visual assessment which corresponds to the results presented in the previous sections. It has been reported that to obtain comparable colour levelness, either longer dyeing period is required or each element of the package needs to be exposed to the same dye concentration for the same time [25]. Therefore, for the same dyeing time but using different dye concentrations, obtaining different levelness values seems logical. For higher dye concentration, the initial dye uptake may consume the majority of available free volumes easily which makes for the remaining dye molecules difficult to access unoccupied free volumes requiring a relatively longer dyeing time. For lower dye concentration, instead, the available free volumes are enough and easily accessible to accommodate the small number of dye molecules achieving level dyeing in a short time. Thus, the colour uniformity of samples dyed under lower dye concentration is better than those developed with higher dye concentrations. The obtained levelness value at all dye concentrations is still ranked from excellent to fair, which is sufficient for commercial applications.

Table 5.4 Effect of dye concentration on the colour levelness at a constant pressure of 25MPa, temperature of 120 °C, and 60 min dyeing time

Dye concentration (wt. %)	$\sum_{\lambda=400}^{700} S_r(\lambda)$	U	L	Visual observation*
0.1	4.15	1.91	1.621	♦
0.5	4.94	1.99	1.574	○
1	5.24	2.32	1.392	Δ

*♦ Excellent, ○ good, Δ fair, × poor, ×× bad

The colour LAB values of curcumin dye polyester fabric in $scCO_2$ are represented in **Table 5.5.** These samples are developed by using the high purity curcumin to investigate its functional properties when applied to polyester from $scCO_2$ medium. The results in the table show that both the colour strength and yellowness increase (increase in b* value) when the dye concentration increase. The obtained yellowness value using such a low dye concentration is better than the conventionally dyed sample that used the same curcumin [204], suggesting the better efficiency of the $scCO_2$ dyeing method.

Table 5.5 Colour values of curcumin dyed polyester fabrics produced at a constant pressure of 25MPa, temperature of 120 °C, and 60 min dyeing time in $scCO_2$

Concentration (wt. %)	L*	a*	b*	K/S (430 nm)
0.25	88.20	-6.58	84.15	10.4
0. 5	86.78	-4.03	87.29	11.8
0.75	85.99	-0.14	93.75	17.3
1	83.81	4.43	93.34	17.7

5.2.5 Colour fastness properties

The colourfastness against washing and rubbing was evaluated according to ISO 105-C06 standard test method using greyscale ratings as summarised in **Table 5.6.** From the results, the samples developed under higher pressure, temperature, time, and lower dye concentration displayed better fastness properties. While those developed under low pressure, temperature, dyeing time, and higher dye concentration resulted in inferior fastness properties towards certain adjacent fabrics such as polyamide, cotton, and acetate. Besides, all samples exhibited good colour fastness to dry and wet rubbing with ratings between 4 and 5. Thus, excellent fastness properties could be attained using the optimum dyeing condition. The fastness properties could be further improved at the industrial level as the industrial scCO$_2$ dyeing process involves a short rinsing time with a supercritical fluid to remove unfixed dyes [192], something which is absent in our lab-dyeing facility.

Table 5.6 Fastness data of samples developed under different scCO$_2$ dyeing conditions

Wash fastness								Rub fastness	
Sample	Fading	Staining						Dry	Wet
		Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate		
S1	3-4	5	5	5	2-3	2-3	2-3	4-5	4
S2	4	5	5	5	3-4	3-4	3-4	4-5	4-5
S3	4-5	5	5	5	5	5	5	5	5
S4	4	5	5	5	2-3	2-3	2-3	4-5	4-5
S5	4-5	5	5	5	3-4	3-4	3-4	5	4-5
S6	4-5	5	5	5	4	4-5	4-5	4-5	4-5
S7	5	5	5	5	5	5	5	5	5
S8	4	5	5	5	4	4-5	4-5	4-5	4-5
S9	4	5	5	5	4	4	4-5	4	4

In terms of fastness to light, all chitosan dyed samples exhibited a rating between 1 and 2 according to the blue wool scale. This shows the poor lightfastness property of curcumin dyed samples and further investigations are required for possible improvement in this regard. A similar poor lightfastness of curcumin dyed polyester and cotton fabrics were reported, and the chromophore group of curcumin structure was suggested a possible cause of its poor lightfastness [212]. Indeed, most natural dyes are known to display poor light fastness properties [214].

5.3 Functional properties

The results of the functional properties of curcumin dyed samples such as UV protection ability, antioxidant property, and antibacterial properties are discussed in this section.

5.3.1 UV protection ability

Fabrics with UV protection functions are more demanded nowadays due to the threat caused by ozone layer depletion. Due to many health problems of UV exposure, functionalized textiles for the protection of skin from UV radiation becomes more important. Various UV absorbent organic and inorganic materials with strong absorption in the UV region are generally applied on textile fabrics to impart UV protection function. Certain nanostructures and natural materials are the most active and effective agents mostly chosen because of their small molecular size and safety [215]. Natural colourants are considered as safer and sustainable agents and have been confirmed appreciable UV blocking ability and the UV blocking property of curcumin incorporated to textiles have been reported [216]. In this study, samples dyed with different curcumin concentration and without curcumin were tested from the face and back sides of the fabric. As presented in **Fig. 5.5**, the samples dyed with curcumin showed higher UPF value compared with the one treated in the absence of curcumin. According to Australian/New Zealand standard (AS/NZS4399:2017), fabrics can be rated as providing good, very good, and excellent protection if their UPF values range from 15 to 24, 25 to 35, and above 40, respectively [156]. According to the results, all curcumin dyed samples provided UPF values above 35%, which means a very strong UV protection level according to the standard stated above. However, there was no clear trend between the dye concentration and UPF value in which those dyed with 0.5 wt. % curcumin concentration exhibited a relatively higher average UPF value (above 42%). There was also no clear and significant difference between the UPF value of the back and face of the fabric samples.

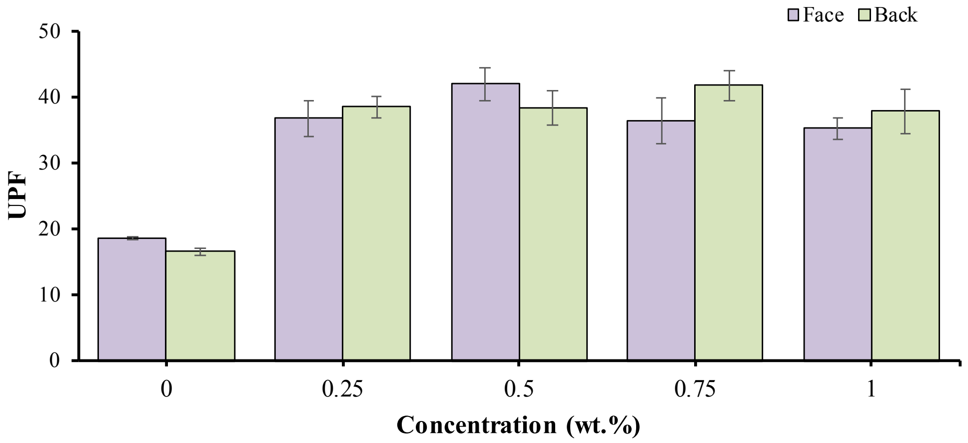
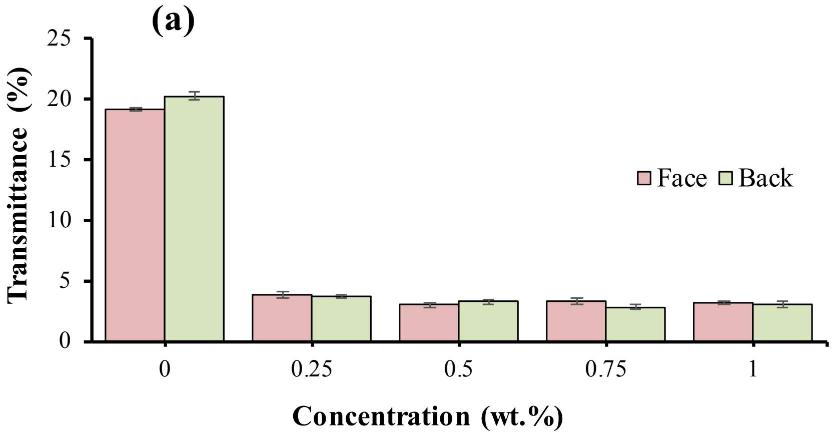


Fig. 5.5 UPF values of samples obtained at different curcumin concentration.

Furthermore, the UV transmittance level of samples was also examined as illustrated in **Fig. 5.6. (a) and (b).** Generally, there are three types of UV radiations such as UVA (400-320 nm), UVB (320-290 nm), and UVC (290-100 nm). Knowledge of which wavelength are transmitted through the fabric is important as each type of radiation has a different impact on human health. Exposure to UVA causes skin ageing and UVB irradiation is associated with skin cancer, cataracts, and immune suppression [217]. UVC is the most dangerous and potentially lethal even in moderate doses. Fortunately, most UVC is filtered by the ozone layer and does not reach to the earth [215]. From the results, the UVA and UVB transmittance levels of curcumin dyed samples were significantly low compared with the undyed sample (i.e. treated without curcumin). This clearly shows the UV blocking capability of curcumin natural dye even in small concentrations. About four-fold increase in UV blocking property could be obtained using only 0.25 wt. % curcumin concentration. Increasing the dye concentration further decreases the UV transmittance. According to the Australian/New Zealand standard (AS/NZS4399:2017), UVA transmission should be less than 5%. Based on the results, all curcumin dyed samples exhibited UVA and UVB transmittance values less than 5% (see **Fig. 5.6 a** and **b**), which meets the standard requirement. Therefore, the results indicate that it is possible to produce polyester fabrics with enough UV protection ability using a significantly lower amount of curcumin without using any auxiliary chemical in $scCO_2$. A previous study showed that polyester fabric dyed with 3 wt. % curcumin almost completely blocks UV from passing through the fabric [206]. Therefore, increasing the dye concentration may also improve the UV protection ability even further.



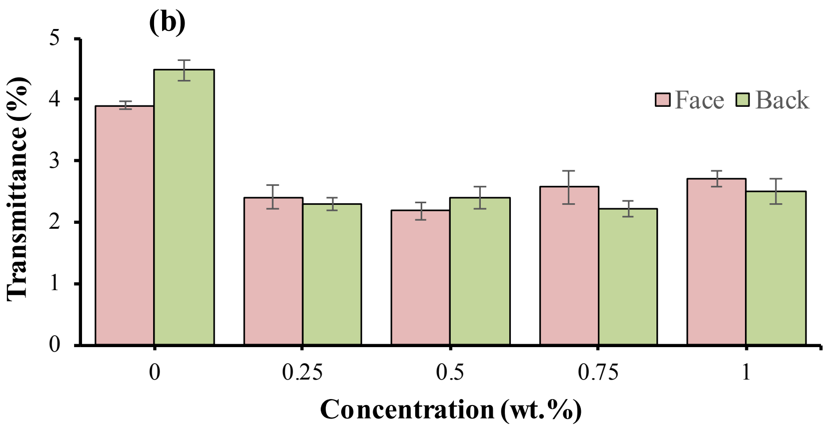


Fig. 5.6 UVA (a) and UVB (b) transmittance percentage of polyester fabric samples at different curcumin concentrations

5.3.2 Antioxidant property

Antioxidants can protect the human body from free radicals and radical oxygen species. Textiles in contact with skin are required to possess antioxidant activity to protect humans from these free radicals [218]. The most widely used synthetic antioxidants are butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). However, these antioxidant agents have been suspected to cause side effects such as liver damage and are carcinogenesis [219]. Therefore, there is a growing interest to replace these synthetic antioxidants with more safe and natural antioxidants. Among the available natural antioxidants, curcumin has been reported an effective antioxidant phenolic compound possessing many including antioxidant activity. [220-222]. In this work, the antioxidant activity of curcumin dyed polyester fabrics have been examined and results are presented in **Fig. 5.7**. Results showed that all the samples treated with curcumin showed a significantly higher antioxidant activity compared with the sample treated in $scCO_2$ without curcumin (non-dyed). The non-dyed polyester exhibited the lowest antioxidant activity (17 %) revealing its poor radical scavenging activity compared with curcumin-treated polyester samples. An increase in the antioxidant activity was observed with increase in the dye concentration attaining an activity of more than 60 % using only 1 wt. % curcumin concentration. According to this trend, a further increase in dye concentration could lead to a more efficient antioxidant activity. Antioxidant activity of more than 70 % was reported using 3 % curcumin concentration applied to silk fabric [201] suggesting improvement of the antioxidant activity could be possible through increasing the dye concentration.

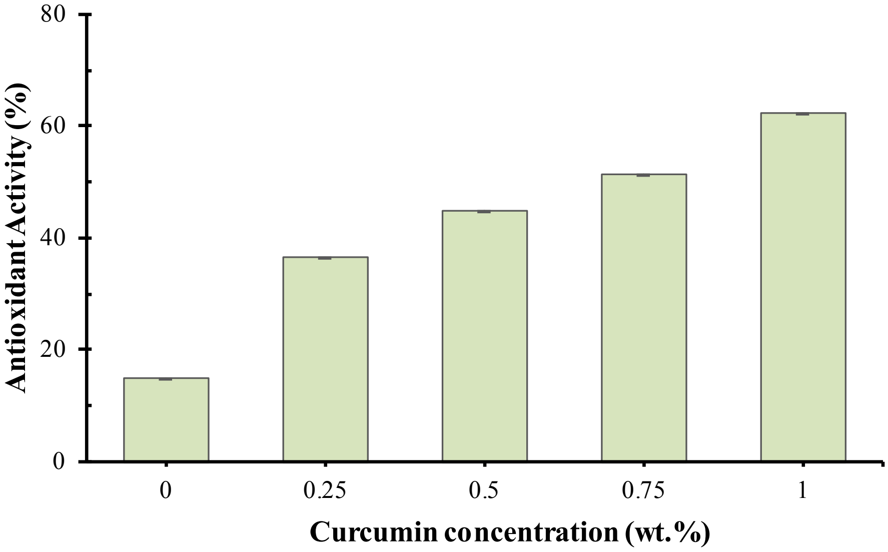


Fig. 5.7 Effect of curcumin concentration on the antioxidant activity of samples

According to previous studies, curcumin has been an effective antioxidant phenolic compound possessing comparable activity to those standard antioxidants [223]. The antioxidant property of curcumin dyed textiles has also been reported with varied level of activities based on the quality of curcumin and application conditions [224]. Different antioxidant mechanisms of curcumin have been suggested. Generally, the antioxidant mechanism of curcumin is believed to be due to its unique conjugate structure containing two methoxylated phenols in which the enol form of β-diketone structure (**Fig. 3.1**) is believed to possess a typical radical trapping ability as a chain-breaking antioxidant [225]. It is believed that the H-atom donation from the phenolic group is mainly responsible for the antioxidant properties of curcumin [223, 226]. Therefore, the presence of the required amount of enolate form is found to be important in the radical scavenging ability of curcumin.

5.3.3 Antibacterial property

Antimicrobial finishes are usually applied to textiles to prevent a range of undesirable effects both on the wearer and the textile itself due to bacteria growth. Some of these effects are the generation of unpleasant odour, stains and discolouration, strength loss, and user contaminations [161]. The antibacterial activities of polyester fabrics both untreated and treated with different concentrations of curcumin are presented in **Fig. 5.8**. The relationship between the concentration of curcumin and the antibacterial reduction can be seen from the results. From the results, untreated polyester samples had a poor antibacterial activity with an inhibition rate of around 24% against *E. coli.* On the other hand, curcumin-treated polyester fabrics demonstrated higher activity compared with untreated ones. Moreover, the bacteria inhibition increases when the dye concentration increase attaining a bacteria reduction percentage of above 60% using small curcumin concentration (1 wt. %). Similar results were also reported for curcumin-treated wool and cotton fabrics but with mordants [227, 228]. However, in some cases, a higher dye concentration in the range of 3 – 30 wt. % was required to obtain comparable bacteria reduction using conventional treatment [198, 229]. The level of antibacterial activity achieved in this study seems not enough to be applied as true antimicrobial fabric. Still, compared with the conventional dyeing, the current process highly resources-efficient with the possibility of improving the activity by increasing the dye concentration. The obtained antibacterial activity is expected as curcumin is a well-known antibacterial agent against a wide spectrum of bacteria [230]. Different mechanisms of antibacterial activity by curcumin have been suggested. The most accepted one is through damaging the bacterial membrane and the presence of the methoxyl and hydroxyl groups are mainly responsible for antibacterial activity [227, 228]. Furthermore, its antimicrobial activity is believed to increase when gram-positive bacteria is the test strain because according to many reports, gram-positive species are more susceptible to curcumin than gram negatives (used in this study) [231].

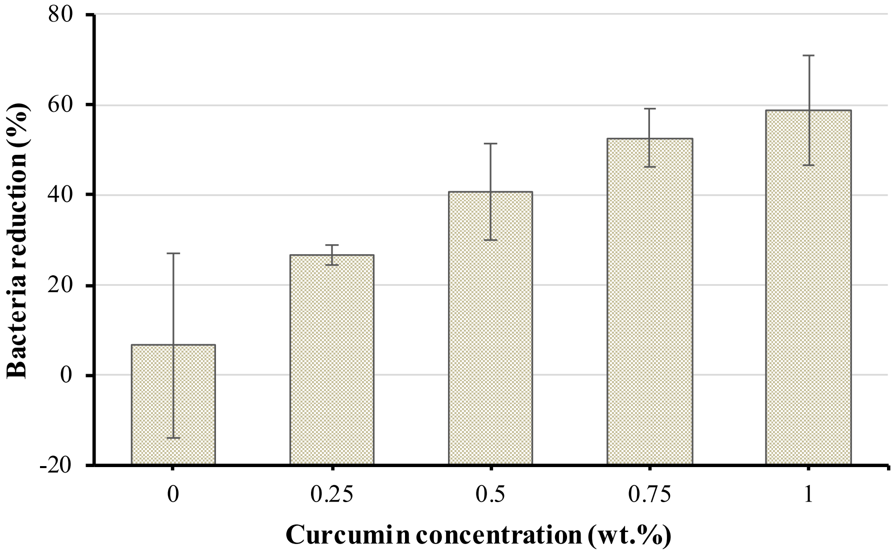


Fig. 5.8 Effect of curcumin concentration on the antibacterial activity of samples

5.4 Conclusion

In this study, novel multifunctional dyeing of polyester fabric with a nontoxic curcumin natural dye based on the use of environmentally friendly $scCO_2$ has been investigated. Being hydrophobic, curcumin is suitable for dyeing and functionalization of polyester fabric in $scCO_2$ medium and this has been proven experimentally in this study achieving excellent colour and functional performances. In this process, fabric pre-or post-treatment and the use of mordant which otherwise are required in the conventional dyeing process of natural dyes could be avoided. Among the variables, the dyeing behaviour of polyester fabric with curcumin in $scCO_2$ is strongly affected by system pressure followed by temperature. The fabrics dyed with curcumin natural dye have demonstrated desirable multiple functionalities such as antioxidant, antimicrobial, and UV protection properties. Moreover, an excellent colour strength, levelness, and fastness property was obtained. The results demonstrated the large potential of $scCO_2$ dyeing technique as a viable and green alternative to the conventional aqueous-based dyeing of polyester fibres which could also improve the economics and environmental sustainability.

