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Improvement of polyester dyeing at low temperature

Shahram Radei

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PhD Thesis

Improvement of polyester dyeing at low temperature

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Terrassa, May 2020

El Doctor **José Maria Canal** Catedrático y Profesor Emérito de la Sección de Ingeniería Textil del Departamento de Ciencia e Ingeniería de Materiales de la Universitat Politècnica de Catalunya y la Doctora **Mònica Ardanuy**, Profesora Agregada de la Sección de Ingeniería Textil del Departamento de Ciencia e Ingeniería de Materiales de la Universitat Politècnica de Catalunya.

Certifican:
Que **Shahram Radei**, ha realizado bajo su dirección el trabajo de investigación titulado "*Improvement of polyester dyeing at low temperature*" que presenta para optar al título de doctor.

Y para que así conste, se expide el presente certificado en Terrassa a fecha de 1 de marzo de 2020

José Maria Canal **Mònica Ardanuy**

Agradecimientos

Los directores hacen constar que durante el inicio de la tesis esta fue co-dirigida por el Doctor **Fracisco Javier Carrión-Fité**, actualmente Catedrático jubilado.

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Abstract

In this thesis the polyester dyeing at low temperatures has been assessed with two different methods: exhaustion method and thermosol method.

Exhaustion dyeing process was performed with high and low molecular-weight disperse dyes in presence of small proportion of two non-toxic and biobased aromatic auxiliaries, namely o-vanillin and coumarin with an organic co-solvent (n-butylacetate) in a micro-emulsion system. The kinetic and thermodynamic parameters of this process were analysed. The values of entropy and activation diffusion coefficients were obtained from the theory of absolute rates of dyeing. Moreover, color fastness to washing and ironing were determined. The study proved that color strength and dyestuff absorption on the polyester with this new micro-emulsion formulation at low temperature (95ºC) are similar to those achieved with high temperature exhaustion system at 135 ºC. Moreover, this new micro-emulsion system has the advantage of using eco-friendly auxiliaries being the dyeing system favorable from both economic and environmental points of view. Comparing both auxiliaries, it was found that, in general, polyester samples dyed with o-vanillin/n-butylacetate system yielded higher colour strength (K/S) and exhaustion percentage than the ones dyed with coumarin/n-butylacetate. Higher activated energies, activated entropy and diffusion coefficient were found for polyester samples dyed with o-vanillin/n-butylacetate.

Thermosol process was carried out with a low molecular disperse dye using two different impregnation padding baths (with or without lecithin) at two different impregnation times at 20º C (one minute or twenty four hours). The study demonstrated that values of K/S, dyeing efficiency, and dyestuff concentration into the fiber (mg dye/ g fiber) of dyed polyester samples increased due to action of lecithin. This reveals that if the padding solution contains lecithin less quantity of dyestuff will be required to reach same color shade. Moreover, samples dyed with twenty four hours

of impregnation lead to higher color strength, efficiency and dyestuff concentration in the fiber than thermosolated polyester samples treated during one minute of impregnation time.

Resumen

En esta tesis, se ha estudiado la tintura de poliéster a bajas temperaturas con dos métodos diferentes: el método de agotamiento y el método de termosol. El proceso de tintura por agotamiento se realizó con colorantes dispersos de alto y bajo peso molecular en presencia de una pequeña proporción de dos auxiliares aromáticos alternativos biobasados y no tóxicos (o-vainillina o cumarina) en un co-disolvente orgánico (acetato de n-butilo) en un sistema de micro-emulsión. De dicho proceso de tintura se analizaron los parámetros cinéticos y termodinámicos. Los valores de entropía y los coeficientes de difusión de activación se obtuvieron a partir de la teoría de las velocidades absolutas de tintura. También se determinaron las solideces de la tintura al lavado y al planchado. El estudio demostró que la intensidad del color y la absorción del colorante en el poliéster con esta nueva formulación de micro-emulsión a baja temperatura (95ºC) es similar a la lograda con un sistema de alta temperatura a 135 ºC. Además, este nuevo sistema de micro-emulsión tiene la ventaja de utilizar auxiliares biodegradables y no tóxicos, siendo el sistema de tintura favorable desde el punto de vista económico y medioambiental. Al comparar ambos auxiliares, se vio que, en general, las muestras de poliéster teñidas con el sistema de acetato de n-butilo/o-vainillina produjeron una mayor intensidad de color (K/S) y un mayor porcentaje de agotamiento que las teñidas con acetato de n-butilo/cumarina. Se obtuvieron valores de energía de activación, entropía de activación y coeficiente de difusión más altos para las muestras de poliéster teñidas con acetato de n-butilo/o-vainillina con respecto a las de cumarina/n-butilo.

El proceso de termosol se llevó a cabo con un colorante disperso de bajo peso molecular utilizando baños de impregnación diferentes (con o sin lecitina) introduciendo la variable de dos tiempos de impregnación diferentes (un minuto o veinticuatro horas). El estudio demostró que los valores de K/S, la eficiencia de la tintura y la concentración de colorante en la fibra (mg de colorante/g de la fibra) de las muestras de poliéster teñido aumentaron debido a la acción de la lecitina. Esto revela

que si la solución de impregnación contiene lecitina se requerirá menos cantidad de colorante para alcanzar la misma intensidad de color en el tejido de poliéster. Además, las muestras teñidas con veinticuatro horas de impregnación a temperatura ambiente conducen a una mayor intensidad de color, eficiencia y concentración de colorante en la fibra que las muestras de poliéster termosoladas después de un minuto de tiempo de impregnación.

Resum

En aquesta tesi, s'ha estudiat la tintura de polièster a baixes temperatures amb dos mètodes diferents: el mètode d'esgotament i el mètode de termosol. El procés de tintura per esgotament es va realitzar amb colorants dispersos d'alt i baix pes molecular en presència d'una petita proporció de dos auxiliars aromàtics no tòxics i d’origen natural (o-vanil·lina o cumarina) en un co-dissolvent orgànic (acetat de n-butil) en un sistema de micro-emulsió. D'aquest procés de tintura es van analitzar els paràmetres cinètics i termodinàmics. Els valors d'entropia i els coeficients de difusió d'activació es van obtenir a partir de la teoria de les velocitats absolutes de tintura. També es van determinar les solideses de la tintura a la rentada i a la planxada. L'estudi va demostrar que la intensitat del color i l'absorció del colorant en el polièster amb aquesta nova formulació de micro-emulsió a baixa temperatura (95ºC) és similar a l'aconseguida amb un sistema d'alta temperatura a 135 ºC. A més, aquest nou sistema de micro-emulsió té l'avantatge d'utilitzar auxiliars biodegradables i no tòxics, sent el sistema de tintura favorable des del punt de vista econòmic i mediambiental. Al comparar els dos auxiliars, es va veure que, en general, les mostres de polièster tenyides amb el sistema d'acetat de n-butil/o-vanil·lina van produir una major intensitat de color (K/S) i un major percentatge d'esgotament que les tenyides amb acetat de n-butil/cumarina. Es van obtenir valors d'energia d'activació, entropia d'activació i coeficient de difusió més alts per a les mostres de polièster tenyides amb acetat de n-butil/o-vanil·lina respecte a les de cumarina/n-butil.

El procés de termosol es va dur a terme amb un colorant dispers de baix pes molecular utilitzant banys d'impregnació diferents (amb o sense lecitina) introduint la variable de dos temps d'impregnació diferents (un minut o quatre hores). L'estudi va demostrar que els valors de K/S, l'eficiència de la tintura i la concentració de colorant a la fibra (mg de colorant/g de la fibra) de les mostres de polièster tenyit van augmentar a causa de l'acció de la lecitina. Això revela que si la solució d'impregnació conté lecitina es requerirà menys quantitat de colorant per aconseguir la

mateixa intensitat de color en el teixit de polièster. A més, les mostres tenyides amb quatre hores d'impregnació a temperatura ambient condueixen a una major intensitat de color, eficiència i concentració de colorant a la fibra que les mostres de polièster termosolades després d'un minut de temps d'impregnació

CONTENTS

CHAPTER 1. INTRODUCTION AND OBJECTIVES

The thesis has been written as a compendium of research papers as follows:

First article: *Kinetics of Low Temperature Polyester Dyeing with High Molecular Weight Disperse Dyes by Solvent Microemulsion and AgroSourced Auxiliaries. Polymers 2018 10 (2), 200.*

This article is focused on developing new formulation for polyester dyeing at low temperature with high molecular weight disperse dyes by using bio-based, non-toxic and biodegradable auxiliaries in a micro-emulsion system, in order to have an alternative efficient dyeing system instead of the industrial dyeing processes at high temperatures or dyeing processes with using toxic auxiliaries. In this article we have focused on environmentally friendly auxiliaries in a micro-emulsion system. The kinetic and activation energies have been studied at four temperatures below 100°C.

Second article: *Thermodynamic and kinetic parameters of polyester dyeing with Disperse Blue 56 using bio-based auxiliaries and co-solvent microemulsion. Textile Research Journal, 9 (5-6), 523–536.*

This article is focused on evaluating kinetic and thermodynamic parameters of polyester dyeing at low temperature using bio-based auxiliaries with a low molecular weight disperse dye in a micro-emulsion system in the activated state (before equilibrium) which is more similar to the industrial processes. Moreover, in this article we have compared the efficiency of our proposed process at low temperature to conventional process at high temperature, and there were no adverse different between the two processes, revealing the effectiveness of our process.

Third article: *Effect of a bio-based amphoteric surfactant on polyester thermosol dyeing process. Journal of the Textile Institute, under review.*

This article is focused on continues thermosol polyester dyeing using bio-based auxiliary in two different impregnation time, the efficiency, impregnation and colour strength of the fabric was evaluated. The study revealed that using of Lecithin in the padding bath increased all parameters (colour strength, efficiency and impregnation).

As it has been shown, these three articles were focused on polyester dyeing using environmentally friendly auxiliaries biobased and biodegradables. Moreover, all dyeing processes were carried out at low temperature. These articles revealed that natural bio-based compound can substitute toxic compounds, with maintaining good quality of dyeing. Dyeing processes indicated us acceptable absorbance level, efficiency and there were no significant changes on fastness properties of the dyed samples.

1.1. Objectives

The general objective of the thesis is to develop low temperature dyeing processes for polyerster dyeing with disperse dyes by using biobased, low cost and non-toxic auxiliary compounds via exhaustion or thermosol dyeing systems.

Other objectives of the thesis are the following:

1) To evaluate the kinetic and thermodynamic parameters of polyester dyeing at low temperature in a micro-emulsion system in the activated state.
2) To evaluate the fastness properties like fastness to washing and ironing of dyed samples in both thermosol and exhaustion dyeing processes.

CHAPTER 2. BACKGROUND AND STATE OF THE ART

2.1. Polyester (PET) fibers

Wallace Carothers designed the plan for production of filaments similar to the polyester in the late 1920s. Later the idea of Carothers was developed in the United Kingdom by Calico Printers Association being the first production of polyester achieved by in 1941. The right was later patented by DuPont for the United States and ICI obtained the patent right for rest of the world. In the 1950s commercializing of the polyester happened, and polyester transformed to the "wash and wear" fabric which was a revolution in the textile industry (Koh, 2011).

Polyester fibres (PES or PET) are defined as long-chain polymers chemically composed of at least 85% by weight of an ester of dihydric alcohol and terephthalic acid among others (Figure 1).

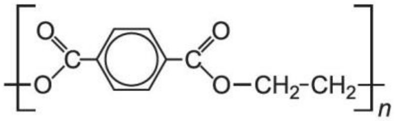

Figure 2.1. Chemical structural unit of PET

Polyester fibres have the highest usage among all synthetic fibres in the world, being higher than the total production of poly-acrylic and polyamide fibres in 1990. In 2017 global production of polyester fibres reached 53 million metric tons (Statisa.com, 2019; Pasquet et al, 2013).

The main world producers of polyester are China, Japan and India although other Asian countries such as Indonesia, Thailand, Malaysia, Pakistan, Vietnam and Bangladesh are also important. Table 1 indicates annual production of PET in 2017 (Statisa.com, 2019).

Table 2.1. Annual production of polyester

World	53.3 million tonnes
Europe	3.9 million tonnes
North America	7.2 million tonnes
USA	7.0 million tonnes
China	18.9 million tonnes
Japan	1.5 million tonnes
Rest of Asia	16.4 million tonnes

As polyester fibres are the most important synthetic fibre worldwide in terms of production volume and applications, therefore is a prominent subject to research on.

Fibre forms

The four basic forms of PET fibres are filament, staple, tow, and fibrefill. In the filament form, each individual strand of polyester fibre is continuous in length, producing smooth-surfaced fabrics. In staple form, filaments are cut to short, predetermined lengths. In this form polyester is easier to blend with other fibers. Tow is a form in which continuous filaments are drawn loosely together. Fiberfill is the voluminous form used in the manufacture of quilts, pillows, and outerwear. The two forms used most frequently are filament and staple.

Production of PET filaments

The types of processes that manufacturers use to produce PET vary among them, and little is known about specific manufacturing processes, because the companies want to keep them a secret in order to remain competitive. Nonetheless, there are common steps to produce the polyester that are described as follows (Corbman & Bernard 1983; Denton & Daniels, 2002):

Polymerization

To manufacture PET, ethylene glycol reacts with terephtalic acid or dimethyl terephthalate (Figure 2) in the presence of a catalyst at around 300 ºC (Lewin & Pearce, 1985).

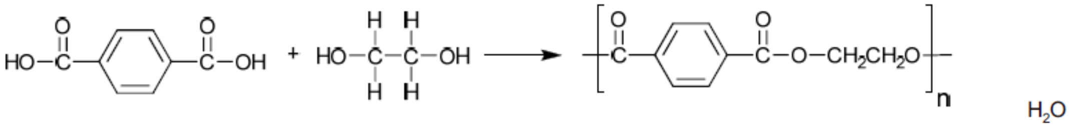

Figure 2.2. Polymerization reaction of PET

Drying

After the polyester emerges from polymerization, the long molten ribbons are allowed to cool until they become brittle. Then, the material is cut into tiny chips and completely dried.

Melt-Spinning

The chips are dried and then put into extrusion system for melt-spun the fibres. Polyester is a melt spun fibre, which means that it is heated, extruded via the spinnerets, and cools upon hitting the air. From there it is loosely wound around cylinders. The number of holes in the spinneret determines the multifilament count, as the emerging fibers are brought together to form a single strand.

Drawing the fibre

When polyester emerges from the spinneret, it is soft and easily elongated up to five times its original length. The stretching forces lead orientation on axis direction of the the random polyester molecules aligend in a parallel formation. This increases the strength, tenacity, and resilience of the fibre. This time, when the filaments dry, the fibres become solid and strong instead of brittle. Drawn fibres may vary greatly in diameter and length, depending on the characteristics desired of the finished material. Also, as the fibres are drawn, they may be textured or twisted to create softer or duller fabrics.

Winding

After the polyester yarn is drawn, it is wound on large bobbins or flat-wound packages, ready to be transformed into fabrics.

Polyester fibre's properties

Polyester fibres have advantages such as high chemical resistance, lightweight, relatively low price, good tensile strength and abrasion resistance, stable to sunlight, acids, reduction and oxidation products and most organic solvents, very good wrinkle recovery and resistance to deformation, high sponge capacity, high resistance to insects (moths) and microorganisms (bacteria), exceptional wash and wear and permanent press properties among others. Moreover in the case of combination with cotton and wool, PET fibres increase the quality of the blended fabric such as: presence of polyester avoids wrinkle problem of the blended fabric, it increases the strength of the blended fabric and it accelerates the drying process after washing (Moncrieff, 1970; Nunn. 1979). Table 2 summarizes the main physical properties of the polyester.

Table 2.2. Physical properties of polyester

Properties	Value
Density	1.38-1.40 g/cm3
Melting point	252-256ºC
Glass transition temperature (Tg)	68-78ºC
Specific heat	At 20ºC→ 1.5 J/g·ºC
	At 150ºC → 1.75 J/g·ºC
	At 175ºC → 3.15 J/g·ºC
Tensile strength	Filament: 3.5-4.5 g/dtex
	Cut fibre: 2.7-3.5 g/dtex
	High strength: 5.4-7.2 g/dtex
Loss of resistance due to wetting	0%
Moisture absorption under normal conditions	0.4%
Ironing temperature	150-170ºC

Polyester fibres have high resistance to reducing and oxidizing agents, also to bleaching treatments with hydrogen peroxide or sodium hydrochloride, although the high degree of white polyester fibre usually makes this operation unnecessary. Polyester fibres lose their strength in high concentration of formic acid, acetic acid and oxalic acid at 80 ºC, while they exhibit high resistance to dilute solutions of mineral acids even at 100 ºC. PET fibres are weak to caustic alkaline solutions, while they have good resistance to dilute alkaline solutions. PET fibres are weak in acidic conditions below pH=4 or alkaline conditions above pH=8. However these fibres can maintain their properties during textile processing such as dyeing at 135 ºC for one or two hours, given that the pH of the bath should be maintained around 5, in the case of dyeing with PET/CO the pH is over 8 (Nunn, 1979). In an acidic bath of pH less than 4 or in an alkaline bath of PH above 8, the chance of damage to the fibre increases.

Polyester fibres have hydrophobic nature due to their compact and semi-crystalline structure. It is because this, polyester dyeing is achieved with special dyes namely disperse dyes.

2.2.Disperse dyes

Disperse dyes are referred to the dyes which are insoluble in water. These dyes are used to dye hydrophobic fibres such as polyester among others (rayon triacetate, polyamide and acrylic).

ICI established a method for the cataloguing disperse dyes in the 1970, based on their fastness and dyeing characteristics, and divided them into four types from A to D: A class refers to low molecular weight dyes, which have better dyeing properties such high exhaustion, good leveling and colour strength, however their fastness properties such fastness to washing and ironing are medium. Generally the diffusion of low molecular weight dyes is quicker and higher than high molecular weight dyes. Class D refers to dyes with higher molecular weight, with poor dyeing properties such levelling, exhaustion and colour strength but better fastness properties. Class B and C refers to medium molecular weight of disperse dyes.