Chapter 6

Functionalization of polyester fabric with photosensitive dyes in $scCO_2$ for UV sensing smart textile application

This chapter presents the experimental results concerning the development of a smart textile UV sensing fabric with the commercially available photochromic colourants using $scCO_2$ dyeing technique. The study investigated the behaviour of photochromic dyes applied to polyester fabric from $scCO_2$ solvent and compared the outcome with those applied using the traditional dyeing and printing methods. An introduction about photochromism, the research reported regarding photochromic textiles and application methods, and the properties of the photochromic dyes used in this study will be presented. The evaluations made about the photochromic properties of dyes applied on polyester fabric using $scCO_2$ dyeing and a comparison between the photochromic property of the dyes in solution and on polyester fabric will be discussed. The content of this chapter has been published as part of paper IV and V.

6.1 Introduction

Photochromism is a phenomenon whereby the absorption spectrum (colour) of a given molecule or crystal changes reversibly when irradiated by the light of a given wavelength [232]. Photochromic compounds are chemical species which change their colour upon exposure with the light of certain wavelength (mostly UV light) and revert to their original colourless state when the light is removed or by increasing the temperature. Nowadays, these photochromic materials have been the subject of active research because of their wide applications in various areas such as ophthalmic and sunglasses, optical recording, lenses, solar energy storage, light control filters, security printing, sensors and displays [233, 234]. Recently, their applications have also been extended to smart and functional textiles including in fashion and intelligent design, security and brand protection, anti-counterfeit, camouflage, textile UV sensors, and active protective clothes [235, 236]. Generally, textile-based UV sensors have the advantage of higher flexibility, easily customizable and require low maintenance compared to conventional sensor systems [237]. Despite the availability of significant interest, limited commercial development is believed to be due to technical issues associated with application methods and the associated performance issues [233]. The major technical reasons are the difficulties encountered when applying photochromic dyes to textiles by using the conventional textile dyeing techniques. Owing to the sensitive structure and poor water solubility (even with the common organic solvents), it is difficult to apply them to the textiles with the conventional exhaust or padding methods. Several reports also showed that they have poor fastness performances [236].

Many organic and inorganic compounds which exhibit photochromism are available today. Among these, spirooxazine and naphthopyran are the most commercially important class of photochromic molecules because of their high colour build-up, reversibility, and fatigue resistance [238]. These photochromic dyes have been applied as dyes to various textile substrates to produce photochromic smart and functional textiles. Several techniques such as exhaust dyeing [239-243], screen-printing [244-248], sol-gel coating [155, 249], pad-dry method [250, 251], electrospinning [252, 253], and mass colouration [254, 255] have been used to apply photochromic molecules to textiles. However, most of the conventional techniques have some common issues such as the requirement of a large amount of water, auxiliaries and the subsequent wastewater, higher cost of production, lower level of colour development, and insufficient durability, that need to be addressed for industrial-scale application [235]. Recently, application of photochromic colourants using resource-efficient digital inkjet printing has shown promising results [256-258]. Despite having several advantages over the conventional screen-printing concerning resource efficiency and process flexibility, the requirement of stable inks that meet a strict physicochemical and environmental criterion along with the associated print qualities remain a challenge. Therefore, given the high cost of photochromic dyes, appropriate resource-efficient production techniques that can meet the necessary commercial requirements are still required.

In response to addressing these issues, the application of photochromic dyes to polyester fabric using $scCO_2$ dyeing method is investigated in this study.

Photochromic dyes are structurally similar to the traditional disperse dyes in that they are nonpolar molecules with a balance of hydrophilic and hydrophobic character. Their dyeing behaviour is reported similar as disperse dyes when applied to polyester fabric in exhaust dyeing method [259]. Therefore, they are believed suitable colourants to dye polyester as disperse dyes and this was the motivation behind selecting these functional dyes to use in $scCO_2$ system to apply to polyester. Some photochromic dyes are proven soluble in $scCO_2$ medium [260] and $scCO_2$ dyeing technique has also been successfully used to produce some photochromic materials. Glagolev *et al.* [117, 118, 261, 262] used various photoactive compounds to impregnate different polymeric materials in $scCO_2$ obtaining promising results. Photochromic lenses were also produced via $scCO_2$ impregnation of polycarbonate and silica gel composite film with a photochromic dye reversacol graphite [263]. Thus, $scCO_2$ has been proven as a feasible method to apply photochromic compounds to various polymeric materials. To the best of our knowledge, however, the application of commercially important photochromic spirooxazine and naphthopyran based dyes to polyester fabrics using $scCO_2$ dyeing technique has not been reported.

In this study, a novel UV-responsive polyester fabric has been developed with selected commercial photochromic dyes based on spirooxazine and naphthopyran dye classes using $scCO_2$ dyeing technique. The photochromic behaviour of these dyes in solution and applied on polyester fabric has been compared. The colourability and reversion properties of photochromic dyed samples were evaluated using a specially designed online colour measurement system which can measure the photochromic colour change continuously during UV-irradiation and after the UV source is removed. The photochromic properties such as the colour yields (*K/S* values), colour switching rates, and the colour fastness against washing and abrasion were examined.

6.2 Results and discussion

6.2.1 Data fitting

For each sample type, at least three replicates were measured, and each measurement contains three cycles of colouration and two cycles of decolouration. Therefore, for each sample type (dye type) a total of nine and six data sets were collected for colouration and decolouration, respectively. The colour reflectance data (latter converted into *K/S* values) in each cycle was collected every two seconds interval. For ruby-red dyed samples, 500 s activation and 1000 s deactivation time were used, which account for 250 and 500 data points, respectively. For samples dyed with sea green, the photochromic textile is activated for 300 s (150 data points) and deactivated for 400 s (200 data points). These time intervals were selected during a setting up the test conditions before the main measurement. The obtained experimental data set was then fitted to a first-order kinetic model using **Equation (3.10)** for all-inclusive analysis. The normalized experimental data and fitted curves for unwashed ruby red and sea green dyed samples are presented in **Fig. 6.1** as a representative to show the fitting procedure.

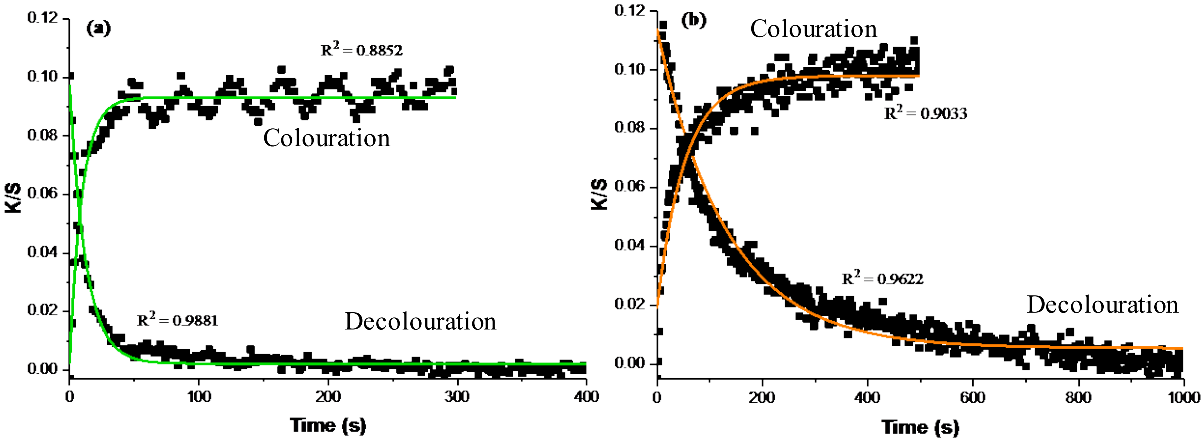


Fig. 6.1 Fitting of the average experimental data (colouration and decolouration) of polyester fabric samples dyed with (a) sea green and (b) ruby red photochromic dyes. The smooth lines indicate the fitted data curves.

According to the obtained R^2 values, the model could describe more than 90% of the variability in the response variable (*K/S*) which is fair to analyse the kinetics of the photochromic dyes applied to polyester fabric. Based on our observation, the model fits well for all samples except for colouration data of ruby red samples (unwashed sample only) which seems its degree of photo colouration is underestimated compared with the distribution of the experimental data. However, for this study, the obtained fitted data and the observations made was enough to make comparisons between the behaviour of the dyes on the fabric as the degree of photo colouration exhibited by both dyes is almost similar.

6.2.2 Photochromic behaviour of dyes in solution and on polyester fabric

The first experiment was concerning about studying the behaviour of the two commercial photochromic dyes, sea green from spirooxazine and ruby red from naphthopyran dye classes in solution and after incorporated into the polyester fabric using $scCO_2$ dyeing technique. Thus, the photochromic behaviour of the dyes in solution and on polyester fabric has been compared. To study their behaviour in solution, a non-polar solvent, hexane, which have similar polarity with CO_2 [264] was used to minimize the solvent effect and establish a better comparison. In solution, the absorbance was measured by exposing the dye solutions (0.05mg/ml) using UV light (UV torch with a maximum emission wavelength at 395-400 nm) for different exposure times. Absorbance at their maximum wavelength (i.e. 472 nm for ruby red and 600 nm for sea green) were collected. To examine the photochromic behaviour of dyes incorporated into the fabric, $scCO_2$ dyed fabric samples were used. Continuous measurement of the photo-colouration during UV irradiation and the decolouration after removal of the UV light was performed using a specially designed photochrom instrument as presented in the method section to assess the photochromism. A bathochromic shift (red shift) of the wavelength maxima was observed after incorporated into the fabric compared to the corresponding dye solution. For ruby red, the peak was shifted from 472 nm in solution to 500 nm on the fabric, while for the sea green the peak was shifted from 600 nm in solution to 620 nm on the fabric. Thus, the colour analysis of each dye on the fabric was made at their dominant wavelength (i.e. 500 nm for ruby red and 620 nm for sea green). Since different UV-sources and powers are used for activation of the samples (the fabric and solution), a direct and quantitative comparison of $\Delta K/S$ and absorbance values was not possible. Nevertheless, the data can give enough information on trends of maximum colour yields. According to the results, both dyes showed a reversible colour changing properties during UV light exposure and reverted to their original non-coloured state when the UV light is removed in both media (on the textile and in solution).

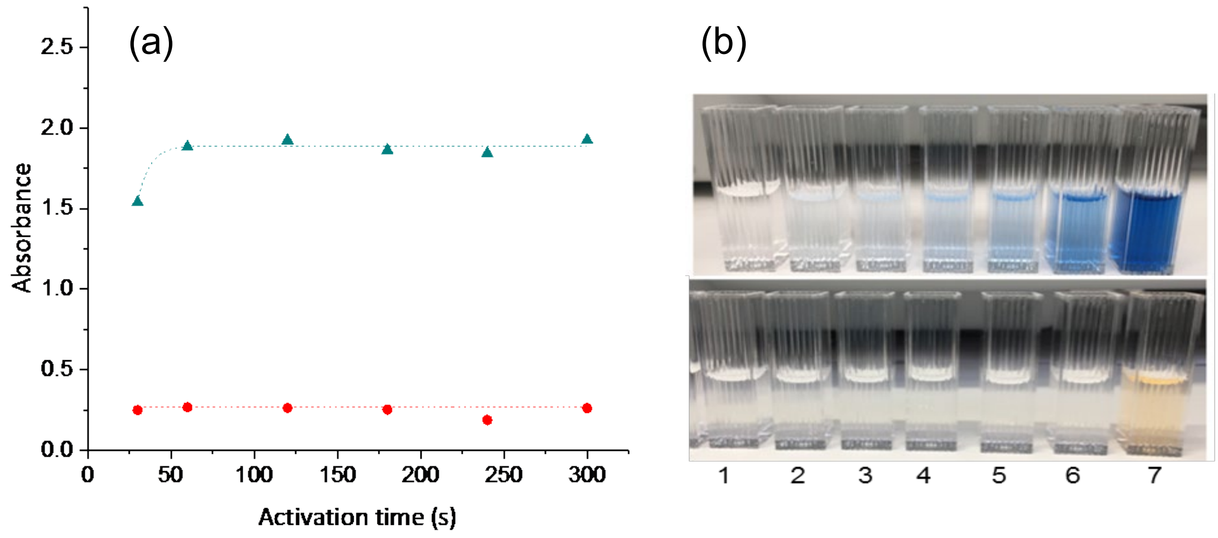


Fig. 6.2 (a) Absorption spectra of ruby red (●) and sea green (▲) in hexane at different UV activation times and (b) Colour reversion of the dye solutions directly after removal of the UV source after each activation times. The cuvettes on the top are sea green and those at the bottom are ruby red dye solutions in hexane. Cuvettes from left: (1) reference cuvette with solvent only, (2) 30 s, (3) 60 s, (4) 120 s, (5) 180 s, (6) 240 s and (7) 300 s activation [265].

As illustrated in **Fig. 6.2** and **Fig. 6.3**, the colour yield of sea green was relatively higher both in solution and on the fabric compared with ruby red but the difference was only marginal. However, the rates kinetics of the dyes applied to the fabric showed contrasting behaviour compared with their behaviour in solution. Ruby red showed faster photo colouration and fading rates in solution while its kinetics became slower when incorporated into the polyester matrix. On the other hand, sea green showed slower switching speeds in solution and faster rate of colouration and decolouration on the fabric. In solution, (referring to **Fig. 6.2 (a)**), the maximum absorbance of ruby red reached within 30 s of UV activation (linear fit) while for sea green it needs at least 60 s to reach maximum absorbance (exponential fit). **Fig. 6.2 (b)** illustrates the reversion to uncoloured state of the dyes in the same solution (in hexane). Upon UV exposure, colourless dye solutions become coloured, sea green becomes deep blue, and ruby red becomes light orange. All the cuvettes of the sea-green dye still show a colour (top) while for ruby red dye solution (bottom), only the cuvette used for the last activation was coloured, which confirms fast decolouration for ruby red and slow fading rate for sea green in solution.

On the textile (**Fig. 6.3**), sea-green showed faster colouration upon UV exposure and decolouration when the UV light is removed. For example, sea-green dyed samples took less than 20 s to revert to their uncoloured state but for samples dyed with ruby red, more than 200 s was needed to fade back to its original colour, which is significantly slower. Differences in the kinetic behaviour of photochromic dyes in solution compared to the behaviour in the solid-state applied in matrices were reported. Generally, photochromic dyes tend to give slower switching speeds when incorporated into fabric structure as the dye molecules become physically restricted by the rigid polymer matrix, which slows down their photochromic transformations [232, 266]. In addition to the surrounding media, the inherent structure of the photochromic dyes also plays a significant role in the photochromic properties. Spirooxazine dye classes are relatively bulky and rigid in their molecular structure compared with naphthopyran dye classes due to the indoline ring [245, 267]. This may restrict their photochromic conversion, which makes the conversion speed relatively slower in solution. On the fabric, however, this rigidity behaviour prevents from efficient penetration of the dye molecules into the rigid polymer matrix resulting the dye molecules to be located close to the fabric surface [241]. Thus, this can give them better space and freedom favouring faster photochromic conversion as the conversion involves a significant change in geometry facilitated by more free space. On the other hand, naphthopyran dyes are more flexible favouring faster photoisomerization in solution as well as easy penetration into the polymer matrix when applied on the fabric. Being penetrated inside the polymer matrix, they are in a more restrictive polymeric environment which slows down the configuration change of photochromic molecules. Similar to our result, naphthopyran based dyes applied to polyester by using exhaust dyeing and printing techniques consistently showed slower switching speeds compared to spirooxazines, which are fast-switching, but more temperature-sensitive [242, 245, 256].

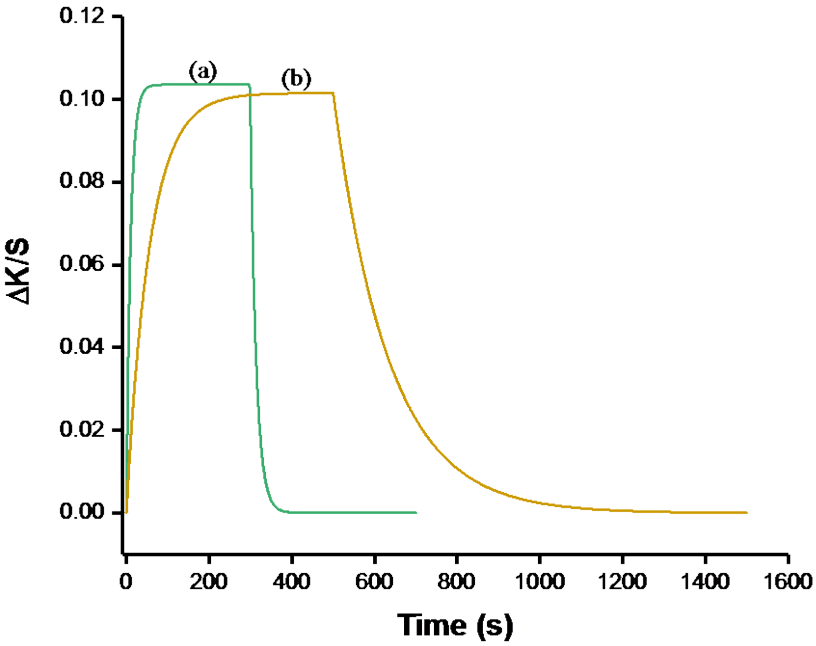


Fig. 6.3 Fitted curves for colouration and decolouration of photochromic dyed polyester fabric upon UV exposure and relaxation (a) sea green and (b) ruby red. The values are normalized to have the same initial and final value.

6.2.3 Colour yield (*ΔK/S*) of photochromic dyed fabrics

The ability to impart intense photo colouration on exposure to UV light is a very important property of photochromic materials because it is useful in detecting UV irradiations easily. Both dyes showed intense colour development characteristics upon exposure to UV light. **Fig. 6.4** shows the fitted average colour strength values of dyed polyester fabric samples upon UV irradiation. According to the results of the fitted data, the average colour strength values (*ΔK/S*) of the samples was 0.096 and 0.088 for samples dyed with sea-green and ruby red, respectively upon UV irradiation. However, the difference in the colour yield values between the two dyes is not statistically significant suggesting their similar colourability property. Generally, photochromic dyes often display different performance in terms of colour yield due to their inherent specific structural differences. According to some reports, a relatively higher degree of photo colouration by some specific dyes from spirooxazine dye classes has been obtained compared with naphthopyran based dyes. However, there was no obvious correlation between the degree of colouration and a chemical class of dyes. Differences in the level of photocolouration are mainly due to dissimilarities in the particular chemical nature of individual dye structures [242]. The washing and abrasion tests caused a significant reduction on the colour strength of the sea green dyed samples compared with samples dyed with ruby red (see **Fig. 6.4**). This suggests the limited dye penetration of sea-green dye molecules which could affect the colourability of these dyes. According to reports, some spirooxazine based dyes are relatively bulky and rigid in their molecular structure. This may limit the dye molecules from penetrating the polymer matrix to become concentrated near the fibre surface [241]. Therefore, these dye molecules concentrated close to the surface of the fibre could have better space for effective photoisomerization, resulting in a relatively higher colour yield. On the other hand, for ruby red dyed samples, the higher background colour as established from background colour result (**section 6.2.6**) indicates the presence of a higher number of permanently coloured ring-opened dye molecules trapped inside the polymer matrix. This means the number of ring-closed dye molecules which are capable of reversibly opening and closing the heterocyclic ring structure decreases. Consequently, this may lead to a relative decrease in the colour yield during photoisomerization [256]. However, these suggestions are based on the general dye structure of the two dye classes which could not be exactly true for the specific dyes used in this study in which their colour yield is almost similar.

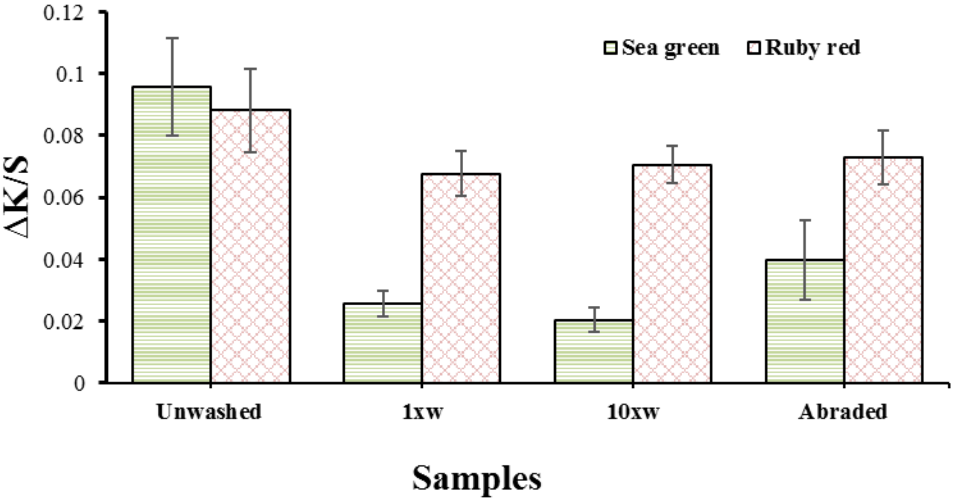


Fig. 6.4 Comparison of average colour strengths of samples dyed with sea green and ruby red photochromic dyes in $scCO_2$ upon UV exposure. (Sample notation: 1W = one wash cycle, 10W = ten wash cycle)

6.2.4 Colouration and decolouration rates

The rate of colourability and reversion indicates the detection speed of photochromic colourants towards UV light which have important practical implications. The average rate constants of the experimental data fitted to the first-order kinetic model are presented in **Fig. 6.5** and **Fig. 6.6**. Results showed that samples dyed with ruby red had a significantly slower colour development upon UV exposure and faded much more slowly when the UV source is removed regardless of the washing condition. On the other hand, sea-green dyed samples consistently displayed faster colouration and decolouration speeds compared with ruby red dyed samples. One reason for faster colour development by spirooxazine based sea-green dye molecules is possibly due to the limited dye penetration owing to their non-planar and bulky molecular structure. Being located close to the surface might lead to a fast response as they are relatively free, favouring faster ring-opening and closing.

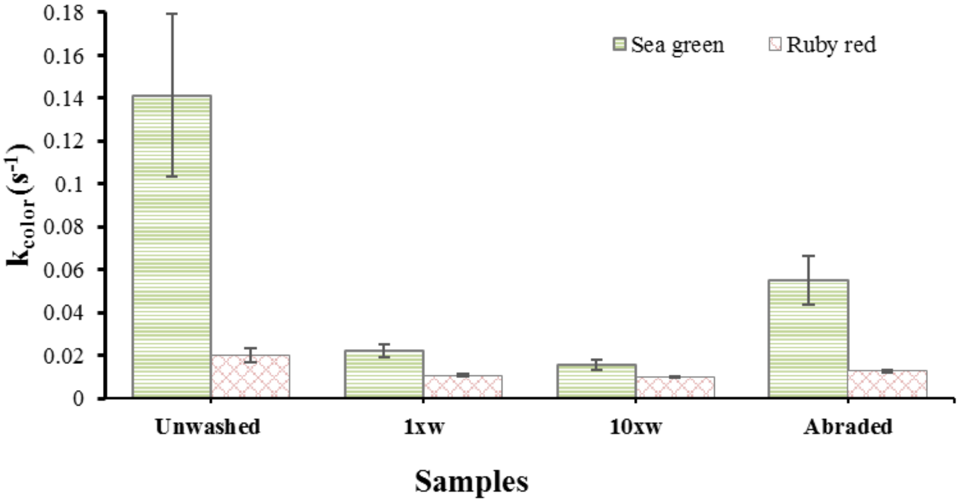


Fig. 6.5 The rate of colouration of $scCO_2$ dyed photochromic polyester fabric samples upon UV irradiation

Similar fast colour development was reported by spirooxazines printed on the cotton fabric compared with naphthopyrans. A more pronounced photochromic effect was also reported when the dye molecules are located close to the fabric surface in the case of screen printing [244]. For samples dyed with ruby red, on the other hand, the dye molecules are believed deeply penetrated the polymer matrix as demonstrated from their better wash fastness result and higher background colour. These deeply penetrated ruby red dye molecules are thus physically restricted by the polymer matrix environment leading to slower response speed. Generally, a considerable change of molecular geometry happens during photo colouration (from non-planar to planar form) which may be inhibited by the semi-crystalline nature of polyester. In all the cases, the fading rates are lower than the rate of colour build-up irrespective of the dye type and washing or abrasion conditions. For example, the rate of colouration for ruby red dyed samples is more than twice higher than the decolouration rate (see **Fig. 6.5** and **Fig. 6.6**).

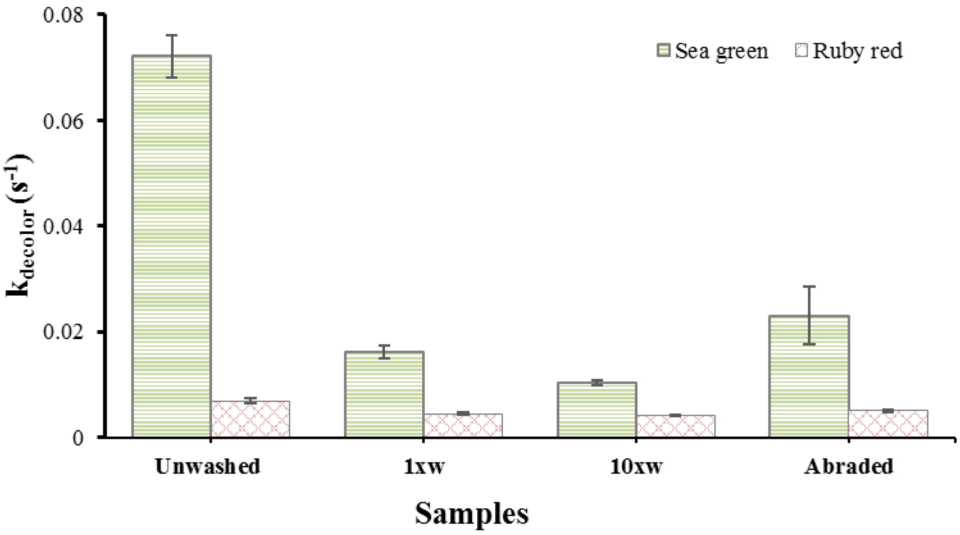


Fig. 6.6 The rate of decolouration of $scCO_2$ dyed photochromic polyester fabric samples after UV is off.

6.2.5 Halve-lives ($t_{1/2}$)

The rate of colour development and fading of photochromic materials can also be explained by analysing the half-lives ($t_{1/2}$) of colouration and fading. The half-life of colouration ($t_{1/2col}$) is the time required for absorption to reach half of its maxima upon UV irradiation and similarly, the half-life of fading ($t_{1/2deco}$) is the time taken to fade from absorbance maxima (K/S_∞) when the UV light is removed [155]. The half-life values give information about the rate kinetic behaviour of the dyes during their initial part of colouration and decolouration. **Table 6.1** presents the half-life values of samples recorded during colouration and fading before and after washing. Lower numerical values of $t_{1/2}$ indicate faster colouration and decolouration speeds and vice versa. According to the results, ruby red dyed samples showed relatively slower colouration and fading rates, expressed by larger half-lives of colouration and fading, compared with sea-green dyed samples regardless of the washing condition. The rate kinetics generally becomes slower after every washing cycle for both dyes. These results are consistent with the rate of kinetic results presented in the previous section. A similar trend of rate kinetics was also observed in a previous study of the same classes of photochromic dyes applied to polyester fabric using exhaust dyeing method [242]. Based on previous reports, spirooxazine based dyes consistently exhibited a higher rate of colouration and fading compared with naphthopyrans in agreement with the current study. One notable observation was that (see **Table 6.2)** the half-life of fading values of the same class of dyes applied by $scCO_2$ dyeing is significantly lower than those obtained when applied by aqueous or solvent-based dyeing methods [242, 251] and comparable with the values obtained by digital inkjet printing method [256, 257, 268].

Table 6.1 Half-lives ($t_{1/2}$) of colouration and decolouration of dyes applied to the polyester fabric using $scCO_2$ dyeing.

Sample	Half-lives (s)					
	Colouration			Fading		
	Unwashed	Washed (1W)	Washed (10W)	Unwashed	Washed (1W)	Washed (10W)
SO-SG	5.2±1.3	31.5±4.3	44.9±6.3	9.6±0.5	43.2±3.2	66.3±3.0
NP-RR	35.6±4.9	65.3±4.2	69.8±1.3	100.2±6.2	155.3±8.6	163.7±3.3

(*1W = one wash cycle, 10W* = ten wash cycles)

As can be seen from the comparison in **Table 6.2,** the smallest half-life of fading (0.15 min) was achieved by $scCO_2$ dyed samples with spirooxazine (Sea green) followed by inkjet printed spirooxazine dye using UV-curable ink and solvent-based ink. Thus, in addition to the environmental, resource efficiency, and uniform treatment advantages of $scCO_2$ dyeing method, improvement of the kinetics switching speed is another commercially important advantage. In general, it could be suggested that the nonplanar molecular structure of photochromic dyes limit the penetration level into the rigid polyester matrix as demonstrated by poor wash fastness properties and faster fading rates.

Table 6.2 Comparison of the half-life of fading of photochromic dyes applied to the polyester fabric by using different application methods

Application method	Dye class	$t_{1/2decol}$ (min)	Reference
Exhaust dyeing	SO	3.1*	[251]
	NP	18.1*	
Solvent dyeing	SO	3.1*	[251]
	NP	11.5*	
Digital inkjet printing	SO	1.0, 0.9*	[256], [268]
	NP	5.1, 0.8*	
$scCO_2$ dyeing	SO	0.15	Current work
	NP	1.8	

*The minimum half-life of fading values achieved

6.2.6 Background colour

The permanent shade of the photochromic fabric samples developed during high-temperature dyeing process was also evaluated. According to previous reports, the background colour influences the photochromism of the photosensitive dyes applied to textile. The background colour of the samples was measured in terms of *K/S* and colour difference (CIE ΔE) before UV exposure. The ΔE values are the colour difference between the undyed fabric and fabric after dyeing without UV irradiation. Large numerical value means higher background colour or deep shade. Generally, samples with ΔE value from 2 to 4 have perceivable colour difference and those between 4 and 5 have significant colour difference [269, 270]. From the results in **Table 6.3**, samples dyed with ruby red had a relatively higher ΔE value (deeper colour) with values above 2 illustrating perceivable colour difference (higher background colour). On the other hand, the samples dyed with sea-green displayed ΔE values less than 2 assuring less significant (non-perceivable) colour difference. Similar results were also observed from the results of the *K/S* value **(Fig. 6.7)**, in which samples dyed with ruby red had a relatively higher K/S value compared with sea green-dyed ones.

Table 6.3 Average CIE ΔE values of photochromic dyed polyester fabrics and their washed counterparts

	Treatment		
Samples	Unwashed	Washed (1W*)	Washed (10W*)
Sea green	1.47±0.12	1.35±0.13	1.28±0.08
Ruby red	2.81±0.15	2.69±0.08	2.62±0.07

Photochromic dyes which are normally uncoloured becomes coloured when applied to textile because of the application conditions. The presence of thermochromism and thermal instability of the dyes during dyeing are the main causes for the development of background colour in which the later one is believed to be the dominant one [242, 251]. At a higher treatment temperature, the non-planar ring-closed form of some photochromic dye molecules is converted thermally to their coloured planar merocyanine form and subsequently locked in this form within the textile structure, resulting in permanent colour. This phenomenon is more pronounced in the case of naphthopyran based ruby red dye molecules as they are believed to have better penetration as demonstrate form its better wash fastness results. Because, once they are penetrated in their open form, it could be more difficult to switch back to their uncoloured state due to the matrix effect resulting in a higher background colour. Conversely, sea green dye molecules located close to the fabric surface have a relatively better free space suitable for effective thermal fading, resulting in a reduced background colour [233, 244]. Furthermore, the effect of background on the photo colouration could be noticed from the results. Ruby red with higher background colour exhibited a slightly lower colour yield. It seems the developed colour decreased as a result of increased background colour due to the presence of relatively higher ring-opened dye molecules (lower ring-closed molecules) and the reverse is true for sea green-dyed samples. This suggests that the background colour is mainly derived from the ring-opened dye molecules formed during the dyeing process.

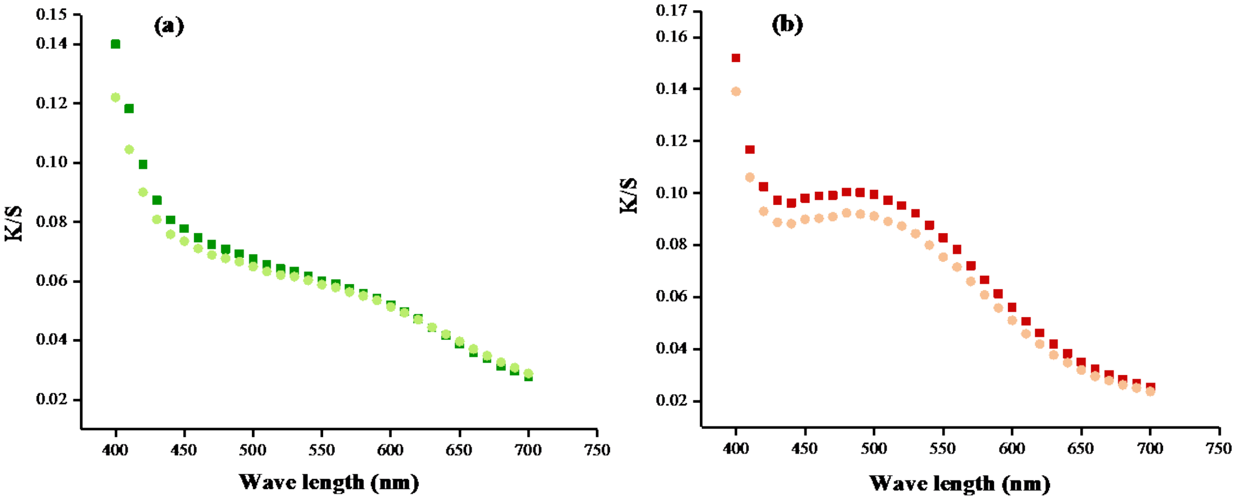


Fig. 6.7 Background colour of polyester samples dyed in $scCO_2$ (a) Sea green and (b) Ruby red before (■) and after (●) washing.