In 1992 Colour Index classified around 1,150 disperse dyes according their chemical structure such as azo, antraquinone, meethine, nitrodiphenylamine, xanthene, aminoketone, quinoline and miscellaneous (Broadbent, 2001; Trotman, 1970). Following, the main characteristics of the most common groups are presented:

Azo disperse dyes

Azo disperse dyes are dyes which have at least one azo group (Figure 5) attached to different substituents like naphthalene, benzene or thiazole among others. These dyes are one of the most important dye classess in polyester dyeing and cover all ranges of shades.

Azo dyes have advantages like powerful electron donating groups; tinctorial strength and low cost in comparison to other disperse dyes. Their disadvantages are low shade and low fastness to the light (Gordon & Gregory, 1983; Koh, 2011).

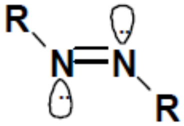

Figure 2.3. Azo group

Antraquinone disperse dyes

Antraquinone disperse dyes were among early acetate dyes and had important influence on violet and blue shade series. Antraquinone disperse dyes are the oldest disperse dyes and have advantages such as excellent fastness properties and particularly high light fastness, bright shades and good stability. These dyes cover all ranges of colours from yellow to even turquoise blue (Griffiths, 1984; Weaver & Shuttleworth, 1982; Koh. 2011). Figure 6 shows the chemical formula of antraquionone.

Different shades can be made by these dyes. For instance C.I disperse red 60, C.I. disperse blue 56 and C.I. disperse violet 26 have been used hugely in the industry, especially C.I. disperse red 60 which acts as an elementary colour for shades that obtained by combination of three dyes, in pale shades and it is a dye available for heat transfer printing. These disperse dyes show excellent brilliance and high light fastness properties compared to similar colorants of azo dye. Additionally these dyes have fluorescence properties.

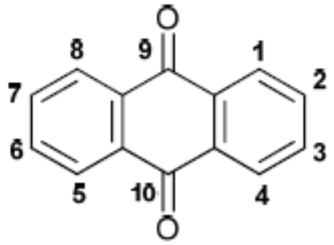

Figure 2.4. Chemical formula of antraquionone

Other classes of disperse dyes

Even though antraquinone, monoazo and diazo disperse dyes are the most important and common dyes for polyester dyeing, in terms of the market share and industrial uses, there are other important classes such as nitroarylamino disperse dyes, coumarin disperse dyes, methine disperse dyes, naphthostyryl disperse dyes, quinophthalone disperse dyes, formazan disperse dyes and benzodifuranone disperse dyes (Koh 2011).

Antraquinone and azo type of disperse dyes has been used in the thesis due to their high importance. Dyes with different molecular weight have been used in order to compare their efficiency, absorbance level and fastness properties.

2.3.Dyeing mechanism with disperse dyes

Disperse dyeing's mechanism involves the diffusion of a a solid (dyestuff) in other solid (polyester fibers) and is produced in four stages (Murray & Mortimer, 1971):

a. The dyestuff is dispersed in the water dye-bath.

b. Dye molecules are transferred to the fibre surface from the dye-bath solution.

c. The adsorbed dyestuff penetrates in a monomolecular way into the fibre and diffuses into it.

d. The dyestuff remains absorbed on the polyester fibre surface and must be erased by reductive washing to obtain an adequate rubbing fastness.

The transfer process to the fibre from the aqueous solution is similar to the extraction of a solute from of one solvent by a second solvent, so immiscible solvent and laws of partition are similar. The distribution coefficient, which is linked to the solubility of the dye in the fibre and aqueous phases, can be determined at different temperatures. However, they can be influenced by the concurrent equilibrium between the aqueous and solid phases of the dye. The rate of the first and second stages of the process mechanism is ruled by this solubility.

Disperse dyeing process is strictly reversible and the results follow to a straight-lined isotherm. Typical results show linear relationship in the distribution of dye between polyester and water indicates a linear relationship with results of disperse dyeing system.

Dyeing processes with disperse dyes is the transfer of dye molecules from a dispersion into the fibre and, due to the linearity of the isotherms obtained, the amount of dye adsorbed ($[D]_{ad}$) relative to the dye concentration in the bath ($[D]_s$) can be expressed by the partition coefficient (K) (Equation 2.1).

$$\frac{[D]ad}{[D]s} = K \quad (2.1)$$

The dye molecules that have been adsorbed on the fibre surface diffuse into the inner of the fibre by a relatively simple mechanism, which seems to obey Fick's equation (Patterson & Sheldon, 1959).

The Fick's equation quoted that 'the rate of diffusion of dye through unit area (transverse to the direction of diffusion) at any point in the fibre is directly proportional to the concentration gradient of the dye at that point'. As would be expected, the amount of dye taken up by polyester fibres from a bath of constant concentration is found to be proportional to the square root of the dyeing time, until a saturation value is reached.

Very similar results are observed during the earlier stages of the process in dye-baths of normal composition and concentrations, such as are employed in commercial 'exhaust dyeing' processes. It is found that the rate of dyeing is quite independent of the initial dyestuff concentration in the dyebath, practically up to the point at which equilibrium is established (Waters, 1950). 'For dyeing carried out at a constant temperature, a plot of the instantaneous fractional 'dye uptake' (C_t/C_∞) against time of dyeing gives a steeply-rising asymptotic curve, which appears to fit a law based on the hyperbola or, possibly, on the hyperbolic tangent' (Cegarra & Puente, 1967).

2.4. Polyester dyeing processes

Polyester dyeing is generally performed with three different systems depending on the amount or special shades needed. These systems are exhaustion high temperature (130-140ºC), exhaustion low temperature (≤100ºC) and continuous processes like thermosol and pad-steam. When small quantity or special shades of dyed fabrics are needed, exhaustion process is the most suitable process; while for larger quantity with shorter dyeing time thermosol dyeing process is more desirable.

Exhaustion High Temperature (HT) dyeing

This method is one of the most common systems used for polyester dyeing. HT dyeing is carried out at 135-140 ºC under high pressure with dispersing agents. The dyeing process occurs in three phases: namely absorption phase (absorption of dye onto the surface of the fibre, diffusion phase (diffusion of the dye on the inner of the fibre) and cleaning phase (removing of dyestuff from the surface of the fibre).

Normally HT dyeing is achieved in absence of carrier. This method has advantages such as excellent diffusion, short time of dyeing, and high colour strength. Also this method in some circumstances leads to better fastness properties. However, HT dyeing has disadvantages such as: it requires high energy consumption to remain heat, in some cases it causes deformation of the fibre, and the process should be done in enclosed machinery (Burkinshaw, 1995).

Exhaustion Low temperature dyeing

This process is done at atmospheric pressure and temperature below 100 ºC with the aid of carriers. However, most of the carriers used have toxicity for the human and are not environmentally friendly. In all parts of the industrial processes environmental issues are becoming so important (McCarthy, 1998), and to reduce the undesirable effects of dyeing processes on the environment, several legislative requirements have emerged with increasing consistency. In response, the industry has been forced to become increasingly innovative in order to develop new products and practices that are more environmentally friendly than the existing ones (Lewis, 1999). Therefore, nowadays dyeing processes have more environmental restrictions, due to innovation and developments in colour chemistry, in order to create novel effects, and reduce processing costs.

In general, there are two types of carriers for polyester exhaustion dyeing at low temperature, hydrophobic and hydrophilic carriers, which have different mode of action during the dyeing process. Hydrophobic carriers are the most efficient carriers for polyester dyeing in textile industry;

hydrophobic carriers like dichloro and trichloro-benzene are substituted by hydrophilic carriers such as benzoic acid, due to their lower toxicity than benzoic acid (Pasquet, 2013; Vigo, 1994).

Hydrophilic carriers have different mode of action, they increases the solubility of the disperse dyes in the water which decreases their diffusion into the fibre (Burkinshaw, 1995; Arcoria, 1989; Pasquet, 2103). The absorption process of carriers to the PET fabric are quite similar to the absorption process of the disperse dyes to polyester, and aromatic parts of the carriers are linked to polyester fabric. The molecular weight of carriers are smaller compare to molecular weight of the disperse dyes, therefore due their smaller molecular weight, carriers penetrate faster to the amorphous regions of the fibre, so this phenomena cause swelling of the polyester and it opens sites and free spaces in the macromolecule chains of the fibre for dye absorption (Murray and Mortimer, 1971; Vigo, 1994; Burkinshaw, 1995; Pasquet, 2013).

Several studies have been done in the way of more environmentally friendly practices of polyester dyeing via exhaustion system at low temperature. There has been significant interest in dyeing polyester with carriers or additives at lower temperatures, considering their biodegradability, low toxicity and environmentally friendly practices.

Carrión-Fite (1995) developed an alternative method for dyeing polyester with reduced energy costs, lower investment, and without the unwanted effects of auxiliaries (Carrión-Fite, 1995; Spanish patent, 1995)). The method used temperatures as low as 40 ºC, or even lower, in combination with disperse dyes in a micro-emulsion containing a low proportion of an organic solvent (an alkyl halogen) and phosphoglyceride as emulsifier that is prepared under ultra-sonic agitation. In 2016 he replaced the organic solvent with n-butylacetate, a non-toxic solvent, and he used lecithin (an agro-sourced auxiliary) as an emulsifier (Carrión-Fite, 2016; Spanish patent, 2016).

Pasquet et al. (2013) dyed polyester fabric with p- and o-vanillin at low temperature in the presence of two disperse dyes (C.I Disperse Blue 56 and C.I Disperse Blue 79). The study confirmed that color strength of polyester dyed with these auxiliaries was good, mainly when o-vanillin was used. Moreover, the level of the toxicity of these compounds was shown by the USEtox model (Pasquet et al., 2013).

With the aim of avoiding disadvantages effects of carriers, Montazer and Harifi, 2013 developed an alternative method by thermally treating with nano TiO_2 and two different disperse dyes. Their study confirms colour strength of PET fibre increased with nano TiO_2. But this process is expensive and not able for industrial dyeing.

Hamada et al, 2013, established a new method of dyeing polyester by using nano disperse dyes and developing light fastness by using nano ZnO powder.

Choi et al 2001, investigated comparison of dyeing behavior of disperse dyes on polyester fabric with two cationic gemini surfactants namely propanediyl 1-α, ω-bis (dimethyldodecylammonium bromide) (DC3-12) and hexanediy 1-α, ω-bis (dimethyldodecylammonium bromide) (DC6-12) as auxiliaries or a conventional surfactant namely dodecyltrimethylammonium bromide (C12C1NBr). Study proved that colour strength with gemini surfactants is higher than achieved in conventional one, also with increasing concentration of surfactants dye hydrophobicity decreases above the critical micelle concentration (CMC), in general dyeing of polyester with gemini surfactants has benefits such as controlling dyeing kinetics and improving dye absorbed by PET fabric, dye which used in this study was C.I. disperse blue 56.

Thermosol dyeing process

Thermosol dyeing process was established by Du Pont in 1949. To dye batch of 5,000 m or more polyester fabrics prepared to width or the polyester component of a blended fibers fabric at continuous speed (10-50 m/min), thermosol continuous dyeing is one of the most efficient process. The general industrial process comprises:

1- Polyester fabric preparation at width
2- Padder + automatic wet colorimetric control
3- Pre-dryer
4- Dryer
5- Thermosol: dye fixation + fabric thermofixation
6- Continuous washing + finishing
7- Dryer
8- Continuous inspection by artificial vision

This process normally is carried out by impregnation and padding of the fabric in the padding bath followed a drying with infrared radiation or hot air at 100-140 ºC followed by dye fixation achieved by a thermal treatment at 160-225 ºC during 120-20 seconds (Pasquet, 2013). Compared to the exhaustion process, thermosol dyeing process requires shorter time and has advantages such as lower consumption of water, labor costs and production time, faster production range, and also fiber thermofixed besides dyeing. Thermosol dyeing process is highly dependent on characteristics of the disperse dyes, and it is important to control the dye migration during drying and the thermosol sequence. Therefore choosing the most efficient migration inhibitors, auxiliary products and disperse dyes are crucial (Pasquet, 2103). In the continuous thermosol dyeing process, a disperse dye in an aqueous medium is deposited on the surface of the polyester fabric by padding, and then, with the drying process by hot air, a multilayer of disperse dye in solid form, with the auxiliary products, are located on the polyester fibres surface. By means a thermal treatment by hot air at temperatures between 160 °C to 210 °C, during a short time (between 120 s and 30 s), the diffusion of the dye inside the fiber is achieved. Thermosol process is industrially suitable for dyeing productions from 8,000 m / shade of polyester fabric, and also for the dyeing the PET component of the PET/CO, or PET/CV fabrics. The production speed ranges are comprised between 20 to 80 m/min, and compared to discontinuous dyeing, the personnel costs are 40% lower, the water consumption is 20% lower, and additionally the fabric is thermofixed during the dyeing operation. In the process design is essential the choose disperse dyes and auxiliary products to obtain high exhaustion of the dye into the fibre, so that the colour contamination of the subsequent washing baths is minimal and may facilitate the reuse of the washing baths (Trotman, 1970). After thermosol dyeing, posterior reductive washing is essential to remove the dyes absorbed onto fiber surfaces.

2.5. Factors that affect the polyester dyeing

There are several factors which can influence on polyester dyeing such as dispersing agents, particle size in the dye-bath, pH of the dye-bath, and temperature of dyeing. Due to low solubility of the disperse dyes in water, dispersing agents are used in polyester dyeing in order to achieve acceptable distribution and particle size in the dye-bath, dispersing agents prevent agglomeration of the dye particles (Heimanns, 1981; Derbyshire et al, 1972). Reduction in particle size of the dye-bath increases the solubility of the disperse dye in a dispersion, also reduction of the particle size, increases the dye absorption on the fibre (Kenneth & Skelly, 1973).

In general polyester dyeing is achieved at pH ranging 5.5 to 6.5, high acidic or alkaline conditions, such as lower than pH=4 or higher than pH=9 can damage polyester fibers, as well as some disperse dyes (Nunn, 1979, Koh, 2011). Dye absorption and diffusion into the polyester is highly influenced by the temperature of dyeing, as dyeing temperature increases it cause an increase the mobility in the amorphous macromolecule segments chains of the fiber, which increases the dye absorption speed (Nunn, 1979).

2.6.Fastness to wet treatment

It has been increasing the demand of high wet fastness for environmentally friendly dyes on polyester. Fastness to washing is highly dependent on dye diffusion. Also, the fastness is dependent to size and polarity of the dye molecule. For instance if the size and polarity of the dye molecule increases, it decreases the mobility inside the fiber, which causes an increase in fastness to washing (Choi et al, 2000). Due to hydrophobicity and crystallinity of polyester fabrics, these fabrics have better fastness properties to wet like washing and moisture fastness than nylon and acetate with a given dye. Furthermore, choosing the proper dye has important role on polyester wash fastness (Choi et al, 2000).

2.7.Fastness to dry heat

Fastness to dry heat or ironing is really important property of the disperse dye in polyester dyeing, as after dyeing, heat treatments are common in the finishing processes such as thermofixation, or calendering among others. The dry heat fastness is highly dependent on the size and polarity of the molecules, increases in size or polarity, will reduce the diffusion rate in the fiber as well as the vapor pressure of the dye, therefore this phenomena increase heat fastness (Gordon & Gregory).

In this thesis, the exhaustion low temperature process was carried out in presence of non-toxic, biodegradable and environmentally friendly auxiliaries such as: ortho-vanillin and coumarin.

O-vanillin and coumarin have been dispersed in water with an organic non-toxic solvent namely n-butylacetate. On the other hand, for thermosol process, lecithin has been used as a natural bio-based auxiliary.

2.8.Natural auxiliaries for polyester dyeing

Vanillin is a white or yellow crystalline compound, which can be finding in plants in the nature, normally as a glycoside bound to sugar. Vanillin is environmentally friendly and normally is used as an additive in beverages and foods (60%), flavours (20-25%) and 5-10% for pharmaceuticals. During the years 1993 to 1995 worldwide production of vanillin was estimated 10,000 tons per year with an annual increase of 2%. Vanillin has properties such as antimicrobial, antioxidant and anti-mutagenic influences (Food chemicals, 1994; Pasquet et al, 2013; Cha et al, 2011). Melting point is 81 ºC and its boiling point 285 ºC. Figure 7 shows chemical formula of ortho vanillin (o-vanillin):

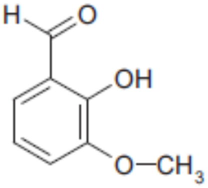

Figure 2.5. Chemical structure of o-vanillin (2-hydroxy-3-methoxybenzaldehyde)

The solubility parameter of o-vanillin is similar to conventional carriers, and its solubility in water is 10 g/L. The molecular weight is 152.15 g·mol^{-1}. Moreover is a biodegradable. There has been studied abiotic degradation, photodegradation and hydrolytic degradation of vanillin in water. By sunlight in air, during the time of half-life of 4.7 hours, vanillin will be degraded. The hydrolysis measurements in water at different pH levels revealed that the compound is stable in the water and hydrolyses did not occurred. In order to study the biotic degradation of vanillin, vanillin was in soil and water after inoculation with Aspergillus terrus, anaerobic sludge or benthic microorganisms from a eutrophic lake. The biodegradation in unamended garden soil was slow (about 10 % after 4 weeks), but in amending garden soil with "active garden soil" the degradation was 41% after 21 days. 62.5% degradation was achieved with aerobic conditions in water after inoculation with Aspergillus terrus within 6 days.72% of degradation was achieved in water under anaerobic conditions after inoculation with anaerobic sludge in water, within 28 days. From these studies it can be concluded that vanillin is biodegradable. (Peery, 1965; Pool, 1982).

Coumarin (2H-chromen-2-one) is obtained from natural sources via extraction from tonka beans. Also coumarin can obtained in vanilla extract with a photometric method, it is possible from reading the transmittance or absorbance at 490 nm, and comparing it against a standard (LARC, 1987). Coumarin has usage in toothpastes, antiperspirant deodorants, bath products, body lotions, face creams, fragrance creams, hair sprays, shampoos, shower gels and toilet soaps (Cohen, 1979; Lake, 1999). Also has usage in medicine such as cancer treatment and prevention of dental caries and food industry. Coumarin has boiling point of 301.7 ºC, melting point of 71 ºC and density of 0.935 cm^3/g and its solubility in water is 1.7 g/L. Like o-vanillin solubility parameter of coumarin is similar to the conventional carriers, and its molecular weight is 146.15 $g{\cdot}mol^{-1}$ (LARC, 1987). Figure 8 shows chemical formula of the coumarin.