6.2.7 Durability and fastness properties

The colour fastness of the background colour was evaluated through measurement of the colour strength after washing cycles. For evaluation of the durability of photochromic property against washing, a comparative study of the photochromic colour build-up and fading properties were examined before and after washing. As can be seen from the results of the background colour strength and ΔE values, (**Fig. 6.7** and **Table 6.3)** the washing had a minimum influence on the background colour of both dyes. On the other hand, as presented in the figures of the previous sections (**Fig. 6.4, Fig. 6.5,** and **Fig. 6.6**), the degree of photo colouration decreased progressively with washing cycles irrespective of the type of photochromic dye used. A larger reduction in colour yield, a slower rate of photoisomerization, and larger half-lives were observed after the first wash but the effect after ten washing cycles was less significant. Among the two dye classes, samples dyed with sea-green showed a significantly lower wash fastness (27%) while ruby red dyed samples exhibited better wash fastness (77%). The relatively better wash fastness behaviour by ruby red dyed samples suggests enhanced penetration or better affinity towards polyester compared to samples dyed with sea green. As presented in **Table 6.4**, the colour switching speeds decreased for both dyes after washing while their performance was significantly different when compared to each other. For sea-green dyed samples, a reduction of more than six times in $k_{colouration}$ and more than four times in $k_{decolouration}$ was observed after the first washing cycle. On the other hand, the reduction in the rate of fading after washing was minimum for ruby red dyed samples. When we look the effect of the washing cycles, much of the colour was lost during the first washing cycle while the colour lost after ten washing cycles was small compared with the colour lost during the first wash

Table 6.4 Rate constants of $scCO_2$ dyed photochromic samples before and after washing

	Rate constants (k in s^{-1})					
	$k_{colouration}$			$k_{decolouration}$		
Sample	Unwashed	1xw	10xw	Unwashed	1xw	10xw
SO-SG	0.1413	0.0222	0.0157	0.0721	0.0161	0.0105
NP-RR	0.0199	0.0107	0.0099	0.007	0.005	0.0042

After abrasion, a fluffy surface with protruded fibres coming out to the surface of the fabric was observed for both samples. As illustrated in **Fig. 6.4**, the colour yield of sea-green dyed samples decreases significantly after abrasion while a slight decrease in colour yield was observed for ruby dyed samples. This result further confirms the limited dye penetration of sea-green dye molecules in which those dye molecules near the surface are removed easily during rubbing cycle. However, for ruby dyed samples, only a slight decrease in colour strength was observed after abrasion suggesting the presence of a small number of dye molecules on the fabric surface. Abrasion had the same but intermediate effect on both the colour build-up and fading rates in which the effect is more pronounced for sea-green dyed samples exhibiting slower kinetics after abrasion (see **Fig. 6.5** and **Fig. 6.6)**. In conclusion, the weak washing and rubbing fastness property displayed by sea-green dyed samples indicate the limited dye penetration while the relatively better wash fastness behaviour exhibited by ruby red dyed samples suggests enhanced penetration of the dye molecules into the fibre structure. The non-planarity and bulk characteristics of sea-green dye molecules as explained earlier or presumably a weak affinity property towards polyester fibre could be the reasons for the limited penetration into the compact polyester structure [241]. Nevertheless, the colour yields and rate kinetic values of sea green are still better than ruby red even after repeated washing and rubbing cycles when compared with each other.

6.3 Conclusions

In this study, the two most important commercial photochromic dyes from spirooxazine and naphthopyran dye classes are successfully applied on polyester fabric using $scCO_2$ dyeing technique. The photochromic behaviour of these dyes in solution and applied on polyester fabric has been investigated. Both dyes exhibited reversible colour changing behaviour when exposed to UV light and revert to their original colour fast enough when the UV light is removed both in solution as well as applied on polyester fabric. When incorporated into the polymeric matrix, photochromic molecules showed a similar trend of colour strength but contrasting reaction kinetics was observed compared with their behaviours in solution. On the fabric, the sea-green from the spirooxazine family had a slightly higher colour yield, faster colouration, and decolouration, and poor wash fastness properties compared with the ruby red from naphthopyran dye class. However, the colour yield and rate kinetics were significantly reduced after washing and abrasion of sea-green dyed samples while the effect was almost negligible for ruby dyed samples. One interesting observation was that the half-lives of fading of both dyes applied from $scCO_2$ solvent were found to be relatively low compared to conventional exhaust and solvent dyeing techniques and are comparable with samples produced with digital inkjet printing method. Overall, the results showed that supercritical CO_2 dyeing is a viable technique to incorporate photochromic spirooxazine and naphthopyran based dyes into the polyester fabrics. The obtained photochromic dyed polyester fabrics showed the required technical performances suitable to develop a flexible textile-based sensor for applications such as identification of the intensity of UV radiation. Moreover, as photochromic dyes are relatively expensive, $scCO_2$ dyeing would be an ideal technique to develop photochromic textiles in a resource-efficient and eco-friendly way.

Chapter 7

Functionalization of cotton fabric with pH indicator dye using photo grafting technique for pH sensing smart textile application

In this chapter, the experimental results concerning the production of a smart textile pH sensing fabric with a pH indicator dye, Nitrazine yellow (NY) modified with methacrylate moiety (GMA-NY) by photo grafting technique is presented. The study explored the photo grafting reaction and the halochromic property of the functionalized fabric at different pH conditions. This work was aimed to compare the performances of the functionalized fabrics produced by photo-grafting and $scCO_2$ dyeing methods. Unfortunately, dyeing of cotton with NY using $scCO_2$ was not successful and only the results concerning photo grafting is presented here. The content of this chapter has been published as part of paper VII.

7.1 Introduction

Chromic materials change their colour upon alteration of external stimuli, such as temperature (thermochromism), light (photochromism), electricity (electrochromism), solvent polarity (solvatochromism), pH (halochromism), and so on. They are very useful materials that can be used as a warning signal when there is a change in these external sources. Consequently, studies about such materials that undergo a reversible change in colour upon the application of an external stimulus have been extensive [266]. In recent years, there has been an increasing interest in the development of textile-based sensors by incorporating these chromic materials to the textile structure owing to several advantages. Specifically,textile-based sensor systems are flexible, breathable, easy to handle, and comfortable compared with the conventional sensor systems. They also have an advantage of large area coverage while providing local signals which have a wide variety of applications [271]. However, researches are mainly focused on thermochromic and photochromic functionalities while studies about-sensitive textiles are much limed despite its great value for various textile applications.

Materials with pH-sensitive capability are very useful as the degree of acidity or basicity is an important parameter in different situations [272]. These materials can have important textile applications in the area of medical textile such as wound dressing to follow up the healing process [273]; in protective clothing to identify toxic or harmful vapour, and in the filtration process to assess the acidity of water [274]. They can be also used to monitor biochemical changes in body fluids, such as sweat. For example, a wearable textile pH sensor can measure the dehydration level of athletes during exercise by directly monitoring the sweat pH [275]. Because of this, there has been an increasing interest in the development of pH-sensitive textiles by incorporating various functional dyes to the textile structure [276]. Nitrazine yellow, 2-(2,4- dinitrophenylazo)-1-hydroxynaphthalene-3,6-disulfonic acid disodium salt) is among these indicator dyes, that have been studied widely especially for refined pH determination [277, 278]. Several techniques such as conventional printing [279], exhaust dyeing [276, 280, 281], sol-gel method [274, 282-285] and electrospinning [286-290] have been used to develop halochromic textiles. However, the conventional dyeing processes have some issues such as the requirement of long dyeing time at high temperature, insufficient exhaustion and fixation levels, and discharge of contaminated dye as a waste which makes it environmentally unsafe. In addition, some challenges such as compatibility between pH indicators and the textile, dye leaching, and slow response speed of the dyes when incorporated into the textile matrices have been reported [282]. Therefore, an alternative method to incorporate these functional dyes on textiles durably with minimal amounts of water, time, and energy is highly needed.

Photo-induced grafting using UV radiation is among the most useful and feasible methods of graft polymerization because of its simplicity, safety, and least deteriorating effect as lower radiation energy is used. It has been widely used to modify fibre properties for specific end uses using different kinds of monomers. The common grafting process is based on a mechanism that the UV induced radical abstraction of hydrogen from the polymer, and these formed polymeric radicals initiate graft polymerization [291]. Photoinduced copolymerization of cellulose with the use of various photoinitiators has been reported. Graft copolymerization of glycidyl methacrylate and hydroxyethyl methacrylate onto cotton using suitable photoinitiators has been used to modify the property of cellulose [292, 293]. Hong *et al.* [294] grafted polyacrylamide onto cotton fabrics using longer UV wavelength irradiation to improve the thermal stability of cotton. Unsensitised, photoinitiated grafting of GMA onto cotton fabrics has been successfully carried out by Harris *et al.* [295]. Recently, Dong *et al.* synthesized a novel bifunctional quinizarin dye-containing photoactive methacrylate groups and photo-grafted onto cotton and wool fabrics using the same technique [296].

This study aims to develop textile-based pH sensing fabric using simple and economical photo grafting technique. An azo pH indicator dye, Nitrazine Yellow modified with photoactive glyceryl methacrylate (GMA-NY) group was photo grafted onto cotton fabric using benzophenone as a photoinitiator at room temperature. The photo grafting reaction and the halochromic property of functionalized fabrics were evaluated.

7.2 Summary of results

7.2.1 Photo grafting mechanism

The photo grafting mechanism of GMA-NY dye onto cotton fabric can be described as illustrated in **Fig. 7.1**. During UV irradiation, the photoinitiator molecules in their ground state absorb photons and produce triplet state excited species. The photoexcited photoinitiator abstracts hydrogen from the hydroxyl group of cellulose and the cotton substrate acquires free radicals [297]. These cellulose free radicals initiated GMA-NY to undergo photoinitiated graft polymerization and crosslinking of the dyes containing methacrylate groups onto cotton [296]. The cellulose radicals can attack the carbon double bond of methacrylate groups of GMA-NY forming a covalent bond between monomer and cellulose initiating the chain propagation reaction. Thus, upon irradiation of UV light and in the presence of a photoinitiator (PI), graft chains of GMA-NY can be grown from the cellulose backbone of cotton fabric as schematized in **Fig. 7.1 b**.

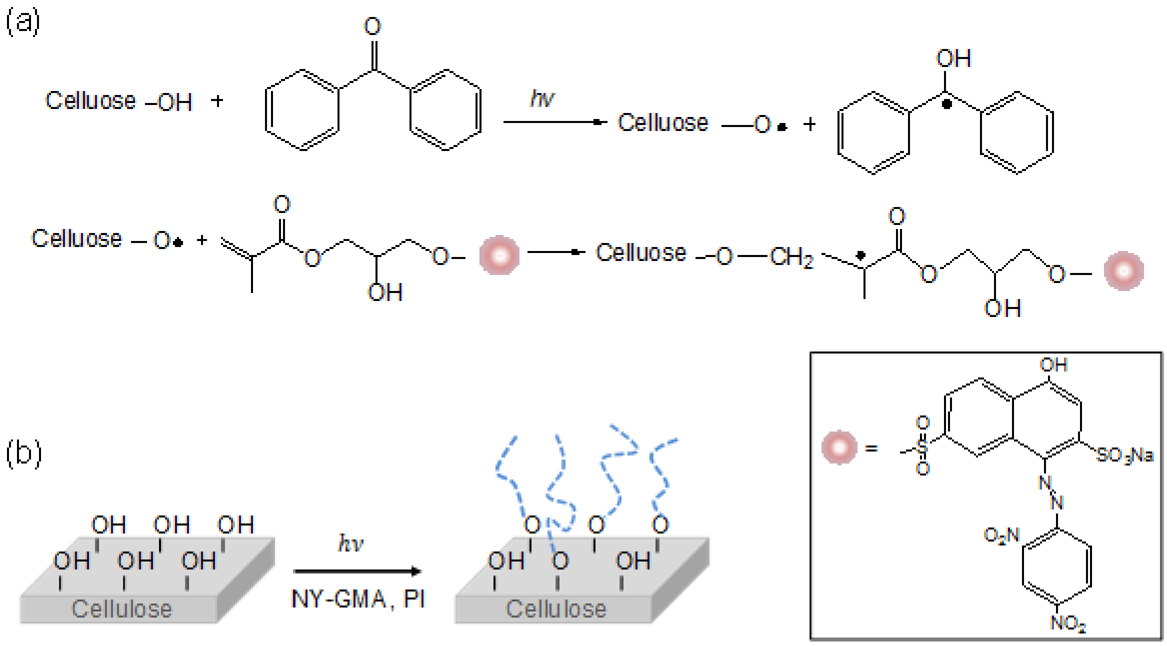


Fig. 7.1 Photo grafting of GMA-NY onto cotton fabric in the presence of photoinitiator (Benzophenone): (a) Mechanism of photo grafting reaction of GMA-NY onto cotton (b) scheme of the photo grafting process.

7.2.2 Impregnation and grafting process

Initially, the optimized impregnation time was determined by immersing the fabric samples into the dye solution for different periods between 10 and 60 s and subsequently measuring the wet pick up. The results showed that the impregnation of the samples was very fast reaching plateau in a few seconds. For this study, impregnation time of 30 s with a wet pick up of around 85% was selected. After impregnation, the photo grafting process was performed in which the cotton fabric samples were subjected to UV irradiation, washing, and drying.

After the photo grafting process, ATR-FTIR measurements were performed to investigate the grafting of GMA-NY monomers onto cotton fabric. A comparative analysis of the FTIR spectrum of the dye solution, cotton fabric grafted with GMA-NY after thoroughly rinsing with the dye, and non-treated reference fabric was performed to confirm the occurrence of photo grafting (see Fig. 7.2). From the FTIR spectrums, the main characteristic peaks of cellulose are present at 3500 – 3000 cm^{-1} for O-H stretching, 3000-2800 cm^{-1} corresponds to C-H stretching, 1429 – 1202 cm^{-1} assigned to C-H wagging, C-H deformation stretching and O-H in-plane bending, and 1160 – 895 cm^{-1} is a contribution from asymmetric bridge C-O-C, asymmetric in-plane and out-of-phase ring stretch, C-O stretch [298].

In the FTIR spectrum of GMA-NY dye solution, the peaks at 3000-2800 cm $^{-1}$ are assigned to C-H asymmetric stretching vibrations, 1716 cm $^{-1}$ corresponds to ester carbonyl stretching, 1637 cm $^{-1}$ for C-C stretching (in the acrylic moiety of GMA), and 940 cm $^{-1}$, assigned to C=C wagging (in the acrylic moiety of GMA). In the FTIR spectrum of photo grafted cotton, the peaks attributed to the dye solution are present, but it seems the main GMA-NY peaks are covered by the strong vibrational peaks of the cellulose structure making it difficult to characterize the functionalization process. However, the band at 1720 cm^{-1} (C=O stretching) can be recognized as a characteristic peak of the GMA-NY dye grafted on cotton. The intensity increase observed at 2851 cm^{-1} for GMA-NY grafted sample may be due to a combined effect of C-H stretching vibration of the methyl group of GMA and C-H stretch of cellulose. Moreover, the absence of C=C wagging at 942 cm-1 confirms the successful grafting of GMA-NY onto cotton [299-301]. Overall, the results of the FTIR analysis demonstrate that the GMA-NY has been successfully grafted onto cotton fabric using the photo grafting technique.

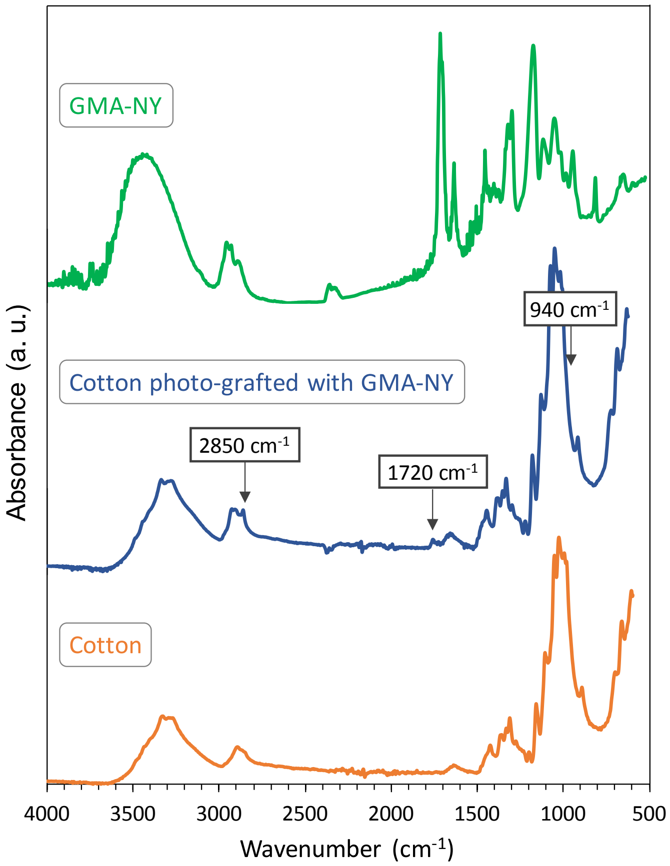


Fig. 7.2 Comparison of FTIR –ATR spectra of NY – GMA dye solution, non-treated cotton fabric, and photo grafted cotton fabric with NY - GMA

7.2.3 Halochromic property

Initially, the pH response of GMA-NY dye solution was examined through UV-vis measurement of the dye solution before and after exposure to UV light to confirm the influence of UV irradiation on the halochromic property. According to the result, it was concluded that the pH response of GMA-NY was not affected by the UV irradiation. According to the UV-vis measurement, absorbance maximum of the GMA-NY solution was 463 nm and 590 nm in acidic and alkaline conditions, respectively. It was also observed that the halochromic response to acidic and alkaline conditions takes place in the pH range between 6 and 7. The halochromic behaviour of functionalized cotton fabric samples was evaluated by measuring their colour change through spectrophotometer analysis at different pH condition both in wet and vapour environments. Non-treated cotton fabric was used as a standard sample and photo grafted cotton fabric before exposure to different pH conditions was used as a control sample. All grafted samples demonstrated a visible and fast colour change when introduced to pH environments: turned into yellow in acidic condition and blue in alkaline condition. This change in colour was also quantitatively confirmed by the *K/S* versus wavelength spectra under various pH conditions as shown in **Fig. 7.3**. A typical *K/S* spectrum of yellow colour can be observed at acidic pH condition and the alkaline pH condition showed a typical *K/S* spectrum of blue colour. When the pH response of samples was compared in wet and vapour conditions, the response to alkaline pH in vapour condition is more pronounced, while the response was more pronounced to acidic pH in wet condition. This could be due to the difference in the accessibility of the dye molecules by the vapour and liquid pH media. In the case of vapour condition, the vapour molecule can easily penetrate and access the dye molecules better than the liquid molecules resulting in a more pronounced response. Besides, the alkaline media used (ammonia) in the vapour condition is more volatile than the acidic media used (HCl) that could cause a relatively higher level of exposure towards alkaline pH resulting in a more pronounced response for alkaline pH compared with acidic pH. Also, the longer exposure time used (24 h) during testing in vapour media could affect the halochromic response.