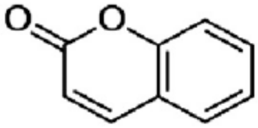

Figure 2.6. Chemical structure of coumarin

Butyl acetate can be finding in the nature and various plant tissues. N-butylacetate has usage in food industry as flavouring. Inhalation of n-butylacetate can cause slight eye, nose and throat irritation on human, but no serious hazard has been reported (World health organisation, 2005). Figure 9 shows chemical structure of n-butylacetate.

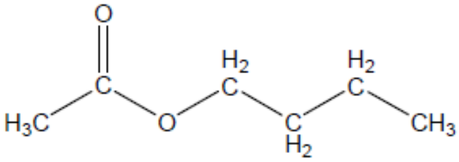

Figure 2.7. Chemical structure of n-butylacetate

Lecithin is a bio-based fatty substance with brown to light yellow colour. The density of lecithin is 0.97 g/mL (liquid) and 0.5 g/mL (granule) and its molecular weight is 750 g·mol^{-1}. Lecithin colour is dependent on its origin, procedure conditions, and whether. Lecithin is biodegradable, and there is no health hazard involved in the production of commercial lecithin from crude vegetable oils. Lecithin has usage in food industry, cosmetic and pharmaceuticals. Lecithin is used in the textile industry as wetting, dispersing, emulsifying, softening, and stabilizing agent (Kartal et al, 2018). Figure 10 shows chemical structure of Lecithin.

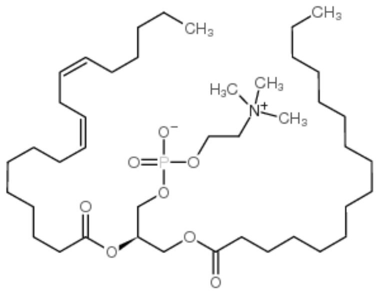

Figure 2.8. Chemical structure of Lecithin

2.9.Dyeing kinetics

Studying kinetic parameters is important in polyester dyeing system to evaluate the effects of different conditions such as temperature and auxiliary products during the dyeing kinetic process. Also these data are important to reference dyeing behavior of the polyester in different conditions and understand in depth the dyeing process. The kinetic of dyeing systems are normally determined as function of temperature and time. Study the adsorption isotherms assist to understand the dyeing mechanism and to control the finishing process, however only there is lack of data so far on the thermodynamic and kinetic aspects of polyester dyeing in the activated state (before equilibrium). Most of the dyeing processes imply adsorption and also absorption of dyes in the fiber, therefore is difficult to differentiate them in the dyeing systems. Thus, the term of sorption of the colorants can be employed in research methods and was measured to study thermodynamics and kinetics of the processes. Adsorption of colorants on fibres follow three most general isotherms, mostly determined by interactions between colorant molecules and polymers, and absorption of colorants into fibers is a little more complicated, affected by colorant molecules, dyeing conditions, and concentrations. Several theoretical models were found effective in describing the overall sorption processes regardless of the complexity of molecular interactions and sizes of colorants. However, the adsorption and absorption processes are reversible, i.e., sorption and desorption of the dyestuff occur simultaneously, the equilibrium processes. Thus, most thermodynamic and kinetic investigations of the dyeing processes have been mostly based on these equilibrium processes as well.

Kinetic equations

One of the most appropriate ways to define the dyeing rate constant is through empirical kinetic equations, which allow us to calculate specific rate constant. The most simple and usable dyeing kinetic equations among all of authors, including Patterson and Sheldon, is the deduction of the reduced equations of diffusion, which tells us that the amount of dye per unit of the weight of fibre absorbed at time t (Cegarra et al, 1982) (Equation 2.2).

$$C_t = k\sqrt{t} \qquad (2.2)$$

where C_t is the concentration of dye inside fabric in time t, k is the dyeing rate constant and t is the time.

First order equation (Equation 2.3)

$$\ln\left(1 - \frac{ct}{c\infty}\right) = -kt \qquad (2.3)$$

This is a linear equation that passes through the origin and its slope is k. This equation is appropriate for the experimental results of the bath with constant dyestuff concentration.

Equation of Vickerstaff

Vickerstaff for his kinetic studies proposed a hyperbolic type equation (Equation 2.4):

$$\frac{1}{ct - c\infty} - \frac{1}{c\infty} = kt \qquad (2.4)$$

Equation of Cegarra-Puente

This equation is based on a fundamental property of the dyeing equilibrium, which establishes their reversibility. That is, in the dyeing processes there is a direct dye velocity of the bath towards fiber and an inverse rate of the fiber towards the bath, which is the same (Equation 2.5).

$$\ln\left(1- \frac{ct^2}{c\infty^2}\right) = -kt \quad (2.5)$$

Equation of a line that passes through the origin and that adapts quite well to all the experimental points of the bath with constant concentration and meet the second law of Fick.

Equation of Carrión-Fité

Carrión-Fité proposed new equation for calculating the dyeing rate constant as below (Equation 2.6):

$$\frac{x}{(1-x)^2} + 0.5\ln\frac{(1-x)}{(1+x)} = kt \quad (2.6)$$

where x is the quotient between the dye concentration on the fibre in time t and the initial dye concentration in the dye-bath (C_t/C_∞), k is the dyeing rate constant, and t is the time.

However, choosing the appropriate equation to obtain the linearity adjustment for kinetic results is challenging, in our thesis first we have used the equation of Cegarra-Puente, but results were not satisfactory for further calculation such as activation energies. Therefore, in this thesis the equation of Carrión-Fite has been used in order to adjust the results.

Thermodynamic parameters

Activation energy

Activation energy parameter usually is used for characterizing temperature sensitivity in the chemical reactions; the most common method to measure the activation energy is the Arrhenius equation. The Arrhenius equation defines a relationship between the temperature and the rate constant as follows (Arrhenius, 1967) (Equation 2.7).

$$\ln k = \ln k_0 - \frac{E}{RT} \qquad (2.7)$$

where k is the rate constant, k_0 is a constant proportional to the collision frequency, E is the activation energy, T is the absolute temperature and R is the constant of ideal gases.

E represents the minimum energy for an effective collision.

Enthalpy

The amount of heat releases in the reaction can be determined by enthalpy changes. When the enthalpy of the reaction is positive, it indicates that, the reaction absorbs heat and it will cool down its surrounding, therefore that reaction is endothermic. A reaction that releases heat to the system is exothermic and its enthalpy will be negative and the surrounding will increase the temperature because of the gain of heat the system releases (Otutu & Ameuru, 2014).

Entropy

In a thermodynamic system, entropy referred with the amount order or disorder, measure of molecular disorder and the amount of wasted energy. When a change of the entropy in the reaction is positive, it indicates that, the disorder of the system increases. In the textile dyeing system, entropy shows 'the extent of the reduced freedom of dye molecules after the dyeing completion'. When the mobility of the dye molecules decreases dramatically, it represents that the entropy changes are significantly negative (Otutu & Ameuru, 2014).

Theory of absolute rate of dyeing

For this theory, it was assumed that the fibre could be compared to a cylinder in which the dye on the surface at constant concentration, diffused into the inner of the fiber following a process based on an heterogeneous reaction. For such a process the following kinetic equation was proposed. The theory has advantages for explanation of absorption kinetic dyeing system in the activated state, while this the theory has limitation for investigating the dye absorption process in the equilibrium state (Barrer, et al 1958; Eyring & Gershinowitz 1935; Eyring, 1935; Glasstone, 1940) (Equations 2.8 and 2.9).

$$\frac{dCt}{dt} = \frac{Kd}{Ct} - Ki.\mathrm{Ct} \qquad (2.8)$$

$$\frac{dCt}{dt} = -D.A.dc/dx \qquad (2.9)$$

In both, Ct is the amount of dye referred to one gram of fibre that diffuses through a surface A at a time t; K_d is the direct speed constant, K_i the inverse velocity constant, D diffusion coefficient and dc /dx the concentration gradient.

The solution of equation (9) for diffusion in semi-infinite medium through a surface A, of constant concentration C∞, which is precisely the particular case of desorption of dyes in its early stages, is given according to Crank equation as indicated below: (Crank, 1968) (Equation 2.10).

$$\frac{\mathrm{Ct}}{AC\infty} = 2\left(\frac{D.t}{\pi}\right)^{0.5} \qquad (2.10)$$

The variation of the diffusion coefficient with temperature is expressed by the known Arrhenius equation (Equation 2.11):

$$D = D_0 . e^{-E/RT} \quad (2.11)$$

where D_0 is the absolute diffusion coefficient, E activation energy, R constant of the gases and T absolute temperature; and according to the theory of speeds absolute values of Eyring applied to the diffusion (Equation 2.12).

$$D^* = \lambda^2 . \frac{kT}{h} . e^{\Delta S^*/R} . e^{-\Delta H^*/RT} \quad (2.12)$$

Where λ is the distance between two consecutive positions of the colorant on the coordinate of reaction, k is the Boltzmann constant, h is Planch constant , T is the absolute temperature, ΔS^* is the activation entropy and ΔH^* increase in calorific content between the activated state of the colorant and its normal state (Equation 2.13).

$$D_0 = \lambda^2 . e . \frac{kT}{h} . e^{\Delta S^*/R} \quad (2.13)$$

As the ΔH^* is approximately equal to the activation energy of Arrhenius, this equation allows calculating the activation entropy from the coefficient of absolute diffusion, and the distance between two consecutive positions of the molecule of the colorant within the fibre (Eyring & Gershinowitz 1935; Eyring, 1935; Glasstone, 1940; Crank, 1975).

CHAPTER 3. MATERIALS AND EXPERIMENTAL PROCEDURES

3.1.Materials

Fabric

Standard polyester, Type 30 A (Code 30,000), from wfk Testgewebe GmbH (Brüggen, Germany) (ISO 105-F10) was used for exhaustion dyeing processes and Polyester/cotton (51%, 49%) plain woven 215 g/m^2 industrially prepared for dyeing was used for continuous thermosol dyeing processes.

Chemicals for exhaustion dyeing processes

The low-molecular weight disperse dyes Rubin Foron E-5R (C.I. Disperse Red 73), and high molecular weight disperse dyes Blue Foron E-BL (C.I. Disperse Blue 56), S-2GFL (C.I Disperse Red 167) and Navy Blue Foron S-BRL (Disperse Blue 79), all supplied by Clariant were used.
Coumarin and o-vanillin (99% purity) both were supplied by Acros (USA) were used as auxiliaries. Pure n-butyl acetate (Mw = 116.16 g_mol–1), supplied by Panreac (Barcelona, Spain), was used as the co-solvent. N,N-Dimethylformamide (Mw = 73.10 g_mol–1), 99.8% purity and supplied byPanreac (Barcelona, Spain), was used as the solvent to extract the dyes from the PES fabrics. Hostapal non-ionic surfactant detergent, supplied by Archroma GmbH (Sulzbach, Germany), was used as for pre-dyeing washing. QP-grade 85% pure sodium dithionite (Mw = 174.11 g_mol–1) and analytical-grade sodium hydroxide, both supplied by Panreac, were used as a post-reductive washing.

Chemicals of thermosol process

Antraquinone type of low molecular weight disperse dye Serilene Blue RL 100 (C.I. Disperse Blue 56) supplied by Yorkshire was used. Pure Lecithin of soya was purchased from Carlo Erba (Spain) was used as an auxiliary. N,N-Dimethylformamide (DMF), (MW = 73.10 $g \cdot mol^{-1}$) with 99.8% purity supplied by Panreac (Barcelona, Spain) was used to determine the concentration of the dye into the polyester fibre. Sodium Hydrosulfite, supplied by BASF (MW = 174.11 $g \cdot mol^{-1}$), and analytical-grade sodium hydroxide, supplied by Panreac were used for post reductive washing. As dispersing agent Lyogen DFTN liq a non-ionic surfactant supplied by Clariant with properties as wetting and dispersing agent. Solidikoll N (Clariant) was used, as anionic migration inhibitor.

3.2.Experimental procedures

Exhaustion Dyeing conditions

The dyeing bath containing 3g of polyester fabric, a 2% concentration of disperse dye, a 1 ml/1 g o.w.f. concentration of solvent (*n*-butyl acetate) and a 4% o.w.f. concentration of auxiliary. The bath ratio was 1:60 and the temperature were 65, 75, 83 or 95 ºC with low molecular weight disperse dyes and for high molecular weight disperse dyes were 83, 90, 95 and 100 ºC. The dyeing apparatus was used with closed containers at a constant agitation rate (40 rpm) and temperature. The operation time was 120 min by exception that used at the lowest temperature (65 ºC) was 150 min.

Exhaustion dyeing equipment

Dyeing. A Linitest dyeing apparatus furnished with 300 ml sealed cans that was purchased from Atlas MTT GmbH (Germany)

Washing: A Launder-Ometer with 550 ml sealed cans also purchased from Atlas (Illinois, USA).

Spectrophotometry: A model M 330 UV–Visible spectrophotometer from Camspec, Ltd. (Cambridge, UK).

Sonication: A Labsonic 1510 shaker equipped with a standard probe of 19 mm Ø that was supplied by B. Braun (Hessen, Germany).

Zetasizer nano series device from Malvern (Malvern, UK) at 90 with respect to the incident laser beam at 25 ºC was used for particle size analysis.

Thermosol dyeing equipment

The thermosol equipment was a pneumatic pressure padder (Te-Pa- Spain) and a Werner Mathis AG laboratory stenter(Switzerland).

Exhaustion dyeing procedure

Each dyeing bath was prepared from a 4% o.w.f. concentration of auxiliary (*o*-vanillin or coumarin) that was dispersed in 3 ml of *n*-butyl acetate and made to 180 ml (B.R: 1:60) with distilled water. Emulsification was facilitated by mechanical stirring with a propeller shaker, followed by ultrasound during 1 minute. The auxiliary emulsion contained a 2% o.w.f. concentration of disperse dye previously dissolved in the solvent in the required volume for the applicable bath ratio (180 ml). Each emulsion was warmed to the present temperature for each assay, which was kept constant throughout the dyeing process. One-half of all tests used *o*-vanillin and the other half coumarin as auxiliary.

After dyeing, the fabric was washed in a reductive medium to remove all dye absorbed onto fiber surfaces. The reduction washing process consisted of 0.5 g/L Sodium hydroxide (sosa) and 2 g/L sodium hydrosulphite in distilled water and was followed by washing at 50 °C for 30 min. The bath ratio was 1:50 (150 ml per sample). The equipment used to wash dyed fabric was a Launder-Ometer with 550 ml cans for each specimen. An amount of 3g of specimen was washed in a 150 ml wash bath under the above-described conditions.

Determination dye absorption

The amount of dye absorbed by the polyester fabric was determined by extraction with *N,N*-dimethylformamide (DMF) and calculated from a linear line for the calibration of each disperse dye. As per the Beer–Lambert law, the absorbance at the maximum wavelength in the visible spectrum was a linear function of the concentration of dye dispersed in DMF.

Determination of Color Strength for exhaustion process

The colour strength (K/S) of the dyed fabrics was calculated with the Kubelka-Munk equation using a spectrophotometer Datacolor SF600 plus-CT. The values from the average of four random measures of the fabrics were obtained. The illuminant D65 and observer 10 º were used.

$$(\mathrm{K/S}) = \frac{(1-R)^2}{2R} \qquad (3.1)$$

where R is the % Reflectance/100 of dyed samples at λ_{min}, and K and S are the absorption and scattering coefficients, respectively.

Determination of exhaustion

Exhaustion of the dyed samples was determined using equation.

$$\text{Exhaustion } \% = 100 - \frac{C\infty - Cf}{Cf} \times 100 \qquad (3.2)$$

Where C_f is the measured concentration of dye inside the fibre (mg dye/ g of fibre) and C_∞ is the maximum concentration of dye inside the fibre (mg dye/ g of fibre) in our experimental conditions.

Colour Fastness

Color fastness to washing was tested according to the UNE-EN ISO 105-C06 method using the A2S test showed in aforementioned standard test. The samples were washed with 2g/L of IEC 60456 Base Detergent Type A at 40 °C for 30 min and ten steel balls, at liquor ratio 50:1. ATLAS LAUNDER-O-METER was used. The colour fastness to ironing was analyzed according to the UNE-EN ISO 105-X11 method, at three temperatures (110, 150 and 200°C).

Thermosol dyeing process

Samples of polyester/cotton fabrics (51% / 49%) were cut 12 cm in warp, 42 cm in weft, with a weight of 11 gram approximately. The fabric samples were impregnated, during 1 minute and 24 hours at room temperature, with orbital agitation.

Table 3.1. Formulation of the padding baths

Padding bath without Lecithin	Padding bath with Lecithin
Dye: 20 g/L Lyogen DFTN: 1.007 g/L Solidokoll N: 7.6 g/L pH= 5.5 (adjusted with citric acid) Mechanical stirring: 120 sec Ultra-sonic agitation: 180 sec at the frequency of 20 Hz and potential of 300 w	Dye: 20 g/L Lyogen DFTN: 1.007g/L **Lecithin: 1.45 g/L** Solidokoll N: 7.6 g/L pH= 5.5 (adjusted with citric acid) Mechanical stirring: 120 sec Ultra-sonic agitation: 180 sec at the frequency of 20 Hz and potential of 300 w

Fabrics were padded with the padding baths indicated in the Table 3.1, at pressure of 3 kg/cm^2 and velocity of 2 m/min. Then padded fabrics were dried for 2 minutes at 110 ºC, and the thermosol dyeing process was carried out at 160 ºC, 180 ºC and 200 ºC during 1 minute. Then reductive washing was carried out by using 4g/L of Sodium Hydrosulfite, 4g/L of NaOH and 2g/L of Lyogen DFTN at 80 ºC during 10 minutes, at a liquor ratio of 20:1, followed by rinsing and neutralizing, and samples were dried at room temperature for 24h.

Cotton fibre elimination from the PET/CO dyed fabrics

The cotton elimination bath was prepared, as follows: 2 parts sulphuric acid (600mL) was slowly mixed with continuous stirring, with 1 part of water (300mL) in a refrigerated beaker.

Each dyed fabric sample was treated with aforementioned solution at a bath ratio 50:1 during 60 minutes with continuous agitation at room temperature.

The neutralization bath was prepared as follows:

Cotton-eliminated samples were treated with 3g /L of Sodium Carbonate during 5 minutes at room temperature, followed by rinsing with cold water, and drying at room temperature during 24 hours.

Dye concentration measurement of fabrics with PET component

The dyestuff inside the thermosolated polyester samples was extracted with DMF to measure dye concentration into the fiber (mg dye/g of fibre). All determinations were done at the maximum absorbance of the dye ($\lambda_{max=}$ 640nm). A spectrophotometer model M 330 UV–Visible, Camspec (UK) was used.

Vertical wicking and Drop tests

Vertical wicking test was performed according to AATCC standard. Drop test was performed by applying a constant volume drop of distilled water on each fabric surface, and measuring the time to reach the complete the absorption of the drop on each fabrics surface of PET/CO and PET.

Determination of Colour Strength for thermosol process

The colour strength $(K/S)_{corrected}$ of the thermosolated fabrics after cotton elimination was calculated with the Kubelka-Munk equation (equation) using a spectrophotometer Datacolor SF600 plus-CT. The values from the average of four random measures of the fabrics were obtained. The illuminant D65 and observer 10 ° were used.

$$(\mathrm{K/S})\ corrected = \frac{(1-R)^2}{2R} - \frac{(1-\mathrm{Rw})^2}{2\mathrm{Rw}} \qquad (3.3)$$

where R= % R/100 is the reflectance of the PET component after the dyeing process and Rw=% Rw/100 which is the reflectance of white PET fabric at $\lambda_{min= 630nm}$ and K and S are the absorption and scattering coefficients respectively.

Determination of dyeing efficiency

Efficiency was determined using equation 3.4.

$$\text{Efficiency}\,\% = 100 - \frac{C\infty - Cf}{Cf} \times 100 \qquad (3.4)$$

Where C_f is the measured concentration of dye inside the fibre (mg dye/ g of fibre) and C_∞ is the maximum concentration of dye inside the fibre (mg dye/ g of fibre) in our experimental conditions.

Colour Fastness

Colour fastness to washing was tested according to the UNE-EN ISO 105-C06 method using the A2S test showed in aforementioned standard test. The samples were washed with 2g/L of IEC 60456 Base Detergent Type A at 40 °C for 30 min and ten steel balls, at liquor ratio 50:1. ATLAS LAUNDER-O-METER was used.

CHAPTER 4. KINETICS OF EXHAUSTION POLYESTER DYEING

Investigating kinetics of exhaustion polyester dyeing via sustainable approach at low temperature with high molecular weight disperse dyes

Abstract: This work focused on the evaluation of the kinetics of dyeing polyester fabrics with high molecular weight disperse dyes, at low temperature by solvent microemulsion. This study also compared the effect of two non-toxic agro-sourced auxiliaries (o-vanillin and coumarin) using a non-toxic organic solvent. A dyeing bath consisting of a micro-emulsion system involving a small proportion of n-butyl acetate was used, and the kinetics of dyeing were analysed at four temperatures (83, 90, 95 and 100ºC). Moreover, the dyeing rate constants, correlation coefficient and activation energies were proposed for this system. It was found that o-vanillin yielded higher dye absorption levels than coumarin, leading to exhaustions of 88% and 87% for Disperse Red 167 and Disperse Blue 79, respectively. K/S values of dyed polyester were also found to be higher for dye baths containing o-vanillin with respect to the ones with coumarin. In terms of hot pressing fastness and wash fastness, generally no adverse influence on fastness properties was reported, while o-vanillin showed slightly better results compared to coumarin.

Keywords: polyester dyeing, microemulsion, o-vanillin, coumarin, n-butyl acetate, kinetics

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4.1. Introduction

Polyester (Polyethylene terephthalate) (PES) fibres are the most used fibres in the global apparel industry, and therefore are a prominent topic of research. The hydrophobic nature PES fibres, combined with a glass transition temperature of around 80ºC, make their dyeing process challenging, since it is high-energy and consumes a significant amount of water [1]. The most common dyestuffs used to dye PES fibres are disperse dyes. These dyes are almost insoluble in water, making it necessary to use them in combination with dispersing agents and carriers, if the dyeing processes are performed in water under 100ºC [2,3]. The carriers, which have smaller size than the dyes, are capable of penetrating the amorphous regions of fibres, like polyester, and opening the macromolecular structure of the polymer at temperatures higher than the Tg. However, the nature and high molecular weight of the organic compounds used generally as carriers involves problems of non-biodegradability and toxicity. These agents can also partially plasticize polyester fibres, decreasing their glass transition temperature [4,5].

Dyeing and avoiding the use of carriers in the conventional industrial process is only possible at higher temperatures, such as 130-135 ºC, to produce a sufficient absorption level. Although this system is the most used process in the world, it requires costly machinery in relation to the material processed, and a considerable amount of energy to heat and maintain the dye bath at the operating temperature [6].

Recent studies have attempted to look for alternative processes for polyester dyeing with non-hazardous and more environmentally friendly compounds that also require less energy in the overall dyeing process. With the aim of avoiding negative effects of the carriers, Harifi and Montazer [7] studied the effect of nano-TiO2 on the dyeing process of PES with disperse dyes. They found that the colour strength of the PES fabric increased by the effect of the pre-treatment, consisting of an immersion in aqueous dispersions of nano-TiO2 particles (0.25–2% (W/V)). This method was free from the aforementioned disadvantages of carriers, but its industrial application is costly and very difficult to perform [7].

Choi et al. [8] compared the dyeing behaviour of PES fabrics with Disperse Blue C.I. 56 dye, and used two environmentally friendly cationic gemini surfactants as auxiliaries, namely propanediyl-1-α,ω-bis-(dimethyldodecylammoniumbromide) (DC3-12) and hexanediyl 1-α,ω-bis (dimethyldodecylammoniumbromide) (DC6-12) or a conventional surfactant (dodecyltrimethylammonium bromide) (C12C1NBr). The study proved that colour strength with gemini surfactants was higher than achieved with the conventional one. They found also that increasing the concentration of gemini surfactants led to a decrease of the dye hydrophobicity above the critical micelle concentration (CMC). Moreover, it was found that dyeing with gemini surfactants had benefits such as controlling dyeing kinetics and improving dye absorption by the PES fabric [9].

On the other hand, several studies propose dyeing processes with more environmentally friendly carriers at temperatures lower than 100 ºC. Pasquet et al. [10], used a high concentration of o- and p-vanillin as carriers for low-temperature dyeing of polyester fabrics (90º C), with low and high molecular weight disperse dyes in the presence of ethanol as a co-solvent [10]. This study proved that o- and p-vanillin can be a substitute for conventional carriers. Additionally, PES fabric dyed with these carriers presented acceptable absorption and fastness. Furthermore, Pasquet et al. [10] analysed the toxicity of o- and p-vanillin with the USEtox system, confirming that these carriers are not toxic. Carrión-Fite proposed a low-temperature dyeing process in the presence of a micro-emulsion obtained by ultrasonic agitation, composed of a low proportion an alkyl halogen solvent and a phosphoglyceride emulsifier [11]. In this sense, it was proved that ultra-sonic cavitation improves the dyeing rate constant, and the dye absorbed by the fibre [12, 13].

More recently, Carrión-Fite and Radei [14] proposed the use of more environmentally friendly dyeing auxiliaries based on o-vanillin or coumarin in an n-butylacetate co-solvent (an organic non-toxic solvent) for low molecular weight disperse dyes (C.I. Disperse Blue 56 and C.I. Disperse Red73). The study confirmed that o-vanillin and coumarin had a positive and significant influence on dyeing behaviour of polyester in this system. At a temperature of 95 ºC, the absorption levels of the fibres after 120 minutes were excellent: the content of Disperse Blue 56 dye absorbed by the PES in the presence of o-vanillin or coumarin was 97% and 96%, respectively. In the case of Disperse Red 73, the amount absorbed was 81% and 82%, respectively, for of o-vanillin or coumarin. Moreover, wash fastness was similar to the conventional process of dyeing polyester [14, 15]. However, it was necessary to study more in more depth the effect of the carriers by analysing the thermodynamic parameters and heat fastness, among others, to establish this new methodology. Moreover, another limitation of this study was that only low molecular weight disperse dyes were analysed.

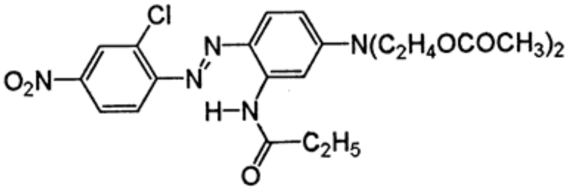
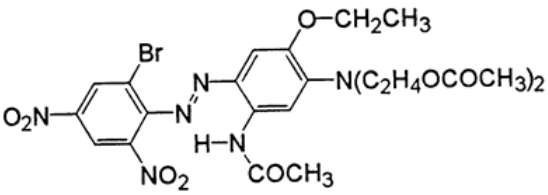
In this paper, we investigated the kinetics of dyeing PES fabrics with two high molecular weight disperse dyes (Disperse Red 167 and Disperse Blue 79), in a micro-emulsion system involving a small proportion of a non-toxic organic solvent (n-butyl acetate), and two potential auxiliaries (o-vanillin & coumarin). Moreover, the activation energies were determined for this system.

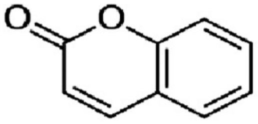
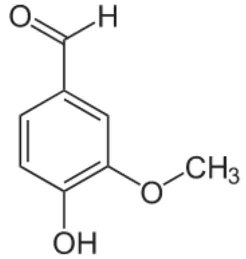
4.2. Experimental

Chemicals

The fabric used was a PES 100% woven standard polyester, Type 30 A (Code 30,000), from Testgewebe GmbH (Brüggen, Germany) (ISO 105-F10). The high molecular weight disperse dyes used were Rubi Foron S-2GFL (C.I Disperse Red 167) and Navy Blue Foron S-BRL (Disperse Blue 79). All dyes were supplied by Clariant (Switzerland). Coumarin (99% purity) was supplied by Acros (New Jersey, USA) and o-vanillin (99% purity) was supplied by Acros (New Jersey, USA). Both carriers use agro-sourced alternative compounds with additional properties, such as antimicrobial, antioxidant, biodegradability and antimutagenic. Also, these carriers are hydrophobic with no toxicity, and we expect them to have better influence on polyester dyeing [10,16]. The chemical structure of these chemicals is presented in Table 4.1.

Table 4.1. Chemical structure of dyes and auxiliaries.

Dyes and chemicals	**Chemical structure**
C.I. Disperse Red 167 CAS No. = 61968-52-3/26850-12-4 M_W = 519.93 g·mol–1	
C.I. Disperse blue 79 CAS No.= 12239-34-8 M_W = 639.41 g·mol–1	

Coumarin 2H-chromen-2-one CAS No=. 91-64-5 M_W = 146.15	
o-vanillin 2-hydroxy-3-methoxybenzaldehyde CAS No.= 148-53-8 M_W = 152.15,	

Pure n-butyl acetate (Mw = 116.16 g·mol–1), supplied by Panreac (Barcelona, Spain), was used as the co-solvent. N,N-Dimethylformamide (MW = 73.10 g·mol–1), 99.8% purity and supplied by Panreac (Barcelona, Spain), was used as the solvent to extract the dyes from the PES fabrics. Hostapal non-ionic surfactant detergent, supplied by Archroma GmbH (Sulzbach, Germany), was used as for pre-dyeing washing. QP-grade 85% pure sodium dithionite (MW = 174.11 g·mol^{-1}) and analytical-grade sodium hydroxide, both supplied by Panreac, were used as a post-dyeing washing reductant.

Experimental Methods

Dyeing procedure

Figure 4.1 shows the dyeing process for the proposed methodology.

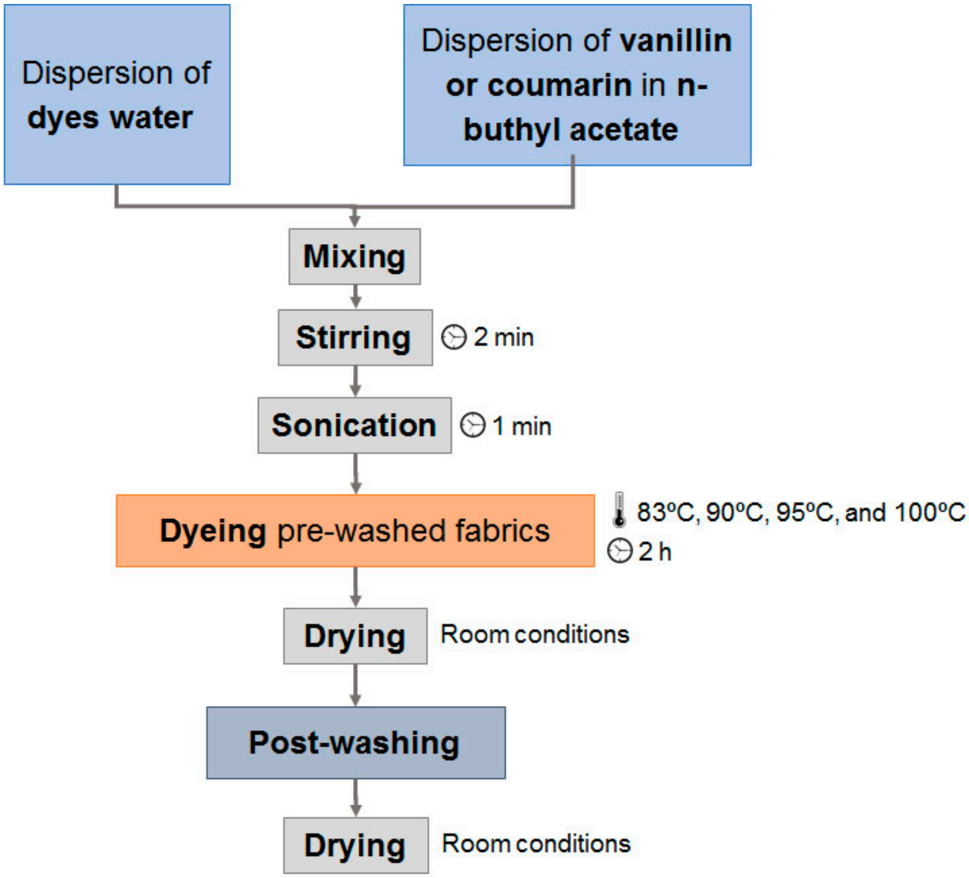


Figure 4.1. Experimental dyeing process used for this study.

PES fabrics were prepared for dyeing by cutting 16 cm in warp and 11cm in weft, and weighing 3.0 g. Fabric pre-washing was done by using Hostapal detergent at a 0.5 $g \cdot L^{-1}$ concentration at 40 ºC for 30 min.

The dye bath was prepared by dissolving carriers in n-buthylacetate and then adding the dye solution. The mixture was stirred for 2 minutes followed by sonication for 1 minute. The bath ratio for each dyeing operation was set to 1:60. The quantity of dyes and chemicals used were 2% o.w.f of disperse dye, 4% o.w.f. of auxiliaries and 3 ml of n-buthylacetate, for a total amount of 180 ml of dye bath. The dyeing process was carried out in a Linitest dyeing apparatus, furnished with 300 ml sealed cans that were purchased from Atlas MTT GmbH (Germany). The dyeing temperatures were 83, 90, 95 and 100 ºC for a fixed time of 120 min. One-half of all tests used o-vanillin and the other half coumarin as auxiliaries.

After the dyeing process, the samples were rinsed with water two times and dried at ambient conditions. Post washing was performed in a reductive medium to remove all dye absorbed onto the fibre surfaces. The reductive medium consisted on a mixture of 0.5 g/l sodium hydroxide and 2 g/l sodium hydrosulphite in distilled water (bath ratio 1:50). This process was followed by washing at 50 °C for 30 min, rinsing three times with water and drying at room temperature for 24h.

Colour fastness

Wash fastness of the samples was tested according to the UNE-EN ISO 105-C06 method. The samples were washed with IEC 60456 Base Detergent Type A at 40 °C for 30 min, keeping liquor to material ratio as 1:50. The colour fastness to hot pressing was tested according to the UNE-EN ISO 105-X11 method.

Dye absorption

The amount of dye absorbed by the PES was quantified by spectrophotometric analysis after dye extraction with N,N-dimethylformamide (DMF). The absorbance at the maximum wavelength in the visible spectrum is a linear function of the concentration of dye dispersed in DMF following the Beer–Lambert law. The maximum absorbance was determined for each dye at different concentrations, obtaining linear regressions with R values ranging from 0.9758 to 0.9845. A model M 330 UV–Visible spectrophotometer was used that was purchased from Camspec (United Kingdom).

Particle size analysis

To evaluate the homogeneity of the dye baths, particle size measurements were performed using a Zetasizer nano series device at 90° with respect to the incident laser beam at 25°C [17].

Determination of exhaustion

The exhaustion was determined using Equation 4.1:

$$\%Exhaustion = \frac{C_0 - C_s}{C_0} \times 100 \quad (4.1)$$

where C_0 is initial concentration of dye and Cs is final concentration of dye.

Determination of Colour strength

The colour strength, expressed as K/S value, was determined from the spectral diffuse reflectance using a spectrophotometer (Gretag Macbeth 7000). Reflectance values of the samples (R) were used to calculate K/S based on Kubelka-Munk, as shown in Equation 4.2 [18]:

$$K/S = \left[(1 - R)^2/2R\right] \quad (4.2)$$

where R is the % Reflectance/100 of coloured samples at λmax, and K and S are the absorption and scattering coefficients, respectively.

4.3. Results and Discussion

Emulsion particle size

Before dyeing, the particle size of the dye bath emulsions was determined and compared with the bath in the presence of high molecular weight disperse dyes without any auxiliaries. The average values are presented in Table 4.2.