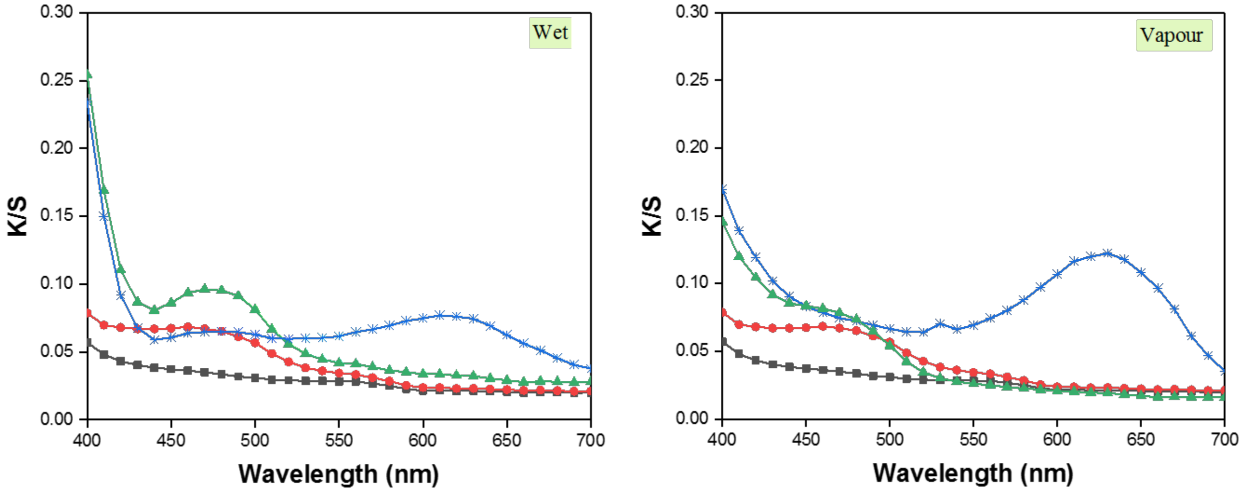


Fig. 7.3 Comparison of the pH response of samples, when subjected to aqueous (wet) and vapour pH environments: (■) standard- untreated, (●) control-treated, (▲) acid pH, (*) alkaline pH

Furthermore, ΔE and Δb values obtained from spectrophotometer measurements were also used to evaluate the colour difference of photo grafted samples before and after introduction to different pH conditions. These ΔE and Δb values provide a numerical descriptor of the colour difference between the sample (photo grafted cotton fabric after introduced to different pH baths) and a standard (photo grafted cotton fabric). The obtained ΔE values confirmed the presence of colour change when the samples are subjected to acidic and alkaline conditions (see **Fig. 7.4**). The ΔE values in a wet condition for both alkali and acidic conditions were almost similar while the alkali media showed a relatively higher ΔE value compared with acidic media in vapour condition. The measured Δb values showed an obvious colour change when subjected to acidic to alkaline pH conditions both in aqueous and vapour environments. The Δb values represent blueness – yellowness difference between a sample and standard colour. As seen from the results in **Fig. 7.4,** the photo grafted samples exhibited positive Δb (yellow) in acidic condition and negative Δb values (blue) colour in alkaline media. The photo grafted samples subjected to alkaline environment exhibited larger negative Δb value (Δb < -5) compared with those subjected to acidic media.

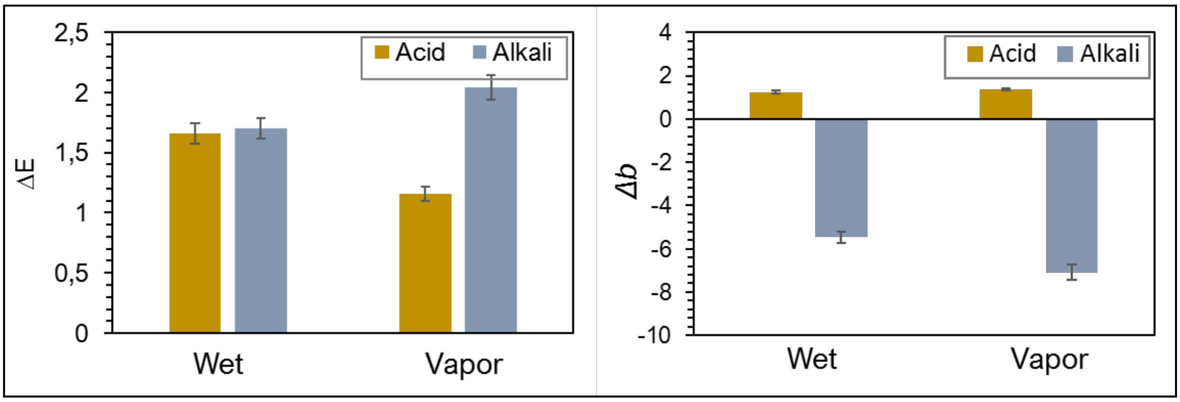


Fig. 7.4 ΔE and Δb values of GMA-NY grafted cotton fabric samples subjected to acidic and alkaline pH bath both wet and vapour environments

7.2.4 Conclusion

This study investigates surface functionalization of cotton fabric with a modified NY dye with a methylate group (GMA-NY) by using photo grafting technique. A simple fabric immersion technique was optimized, and subsequent photo grafting was performed by using UV irradiation in the presence of photoinitiator (benzophenone) under an inert atmosphere. The FTIR spectra of the cotton fabric samples before and after modification have been analysed to confirm the occurrence of the photo grafting. Furthermore, the halochromic property of fabric samples was analysed through CIELAB colour changes using UV-Vis reflectance measurements. The results of the FTIR demonstrated that the photo grafting was successful. The grafted fabrics with GMA-NY showed a visible colour change when subjected to acidic and alkaline environments (both in aqueous and vapour conditions). Thus, the photo grafting technique used in this study is a promising and economical alternative for surface functionalization of textile fabrics. Further investigation is necessary to test the halochromic performance of the photo-grafted cotton fabric with GMA-NY fabric in terms of on-body trials for potential applications in sport, fitness, healthcare, and medical fields.

Chapter 8

Conclusions and perspective

8.1 Conclusions

This thesis explores the production and characterization of functional and smart textiles using a resource-efficient and eco-friendly $scCO_2$ processing technology. It aimed at investigation of the feasibility of $scCO_2$ processing technology towards sustainable and economic production of functional and smart textiles. Besides, photo grafting of cotton fabric with a halochromic dye was also investigated as an alternative technique to functionalize textiles. The results obtained in this thesis are encouraging and gives an insight for a wider application of $scCO_2$ technology in the textile processing industry in the future. It will also open more opportunities in innovative green processing of materials useful for the development of new functional products. Based on the obtained results and observation made during the study, the following conclusions have been drawn.

- The results obtained in this thesis showed the feasibility and significant potential of $scCO_2$ impregnation and dyeing technique to produce various functional and smart textile materials
- In this work, we have identified suitable functional finishing agents such as chitosan biopolymers, curcumin natural dye, and photochromic colourants which are successfully applied to polyester fabric using $scCO_2$ processing technique.

- An approach towards combining the dyeing and functionalization processes through single bath (i.e. the dye and functional agent in a single formulation) as well as employing multifunctional colourants was proven effective which is important from economical production and environmental safety viewpoints for the designing of sustainable production processes.

- Novel single-step dyeing and functionalization of polyester using green agents such as curcumin and chitosan biopolymers in $scCO_2$ medium have achieved promising results. Using $scCO_2$, it was possible to avoid the substrate pre/post-treatment and use of the toxic metallic mordants which otherwise are required procedures in the case of conventional natural dyeing. This will be highly useful in the designing of an innovative and eco-friendly process to develop new functionalized materials in the future.

- The study showed that $scCO_2$ is a viable technique for dyeing of polyester fabric with photochromic spirooxazine and naphthopyran based dyes to produce photochromic smart textiles in a resource-efficient and eco-friendly way achieving faster colourability and fading kinetics compared to exhaust dyed and screen-printing methods and comparable performance with inkjet printing.

- The experimental studies showed that $scCO_2$ processing parameters greatly influence the colour and functional performances and an optimum processing condition has been determined. Among the processing variables, pressure and temperature were identified as the two important factors that affect the colour and functional performances.

- The results of the study demonstrated that the photo grafting technique is proven an effective alternative for surface functionalization of textiles. The photo grafted fabrics with GMA-NY showed good halochromic property when subjected to acidic and alkaline conditions both in aqueous and vapour environments.

Overall, in this thesis, an attempt has been made to address important challenges related to the conventional textile dyeing and functionalization processes and new knowledge has been gained to widen the application of $scCO_2$. The obtained results showed that $scCO_2$ processing is a feasible technique for the production of functional and smart textiles and could be an attractive alternative to conventional aqueous dyeing and impregnation methods with significant environmental and economic advantages. Thus, adopting this technique is highly important in improving the economics and environmental safety of textile dyeing and finishing processes eliminating wastewater discharge, reducing water, chemical, and energy consumptions, reducing drying and the associated air emissions.

8.2 Future work

This study can be considered as the first attempt that focused entirely on the functionalization of polyester fabrics with selected functional finishing agents using $scCO_2$ dyeing technique. This could motivate researchers and stimulate further investigations so that the advantages of $scCO_2$ impregnation technique can be effectively utilized for eco-friendly and resource-efficient textile dyeing and functional finishing processes. To fully exploit the advantages of this technology for the development of novel functional materials, it is important to explore other additional functionalities and associated functional finishing agents suitable for $scCO_2$ processing. The investigation carried out in this thesis used only polyester fabric as a model substrate. Thus, focus on other textile fibres apart from polyester could also be of interest to expand its application in the textile industry. Furthermore, studies regarding the solubility of functional finishing agents in $scCO_2$ could help to fully understand their behaviour in $scCO_2$ medium and their suitability in this technique. Within this, investigations focusing on the structure-solubility relationship of the functional agents would also be important for selecting or designing new functional agents suitable for $scCO_2$ processing. Concerning the functionalized cotton fabric using UV grafting, further studies on body trials would be necessary to test the pH sensing performance for potential practical applications such as sport, fitness, medical and healthcare fields.

References

[1] Smart Textile Market Growth & Trends, Grand View Research Inc., https://www.grandviewresearch.com/press-release/global-smart-textiles-industry, (2019), [cited October 30, 2019].

[2] Functional textile market: Global industry analysis and forecast 2016-2024, Persistence Market research, https://www.persistencemarketresearch.com/market-research/functional-textiles-market.asp, (2019), [cited October 30, 2019].

[3] Polyester fiber production globally 1975-2017, Statista Inc., https://www.statista.com/statistics/912301/polyester-fiber-production-worldwide/, (2019), [cited Oct 30, 2019].

[4] Z. Wang, M. Xue*, et al.*, Textile dyeing wastewater treatment, in: *Advances in treating textile effluent*, IntechOpen, (2011), 91-116.

[5] U. Rott, Multiple use of water in industry - the textile industry case, *Journal of Environmental Science and Health, Part A*, 38(2003), 1629-1639.

[6] A. A. Vaidya, Environmental pollution during chemical processing of synthetic fibers, *Colourage*, 14(1982), 3-10.

[7] J. Shore, *Cellulosics dyeing*, Society of Dyers and Colourists, (1995).

[8] F. M. D. Chequer, G. A. R. de Oliveira*, et al.*, Textile dyes: dyeing process and environmental impact, in: *Eco-friendly textile dyeing and finishing*, IntechOpen, (2013), 151-176.

[9] R. Kant, Textile dyeing industry an environmental hazard, *Natural science*, 4(2012), 22-26.

[10] C. R. Holkar, A. J. Jadhav*, et al.*, A critical review on textile wastewater treatments: Possible approaches, *Journal of Environmental Management*, 182(2016), 351-366.

[11] T. Robinson, G. McMullan*, et al.*, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource Technology*, 77(2001), 247-255.

[12] F. I. Hai, K. Yamamoto, *et al.*, Hybrid treatment systems for dye wastewater, *Critical Reviews in Environmental Science and Technology*, 37(2007), 315-377.

[13] F. Mohammad, Emerging green technologies and environment friendly products for sustainable textiles, in: *Roadmap to sustainable textiles and clothing*, Springer, (2014), 63-82.

[14] T. Abou Elmaaty, E. Abd El-Aziz, Supercritical carbon dioxide as a green media in textile dyeing: a review, *Textile Research Journal*, 88(2017), 1184-1212.

[15] M. V. D. Kraan, Process and equipment development for textile dyeing in supercritical carbon dioxide [PhD Thesis], The Netherlands: Delft University of Technology, (2005).

[16] E. Bach, E. Cleve, *et al.*, Past, present and future of supercritical fluid dyeing technology – an overview, *Review of Progress in Coloration and Related Topics*, 32(2002), 88-102.

[17] M. Banchero, Supercritical fluid dyeing of synthetic and natural textiles - a review, *Coloration Technology*, 129(2013), 2-17.

[18] T. Fall, Supercritical CO_2: an eco-friendly option and a commercial reality, *International Dyer*, 2018(2015), 24-25.

[19] S. G. Kazarian, Applications of FTIR Spectroscopy to supercritical fluid drying, extraction and impregnation, *Applied Spectroscopy Reviews*, 32(1997), 301-348.

[20] S. P. Nalawade, F. Picchioni, *et al.*, Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications, *Progress in Polymer Science*, 31(2006), 19-43.

[21] R. B. Gupta, J. J. Shim, *Solubility in supercritical carbon dioxide*, CRC press, (2006).

[22] A. A. Clifford, J. R. Williams, Introduction to supercritical fluids and their applications, in: *Supercritical fluid methods and protocols*, Humana Press, (2000), 1-16.

[23] E. W. Lemmon, Thermophysical properties of fluid systems, NIST chemistry WebBook, NIST standard reference database number 69, http://webbook.nist.gov, (2005), [cited December 12, 2019].

[24] H. Weingärtner, E. U. Franck, Supercritical water as a solvent, *Angewandte Chemie International Edition*, 44(2005), 2672-2692.

[25] G. A. Montero, C. B. Smith, *et al.*, Supercritical fluid technology in textile processing: an overview, *Industrial & Engineering Chemistry Research*, 39(2000), 4806-4812.

[26] J. A. Hyatt, Liquid and supercritical carbon dioxide as organic solvents, *The Journal of Organic Chemistry*, 49(1984), 5097-5101.

[27] Y. Li, Z. Tang, *et al.*, Binary and ternary solubility of amino- and nitro-benzoic acids in supercritical carbon dioxide, *Fluid Phase Equilibria*, 344(2013), 71-78.

[28] T. Kim, G. Kim, *et al.*, Solubility measurement and dyeing performance evaluation of Aramid NOMEX yarn by dispersed dyes in supercritical carbon dioxide, *Industrial & Engineering Chemistry Research*, 45(2006), 3425-3433.

[29] J. M. DeSimone, Z. Guan, *et al.*, Synthesis of fluoropolymers in supercritical carbon dioxide, *Science*, 257(1992), 945-947.

[30] J. B. McClain, D. Londono, *et al.*, Solution properties of a CO_2-soluble fluoropolymer via small angle neutron scattering, *Journal of the American Chemical Society*, 118(1996), 917-918.

[31] W. A. Hendrix, Progress in supercritical CO_2 dyeing, *Journal of Industrial Textiles*, 31(2001), 43-56.

[32] B. Guzel, A. Akgerman, Solubility of disperse and Mordant dyes in supercritical CO_2, *Journal of Chemical and Engineering Data*, 44(1999), 83-85.

[33] S. L. Draper, G. A. Montero, *et al.*, Solubility relationships for disperse dyes in supercritical carbon dioxide, *Dyes and Pigments*, 45(2000), 177-183.

[34] K. Tamura, R. S. Alwi, Solubility of anthraquinone derivatives in supercritical carbon dioxide, *Dyes and Pigments*, 113(2015), 351-356.

[35] I. Tabata, J. Lyu, *et al.*, Relationship between the solubility of disperse dyes and the equilibrium dye adsorption in supercritical fluid dyeing, *Coloration Technology*, 117(2001), 346-351.

[36] H. K. Bae, J. H. Jeon, *et al.*, Influence of co-solvent on dye solubility in supercritical carbon dioxide, *Fluid Phase Equilibria*, 222(2004), 119-125.

[37] M. Banchero, L. Manna, *et al.*, Effect of the addition of a modifier in the supercritical dyeing of polyester, *Coloration Technology*, 126(2010), 171-175.

[38] J. J. Long, R. L. Ran, *et al.*, Solubility of a reactive disperse dye in supercritical carbon dioxide, *Coloration Technology*, 128(2012), 127-132.

[39] H.-M. Lin, C.-C. Ho, *et al.*, Solubilities of disperse dyes of blue 79: 1, Red 82 and modified yellow 119 in supercritical carbon dioxide and nitrous oxide, *The Journal of Supercritical Fluids*, 32(2004), 105-114.

[40] S. K. Liao, Dyeing nylon-6,6 with some hydrophobic reactive dyes by supercritical processing, *Journal of Polymer Research*, 11(2005), 285-291.

[41] Y.-S. Ting, C.-M. Hsieh, Prediction of solid solute solubility in supercritical carbon dioxide with organic cosolvents from the PR+COSMOSAC equation of state, *Fluid Phase Equilibria*, 431(2017), 48-57.

[42] J. Sang, Y. Wang, *et al.*, Simplified calculation of solubility of solid solutes in supercritical carbon dioxide by EoS models, *Fluid Phase Equilibria*, 432(2017), 54-61.

[43] J. W. Lee, M. W. Park, *et al.*, Measurement and correlation of dye solubility in supercritical carbon dioxide, *Fluid Phase Equilibria*, 173(2000), 277-284.

[44] W. Wang, X. Gui, *et al.*, New models for correlating and predicting the solubility of some compounds in supercritical CO_2, *Fluid Phase Equilibria*, 430(2016), 135-142.