Table 4.2. Particle size of dyebath in a presence of Coumarin, vanillin and without auxiliaries

Dye-bath	Average diameter (nm)	Polydispersity
2 % o.w.f Disperse Red 167; 4% o.w.f coumarin & 1mL/g o.w.f. n-buthylacetate	183 ± 9.5	0.153 ± 0.03
2 % o.w.f Disperse Blue 79; 4% o.w.f coumarin & 1mL/g o.w.f. n-buthylacetate	160.3 ± 14.2	0.121 ± 0.03
2% o.w.f. Disperse Red 167; 4% o.w.f o-vanillin & 1mL/g o.w.f. n- buthylacetate	236.3 ± 10.97	0.107 ± 0.032
2% o.w.f Disperse Blue 79; 4% o.w.f o-vanillin & 1mL/g o.w.f. n-buthylacetate	249.3 ± 4.5	0.247 ± 0.05
2% o.w.f Disperse Red 167 & 1mL/g o.w.f. n-buthylacetate	238.3 ± 0.6	0.183 ± 0.01
2% o.w.f Disperse Blue 79 & 1mL/g o.w.f. n-buthylacetate	250 ± 15.5	0.3 ± 0.05

According to the table, it can be concluded that all dye-baths were in general homogenous: values obtained were acceptable in this micro-emulsion system. The average for the particle size (200 nm) and the mean of polydispersity (0.2) presented standard values for the dyeing process. Particle sizes of dye-bath in a presence of coumarin showed better results. Indeed, presence of this auxiliary successfully reduced the particle size. Nonetheless, when o-vanillin was used, no significant changes in particle sizes were found with respect to the bath without auxiliaries.

Dyeing kinetics and rate constant

Figures 4.2–4.5 show the dyeing kinetics of two single azo class high molecular weight disperse dyes in the presence of the two auxiliaries used, namely C.I. Disperse Red 167 with 4% o.w.f of coumarin (Figure 2), C.I. Disperse Red 167 with 4% o.w.f of o-vanillin (Figure 3), Disperse Blue 79 with 4% o.w.f of coumarin (Fig. 4) and Disperse Blue 79 with 4% o.w.f of o-vanillin (Figure 5).

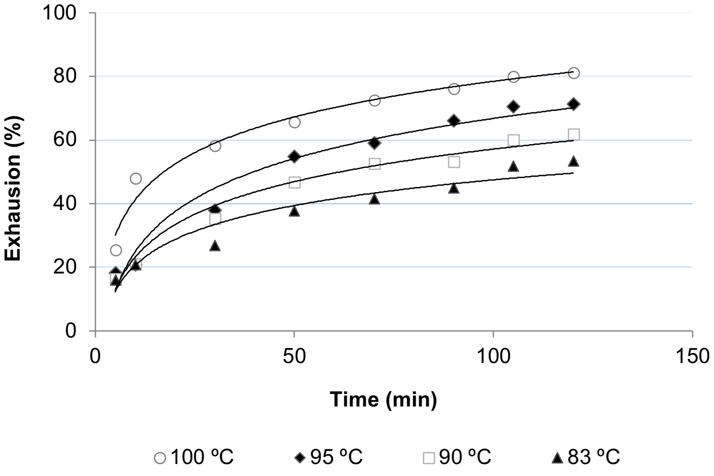


Figure 4.2. Dyeing kinetics for PES fabric dyed with Disperse Red 167 and Coumarin.

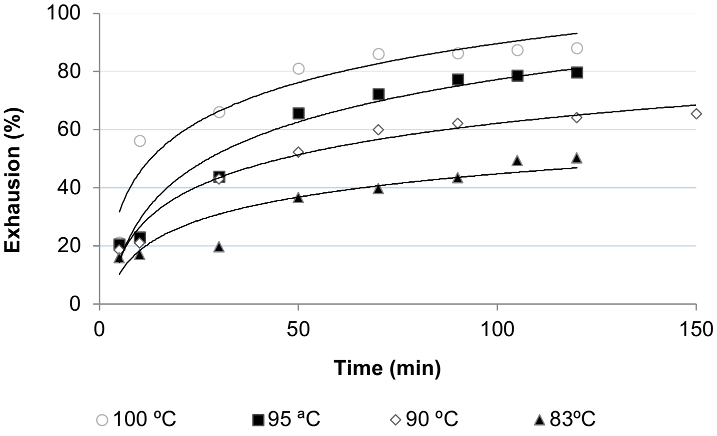


Figure 4.3. Dyeing kinetics for PES fabric dyed with Disperse Red 167 and o-vanillin.

As shown, the initial dyeing rate of coumarin was slightly higher than o-vanillin at almost all temperatures, but final rate of o-vanillin was higher than coumarin. Exhaustion % of o-vanillin at 100°C after 120 minutes was 88.0 %, which is similar to that achieved during the conventional dyeing process of polyester at 130-135°C. Values obtained with o-vanillin were slightly higher than coumarin, except for 83 °C, in which dye absorption level was higher.

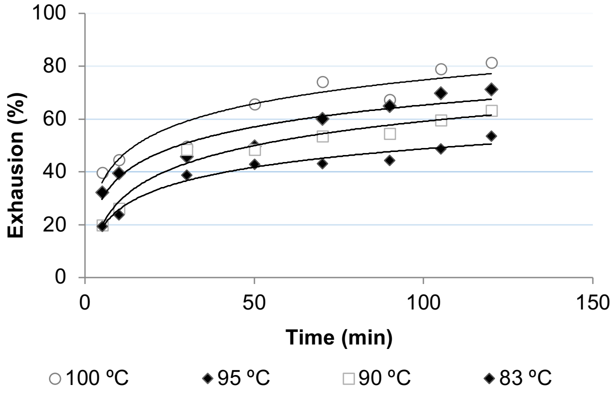


Figure 4.4 Dyeing kinetics for PES fabric dyed with Disperse Blue 79 and Coumarin.

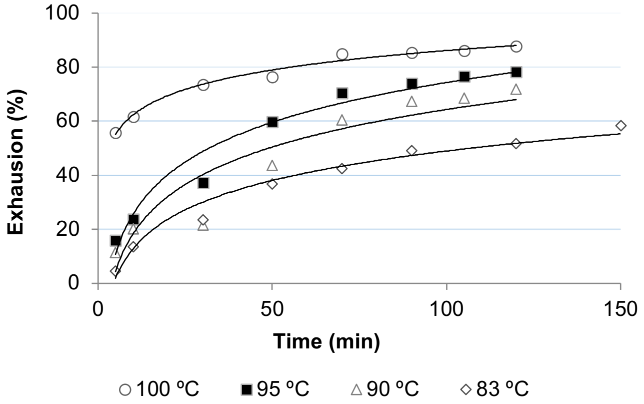


Figure 4.5. Dyeing kinetics for PES fabric dyed with Disperse Blue 79 and o-vanillin.

Concerning to the dyeing with Disperse Blue 79, it was found that the initial dyeing rate with coumarin was significantly higher than for o-vanillin, except at 100º C. However, after 60 minutes of the dyeing process, the PES fabric dyed in presence of o-vanillin presented a higher absorption level. At 100°C, the values of exhaustion of PES fabric dyed with o-vanillin reached 87 % after 120 minutes, which is similar to those achieved in conventional dyeing process of polyester at 130-135°C, as was mentioned above for Disperse Red 167.

From these results it can be concluded that o-vanillin leads to higher absorption dyeing levels than coumarin. This can be due to the higher hydrophilicity of o-vanillin, which makes it more difficult to diffuse it inside of the amorphous phase of PES. However, once diffused, it leads higher absorption.

Tables 4.3 and 4.4 indicate K/S values obtained for the dyed polyester fabrics at 100 ºC at different times.

Table 4.3. K/S values for PES fabric dyed with D167 in presence of 0.666 g·l^{-1} of coumarin or o-vanillin at 100ºC and different times (5, 10, 30, 50, 70, 90 and 105 minutes).

		T= 100ºC		**C.I. Disperse Red 167**			
t (min)	5	10	30	50	70	90	105
Coumarin							
K/S λ=640 nm	4.490	8.820	11.157	16.382	17.025	18.698	19.133
Vanillin							
K/S λ=640 nm	3.487	9.260	13.190	14.934	18.378	19.305	21.383

Table 4.4 K/S values for PES fabric dyed with D79 in presence of 0.666 $g\cdot l^{-1}$ of coumarin or o-vanillin at 100ºC and different times (5, 10, 30, 50, 70, 90 and 105 minutes).

		T= 100ºC		**C.I. Disperse Blue 79**			
t (min)	5	10	30	50	70	90	105
Coumarin							
K/S λ=640 nm	3.298	4.807	3.298	4.807	3.298	4.807	3.298
Vanillin							
K/S λ=640 nm	3.877	5.061	6.982	7.741	9.982	11.166	12.08

As expected, the K/S values increased as time increased for both auxiliaries at 100ºC. As seen, o-vanillin yield higher colour strength than coumarin in all cases. On the other hand, it was found that disperse Red 167 had higher shade depth compared to Disperse Blue 79. Values of K/S were almost similar to those achieved in conventional dyeing process of PES at higher temperatures, with a range between 12 and 21.

The following equation to calculate the dyeing rate constant and correlation coefficient was used [11]:

$$\frac{x}{(1-x)^2} + \frac{1}{2}\ln\frac{1-x}{1+x} = Kt \qquad (4.3)$$

where x is the quotient between the dye concentration on the fibre at time t and the initial time in the dye-bath, K is the dyeing rate constant and t is the time of the kinetics examined.

Table 4.5 shows the dyeing absorption rate constants and their respective correlation coefficients, calculated from Equation 3.

Table 4.5. Absorption rate constant (K), correlation coefficient (R^2) and exhaustion after 120 minutes (%) for the kinetics of dyeing of polyester with disperse dyes in the presence of *o*-vanillin or coumarin auxiliaries.

	o-vanillin			**coumarin**		
Disperse dye	K	R^2	Exhaustion after 120 min (%)	K	R^2	Exhaustion after 120 min (%)
C.I. Disperse Red 167 100ºC	0.5667	0.9855	88.21	0.1759	0.9659	81.22
C.I. Disperse Red 167 95ºC	0.1712	0.9716	79.78	0.0711	0.9704	71.45
C.I. Disperse Red 167 90 ºC	0.0426	0.992	65.65	0.0312	0.989	61.96
C.I. Disperse Red 167 83ºC	0.0128	0.9523	50.29	0.0153	0.9436	53.45
C.I. Disperse Blue 79 100ºC	0.472	0.9764	87.96	0.1892	0.9577	81.42
C.I. Disperse Blue 79 at 95ºC	0.1359	0.9736	78.42	0.0638	0.9268	71.37
C.I. Disperse Blue 79 90ºC	0.0722	0.9305	71.95	0.0294	0.934	63.39
C.I. Disperse Blue 79 83ºC	0.0208	0.9108	58.34	0.0129	0.9105	53.60413

According to the Table 4.5, the absorption rate constant for both dyes increased with increasing temperature, as expected. The rate constant values of o-vanillin were considerably higher than coumarin due to a higher absorption level. Correlation coefficients with the equation used were more than 0.9, demonstrating a good adjustment. In general, values obtained with o-vanillin were more attractive.

Activation energy

The activation energy for each dye during the dyeing process was calculated from the Arrhenius equation:

$$K = K_0 \, e^{-E/RT} \qquad (4.4)$$

where K is the rate constant, K_0 is the pre-exponential factor, E is the activation energy, T is the absolute temperature and R is the constant of ideal gases.

Table 4.6 shows the apparent activation energies for the dyeing of polyester with disperse dyes at a low temperature by the absorption rate constant obtained from Equation 4.

Table 4.6. Activation energy (E) and correlation coefficient (R^2) for the two dyes studied in the presence of o-vanillin or coumarin auxiliaries.

	o-vanillin		**coumarin**	
Disperse dyes	E ($kcal \cdot mol^{-1}$)	R^2	E ($kcal \cdot mol^{-1}$)	R^2
C.I. Disperse Red 167	59.3	0.9869	37.8	0.9763
C.I. Disperse Blue 79	46.6	0.9841	40.8	0.9781

As can be seen, energies ranged from 37 to 59 $kcal \cdot mol^{-1}$ and were similar to those previously reported for the dyeing of polyester with disperse dyes. These values show that temperature significantly influenced this process. The activation energies of the disperse dyes were higher in presence of o-vanillin than coumarin. This means that dyeing PES with o-vanillin requires more energy to diffuse the dyestuff into the fabric than coumarin. Indeed, the higher the activation energy, the higher the barrier to diffusion of the dye molecules into the fabric [11,19]. This can be explained because o-vanillin is more hydrophilic than coumarin, and therefore the penetration inside of the dye molecules with this auxiliary is more difficult. However, once o-vanillin penetrates, it causes higher swelling of polyester and makes the diffusion of the dye easier. Finally, it was found that the correlation coefficients were all acceptable and had values greater than 0.97.

Washing fastness

Table 4.7 shows colour fastness for domestic and commercial laundering for the high molecular weight dyes according to the standard methodology, and using the A2S test indicated in this standard [20].

Table 4.7. Colour fastness by washing of polyester dyed materials.

PET fabric dyed 120 minutes	**o-vanillin**			**coumarin**		
	Gray Scale	**PES**	**Cotton**	**Gray Scale**	**PES**	**Cotton**
C.I. Disperse Red 167 at 83ºC	4-5	4	3-4	5	4	3-4
C.I. Disperse Red 167 at 90ºC	5	3-4	3-4	4-5	4-5	3-4
C.I. Disperse Red 167 at 95ºC	5	4-5	3-4	4-5	4	3-4
C.I. Disperse Red 167 at 100ºC	5	4-5	3-4	5	4	3-4
C.I. Disperse Blue 79 at 83ºC	4-5	4-5	3-4	4-5	4-5	3-4
C.I. Disperse Blue 79 at 90ºC	4-5	4-5	3-4	4-5	4-5	3-4
C.I. Disperse Blue 79 at 95ºC	5	5	3-4	5	5	3-4
C.I. Disperse Blue 79 at 100ºC	5	4-5	3	5	4-5	3-4

It can be reported that the colour fastness by washing in this dyeing process was totally acceptable, because there was no adverse influence on fastness properties. Staining of the white polyester fabric was good for all dyes and auxiliaries tested. With respect to the white cotton fabric, values were almost similar to the regular level. Values of both auxiliaries and disperse dyes were quite similar, but o-vanillin exhibited slightly better colour fastness by washing than coumarin.

Hot pressing fastness

Dry heat was applied to dyed and undyed polyester fabric at three temperatures (110, 150 and 200 ºC) under pressure to measure colour changes and colour migration to the white fabric due to the steam. Tables 4.8 and 4.9 indicate discharge hot pressing fastness and degradation hot pressing fastness of dyes with higher molecular weight.

Table 4.8. Degradation hot pressing fastness.

PET fabric dyed 120 minutes	**Discharge Hot Pressing fastness (Gray Scale)**					
	o-vanillin			**coumarin**		
	110 ºC	150 ºC	200 ºC	110 ºC	150 ºC	200 ºC
C.I. Disperse Red 167 at 83 ºC	5	5	5	5	5	4-5
C.I. Disperse Red 167 at 90 ºC	5	5	4-5	5	5	4-5
C.I. Disperse Red 167 at 95 ºC	5	5	4-5	5	4-5	4-5
C.I. Disperse Red 167at 100 ºC	5	4-5	4-5	5	4-5	4
C.I. Disperse Blue 79 at 83 ºC	5	4-5	4-5	5	5	4-5
C.I. Disperse Blue 79 at 90 ºC	5	5	4-5	5	5	4-5
C.I. Disperse Blue 79 at 95 ºC	5	4-5	4-5	5	5	4-5
C.I. Disperse Blue 79 at 100 ºC	5	5	5	5	5	5

Table 4.9. Discharge Hot Degradation hot Pressing fastness.

PET fabric dyed 120 minutes	**Degradation Hot Pressing fastness (Gray Scale)**					
	o-vanillin			**coumarin**		
	110 ºC	150 ºC	200 ºC	110 ºC	150 ºC	200 ºC
C.I. Disperse Red 167 at 83ºC	4-5	3	2	3	2-3	1-2
C.I. Disperse Red 167 at 90 ºC	4-5	3	1-2	3	2-3	1-2
C.I. Disperse Red 167 at 95 ºC	4-5	4	2	2-3	2-3	2-3
C.I. Disperse Red 167at 100 ºC	4-5	4	2	4	4	4-5
C.I. Disperse Blue 79 at 83 ºC	5	3	1-2	3-4	3	1-2
C.I. Disperse Blue 79 at 90 ºC	4	3-4	1-2	3-4	2-3	2
C.I. Disperse Blue 79 at 90 ºC	4-5	4-5	2-3	3	2	3
C.I. Disperse Blue 79 at 100 ºC	4-5	4-5	2-3	4-5	4-5	4

Generally, heat fastness of this dyeing method was positive, and no significant changes can be seen for the properties. Degradation hot pressing fastness of both dyes and auxiliaries at lower temperatures, like 83 and 90 ºC, were in the regular level (such as 2-3 or 1-2), whereas discharge hot pressing fastness were in the excellent level, as most values were 5. Polyester fabric dyed in this process had good heat stability based on the degradation results. In terms of transforming colour (migration) to the white fabric (discharge hot fastness), the results were in the regular level.

O-vanillin showed remarkably better heat fastness than coumarin, and values obtained with o-vanillin were more convincing. In terms of two disperse dyes, the results indicated that C.I. Disperse Blue 79 was better than C.I. Disperse Red 167.

4.4. Conclusions

Based on the kinetics and K/S analysis, it was found that both auxiliaries at temperatures near to 100ºC led to good a dyeing absorption level in PES fabrics.

Comparing the two auxiliaries studied, it was found that polyester dyed in the presence of o-vanillin yielded, in general, a higher absorption level and colour strength than in presence of coumarin. Moreover, a higher colour strength was found for Disperse Red 167 compared to Disperse Blue 79. It is understandable that temperature would have a significant influence in this dyeing system. The effect of temperature on o-vanillin was more apparent, as dyeing PES with o-vanillin involve more energy to penetrate the polyester fabric than coumarin. Ranges of energies were similar to those achieved in conventional process. In terms of applicability and interaction between fabric and dye molecules, the swelling of polyester dyed with o-vanillin auxiliary was higher than coumarin, therefore this factor led the fabric to absorb more colour. According to wash and hot-pressing fastness, the auxiliaries were almost similar to each other. Fastness property results were positive, and there were no significant changes of the fastness properties. However, polyester fabric dyed with o-vanillin show slightly better wash and heat fastness than coumarin.

Additionally, we attempted to dye polyester in a manner as ecologically friendly and economical as possible. The percentages of auxiliaries and dyes were at a minimum level, and this method had several advantages, such as low-cost materials, low energy costs, no toxic chemicals, no deformation of the fabric due to low temperature and the possibility of reusing the waste water as a fertilizer. Therefore, this process can be suggested as an ecological alternative method of dyeing polyester because it avoids phenolic compounds. Moreover, it can be recommended to the industry due to the antimicrobial, antioxidant, biodegradability and anti-mutagenic activities of the carriers involved.

4.5. References

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CHAPTER 5. THERMODYNAMIC PARAMETERS OF EXHAUSTION POLYESTER DYEING

Investigating thermodynamic parameters of exhaustion polyester dyeing via sustainable approach at low temperatures in the activated state

Abstract

The study aims to dye a polyester fabric with a low molecular weight anthraquinone type disperse dye (C.I. Disperse Blue 56), n-butylacetate as co-solvent in the microemulsion system and the presence of two bio based auxiliaries (o-vanillin and coumarin) at temperatures lower than 100ºC. In order to investigate the influence of the temperature and the aforementioned auxiliaries on the kinetic dyeing process, the energy of the activation by the kinetic rates constants were determined. The activated entropy by the theory of absolute rates of dyeing and diffusion of the activated state of the dye for the disorder state of the dyeing system were obtained. Higher activated energies, and higher activated entropy so higher dye absorption for polyester samples dyed with o-vanillin/n-butylacetate than polyester samples dyed with coumarin/n-butylacetate were found. Color strength values of the polyester fabric dyed for this proposed micro-emulsion dyeing system at low temperature (95ºC) and the polyester fabric dyed with conventional dyeing system at high temperature (135ºC) were similar. According to color fastness to washing and ironing, it was found that the use of these auxiliaries did not modify the fastness values of the dyed samples significantly.

Keywords: Polyester, dyeing kinetic, apparent activation energy, coumarin, o-vanillin, n-butylacetate, microemulsion dyeing

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5.1. Introduction

The kinetic dyeing microemulsion system of the polyethylene terephthalate (PET) with disperse dyes at lower temperatures than conventional dyeing process with the co-solvent (n-butylacetate) were studied previously [1,2].

In this sense due to growing environmental concerns, there has been significant interest in dyeing polyester with carriers or additives at lower temperatures, considering their biodegradability, low toxicity and environmentally friendly practices [1-3].

With the aim of saving water and energy, Gao et al, 2018 proposed an environmentally friendly dyeing process, using silicone nanomicelle technique, which the organic silicone oil was used as nano-emulsion by solvent evaporation, this technique improved the dyeability of the polyester compared to polyester dyed by the traditional dyeing system which requires more energy consumption [4].

Parvinzadeh Gashti and Moradian, 2011 prepared PET/Clay nanocomposite via melt spinning system, and the study confirmed that the presence of the clay on polyester increased the dyeability of the polyester by reducing the glass transition temperature of the PET. This method avoids the disadvantages of the toxic carriers [5].

Additionally, Parvinzadeh Gashti et al, 2015 modified the surface of the polyester by corona discharge ionization process. The Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and reflectance spectroscopy (RS) proved that the corona discharge improved the surface functionality and dyeability of the polyester [6].

Pasquet et al. 2013 dyed polyester fabric with o- and p-vanillin in the presence of two disperse dyes (C.I Disperse Blue 56, and C.I Disperse Blue 79) with ethanol as co-solvent. The study confirmed that color strength of the polyester dyed with these auxiliaries was good, mainly when o-vanillin was used [7].

Radei et al [2,3] proposed the use of two alternative bio-based auxiliaries such as ortho-vanillin (o-vanillin) and coumarin with n-butylacetate as a co-solvent, in the micro-emulsion system for the high molecular disperse dyes (C.I. Disperse Blue 79 and Disperse Red 167) [3]. This new proposed microemulsion system has advantages such as using biodegradable and non-toxic auxiliaries during the dyeing process. Furthermore, the dyeing system is favorable from both economic and environmental point of view. The microemulsion system is formed with micro particles containing the co-solvent, the dyes and the auxiliaries used, and these micro particles including the dye molecules facilitate the transport to the fiber in function of the temperature used [3,8].

Many studies have been done on kinetics and thermodynamic parameters of polyester dyeing processes in the equilibrium state; however, there is a lack of data related to the thermodynamic parameters before the equilibrium state for improvement the exhaustion and levelness during the kinetic dyeing process [9-11].

The aim of this paper is to study the dyeing process of a polyester fabric with a low molecular weight anthraquinone type disperse dye (C.I. Disperse Blue 56), with n-butylacetate as co-solvent (low environmental impact) in the microemulsion system and the presence of two bio based auxiliaries (o-vanillin and coumarin) at temperatures lower than 100ºC. In order to investigate the influences of the temperature and the aforementioned auxiliaries on the kinetic dyeing process, the energy of the activation by the kinetic rates constants were obtained. The activated entropy was calculated by the theory of absolute rates of dyeing and diffusion in the activated state. This entropy was obtained by rate kinetic and diffusion dyeing values, such were obtained by other authors [12; 13, 14]. The theory of absolute rates of dyeing has advantages for explanation of absorption kinetic dyeing system in the activated state. The quality of the dyed fabrics was evaluated by determining color fastness to ironing and washing.

5.2. Experimental

Materials

Fabric

A standard plain-woven 100% polyester fabric, Type 30 A, from Testgewebe GmbH (Germany) (ISO 105-F10) was used as textile substrate. The average fiber diameter of the fabric was 10μ.

Chemicals and auxiliary products

Antraquinone type low molecular weight disperse dye Foron Blue E-BL supplied by Archroma GmbH (Germany) (C.I. Disperse Blue 56, $M_W = 365.18\ g{\cdot}mol^{-1}$) was used as a dye. As a co-solvent pure n-butylacetate from Panreac (Spain) (boiling point 126 ºC) was used. Coumarin ($M_W = 146.15\ g{\cdot}mol^{-1}$) and o-vanillin ($M_W = 152.15\ g{\cdot}mol^{-1}$) with 99% purity supplied by Acros (USA) were used as bio-based auxiliaries, respectively. The chemical structure of the co-solvent, the disperse dye and the two selected auxiliaries are indicated in Figures 5.1, 5.2, 5.3 and 5.4 respectively.

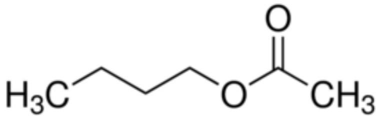

Figure 5.1. n-butylacetate, CAS NO. 123-86-4

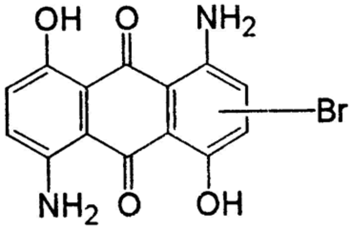

Figure 5.2.C.I. Disperse Blue 56, CAS NO. 12217797

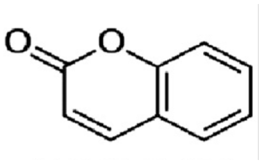

Figure 5.3. Coumarin (2H-chromen-2-one), CAS No. 91-64-5

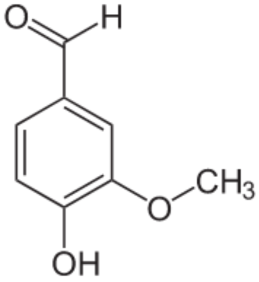

Figure 5.4. O-vanillin (2-hydroxy-3-methoxybenzaldehyde), CAS No. 148-53-8

Hostapal NF liq a non-ionic surfactant supplied by Archroma was used for the pre-dyeing washing. Eganal RAP liq supplied by Archroma (Germany) as a dispersing agent was used. Sodium hydrosulphite (MW = 174.11 g·mol^{-1}) and analytical-grade sodium hydroxide, both supplied by Panreac, were used for the post reductive washing. N,N-Dimethylformamide (DMF) with 99.8% purity supplied by Panreac (Spain) was used to extract the dyestuff from the fabric.

Isothermal dyeing procedure

The dyeing procedure was performed as described by Radei et al. 2018. The standard polyester fabrics were pre-washed (40 ºC for 30 minutes) with 2 g/L of Hostapal NF liq, then rinsed with distilled water and dried at room temperature. Afterwards, fabrics were dyed with 2% o.w.f of disperse dye, 4% o.w.f. of auxiliaries (o-vanillin or coumarin) and 16.66 g/L of n-butylacetate as a co-solvent. Bath ratio was fixed at 1:60**.** An isothermal dyeing process was performed at four temperatures (65, 75, 83 and 95 ºC) for 120 minutes, except for the lower temperature (65 ºC), which the time was 150 minutes. The dyeing process was performed in a Linitest MTT dyeing machine, Atlas MTT GmbH (Germany).

Post reductive washing was done to remove the adsorbed dye at the surface with 0.5 g/L of sodium hydroxide and 2 g/L of sodium hydrosulphite in distilled water (bath ratio 1:50) at 50 °C for 30 min, followed by rinsing three times with cold distilled water, and drying at room temperature for 24 h. Figure 5.5 shows an Scheme of the experimental procedure followed in this research.

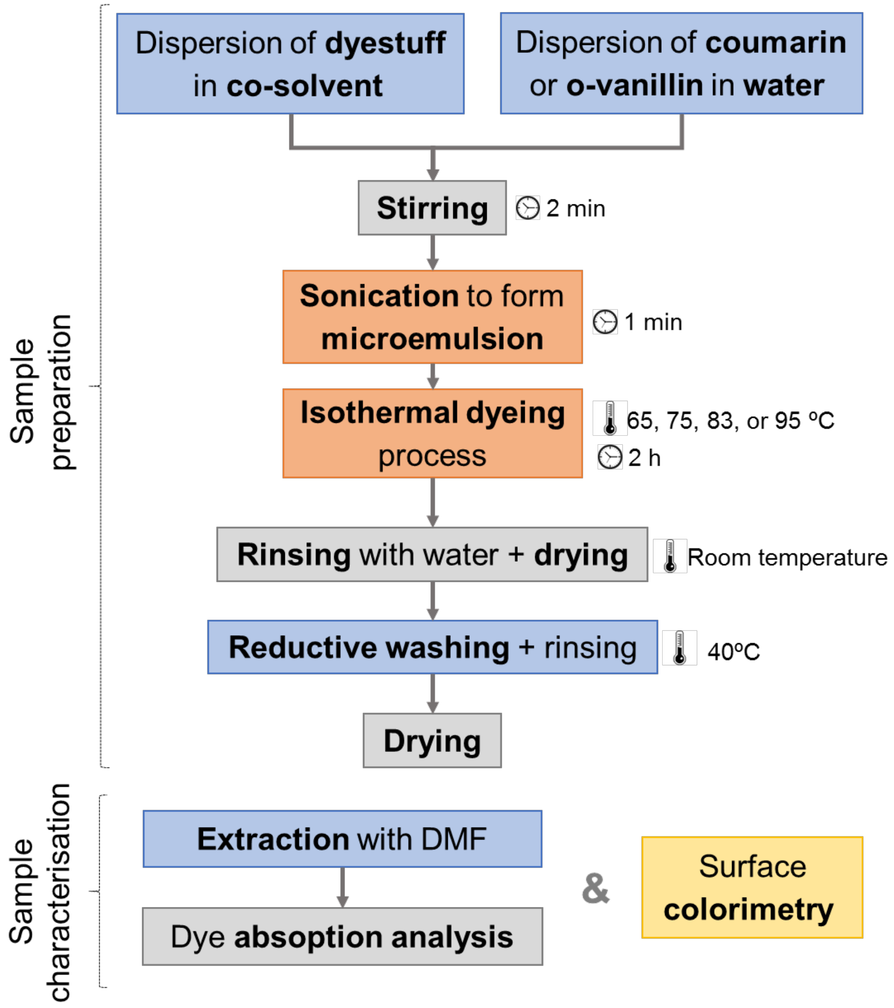

Figure 5.5. Scheme of the procedure for low ~~dyeing~~ temperature dyeing polyester

Particle size measurement

Average values of dye baths particle size were determined with a Zetasizer nano series (Malvern, UK) device at 90° with respect to the incident laser beam at 25 °C. Quartz cells 1 cm thick and volume of 4 mL were used.

Dye absorption measurement

Dye absorbed by the dyed polyester fabric was determined via extraction with DMF. Maximum absorbance was measured at $\lambda_{max=}$ 640 nm for C.I Disperse Blue 56. A model M 330 UV–Visible spectrophotometer Camspec (UK) was used.

The equation (1) shows the linearity of the Beer-Lambert law for C.I. Disperse Blue 56 at different concentrations related to their maximum absorbance [15].

$$(\mathrm{Abs})_{\lambda max\ 640nm} = 15.383[D_f] \qquad (5.1)$$

where D_f is the dyestuff concentration in the fiber (mg dye/g fiber) and $(\mathrm{Abs})_{\lambda max\ 640nm}$ is the maximum absorbance . The correlation coefficient was $R^2 = 0.9982$

Experimental values for the amount of the dye extracted from fiber during the kinetics dyeing process were calculated based on the equation 5.1.

Colorimetric curves analysis

Colorimetric curves were determined using a spectrophotometer Datacolor SF600 plus-CT. The values were obtained from the average of four individual measures rotating 90º the fabric measured, the illuminant D65, and observer 10º were used.

Differential scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) tests performed on a Perkin Elmer DSC **7** to determine changes on thermal characteristics of dyed samples. 4mg samples were heated from 40ºC to 300ºC at a heating rate was 20°C/ min.

Color fastness

The color fastness to ironing was analyzed according to the UNE-EN ISO 105-X11 method, at three temperatures (110, 150 and 200°C).

Color fastness to washing was tested according to the UNE-EN ISO 105-C06 standard using A2S test stated in the standard. Dyed polyester samples were washed with ten steel balls with and IEC 60456 Base Detergent Type A 2g/L at 40°C for 30 min, bath ratio was 1:50. ATLAS LAUNDER-OMETER GmbH (Germany) was used for the washing test, with a vessel of 550ml.

5.3 Results and Discussion

Solubility parameters of auxiliaries, co-solvent, water and polyester used

To study whether the auxiliaries used have the capacity to penetrate inside the fabric, solubility parameters (cohesion energy parameters) were calculated for polyester, o-vanillin, and coumarin with water as the main solvent and n-butylacetate as the co-solvent.

The classic Hansen's formula (equation 2) for solubility parameters was used, where the total parameter is broken down into contributions from the forces involved [16,17].

$$\delta t^2 = \delta d^2{}_{+}\delta p^2{}_{+}\delta h^2 \qquad (5.2)$$

In which δ_d, δ_p and δ_h are the contributions from dispersion forces, polar forces, and hydrogen bonding respectively.

The total solubility parameter and the contributions from dispersion forces, polar forces, and hydrogen bonding for auxiliaries, co-solvent, water, and polyester at 25°C are shown in table 5.1.

Table 5.1. Solubility parameters obtained from the Hansen equation for the auxiliaries, co-solvent, water, and polyester for total dispersion forces, polar forces, and hydrogen bonding, respectively at 25ºc.

Sample	δ_t $(MPa)^{1/2}$	δ_d $(MPa)^{1/2}$	δ_p $(MPa)^{1/2}$	δ_h $(MPa)^{1/2}$
Polyester	17.9	9.8	9.2	11.8
o-vanillin	24.4	19.4	9.8	11.2
coumarin	24.5	20	12.5	6.7
n-butylacetate	17.4	15.8	3.7	6.3
water	47.8	15.5	16	42.3

Based on total solubility parameters, n-butylacetate has the capacity to diffuse inside the polyester and is insoluble in water. Moreover, o-vanillin and coumarin are partially soluble in the co-solvent used, therefore to form a microemulsion system the dye-bath was prepared by ultra-sonic agitation.

Solubility parameters of auxiliaries in the water

To determine hydrophobic or hydrophilic characteristics of the two auxiliaries used, their solubility parameters in the water were found. Solubility parameter values in ~~the~~ water are 1.7 g/L and 10 g/L for coumarin and o-vanillin respectively, which indicates higher hydrophobicity in the case of coumarin [18.19].

Particle size measurement

Before the dyeing process each microemulsion system was controlled with particle size analysis. The obtained average values are presented in Table 5.2.

Table 5.2. Average particle diameter and polydispersity of the dye-bath prepared

Dye-bath	Average diameter (nm)	Polydispersity
0.333 g/l of Disperse Blue 56 0.666 g/l of coumarin 16.66 g/l n-buthylacetate	269.33 ± 3.6	0.249 ± 0.009
0.333 g/l of Disperse Blue 56 0.666 g/l of o-vanillin 16.66 g/l n-buthylacetate	262.33 ± 6.57	0.238 ± 0.012

The particle size of the dye into stable microemulsion particles are similar in presence of both auxiliaries used, at similar polydispersity, but slightly higher values were obtained in presence of coumarin~~.~~

Dyeing kinetics

The Kinetics for the two microemulsion dyeing systems, at four temperatures and at different times was studied in the presence of o-vanillin or coumarin in n-butylacetate. In table 5.3, Figures 5.6 and 5.7 the values of the dye concentration inside fiber and exhaustion % are shown respectively.

Table 5.3. Values of C.I. Disperse Blue 56 dye concentration inside the fiber at the studied temperatures in function of time.

		Time (min)								
	Temperature	5	10	30	50	70	90	105	120	150
Auxiliary products										
4.556 x 10^{-3} mol. L^{-1} of coumarin 16.66 g. L^{-1} of n-butylacetate	mg dye /g fiber (65 ºC)	4.62	6.18	8.10	8.20	9.53	9.71	—	10.52	11.01
	mg dye /g fiber (75 ºC)	4.63	6.96	7.65	10.09	11.40	11.46	11.58	12.32	—
	mg dye /g fiber (83 ºC)	7.72	10.29	13.86	14.66	15.20	15.82	17.30	18.16	—
	mg dye /g fiber (95 ºC)	7.74	8.01	13.90	15.18	16.04	16.93	18.26	19.26	—
Auxiliary products										
4.377 x 10^{-3} mol. mol. L^{-} of o-vanillin 16.66 g. L^{-1} of n-butylacetate	mg dye /g fiber (65 ºC)	2.29	3.23	8.56	8.73	10.48	10.67	—	11.59	11.69
	mg dye /g fiber (75 ºC)	5.32	7.02	10.08	10.99	12.34	13.94	16.08	16.67	—
	mg dye /g fiber 83 ºC	8.74	9.33	12.59	13.14	16.20	16.41	18.12	18.77	—
	mg dye /g fiber at 95 ºC	11.39	14.49	16.49	17.27	18.27	19.12	19.36	19.50	—

It should be noted that the thermodynamic state of equilibrium has not been reached in this dyeing system, as the dyeing time and the amount of the dye-bath were not infinite; therefore, the maximum theoretical concentration (C_∞) is 20 mg dye/ g of fiber for 100% of exhaustion

In general, based on the Table 3, it was observed that, o-vanillin led to higher dye concentration (mg dye/g of fiber) in the fiber than coumarin, and also a higher initial dyeing rate. When the microparticles of the disperse dye, the co-solvent and the auxiliaries are in collision with the surface of the fiber, the free dye molecule in the o-vanillin/n-butyl acetate system is more easily deposited on the fiber surface with greater exhaustion than the coumarin/n-butyl acetate system. The microparticles of the microemulsion collide with the fiber surface and depending on their different instability into the bath system they facilitate more or less their absorption kinetics and consequently the diffusion of the dye. Due to higher hydrophilicity of o-vanillin/bath system, its miroemulsioned particles (i.e. dye molecules) are deposited more easily than on the coumarin/bath system, which is more hydrophobic. The facility of the deposition of the free dye molecules on the surface of the fiber (a hydrophobic solid) after break the microparticle promotes its kinetic absorption and followed diffusion.