[45] J. A. P. Coelho, R. M. Filipe, *et al.*, Semi-empirical models and a cubic equation of state for correlation of solids solubility in $scCO_2$: Dyes and calix 4 arenes as illustrative examples, *Fluid Phase Equilibria*, 426(2016), 37-46.

[46] R. Tabaraki, T. Khayamian, *et al.*, Solubility prediction of 21 azo dyes in supercritical carbon dioxide using wavelet neural network, *Dyes and Pigments*, 73(2007), 230-238.

[47] A. Tarasova, F. Burden, *et al.*, Robust modelling of solubility in supercritical carbon dioxide using Bayesian methods, *Journal of Molecular Graphics and Modelling*, 28(2010), 593-597.

[48] H. L. Engelhardt, P. C. Jurs, Prediction of supercritical carbon dioxide solubility of organic compounds from molecular structure, *Journal of Chemical Information and Computer Sciences*, 37(1997), 478-484.

[49] P. Politzer, J. S. Murray, *et al.*, Relationships between solute molecular properties and solubility in supercritical carbon dioxide, *The Journal of Physical Chemistry*, 97(1993), 729-732.

[50] A. KhazaiePoul, M. Soleimani, *et al.*, Solubility prediction of disperse dyes in supercritical carbon dioxide and ethanol as co-solvent using neural network, *Chinese Journal of Chemical Engineering*, 24(2015), 491-498.

[51] V. J. Krukonis, *Supercritical fluid extraction: principles and practice*, Butterworth-Heinemann, (1994).

[52] O. R. Davies, A. L. Lewis, *et al.*, Applications of supercritical CO_2 in the fabrication of polymer systems for drug delivery and tissue engineering, *Advanced Drug Delivery Reviews*, 60(2008), 373-387.

[53] A. R. C. Duarte, J. F. Mano, *et al.*, Supercritical fluids in biomedical and tissue engineering applications: A review, *International Materials Reviews*, 54(2009), 214-222.

[54] E. Ramsey, Q. Sun, *et al.*, Mini-Review: Green sustainable processes using supercritical fluid carbon dioxide, *Journal of Environmental Sciences*, 21(2009), 720-726.

[55] N. S. E. Ahmed, R. M. El-Shishtawy, The use of new technologies in coloration of textile fibers, *Journal of Materials Science*, 45(2010), 1143-1153.

[56] I. Shahid ul, F. Mohammad, Emerging green technologies and environment friendly products for sustainable textiles, in: *Roadmap to sustainable textiles and clothing: Environmental and social aspects of textiles and clothing supply chain*, Springer Singapore, (2014), 63-82.

[57] E. Weidner, Impregnation via supercritical CO_2 - what we know and what we need to know, *The Journal of Supercritical Fluids*, 134(2018), 220-227.

[58] I. Kikic, F. Vecchione, Supercritical impregnation of polymers, *Current Opinion in Solid State and Materials Science*, 7(2003), 399-405.

[59] M. Champeau, J. M. Thomassin*, et al.*, Drug loading of sutures by supercritical CO_2 impregnation: Effect of polymer/drug interactions and thermal transitions, *Macromolecular Materials and Engineering*, 300(2015), 596-610.

[60] R. Yoganathan, R. Mammucari*, et al.*, Impregnation of ibuprofen into polycaprolactone using supercritical carbon dioxide, *Journal of Physics: Conference Series*, 215(2010), 1-5.

[61] R. Campardelli, P. Franco*, et al.*, Polycaprolactone/nimesulide patches obtained by a one-step supercritical foaming plus impregnation process, *Journal of Supercritical Fluids*, 146(2019), 47-54.

[62] M. Champeau, J. M. Thomassin*, et al.*, Drug loading of polymer implants by supercritical CO_2 assisted impregnation: a review, *Journal of Controlled Release*, 209(2015), 248-259.

[63] S. B. Iversen, T. Larsen*, et al.*, The world's first commercial supercritical wood treatment plant, in:"*Proceedings of the 6th international symposium on supercritical fluids*, Versailles, France (2003).

[64] W. Z. Xu, L. J. Yang*, et al.*, Preparation of antibacterial softwood via chemical attachment of quaternary ammonium compounds using supercritical CO_2, *ACS Sustainable Chemistry & Engineering*, 4(2016), 1551-1561.

[65] Z. Shen, G. S. Huvard*, et al.*, CO_2-assisted fiber impregnation, *Polymer*, 49(2008), 1579-1586.

[66] E. Di Maio, E. Kiran, Foaming of polymers with supercritical fluids and perspectives on the current knowledge gaps and challenges, *The Journal of Supercritical Fluids*, 134(2018), 157-166.

[67] M. Lora, I. Kikic, Polymer processing with supercritical fluids: an overview, *Separation and Purification Methods*, 28(1999), 179-220.

[68] S. G. Kazarian, Polymer processing with supercritical fluids, *Polymer science series C*, 42(2000), 78-101.

[69] A. Ferri, M. Banchero*, et al.*, Dye uptake and partition ratio of disperse dyes between a PET yarn and supercritical carbon dioxide, *Journal of Supercritical Fluids*, 37(2006), 107-114.

[70] A. Rojas, A. Torres*, et al.*, Supercritical impregnation for food applications: a review of the effect of the operational variables on the active compound loading, *Critical Reviews in Food Science and Nutrition*, 2019), 1-12.

[71] S. Üzer, U. Akman, *et al.*, Polymer swelling and impregnation using supercritical CO_2: A model-component study towards producing controlled-release drugs, *The Journal of Supercritical Fluids*, 38(2006), 119-128.

[72] A. R. Berens, G. S. Huvard, *et al.*, Application of compressed carbon dioxide in the incorporation of additives into polymers, *Journal of Applied Polymer Science*, 46(1992), 231-242.

[73] V. Goodship, E. Ogur, *Polymer processing with supercritical fluids*, iSmithers Rapra Publishing, (2005).

[74] J. von Schnitzler, R. Eggers, Mass transfer in polymers in a supercritical CO_2-atmosphere, *The Journal of Supercritical Fluids*, 16(1999), 81-92.

[75] J. M. de Gooijer, C. E. Koning, Chemical modification of polymers in supercritical carbon dioxide, *Supercritical carbon dioxide: In polymer reaction engineering*, 2005), 273-301.

[76] Y. T. Shieh, J. H. Su, *et al.*, Interaction of supercritical carbon dioxide with polymers. I. Crystalline polymers, *Journal of Applied Polymer Science*, 59(1996), 695-705.

[77] E. H. Chimowitz, F. D. Kelley, *et al.*, Analysis of retrograde behavior and the cross-over effect in supercritical fluids, *Fluid Phase Equilibria*, 44(1988), 23-52.

[78] J.-P. Yu, Y.-X. Guan, *et al.*, Preparation of roxithromycin-loaded poly(l-lactic acid) films with supercritical solution impregnation, *Industrial & Engineering Chemistry Research*, 50(2011), 13813-13818.

[79] A. C. de Souza, A. M. A. Dias, *et al.*, Impregnation of cinnamaldehyde into cassava starch biocomposite films using supercritical fluid technology for the development of food active packaging, *Carbohydrate Polymers*, 102(2014), 830-837.

[80] S. Milovanovic, M. Stamenic, *et al.*, Solubility of thymol in supercritical carbon dioxide and its impregnation on cotton gauze, *The Journal of Supercritical Fluids*, 84(2013), 173-181.

[81] T. Kim, B. Seo, *et al.*, Effects of dye particle size and dissolution rate on the overall dye uptake in supercritical dyeing process, *The Journal of Supercritical Fluids*, 151(2019), 1-7.

[82] M. E. M. Braga, V. P. Costa, *et al.*, Effects of operational conditions on the supercritical solvent impregnation of acetazolamide in Balafilcon A commercial contact lenses, *International Journal of Pharmaceutics*, 420(2011), 231-243.

[83] E. Schollmeyer, D. Knittel, *et al.*; *Dyeing process*, Germany Patent DE3906724A1, D 06 P 1, Assigned to Deutsches Textilforschungszentrum and Deutsches Krebsforschungszentrum DKFZ, (1990).

[84] The DyeOx, http://www.dyecoo.com/the-dyeox/, (2019), [cited 2020 March 06].

[85] M. Banchero, S. Sicardi, *et al.*, Supercritical dyeing of textiles apparatus to the pilot plant, *Textile Research Journal*, 78(2008), 217-223.

[86] L. Zheng, H. Zheng*, et al.*, Dyeing procedures of polyester fiber in supercritical carbon dioxide using a special dyeing frame, *Journal of Engineered Fabrics & Fibers*, 10(2015), 37-46.

[87] J. J. Long, H. M. Xu*, et al.*, A novel plant for fabric rope dyeing in supercritical carbon dioxide and its cleaner production, *Journal of Cleaner Production*, 65(2014), 574-582.

[88] D. Gao, D. F. Yang*, et al.*, Supercritical carbon dioxide dyeing for PET and cotton fabric with synthesized dyes by a modified apparatus, *ACS Sustainable Chemistry & Engineering*, 3(2015), 668-674.

[89] B. Gebert, W. Saus*, et al.*, Dyeing natural fibers with disperse dyes in supercritical carbon dioxide, *Textile Research Journal*, 64(1994), 371-374.

[90] J. J. Long, G. D. Xiao*, et al.*, Dyeing of cotton fabric with a reactive disperse dye in supercritical carbon dioxide, *Journal of Supercritical Fluids*, 69(2012), 13-20.

[91] A. Schmidt, E. Bach*, et al.*, The dyeing of natural fibres with reactive disperse dyes in supercritical carbon dioxide, *Dyes and Pigments*, 56(2003), 27-35.

[92] U. Lewin-Kretzschmar, P. Harting, The potential of surfactant modified supercritical fluids for dissolving polar dyes, *Chemical Engineering & Technology*, 27(2004), 160-170.

[93] J. H. Jun, K. Sawada*, et al.*, Application of perfluoropolyether reverse micelles in supercritical CO_2 to dyeing process, *Dyes and Pigments*, 61(2004), 17-22.

[94] J. R. Whinfield, Chemistry of 'terylene', *Nature*, 158(1946), 930-931.

[95] J. Scheirs, T. E. Long, *Modern polyesters: chemistry and technology of polyesters and copolyesters*, John Wiley & Sons, (2005).

[96] Distribution of fiber production worldwide in 2014 by type, Statista Inc., https://www.statista.com/statistics/263154/worldwide-production-volume-of-textile-fibers-since-1975/, (2018), [cited 2020 March 07].

[97] L. Cardozo, H. R. Mazzer*, et al.*, Dyeing of polyethylene terephthalate fibers with a disperse dye in supercritical carbon dioxide, *Textile Research Journal*, 84(2014), 1279-1287.

[98] A. Hou, K. Xie*, et al.*, Effect of supercritical carbon dioxide dyeing conditions on the chemical and morphological changes of poly(ethylene terephthalate) fibers, *Journal of Applied Polymer Science*, 92(2004), 2008-2012.

[99] R. B. Chavan, Environmentally friendly dyes, in: *Handbook of textile and industrial dyeing*, Elsevier, (2011), 515-561.

[100] M. Clark, *Handbook of textile and industrial dyeing: Principles, processes and types of dyes*, Elsevier, (2011).

[101] W. Saus, D. Knittel, *et al.*, Dyeing of textiles in supercritical carbon dioxide, *Textile Research Journal*, 63(1993), 135-142.

[102] J. N. Chakraborty, Dyeing in supercritical carbon dioxide, in: *Fundamentals and Practices in Colouration of Textiles*, Woodhead Publishing India Pvt.Ltd., (2014), 356-364.

[103] J. S. Chiou, J. W. Barlow, *et al.*, Plasticization of glassy polymers by CO_2, *Journal of Applied Polymer Science*, 30(1985), 2633-2642.

[104] L. Herek, R. Oliveira, *et al.*, Impregnation of PET films and PHB granules with curcumin in supercritical CO_2, *Brazilian Journal of Chemical Engineering*, 23(2006), 227-234.

[105] Y. T. Shieh, J. H. Su, *et al.*, Interaction of supercritical carbon dioxide with polymers. II. Amorphous polymers, *Journal of Applied Polymer Science*, 59(1996), 707-717.

[106] Z. Zhong, S. Zheng, *et al.*, High-pressure DSC study of thermal transitions of a poly(ethylene terephthalate)/carbon dioxide system, *Polymer*, 40(1999), 3829-3834.

[107] S. G. Kazarian, N. H. Brantley, *et al.*, Applications of vibrational spectroscopy to characterize poly(ethylene terephthalate) processed with supercritical CO_2, *Vibrational Spectroscopy*, 19(1999), 277-283.

[108] S. Bai, J. Z. Hu, *et al.*, Solid state NMR and wide angle X-ray diffraction studies of supercritical fluid CO_2-treated poly(ethylene terephthalate), *Macromolecules*, 31(1998), 9238-9246.

[109] M. S. Sfiligoj, P. Zipper, WAXS analysis of structural changes of poly(ethylene terephthalate) fibers induced by supercritical-fluid dyeing, *Colloid and Polymer Science*, 276(1998), 144-151.

[110] D. Terada, Y. Kawahara, *et al.*, Structural modification of polyester Shin-Gosen by the treatment in supercritical carbon dioxide fluids, *Sen'i Gakkaishi*, 59(2003), 385-391.

[111] F. Rombaldoni, R. Demichelis, *et al.*, Effect of carbon dioxide dry cleaning on low-stress mechanical properties, air permeability and crease pressing performance of men’s suit fabrics, *Textile Research Journal*, 79(2009), 1168-1177.

[112] M. T. Abate, A. Ferri, *et al.*, Impregnation of materials in supercritical CO_2 to impart various functionalities, in: *Advanced Supercritical Fluids Technologies*, IntechOpen, (2019), 212-227.

[113] Y. Gao, R. Cranston, Recent Advances in Antimicrobial Treatments of Textiles, *Textile Research Journal*, 78(2008), 60-72.

[114] T. Abou Elmaaty, J. Ma, *et al.*, Facile bifunctional dyeing of polyester under supercritical carbon dioxide medium with new antibacterial hydrazono propanenitrile dyes, *Industrial & Engineering Chemistry Research*, 53(2014), 15566-15570.

[115] T. Elmaaty, E. El-Aziz, *et al.*, Eco-friendly disperse dyeing and functional finishing of nylon 6 using supercritical carbon dioxide, *Fibers*, 3(2015), 309-322.

[116] X. Q. Xiong, Y. Y. Xu, *et al.*, Polyester fabric's fluorescent dyeing in supercritical carbon dioxide and its fluorescence imaging, *Journal of Fluorescence*, 27(2017), 483-489.

[117] N. N. Glagolev, A. B. Solov'eva, *et al.*, The photochromic properties of indoline spirooxazine-thermoplastic polymer systems obtained by supercritical fluid impregnation, *Russian Journal of Physical Chemistry A*, 83(2009), 861-867.

[118] A. S. Kopylov, N. N. Glagolev, *et al.*, Dynamics of changes in the colored form of spiroantrooxazine incorporated into polytetrafluoroethylene F-42 in a supercritical carbon dioxide medium, *Russian Journal of Physical Chemistry A*, 89(2015), 1523-1530.

[119] N. P. Prorokova, T. Y. Kumeeva, *et al.*, Modification of the surface of poly(ethylene terephthalate) fabrics by application of a water-repellent coating in supercritical carbon dioxide medium, *Fibre Chemistry*, 41(2009), 29-33.

[120] N. P. Prorokova, T. Y. Kumeeva, *et al.*, Ensuring a high degree of water repellency of polyester textile materials by treating them with supercritical carbon dioxide, *Fibre Chemistry*, 42(2010), 109-113.

[121] Y.-Y. Xu, L.-J. Zheng, *et al.*, Water/oil repellent property of polyester fabrics after supercritical carbon dioxide finishing, *Thermal Science*, 19(2015), 1273-1277.

[122] A. L. Mohamed, M. Er-Rafik, *et al.*, Supercritical carbon dioxide assisted silicon based finishing of cellulosic fabric: A novel approach, *Carbohydrate Polymers*, 98(2013), 1095-1107.

[123] Y. Chen, Q. Zhang, *et al.*, Surface-oriented fluorinated pyridinium silicone with enhanced antibacterial activity on cotton via supercritical impregnation, *Cellulose*, 25(2018), 1499-1511.

[124] Y. Chen, M. Q. Niu, *et al.*, Durable antimicrobial finishing of cellulose with QSA silicone by supercritical adsorption, *Applied Surface Science*, 264(2013), 171-175.

[125] Y. Chen, Q. K. He, *et al.*, Preparation of biocidal 4-ethyl-4-(hydroxymethyl)oxazolidin-2-one-based N-halamine polysiloxane for impregnation of polypropylene in supercritical CO_2, *Journal of Applied Polymer Science*, 135(2018), 1-8.

[126] Y. Chen, Y. Y. Wang, *et al.*, Preparation of silicone containing 2,2,6,6-tetramethyl-4-piperidinol-based N-chloramine for antibacterial polyethylene via interpenetration in supercritical carbon dioxide, *Journal of Applied Polymer Science*, 136(2019), 1-9.

[127] V. V. Zefirov, N. A. Lubimtsev, *et al.*, Durable crosslinked omniphobic coatings on textiles via supercritical carbon dioxide deposition, *The Journal of Supercritical Fluids*, 133(2018), 30-37.

[128] L. H. Peng, R. H. Guo, *et al.*, Synthesis of silver nanoparticles on wool fabric in supercritical carbon dioxide, *Materials Express*, 7(2017), 405-410.

[129] S. D. Gittard, D. Hojo, *et al.*, Antifungal textiles formed using silver deposition in supercritical carbon dioxide, *Journal of Materials Engineering and Performance*, 19(2010), 368-373.

[130] R. K. Boggess, L. T. Taylor, *et al.*, Highly reflective polyimide films created by supercritical fluid infusion of a silver additive, *Journal of Applied Polymer Science*, 64(1997), 1309-1317.

[131] W.-T. Chiu, C.-Y. Chen, *et al.*, Platinum coating on silk by a supercritical CO_2 promoted metallization technique for applications of wearable devices, *Surface and Coatings Technology*, 350(2018), 1028-1035.

[132] W. T. Chiu, C. Y. Chen, *et al.*, Ni-P and TiO_2 codeposition on silk textile via supercritical CO_2 promoted electroless plating for flexible and wearable photocatalytic devices, *Electrochimica Acta*, 294(2019), 68-75.

[133] Y. Iwai, S. Sameshima, *et al.*, Fabrication of conductive cotton by electroless plating method with supercritical carbon dioxide, *The Journal of Supercritical Fluids*, 100(2015), 46-51.

[134] S. Xu, D. Shen, *et al.*, Fabrication of water-repellent cellulose fiber coated with magnetic nanoparticles under supercritical carbon dioxide, *Journal of Nanoparticle Research*, 15(2013), 1577-1589.

[135] M. Belmas, I. Tabata, *et al.*, Supercritical fluid-assisted electroless copper plating of aramid film: The influence of surface treatment, *Sen'i Gakkaishi*, 66(2010), 215-221.

[136] M. Belmas, I. Tabata, *et al.*, Application of dithiol compounds in supercritical carbon dioxide to improve the adhesive properties of copper-plated p-aramid fibers, *Sen'i Gakkaishi*, 66(2010), 229-235.

[137] S. Milovanovic, M. Stamenic, *et al.*, Supercritical impregnation of cellulose acetate with thymol, *The Journal of Supercritical Fluids*, 97(2015), 107-115.

[138] S. Milovanovic, D. Markovic, *et al.*, Application of cellulose acetate for controlled release of thymol, *Carbohydrate Polymers*, 147(2016), 344-353.

[139] D. Markovic, S. Milovanovic, *et al.*, Impregnation of corona modified polypropylene non-woven material with thymol in supercritical carbon dioxide for antimicrobial application, *The Journal of Supercritical Fluids*, 101(2015), 215-221.

[140] A. Torres, J. Romero, *et al.*, Near critical and supercritical impregnation and kinetic release of thymol in LLDPE films used for food packaging, *The Journal of Supercritical Fluids*, 85(2014), 41-48.

[141] A. Torres, E. Ilabaca, *et al.*, Effect of processing conditions on the physical, chemical and transport properties of polylactic acid films containing thymol incorporated by supercritical impregnation, *European Polymer Journal*, 89(2017), 195-210.

[142] S. Milovanovic, T. Adamovic, *et al.*, Cellulose Acetate Based Material with Antibacterial Properties Created by Supercritical Solvent Impregnation, *International Journal of Polymer Science*, 2017(2017), 1-9.

[143] M. L. Goñi, N. A. Gañán, *et al.*, Eugenol-loaded LLDPE films with antioxidant activity by supercritical carbon dioxide impregnation, *The Journal of Supercritical Fluids*, 111(2016), 28-35.

[144] J. E. Mosquera, M. L. Goñi, *et al.*, Supercritical carbon dioxide assisted impregnation of eugenol into polyamide fibers for application as a dental floss, *Journal of* CO_2 *Utilization*, 32(2019), 259-268.

[145] J. Pajnik, M. Radetić, *et al.*, Functionalization of polypropylene, polyamide and cellulose acetate materials with pyrethrum extract as a natural repellent in supercritical carbon dioxide, *The Journal of Supercritical Fluids*, 136(2018), 70-81.

[146] J. Sanchez-Sanchez, M. T. Fernandez-Ponce, *et al.*, Impregnation of mango leaf extract into a polyester textile using supercritical carbon dioxide, *Journal of Supercritical Fluids*, 128(2017), 208-217.

[147] C. Cejudo Bastante, M. J. Cran, *et al.*, Effect of supercritical CO_2 and olive leaf extract on the structural, thermal and mechanical properties of an impregnated food packaging film, *Journal of Supercritical Fluids*, 145(2019), 181-191.

[148] S. F. Zhu, M. W. Shi, *et al.*, Burning behavior of irradiated PET flame-retardant fabrics impregnated with sensitizer, *Materials Letters*, 160(2015), 58-60.

[149] T. Baba, K. Hirogaki, *et al.*, Impregnation of chitin/chitosan into polyester fabric using supercritical carbon dioxide, *Sen'i Gakkaishi*, 66(2010), 63-69.

[150] E. Guido, C. Colleoni, *et al.*, Influence of catalyst in the synthesis of a cellulose-based sensor: Kinetic study of 3-glycidoxypropyltrimethoxysilane epoxy ring opening by Lewis acid, *Sensors and Actuators B: Chemical*, 203(2014), 213-222.

[151] G. Wyszecki, W. S. Stiles, *Color Science*, Wiley, (1982).

[152] Y. Yang, S. Li, Instrumental measurement of the levelness of textile coloration, *Textile Chemist & Colorist*, 25(1993), 75-78.

[153] M. Vikova, M. Vik, Alternative UV sensors based on color-changeable pigments, *Advances in Chemical Engineering and Science*, 1(2011), 224-230.

[154] M. Viková, R. M. Christie, *et al.*, A unique device for measurement of photochromic textiles, *Research Journal of Textile and Apparel*, 18(2014), 6-14.

[155] T. Cheng, T. Lin, *et al.*, Fast response photochromic textiles from hybrid silica surface coating, *Fibers and Polymers*, 9(2008), 301-306.

[156] P. Gies, T. Slevin, *et al.*, Sun protective clothing-evaluation and classification. in: *Australian/New Zealand Standard (AS/NZS 4399:2017)*, (2017).

[157] R. Re, N. Pellegrini, *et al.*, Antioxidant activity applying an improved ABTS radical cation decolorization assay, *Free Radical Biology and Medicine*, 26(1999), 1231-1237.

[158] D. Knittel, E. Schollmeyer, Chitosans for permanent antimicrobial finish on textiles, *Lenzinger Berichte*, 85(2006), 124-130.

[159] B. Tawiah, W. Badoe*, et al.*, Advances in the development of antimicrobial agents for textiles: the quest for natural products. review, *Fibres & Textiles in Eastern Europe*, 24(2016), 136-149.

[160] S. Shahidi, J. Wiener, Antibacterial Agents in Textile Industry, in: *Antimicrobial Agents*, IntechOpen, (2007), 387-406.

[161] D. S. Morais, R. M. Guedes*, et al.*, Antimicrobial approaches for textiles: from research to market, *Materials*, 9(2016), 1-21.

[162] M. Joshi, S. W. Ali*, et al.*, Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products, *Indian Journal of Fibre & Textile Research*, 34(2009), 295-304.

[163] M. Joshi, R. Purwar*, et al.*, Antimicrobial Textiles for Health and Hygiene Applications Based on Eco-Friendly Natural Products, in: *Medical and Healthcare Textiles*, Elsevier, (2010), 84-92.

[164] M. Shahid, F. Mohammad, Perspectives for natural product based agents derived from industrial plants in textile applications–a review, *Journal of Cleaner Production*, 57(2013), 2-18.

[165] K. Murugesh Babu, K. B. Ravindra, Bioactive antimicrobial agents for finishing of textiles for health care products, *The Journal of The Textile Institute*, 106(2015), 706-717.

[166] S. H. Lim, S. M. Hudson, Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals, *Journal of Macromolecular Science-Polymer Reviews*, 43(2003), 223-269.

[167] B. Simoncic, B. Tomsic, Structures of novel antimicrobial agents for textiles - a review, *Textile Research Journal*, 80(2010), 1721-1737.

[168] I. Shahid ul, M. Shahid*, et al.*, Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers-a review, *Industrial & Engineering Chemistry Research*, 52(2013), 5245-5260.

[169] K. Vellingiri, T. Ramachandran*, et al.*, Eco-friendly application of nano chitosan in antimicrobial coatings in the textile industry, *Nanoscience and Nanotechnology Letters*, 5(2013), 519-529.

[170] M. D. Teli, J. Sheikh*, et al.*, Multifunctional finishing of cotton using chitosan extracted from bio-waste, *International Journal of Biological Macromolecules*, 54(2013), 125-130.

[171] T. Agnhage, A. Perwuelz*, et al.*, Eco-innovative coloration and surface modification of woven polyester fabric using bio-based materials and plasma technology, *Industrial Crops and Products*, 86(2016), 334-341.

[172] J. Li, M. Kong, *et al.*, Preparation of biocompatible chitosan grafted poly(lactic acid) nanoparticles, *International Journal of Biological Macromolecules*, 51(2012), 221-227.

[173] R. Carvallo, K. S. Patel, *et al.*, Solubility of chitosan in supercritical carbon dioxide and modeling using SAFT, in:"*AIChE Annual Meeting*, Utah, USA, (2010).

[174] I. S. Chaschin, T. E. Grigorev, *et al.*, Direct deposition of chitosan macromolecules on a substrate from solutions in supercritical carbon dioxide: Solubility and conformational analysis, *European Polymer Journal*, 48(2012), 906-918.

[175] D. P. Chattopadhyaya, M. S. Inamdarb, Chitosan and nano Chitosan: Properties and application to textiles, in: *Handbook of sustainable polymers processing and applications*, Taylor & Francis Group, (2016), 659-741.

[176] K. R. Kirov, H. E. Assender, Quantitative ATR-IR analysis of anisotropic polymer films: surface structure of commercial PET, *Macromolecules*, 38(2005), 9258-9265.

[177] E. Rusu, M. Drobota, *et al.*, Structural investigations of amines treated polyester thin films by FTIR-ATR spectroscopy, *Journal of optoelectronics and advanced materials*, 10(2008), 377-381.

[178] K. Elnagar, T. Abou Elmaaty, *et al.*, Dyeing of polyester and polyamide synthetic fabrics with natural dyes using ecofriendly technique, *Journal of Textiles*, 2014(2014), 1-8.

[179] M. F. Cervera, J. Heinämäki, *et al.*, Effects of spray drying on physicochemical properties of chitosan acid salts, *AAPS PharmSciTech*, 12(2011), 637-649.

[180] R. Gallego, J. F. Arteaga, *et al.*, Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil, *Molecules*, 18(2013), 6532-6549.

[181] T. Luxbacher, T. Pušić, *et al.*, The zeta potential of textile fabrics: a review, in:"*8th International Textile, Clothing & Design Conference*, Dubrovnik, Croatia, (2017).

[182] M. D. Teli, R. D. Kale, *et al.*, Effect of nanoclay loading on zeta potential of polyester nanocomposite fibre, *Indian Journal of Fibre & Textile Research*, 42(2017), 125-131.

[183] A. M. Grancaric, A. Tarbuk, *et al.*, Electrokinetic properties of textile fabrics, *Coloration Technology*, 121(2005), 221-227.

[184] Q. Z. Wang, X. G. Chen, *et al.*, Protonation constants of chitosan with different molecular weight and degree of deacetylation, *Carbohydrate Polymers*, 65(2006), 194-201.

[185] R. C. Goy, D. d. Britto, *et al.*, A review of the antimicrobial activity of chitosan, *Polímeros*, 19(2009), 241-247.

[186] L. Guo, C. Campagne, *et al.*, Zeta potential and surface physico-chemical properties of atmospheric air-plasma-treated polyester fabrics, *Textile Research Journal*, 79(2009), 1371-1377.

[187] N. Ristic, P. Jovancic, *et al.*, Influence of corona discharge and chitosan surface treatment on dyeing properties of wool, *Journal of Applied Polymer Science*, 117(2010), 2487-2496.

[188] I. M. Helander, E. L. Nurmiaho-Lassila, *et al.*, Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria, *International Journal of Food Microbiology*, 71(2001), 235-244.

[189] W. Xie, P. Xu, *et al.*, Preparation and antibacterial activity of a water-soluble chitosan derivative, *Carbohydrate Polymers*, 50(2002), 35-40.

[190] H. K. No, N. Young Park, *et al.*, Antibacterial activity of chitosans and chitosan oligomers with different molecular weights, *International Journal of Food Microbiology*, 74(2002), 65-72.

[191] E. J. Jung, D. K. Youn, *et al.*, Antibacterial activity of chitosans with different degrees of deacetylation and viscosities, *International Journal of Food Science & Technology*, 45(2010), 676-682.

[192] M. Y. Yang, J. Liu, *et al.*, Rope dyeing of fabric in supercritical carbon dioxide for commerical purposes, *Coloration Technology*, 130(2014), 102-111.

[193] M. Shahid, I. Shahid ul, *et al.*, Recent advancements in natural dye applications: a review, *Journal of Cleaner Production*, 53(2013), 310-331.

[194] A. K. Samanta, P. Agarwal, Application of natural dyes on textiles, *Indian Journal of Fibre and Textile Research*, 34(2009), 384-399.

[195] R. Hiserodt, T. G. Hartman, *et al.*, Characterization of powdered turmeric by liquid chromatography mass spectrometry and gas chromatography mass spectrometry, *Journal of Chromatography A*, 740(1996), 51-63.

[196] V. S. Govindarajan, W. H. Stahl, Turmeric chemistry, technology, and quality, *Critical Reviews in Food Science and Nutrition*, 12(1980), 199-301.

[197] Y. Zhou, J. Yu, *et al.*, Inkjet printing of curcumin-based ink for coloration and bioactivation of Polyamide, Silk, and Wool fabrics, *ACS Sustainable Chemistry & Engineering*, 7(2019), 2073-2082.

[198] L. F. Zemljič, J. Volmajer, *et al.*, Antimicrobial and antioxidant functionalization of viscose fabric using chitosan–curcumin formulations, *Textile Research Journal*, 84(2014), 819-830.

[199] W.-H. Lee, C.-Y. Loo, *et al.*, Curcumin and its derivatives: their application in neuropharmacology and neuroscience in the 21st century, *Current Neuropharmacology*, 11(2013), 338-378.

[200] K. I. Priyadarsini, Photophysics, photochemistry and photobiology of curcumin: studies from organic solutions, bio-mimetics and living cells, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 10(2009), 81-95.

[201] Y. Zhou, R.-C. Tang, Modification of curcumin with a reactive UV absorber and its dyeing and functional properties for silk, *Dyes and Pigments*, 134(2016), 203-211.

[202] R. Azarmi, A. Ashjaran, Antibacterial effects and fastness properties of dyed silk fabric with curcumin in presence of organic and bio mordants, *Journal of New Technology and Materials*, 7(2017), 56-66.

[203] G. Dalby, Greener mordants for natural coloration, *Journal of the Society of Dyers and Colourists*, 109(1993), 8-9.

[204] V. Sriumaroum, S. Liprapan*, et al.*, Study on spectroscopic and dyeing characteristics of curcumin on poly (lactic acid) and poly (ethylene terephthalate) fabrics, *Advanced Materials Research*, 233(2011), 1384-1387.

[205] V. Sriumaoum, J. Suesat*, et al.*, Dyeing and spectroscopic properties of natural dyes on Poly (lactic acid) and Poly (ethylene terephthalate) fabrics, *International Journal of Bioscience, Biochemistry and Bioinformatics*, 2(2012), 155-158.

[206] V. Sriumaoum, C. Sodsangchan*, et al.*, Effect of chitosan and turmeric dye on ultraviolet protection properties of polyester fabric, *Applied Mechanics and Materials*, 535(2014), 658-661.

[207] S. Zhan, S. Li*, et al.*, Measurement and correlation of curcumin solubility in supercritical carbon dioxide, *Journal of Chemical and Engineering Data*, 62(2017), 1257-1263.

[208] E. Gracia, M. T. García*, et al.*, Improvement of PLGA loading and release of curcumin by supercritical technology, *The Journal of Supercritical Fluids*, 111(2018), 60-67.

[209] J. J. Long, Y. Q. Ma*, et al.*, Investigations on the level dyeing of fabrics in supercritical carbon dioxide, *Journal of Supercritical Fluids*, 57(2011), 80-86.

[210] D. Knittel, W. Saus*, et al.*, Water-free dyeing of textile accessories using supercritical carbon dioxide, *Indian Journal of Fibre & Textile Research*, 22(1997), 184-189.

[211] H. B. Wen, J. J. Dai, Dyeing of polylactide fibers in supercritical carbon dioxide, *Journal of Applied Polymer Science*, 105(2007), 1903-1907.

[212] M. M. Hasan, M. B. Hossain*, et al.*, Application of purified curcumin as natural dye on cotton and polyester, *International Journal of Engineering & Technology*, 14(2014), 17-23.

[213] B. Becerir, A novel approach for estimating the relation between K/S value and dye uptake in reactive dyeing of cotton fabrics, *Fibers and Polymers*, 6(2005), 224-228.

[214] T. Padfield, S. Landi, The light-fastness of the natural dyes, *Studies in conservation*, 11(1966), 181-196.

[215] A. Bashari, M. Shakeri*, et al.*, UV-protective textiles, in: *The impact and prospects of green chemistry for textile technology*, Elsevier, (2019), 327-365.

[216] D. Grifoni, L. Bacci, *et al.*, UV protective properties of cotton and flax fabrics dyed with multifunctional plant extracts, *Dyes and Pigments*, 105(2014), 89-96.

[217] H. W. Lim, K. Cooper, The health impact of solar radiation and prevention strategies, *Journal of the American Academy of Dermatology*, 41(1999), 81-99.

[218] B. Halliwell, J. M. C. Gutteridge, Role of free radicals and catalytic metal ions in human disease: an overview, in: *Methods in Enzymology*, Elsevier, (1990), 1-85.

[219] N. Ito, S. Fukushima, *et al.*, Carcinogenicity of butylated hydroxyanisole in F344 rats, *Journal of the National Cancer Institute*, 70(1983), 343-352.

[220] V. P. Menon, A. R. Sudheer, Antioxidant and anti-inflammatory properties of curcumin, in: *The molecular targets and therapeutic uses of curcumin in health and disease*, Springer, (2007), 105-125.

[221] A. K. Panda, D. Chakraborty, *et al.*, New insights into therapeutic activity and anticancer properties of curcumin, *Journal of Experimental Pharmacology*, 9(2017), 31.

[222] D. Perrone, F. Ardito, *et al.*, Biological and therapeutic activities, and anticancer properties of curcumin, *Experimental and Therapeutic Medicine*, 10(2015), 1615-1623.

[223] T. Ak, İ. Gülçin, Antioxidant and radical scavenging properties of curcumin, *Chemico-Biological Interactions*, 174(2008), 27-37.

[224] Y. Zhou, J. Zhang, *et al.*, Simultaneous dyeing and functionalization of silk with three natural yellow dyes, *Industrial Crops and Products*, 64(2015), 224-232.