The highest value of dyestuff inside the fiber (mg dye/g of fiber) was obtained for polyester dyed in presence of o-vanillin at 95 ºC reaching after 2 hours of dyeing 19.5 mg dye/g of fiber (which means an exhaustion of 97.5%).

In Figures 5.6 and 5.7 the values of exhaustion with respect to the time at the temperatures studied are shown. As it can be seen C.I. Disperse Blue 56 for the microemulsion system of o-vanillin/n-butylacetate led to higher exhaustion level than microemulsion system of coumarin/n-butylacetate for the isotherms at temperatures of 75ºC, 83ºC and 95ºC. For both cases, as expected, the absorption isotherm at 65ºC led to lower exhaustions.

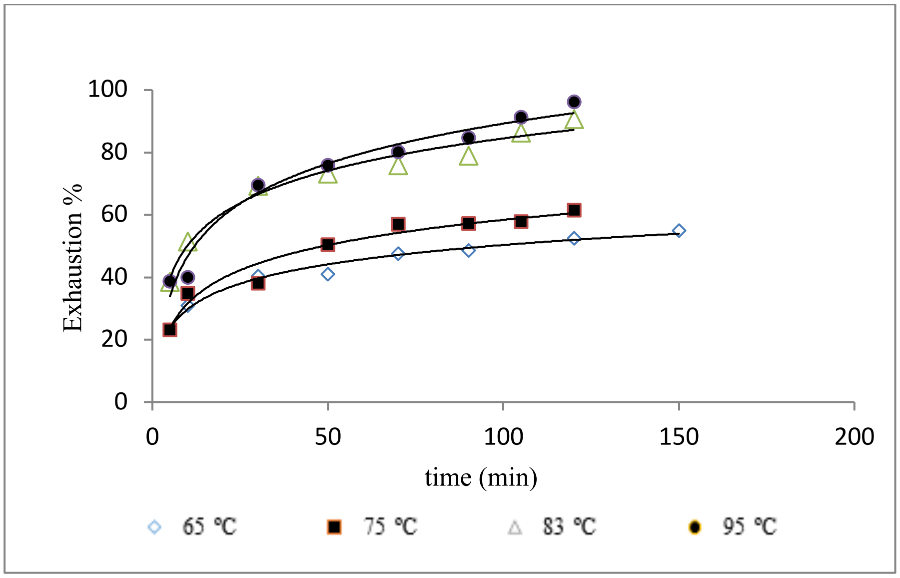

Figure 5.6. Absorption isotherms of exhaustion in function of time of C.I. Disperse Blue 56 in the coumarin/n-butylacetate microemulsion system at four temperatures.

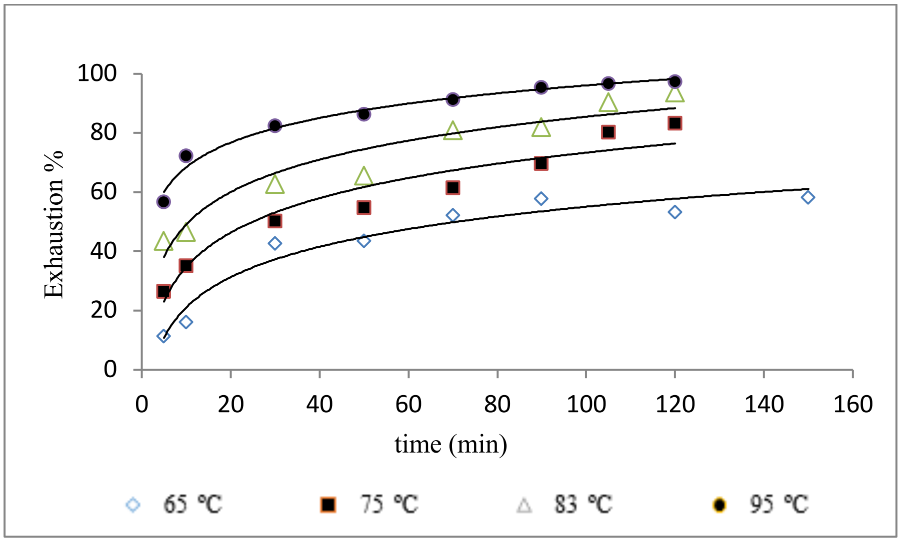

Figure 5.7. Absorption isotherms of exhaustion in function of time of C.I. Disperse Blue 56 in the o-vanillin/n-butylacetate microemulsion system at four temperatures.

In Figure 5.8 the microscopic images of the cross-section of the polyester samples dyed in presence of coumarin/co-solvent or o-vanillin/co-solvent compared with the one dyed without auxiliaries are shown.

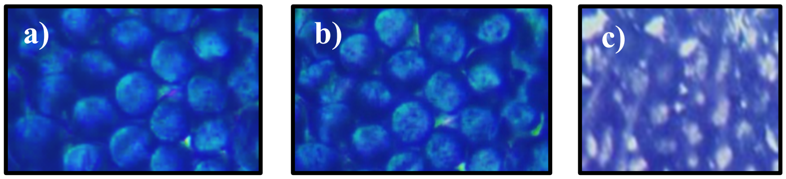

Figure 5.8. Microscopic images of the cross-section of the polyester fabrics: a) dyed with coumarin/co-solvent at 95 ºC during 120 minutes; b) dyed with o-vanillin/co-solvent auxiliaries at 95 ºC during 120 minutes and c) dyed without auxiliaries at 95 ºC during 120 minutes

As it can be seen, the use of auxiliaries led to a significantly better diffusion to the dye. The dyestuff was uniformly distributed into the fibers, demonstrating the efficiency of the dyeing process presented in this research.

Efficiency of the microemulsion dyeing process with respect a conventional process

To demonstrate the efficiency of the dyeing process, colorimetric curves of the polyester fabrics dyed with o-vanillin and co-solvent at 95 ºC after 120 minutes were compared with the ones obtained with the same fabric subjected to a conventional dyeing process at 95ºC and 135 ºC in presence of 2 g/L of dispersing agent Eganal RAP. All dyed samples were washed with a post reductive washing as was described on Figure 5.5. The obtained colorimetric curves are presented in Figure 5.9.

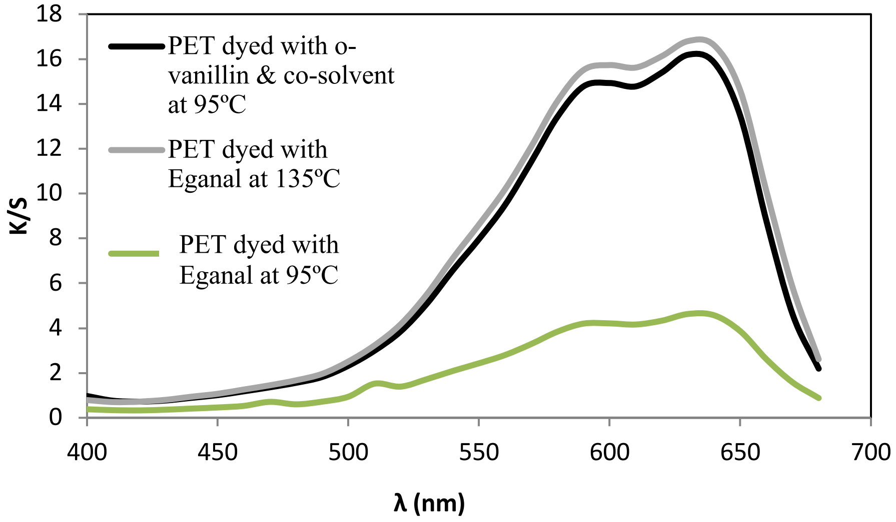

Figure 5.9. K/S reflectance curves in function of wavelength for the polyester fabrics dyed polyester fabrics dyed with o-vanillin and co-solvent at 95 ºC after 120 minutes and the ones obtained with the same fabric

subjected to a conventional dyeing process at 95ºC and 135 ºC in presence of 2 g/L of dispersing agent Eganal RAP.

As shown in Figure 5.9, the microemulsion system at 95ºC led to similar results of K/S to the conventional dyeing at 135ºC. However, the conventional system at 95ºC led to significantly lower color strength. As shown in Table 4, there is no significant difference on the K/S values at the maximum wavelength and exhaustion for the microemulsion system at 95ºC and the conventional system at 135ºC.

Table 5.4. K/S values at λ=630 nm, exhaustion percentage and photographic images of the polyester fabrics dyed with o-vanillin and co-solvent at 95 ºC after 120 minutes and the ones obtained with the same fabric subjected to a conventional dyeing process at 95ºC and 135 ºC in presence of 2 g/L of dispersing agent Eganal.

Dyeing time=120 minutes	K/S (λ=640 nm)	Exhaustion (%)	Photographic image of the dyed fabrics
PET dyed with Disperse Blue 56 and in presence of o-vanillin in n-buthylacetate at 95 ºC (microemulsion system)	16.20	97.5	
PET dyed with Disperse Blue 56 and in presence of Eganal at 135 ºC (conventional system)	16.81	99.1	
PET dyed with Disperse Blue 56 and in presence of Eganal at 95 ºC (conventional system)	4.63	29.1	

From these results, it can be concluded that the dyeing process presented in this paper (using a co-solvent/o-vanillin at 95 ºC) gives color strength similar to a conventional process at 135ºC, after the reductive washing, in both cases. This means that with this new process it is possible to reach 97.5%

exhaustion with only a slight color difference with respect to the dyeing process at 135 ºC, with a reduction of the dyeing temperature by 40ºC.

This new system allows saving thermal energy and makes it possible to perform the dyeing process in open equipment and, in the case of dyeing blended fibers, significantly reduces the risk of damaging the fibers with low resistance to high temperature. These facts demonstrate that the process presented can be appropriate for industrial applications and can be a green alternative method for the industry.

Diferential Scanning Calorimetry (DSC) analysis

In Figure 5.10 the DSC curves of the dyed fabrics with o-vanillin/co-solvent at 95 ºC, with coumarin/co-solvent at 95 ºC, compared with the ones dyed with the conventional system at 95ºC and 135ºC and the undyed fabric. The parameters obtained from these curves are presented in Table 5.5

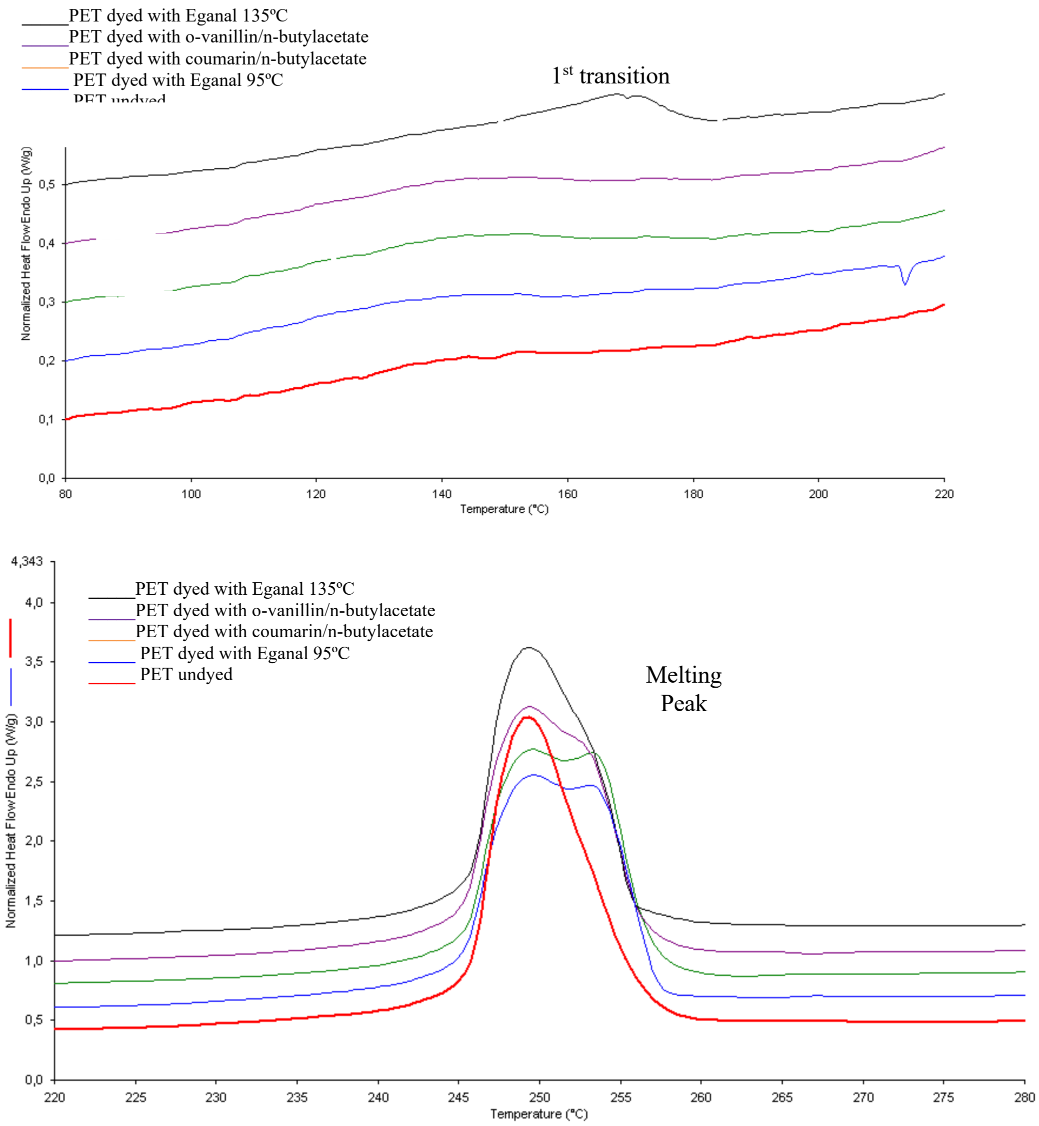

Figure 5.10. DSC endotherms of the of the dyed fabrics with o-vanillin/co-solvent at 95 ºC, with coumarin/co-solvent at 95 ºC, compared with the ones dyed with the conventional system at 95ºC and 135ºC and the undyed fabric: top) zone from 80ºC to 220ºC and down) zone from 220ºC to 280ºC.

Table 5.5. DSC parameters of undyed polyester and polyester samples dyed in different conditions.

Parameters	Original white sample	Conventional dyeing at 95 ºC	Dyed with coumarin/co-solvent at 95 ºC	Dyed with o-vanillin/co-solvent at 95 ºC	Conventional dyeing at 135 ºC
Thermal transition 1 ΔH (J/g)	3.234	5.216	7.524	6.280	6.688
Melting peak ΔH (J/g)	61.092	57.645	57.528	57.392	58.067

As indicated in Table 5 and Figure 9, in general, the presence of o-vanillin and coumarin did not modify significantly the thermal characteristics of the dyed fabrics and the co-solvent is responsible for changes on the microstructure of the fiber. Regarding the first thermal transition (Figure 10a), which is ascribed to a premelting endothermic peak, the conventional dyeing system without auxiliaries at 95 ºC and 135ºC gives an enthalpy of 5.2 J/g of 6.7 J/g respectively. This means that an increase of 40 ºC in the dyeing temperature increased the enthalpy of this transition around 28.2%. Comparing the polyester dyed with conventional system without auxiliaries at 95 ºC to polyester dyed with auxiliaries at 95 ºC it was observed that the enthalpy of this first thermal transition increases around 44% in the case of the coumarin, and by 20% in the case of the o-vanillin, as indicated before this reveals that n-butylaceate affected on the microstructure of the dyed fibers.

Based on the melting peak, as shown, the dyeing treatments have not significantly modified the enthalpy and the maximum temperature of the melting peak. The only observed changes are on the shape of the endotherm, which is wider for the dyed samples. This is related with changes on the crystals formed as a consequence of the hydrothermal dyeing treatment.

Thermodynamic parameters

Since in this work is intended to obtain the influence of temperature in the dyeing process of microemulsified dispersed dyes in the presence of the biobased auxiliaries studied at temperatures below 100ºC, values of dyeing rate constant, apparent activation energy, apparent diffusion coefficient, enthalpy and entropy for the polyester samples dyed have been calculated by the theory of absolute rates of dyeing and diffusion of the activated state of the dye molecule [12-14].

Dyeing rate constant

To calculate the dyeing rate constant from the initial exhaustion values presented in Table 5.3, equation 3 was used [20,21]

$$\frac{x}{(1-x)^2} + 0.5\ln\frac{(1-x)}{(1+x)} = kt \qquad (5.3)$$

where x is the quotient between the dye concentration on the fiber in time t and the initial dye concentration in the dye-bath (C_t/C_∞), k is the dyeing rate constant, and t is the time [22]. The values of the dyeing rate constants calculate from the linearity adjustment of the equation 3 are shown in Table 5.6.