[225] T. Masuda, T. Maekawa, *et al.*, Chemical studies on antioxidant mechanism of curcumin: analysis of oxidative coupling products from curcumin and linoleate, *Journal of Agricultural and Food Chemistry*, 49(2001), 2539-2547.

[226] K. I. Priyadarsini, D. K. Maity, *et al.*, Role of phenolic O-H and methylene hydrogen on the free radical reactions and antioxidant activity of curcumin, *Free Radical Biology and Medicine*, 35(2003), 475-484.

[227] S. Y. Han, Y. Yang, Antimicrobial activity of wool fabric treated with curcumin, *Dyes and Pigments*, 64(2005), 157-161.

[228] N. Reddy, S. Han, *et al.*, Antimicrobial activity of cotton fabrics treated with curcumin, *Journal of Applied Polymer Science*, 127(2013), 2698-2702.

[229] S. M. Ghoreishian, L. Maleknia, *et al.*, Antibacterial properties and color fastness of silk fabric dyed with turmeric extract, *Fibers and Polymers*, 14(2013), 201-207.

[230] S. Zorofchian Moghadamtousi, H. Abdul Kadir, *et al.*, A review on antibacterial, antiviral, and antifungal activity of curcumin, *BioMed research international*, 2014(2014), 1-12.

[231] R. K. B. Bhawana, Harpreet Singh Buttar, V. K. Jain, Nidhi Jain, Curcumin nanoparticles: preparation, characterization, and antimicrobial study, *Journal of Agricultural and Food Chemistry*, 59(2011), 2056-2061.

[232] P. Y. Wang, C. J. Wu, Photochromic behaviour of some phenoxyanthraquinone dyes in solution and on polyester substrate, *Dyes and Pigments*, 35(1997), 279-288.

[233] S. Nigel Corns, S. M. Partington*, et al.*, Industrial organic photochromic dyes, *Coloration Technology*, 125(2009), 249-261.

[234] G. Berkovic, V. Krongauz*, et al.*, Spiropyrans and Spirooxazines for memories and switches, *Chemical Reviews*, 100(2000), 1741-1754.

[235] M. Parhizkar, Y. Zhao*, et al.*, Photochromic fibers and fabrics, in: *Handbook of smart textiles*, Springer (2015), 155-182.

[236] M. A. Chowdhury, M. Joshi*, et al.*, Photochromic and thermochromic colorants in textile applications, *Journal of Engineered Fabrics & Fibers*, 9(2014), 107-123.

[237] M. Vikova, M. Vik, Colorimetric properties of photochromic textiles, *Applied Mechanics and Materials*, 440(2014), 260-265.

[238] R. di Nunzio Maria, L. Gentili Pier*, et al.*, Photochromic, thermochromic, and fluorescent Spirooxazines and Naphthopyrans: a spectrokinetic and thermodynamic study, *Chemphyschem*, 9(2008), 768-775.

[239] P. H. Shah, Azodisperse dyes with photochromic mercury (ii)-dithizonate moiety for dyeing polyester, nylon and cellulose triacetate fibres, *Indian Journal of Textile Research*, 10(1985), 179-182.

[240] S.-J. Lee, Y.-A. Son*, et al.*, Preliminary exhaustion studies of spiroxazine dyes on polyamide fibers and their photochromic properties, *Dyes and Pigments*, 69(2006), 18-21.

[241] S. M. R. Billah, R. M. Christie*, et al.*, Direct coloration of textiles with photochromic dyes. Part 1: Application of spiroindolinonaphthoxazines as disperse dyes to polyester, nylon and acrylic fabrics, *Coloration Technology*, 124(2008), 223-228.

[242] M. Aldib, R. M. Christie, Textile applications of photochromic dyes. Part 4: Application of commercial photochromic dyes as disperse dyes to polyester by exhaust dyeing, *Coloration Technology*, 127(2011), 282-287.

[243] S. M. R. Billah, R. M. Christie*, et al.*, Direct coloration of textiles with photochromic dyes. Part 3: Dyeing of wool with photochromic acid dyes, *Coloration Technology*, 128(2012), 488-492.

[244] A. F. Little, R. M. Christie, Textile applications of photochromic dyes. Part 2: Factors affecting the photocoloration of textiles screen-printed with commercial photochromic dyes, *Coloration Technology*, 126(2010), 164-170.

[245] A. F. Little, R. M. Christie, Textile applications of photochromic dyes. Part 3: Factors affecting the technical performance of textiles screen-printed with commercial photochromic dyes, *Coloration Technology*, 127(2011), 275-281.

[246] M. Kozicki, E. Sąsiadek, UV-assisted screen-printing of flat textiles, *Coloration Technology*, 128(2012), 251-260.

[247] T. Feczkó, K. Samu*, et al.*, Textiles screen-printed with photochromic ethyl cellulose–spirooxazine composite nanoparticles, *Coloration Technology*, 129(2013), 18-23.

[248] T. V. Pinto, P. Costa*, et al.*, Screen-printed photochromic textiles through new inks based on SiO_2@naphthopyran nanoparticles, *ACS Applied Materials & Interfaces*, 8(2016), 28935-28945.

[249] T. Cheng, T. Lin*, et al.*, Photochromic wool fabrics from a hybrid silica coating, *Textile Research Journal*, 77(2007), 923-928.

[250] T. Cheng, T. Lin*, et al.*, Photochromic fabrics with improved durability and photochromic performance, *Fibers and Polymers*, 9(2008), 521-526.

[251] M. Aldib, R. M. Christie, Textile applications of photochromic dyes. Part 5: Application of commercial photochromic dyes to polyester fabric by a solvent-based dyeing method, *Coloration Technology*, 129(2013), 131-143.

[252] E.-M. Lee, S.-Y. Gwon*, et al.*, Photoswitching electrospun nanofiber based on a spironaphthoxazine–isophorone-based fluorescent dye system, *Dyes and Pigments*, 92(2012), 542-547.

[253] E. M. Lee, S. Y. Gwon*, et al.*, Modulation of a fluorescence switch of nanofiber mats containing photochromic spironaphthoxazine and D-π-A charge transfer dye, *Journal of Luminescence*, 132(2012), 1427-1431.

[254] M. Viková, A. P. Periyasamy*, et al.*, Effect of drawing ratio on difference in optical density and mechanical properties of mass colored photochromic polypropylene filaments, *The Journal of The Textile Institute*, 108(2017), 1365-1370.

[255] A. F. Little, R. M. Christie, Textile applications of commercial photochromic dyes. Part 6: Photochromic polypropylene fibres, *Coloration Technology*, 132(2016), 304-309.

[256] M. Aldib, Photochromic ink formulation for digital inkjet printing and colour measurement of printed polyester fabrics, *Coloration Technology*, 131(2015), 172-182.

[257] S. Seipel, J. Yu*, et al.*, Inkjet printing and UV-LED curing of photochromic dyes for functional and smart textile applications, *RSC advances*, 8(2018), 28395-28404.

[258] S. Seipel, J. Yu*, et al.*, Resource-efficient production of a smart textile UV sensor using photochromic dyes: characterization and optimization, in: *Narrow and Smart Textiles*, Springer, (2018), 251-257.

[259] R. M. Christie, *Colour chemistry*, Royal Society of Chemistry, (2001).

[260] P. Coimbra, M. H. Gil, *et al.*, Solubility of a spiroindolinonaphthoxazine photochromic dye in supercritical carbon dioxide: Experimental determination and correlation, *Fluid Phase Equilibria*, 238(2005), 120-128.

[261] A. V. Kotova, N. N. Glagolev, *et al.*, Effect of parameters of a crosslinked polyacrylic Matrix on the impregnation of photoactive compounds in supercritical fluids, *Polymer Science Series A*, 52(2010), 522-531.

[262] A. B. Solovieva, A. V. Cherkasova, *et al.*, Stable "coloured" states of spirooxazine photochrom molecules immobilized in polymer matrixes by supercritical carbon dioxide, *Journal of Molecular Liquids*, 239(2017), 74-82.

[263] F. D. F. de Lima, O. A. A. dos Santos, *et al.*, Impregnation of composite from polycarbonate (PC) and silica gel (Si) films with photochromic dye in supercritical fluid, *Acta Scientiarum-Technology*, 32(2010), 69-74.

[264] P. Mourier, P. Sassiat, *et al.*, Retention and selectivity in carbon dioxide supercritical fluid chromatography with various stationary phases, *Journal of Chromatography A*, 353(1986), 61-75.

[265] M. T. Abate, S. Seipel, *et al.*, Comparison of the photochromic behaviour of dyes in solution and on polyester fabric applied by supercritical carbon dioxide, "IOP Publishing", 459(2018), 212-240.

[266] P. Bamfield, *Chromic phenomena: Technological applications of colour chemistry*, Royal Society of Chemistry, (2010).

[267] A. P. Periyasamy, M. Vikova, *et al.*, A review of photochromism in textiles and its measurement, *Textile Progress*, 49(2017), 53-136.

[268] S. Seipel, J. Yu, *et al.*, Color performance, durability and handle of inkjet-printed and UV-cured photochromic textiles for multi-colored applications, *Fibers and Polymers*, 20(2019), 1424-1435.

[269] G. Wyszecki, G. H. Fielder, New color-matching ellipses, *Journal of the Optical Society of America*, 61(1971), 1135-1152.

[270] Z. Aghaei, B. Emadzadeh, *et al.*, Cellulose acetate nanofibres containing alizarin as a halochromic sensor for the qualitative assessment of rainbow trout fish spoilage, *Food and bioprocess technology*, 2018), 1-9.

[271] R. M. Christie, Chromic materials for technical textile applications, in: *Advances in the Dyeing and Finishing of Technical Textiles*, Woodhead Publishing, (2013), 3-36.

[272] M. Yuqing, C. Jianrong, *et al.*, New technology for the detection of pH, *Journal of Biochemical and Biophysical Methods*, 63(2005), 1-9.

[273] E. Osti, Skin ph variations from the acute phase to re-epithelialization in burn patients treated with new materials (burnshield®, semipermeable adhesive film, dermasilk®, and hyalomatrix®). Non-invasive preliminary experimental clinical trial, *Annals of burns and fire disasters*, 21(2008), 73.

[274] X. Z. Sun, C. Branford-White*, et al.*, Development of universal pH sensors based on textiles, *Journal of Sol-Gel Science and Technology*, 74(2015), 641-649.

[275] D. Morris, S. Coyle*, et al.*, Bio-sensing textile based patch with integrated optical detection system for sweat monitoring, *Sensors and Actuators B: Chemical*, 139(2009), 231-236.

[276] L. Van der Schueren, K. De Clerck, The Use of pH-indicator Dyes for pH-sensitive Textile Materials, *Textile Research Journal*, 80(2010), 590-603.

[277] H. Wenker, Nitrazine Yellow, a New Indicator, *Industrial and Engineering Chemistry*, 26(1934), 350-350.

[278] G. Viscardi, P. Quagliotto*, et al.*, Structural characterisation of Nitrazine Yellow by NMR spectroscopy, *Dyes and Pigments*, 57(2003), 87-95.

[279] T. Salem, F. Simon*, et al.*, Plasma-assisted surface modification of polyester fabric for developing halochromic properties, *Fibers and Polymers*, 18(2017), 731-740.

[280] L. Van der Schueren, K. Hemelsoet*, et al.*, The influence of a polyamide matrix on the halochromic behaviour of the pH-sensitive azo dye Nitrazine Yellow, *Dyes and Pigments*, 94(2012), 443-451.

[281] L. Van der Schueren, K. De Clerck, Textile materials with a pH-sensitive function, *International Journal of Clothing Science and Technology*, 23(2011), 269-274.

[282] E. Guido, C. Colleoni*, et al.*, Influence of catalyst in the synthesis of a cellulose-based sensor: Kinetic study of 3-glycidoxypropyltrimethoxysilane epoxy ring opening by Lewis acid, *Sensors and Actuators B-Chemical*, 203(2014), 213-222.

[283] V. Trovato, C. Colleoni*, et al.*, The key role of 3-glycidoxypropyltrimethoxysilane sol-gel precursor in the development of wearable sensors for health monitoring, *Journal of Sol-Gel Science and Technology*, 87(2018), 27-40.

[284] G. Rosace, E. Guido*, et al.*, Halochromic resorufin-GPTMS hybrid sol-gel: Chemical-physical properties and use as pH sensor fabric coating, *Sensors and Actuators B-Chemical*, 241(2017), 85-95.

[285] L. Van der Schueren, K. De Clerck*, et al.*, Novel cellulose and polyamide halochromic textile sensors based on the encapsulation of Methyl Red into a sol-gel matrix, *Sensors and Actuators B-Chemical*, 162(2012), 27-34.

[286] Z. Aghaei, B. Emadzadeh*, et al.*, Cellulose acetate nanofibres containing alizarin as a halochromic sensor for the qualitative assessment of rainbow trout fish spoilage, *Food and Bioprocess Technology*, 11(2018), 1087-1095.

[287] E. Schoolaert, I. Steyaert*, et al.*, Blend electrospinning of dye-functionalized chitosan and poly(epsilon-caprolactone): towards biocompatible pH-sensors, *Journal of Materials Chemistry B*, 4(2016), 4507-4516.

[288] A. N. Sharifabad, S. H. Bahrami, Halochromic chemosensor from poly(acrylonitrile)/phenolphthalein nanofibers as pH sensor, *IEEE Sensors Journal*, 16(2016), 873-880.

[289] I. Steyaert, G. Vancoillie*, et al.*, Dye immobilization in halochromic nanofibers through blend electrospinning of a dye-containing copolymer and polyamide-6, *Polymer Chemistry*, 6(2015), 2685-2694.

[290] L. Van der Schueren, T. Mollet*, et al.*, The development of polyamide 6.6 nanofibres with a pH-sensitive function by electrospinning, *European Polymer Journal*, 46(2010), 2229-2239.

[291] J.-D. Cho, S.-G. Kim*, et al.*, Surface modification of polypropylene sheets by UV-radiation grafting polymerization, *Journal of Applied Polymer Science*, 99(2006), 1446-1461.

[292] S. R. Shukla, A. R. Athalye, Ultraviolet-radiation induced graft-copolymerization of hydroxyethyl methacrylate onto cotton cellulose, *Journal of Applied Polymer Science*, 44(1992), 435-442.

[293] S. R. Shukla, A. R. Athalye, Graft-copolymerization of glycidyl methacrylate onto cotton cellulose, *Journal of Applied Polymer Science*, 54(1994), 279-288.

[294] K. H. Hong, N. Liu*, et al.*, UV-induced graft polymerization of acrylamide on cellulose by using immobilized benzophenone as a photo-initiator, *European Polymer Journal*, 45(2009), 2443-2449.

[295] J. A. Harris, J. C. Arthur Jr*, et al.*, Photoinitiated polymerization of glycidyl methacrylate with cotton cellulose, *Journal of Applied Polymer Science*, 22(1978), 905-915.

[296] Y. Dong, L. Zheng*, et al.*, UV-grafting coloration of cotton and wool fabrics using bismethacrylated quinizarin dye, *Fibers and Polymers*, 17(2016), 1598-1604.

[297] D. Roy, M. Semsarilar*, et al.*, Cellulose modification by polymer grafting: a review, *Chemical Society Reviews*, 38(2009), 2046-2064.

[298] C. Chung, M. Lee*, et al.*, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, *Carbohydrate Polymers*, 58(2004), 417-420.

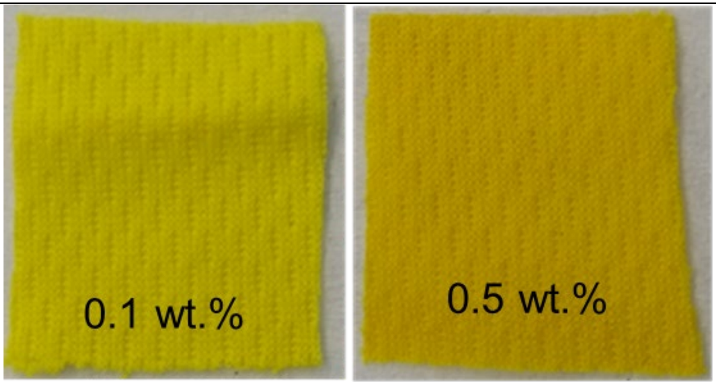
[299] A. Chiappone, J. Nair*, et al.*, Flexible and high performing polymer electrolytes obtained by UV-induced polymer–cellulose grafting, *RSC advances*, 4(2014), 40873-40881.

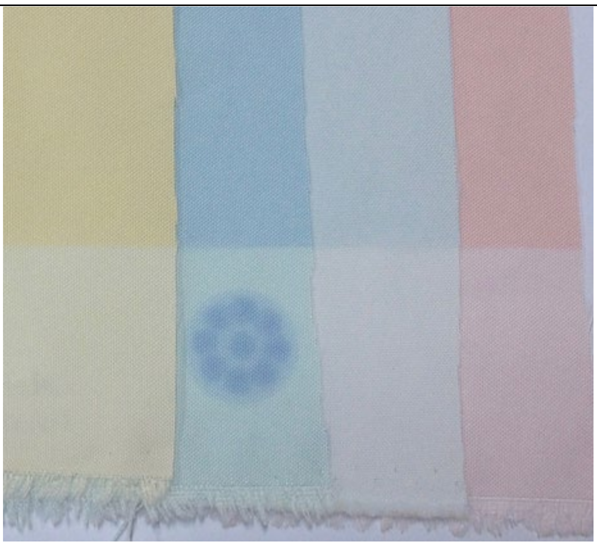
[300] G. Rosace, M. R. Massafra, Marking of cellulose yarn by vinyl monomer grafting, *Textile Research Journal*, 78(2008), 28-36.

[301] T. Xu, Z. Tang*, et al.*, Synthesis of polylactide-graft-glycidyl methacrylate graft copolymer and its application as a coupling agent in polylactide/bamboo flour biocomposites, *Journal of Applied Polymer Science*, 125(2012), 622-627.

Appendix

Images of some representative samples produced in this work

Sample	Image
Combined disperse dyed and chitosan impregnated polyester fabric in $scCO_2$	
Polyester fabrics dyed with curcumin natural dye in $scCO_2$	

Polyester fabrics dyed with photochromic dyes in $scCO_2$	
Photo-grafted cotton fabric with GMA-NY pH indicator dye