Table 5.6. Absorption rate constant (k) for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate at 65 ºC, 75 ºC, 83 ºC, and 95 ºC.

	coumarin	o-vanillin
T (ºC)	k (min^{-1})	k (min^{-1})
65	0.0148	0.0139
75	0.0282	0.1077
83	0.1859	0.7654
95	0.3207	5.6561

As expected, the dyeing rate constant increased as the dyeing temperature increased and generally, except for 65ºC, values of the dyeing rate constant obtained for the polyester dyed with o-vanillin were considerably higher than the values obtained for the polyester dyed with coumarin. Significantly highest value of dyeing rate constant was obtained at 95 ºC for polyester dyed with o-vanillin. This is related with a fast kinetic dyestuff absorption in all studied times and after 120 minutes of dyeing process, the absorption of dyestuff in the fiber was almost reached to the maximum theoretical concentration.

Apparent activation energy

The apparent activation energy of the dyeing process was calculated from the Arrhenius Law, indicated in logarithm form in equation 5.4 [23].

$$\ln k = \ln k_0 - \frac{E}{RT} \qquad (5.4)$$

where k is the dyeing rate constant, k_0 is the pre-exponential factor (slope of the line), E is the apparent activation energy, T is the absolute temperature and R is the constant of ideal gases. Values of apparent activation energies obtained from the linear adjustment of equation 4 are shown in the Table 5.7.

Table 5.7. Values of apparent activation energy for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate.

Polyester dyed with CI Disperse Blue 56, coumarin/ n-butylacetate		Polyester dyed with CI Disperse Blue 56, o-vanillin/ n-butylacetate	
Activation Energy (Kcal·mol^{-1})	Correlation coefficient	Activation Energy (Kcal·mol^{-1})	Correlation coefficient
25.34	0.9383	51.05	0.9879

As shown in Table 5.7, the values of apparent activation energy obtained for polyester dyed with o-vanillin/n-butylacetate is higher than polyester samples dyed with coumarin/n-butylacetate. This is because polyester dyed with o-vanillin/butylacetate during the absorption kinetic process was more influenced by the variation of the temperature; with higher value of activation energy than coumarin/n-butylacetate [24]. Values are almost in the same ranges to those previously achieved in the polyester dyeing at equilibrium [22].

Apparent diffusion coefficient

In order to determine the apparent diffusion coefficient, Crank's equation was used (equation 5.5) [25, 26].

$$\frac{\mathrm{Ct}}{AC\infty} = 2\left(\frac{D.t}{\pi}\right)^{0.5} \qquad (5.5)$$

where C_t is the concentration of dye inside the fabric in the examined time by using the kinetic equation (3), C_∞ is the maximum theoretical concentration inside the fabric, t is the time examined, D is the apparent diffusion coefficient and A is the specific surface area (per gram) of the studied fiber. The specific surface using the equation 6 was obtained.

After surface divided by weight and after simplification for using μ such as diameter of fiber, following equation was applied for obtaining the specific surface area of the fiber.

$$A = \frac{4\times10^4}{\rho.d} \qquad (5.6)$$

Where s is the perimeter of 1 g. length (cm), w is the 1 g. weight (g), ρ is density (cm^3/g) and d (applied in μ) is the diameter of the studied fiber respectively.

Values of apparent diffusion coefficients obtained from the equation (5.5) are shown in the Table 5.8.

Table 5.8. Apparent diffusion coefficients for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate

Apparent diffusion coefficient (D) ($10^{-11}\ cm^2/sec$)			
Disperse Blue 56	T (ºC)	Polyester dyed with CI Disperse Blue 56, coumarin/ n-butylacetate	Polyester dyed with CI Disperse Blue 56, o-vanillin/ n-butylacetate
	65	0.765 ± 0.04	0.531 ± 0.16
	75	0.923 ± 0.04	1.241 ± 0.44
	83	1.833 ± 1.24	2.216 ± 1.41
	95	2.072 ± 0.98	3.775 ± 2.85

As expected, apparent diffusion coefficients increased with increasing temperature. Moreover, polyester samples dyed with o-vanillin lead to higher diffusion coefficients than coumarin/n-butylacetate at all of the temperatures studied. The highest diffusion coefficient was found for polyester dyed in presence of o-vanillin at 95 ºC. According to the definition of diffusion coefficient of the activated dye molecule, it can be concluded that the dyestuff penetration in the polyester samples dyed with o-vanillin is faster compared to the polyester samples dyed with coumarin/n-butylacetate. These values are in good agreement with previous studies for polyester dyeing [22, 24].

Enthalpy and Entropy of activation

The enthalpy and entropy of activation were calculated from the equations 5.7-12 respectively; by the theory of absolute rates of dyeing of Eying equations were used. [27-32].

$$D = \lambda^2 . e . \frac{kT}{h} . e^{-\Delta G^*/RT} \quad (5.7)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (5.8)$$

$$\Delta H^* = E_D - RT \quad (5.9)$$

$$D^* = \lambda^2 . \frac{kT}{h} . e^{\Delta S^*/R} . e^{-\Delta H^*/RT} \quad (5.10)$$

$$D = D_0 . e^{-E_D/RT} \quad (5.11)$$

$$D_0 = \lambda^2 . e . \frac{kT}{h} . e^{\Delta S^*/R} \quad (5.12)$$

After simplification and deduction of the aforementioned equations we have reached to the equation 5.13 for calculating the entropy of activation.

$$\Delta S^* = R\,[\ln D_0 + \ln \lambda^2 . \frac{kT}{h} - 1] \quad (5.13)$$

where ΔH^* is enthalpy of activation, ΔS^* is entropy of activation, E_D is the activation energy of the diffusion, T is the absolute temperature; R is the constant of ideal gases, h is Planck constant, k is Boltzmann constant, λ is the distance between two consecutive positions of the molecule diffused in the reaction coordinate (10 Å). D is the apparent diffusion coefficient at 95 ºC and D_0 is the slope of the line which was obtained from the linear adjustment of equation 7.

The values of D_0 for dyed PET samples with coumarin/n-butylacetae and o-vanillin/n-butylacetate were 1.978 and 3.544 $\mathrm{Kcal \cdot mol^{-1}}$ respectively.

Table 5.9 shows the values of entropy and enthalpy of activation calculated from the theory of absolute rates of dyeing and diffusion of the activated state of the dye molecule with the aforementioned equations.

Table 5.9. Entropy and enthalpy and of activation for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate at 95ºC

Activated state	polyester dyed with auxiliary products in microemulsion systems	ΔS^* ($\mathrm{Kcal \cdot mol^{-1} K^{-1}}$)	ΔH^* ($\mathrm{Kcal \cdot mol^{-1}}$)
		T=95 ºC	T=95 ºC
C.I. Disperse Blue 56 (0.333 g/L)	polyester dyed in microemulsion: coumarin/n-butylacetate/water (0.666/16.666g/L)	0.01305	3.19
	polyester dyed in microemulsion: o-vanillin/n-butylacetate/water (0.666/16.666g/L)	0.01422	6.30

As shown, the enthalpy of activation obtained for polyester dyed with disperse dye C.I. Disperse Blue 56 with o-vanillin/n-butylacetate microemulsion at 95 ºC was significantly higher than polyester dyed with coumarin/n-butylacetate microemulsion. The higher value for the enthalpy of activation indicates a greater energy releases in the dyeing process for absorbing the dyestuff by the polyester [32]. Higher value of the entropy of activation obtained for the polyester dyed with o-vanillin produces higher changes in segmental mobility within the microstructure of the fiber that would produce higher facilities of randomness than coumarin so facility the diffusion inside the fiber.

Both microemulsion systems can be associated with the dye for transport it to the fiber surface. However o-vanillin/n-butylacetate is more hydrophilic, therefore dye transportation to the fiber is made easier than coumarin/n-butylacetate. Such as explained before, deposition of dye molecules in the fiber surface is made dye molecule after breakup. The microemulsion particle in the system of o-vanillin/n-butylacetate, is more realized for their diffusion into the fiber, as indicated for the higher entropy value.

From the thermodynamic results it was found that, the reaction was in a favor of the products.

According to the enthalpy, entropy of activation, it was determined that the absorption process of polyester samples dyed with C.I. Disperse Blue 56 is an endothermic process. Therefore, dye absorption increases with increasing temperatures [33; 34, 35].

This study reported that, before moving to the equilibrium state, the dyeing processes may obtain heat from the system, therefore values of enthalpy and entropy that obtained in the thermodynamic activated state could be larger than the equilibrium state [11, 22]. In this sense, it has to be noted that it is necessary to have the dye molecule in the activated state to overcome the energy barrier to diffuse into the fiber.

Ironing fastness

To analyze the color fastness to ironing, UNE-EN ISO 105-X 11 standard was applied at three temperatures: 110, 150 and 200 ºC. Values of the degradation and discharge ironing fastness of the dyed polyester samples are shown in the Tables 10 and 11.

Table 10. Values of degradation ironing fastness of the polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes.

PET fabric dyed 120 minutes	Degradation values of ironing fastness (Gray Scale)					
	Auxiliary : Coumarin			Auxiliary : O-vanillin		
Temperature	110 ºC	150ºC	200ºC	110 ºC	150ºC	200ºC
C.I. Disperse Blue 56 at 65 ºC	4	3-4	2	4-5	4	2
C.I. Disperse Blue 56 at 75 ºC	4-5	4-5	3	4	4	2-3
C.I. Disperse Blue 56 at 83 ºC	4-5	4	3	4	4	4-5
C.I. Disperse Blue 56 at 95 ºC	4-5	4-5	4	4-5	4	4-5

Both auxiliaries and the co-solvent used did not modify the degradation ironing fastness of the dyed samples; except at 200 ºC of ironing values which are around 2-3. Polyester samples dyed with coumarin/co-solvent showed slightly better values of degradation ironing fastness properties than samples dyed with o-vanillin/co-solvent.

Table 5.11. Values of discharge ironing fastness of the polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes (polyester discharge).

PET fabric dyed after 120 minutes	Discharge ironing fastness (Gray Scale)					
	Auxiliary : Coumarin			Auxiliary : O-vanillin		
Temperature	110 ºC	150ºC	200ºC	110 ºC	150ºC	200ºC
C.I. Disperse Blue 56 at 65 ºC	4-5	4-5	3	5	4-5	3-4
C.I. Disperse Blue 56 at 75 ºC	4-5	5	3-4	5	5	3
C.I. Disperse Blue 56 at 83 ºC	4-5	5	3	4-5	5	3
C.I. Disperse Blue 56 at 95 ºC	5	5	3	5	5	3

In terms of discharge ironing fastness, there were no significant changes on the properties of dyed samples, and both auxiliaries have almost similar values, however at 200 ºC of ironing values are around 3. In general polyester samples dyed with o-vanillin/co-solvent indicated slightly better values of discharge ironing fastness.

Color fastness to washing

To determine color fastness values to washing of the dyed samples, polyester fabrics were washed based on the UNE-EN ISO 105-C06 standard. Values of color fastness to washing are shown in the Table 5.12.

Table 5.12. Values of color fastness to washing of polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes.

PET fabrics dyed after 120 minutes	Auxiliary : Coumarin			Auxiliary : o-vanillin		
	Gray Scale for evaluating change in color	PET (Gray scale for evaluating staining)	Cotton (Gray scale for evaluating staining)	Gray Scale for evaluating change in color	PET (Gray scale for evaluating staining)	Cotton (Gray scale for evaluating staining)
C.I. Disperse Blue 56 at 65 ºC	3	3	2-3	2-3	3	2-3
C.I. Disperse Blue 56 at 75 ºC	4	3-4	2-3	4-5	3	3
C.I. Disperse Blue 56 at 83 ºC	3	4	3-4	4-5	4	3
C.I. Disperse Blue 56 at 95 ºC	4	4-5	4	4	4-5	3-4

Either use of coumarin/co-solvent or o-vanillin/co-solvent did not change the washing fastness properties of the dyed samples significantly, as values are almost in good agreement with previous studies [2; 3, 36]. However values obtained for polyester dyed with o-vanillin/co-solvent were slightly better than the samples dyed with coumarin/co-solvent.

5.4. Conclusions

The purpose of this paper was to study the dyeing process of a polyester fabric with low molecular weight disperse dye (C.I. Disperse Blue 56), included in a microemulsioned system with n-butylacetate as a co-solvent (low environmental impact) and testing two biobased auxiliaries, o-vanillin or coumarin, selected with different affinity for the medium aqueous of dispersion. The studied temperatures were below 100ºC, so lower than the conventional dyeing process around 135ºC that promotes saving of energy during the dyeing process with auxiliaries in form of microemulsion particles including the hydrophobic molecules of disperse dye with low toxicity than conventional carriers.

The particle size of the microemulsioned system o-vanillin /n-butyl acetate and coumarin/n butylacetate were similar including the same dye molecule into the system.

From results of the rate of the absorption kinetic of free disperse dye molecule to the fiber by the transport of the particles for the o-vanillin/n-butylacetate system were higher than for coumarin/n-butyl acetate system. This behavior is explained for the more hydrophilic dyeing bath of o-vanillin than coumarin dyeing bath more hydrophobic. The facility of the deposition of the free dye molecule at the surface in function of the auxiliary used showing their kinetic different absorption behavior and the diffusion later into hydrophobic fiber.

This phenomenon of liberation of free disperse dye molecule was justified for the more instable particle including the auxiliary o-vanillin for its higher hydrophilicity than the particles including coumarin, In consequence at the surface of the fiber the kinetic of the free dye molecule for their diffusion inside the fiber was higher for the system o-vanillin /n-butylacetate .

The highest values of the rate constant of the isotherms absorption and the activation energies of the disperse dye at 65ºC, 75ºC, 83ºC and 95ºC for the microemulsion o-vanillin/n-butylacetate than coumarin/n-butylacetate indicates the higher absorption kinetic process and the higher diffusion coefficient values (at 95 ºC highest exhaustion found) for o-vanillin. From the apparent activation energy at the range of temperatures studied it was found that the action of microemulsion of o-vanillin/n-butyl acetate during the absorption kinetic process was more influenced by the variation of the temperature than coumarin/n-butyl acetate

The activated enthalpy and activated entropy and was calculated by the theory of absolute rates of dyeing and diffusion in the activated state. Higher value for the enthalpy of activation indicates a greater energy releases in the dyeing process for absorbing the dyestuff and higher entropy of activation obtained for in presence o-vanillin/butyl acetate produces higher changes in segmental mobility within the microstructure of the fiber so justify the more efficiency of kinetic and diffusion inside the fiber than coumarin/n-butylacetate~~.~~

According to the first thermal transition observed on the DSC curves, it was found that, presence of the co-solvent changed the thermal characteristics of the dyed polyester samples compared to the dyed polyester sample without using auxiliaries.

The calculated enthalpy and entropy of activation showed that the absorption of the polyester samples dyed with C.I. Disperse Blue 56 was an endothermic process, as expected.

Based on color fastness to washing and ironing tests, it was observed that there were no significant changes on the fastness properties of the dyed samples, as values were in good agreement with previous studies.

Furthermore, comparing this new process with a conventional one at 135 ºC, it was found that similar results in terms of color strength were obtained with the 95 ºC process presented in this paper, while avoiding high temperature, energy and cost of the dyeing process.

5.5. References

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CHAPTER 6. DEVELOPMENT OF POLYESTER THERMOSOL DYEING

Development of polyester thermosol dyeing via sustainable approach

Abstract

The effect of a natural amphoteric surfactant, lecithin, in the padding bath of a polyester thermosol dyeing process was studied. The impregnation treatment, with or without lecithin, was performed for 1 min or 24 h. The presence of lecithin leads to a reduction of the particle size and the polydispersity of the padding bath micro-dispersion. Lecithin increased the impregnation on the fabric independently from the thermosol conditions. Due to action of lecithin, the values of colour strength (K/S), dyestuff concentration into the fibre (mg dye/ g fibre) and efficiency (%) increased. This means that less dyestuff will be needed if the padding solution containing lecithin. Concerning to the effect of the time of impregnation, higher colour strength, efficiency and dyestuff concentration was found for 24 h treatment with respect to the 1 min treatment. The study also proved that higher thermosol temperature lead to higher dye fixation into the fabric. The highest value of efficiency (99.81%) was obtained for polyester thermosolated with lecithin at 200 °C with a previous impregnation for 24 h. It was found that either lecithin or impregnation time (1 minute or 24 h) did not modify the washing fastness values of the thermosolated fabrics.

Keywords: Continuous dyeing polyester; Thermosol, Disperse dyes, Lecithin, Impregnation times, Micro-dispersion

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6.1. Introduction

Polyester (polyethylene terephtalate (PET)) fibres are one of the most used fibres in the world; reaching a global production of 53.7 million metric tons in 2017 [1]. Due to the hydrophobic nature of PET the dyeing is achieved with disperse dyes. Disperse dyes are non-ionic dyestuff with low solubility in water and with molecular weights in the range of 300 to 600 $g \cdot mol^{-1}$ [2].

The thermosol dyeing of polyester fabrics with disperse dyes is a process in which a dye molecule in solid form diffuses inside the polyester fibre, also in solid state. A physicochemical process of this nature is dependent on the padding bath preparation, the thermosol conditions (temperature and time), and the auxiliary products [3,4].

In a continuous thermosol dyeing process, the disperse dye in an aqueous medium is deposited on the surface of the fabric by padding, and then, after a drying process with hot air, a multilayer of disperse dye in solid form, with the auxiliary products, is located on the polyester fibres surface. Then, by means a thermal treatment with hot air at temperatures between 160 °C to 210 °C, during a short time (between 30 s and 120 s), the diffusion of the dye inside the fiber is achieved [5,6].

The thermosol process is industrially suitable for high dyeing fabric productions (from 8,000 m) of 100% PET or PET/CO, and PET/VIS blends. The production speed ranges are comprised between 20 to 80 m/min, and compared to discontinuous dyeing, the labour force costs are 40% lower, the water consumption is 20% lower, and additionally the fabric is thermfixed during the dyeing operation. In the design of the process is of crucial importance the right selection of the disperse dyes and auxiliary products to obtain high content of the dye into the fibre and avoid or minimize colour contamination of the subsequent washing baths to facilitate the reuse of the washing baths [7,8].

Noonari et al. (2014) investigated the possibility of controlling dye migration during drying and thermosol sequences by using both natural and synthetic migration inhibitors. The natural migration inhibitors studied were guar gum, sodium alginate and carboxymethyl cellulose, and the synthetic inhibitors Thermacol MIN, Primasol FFAM, and Thermacol MP. Parameters such as migration test, tensile strength, colour strength, bending length and light fatness were analysed. This study proved that synthetic migration inhibitors exhibit better results for all proposed tests than natural migration inhibitors [9].

Jeong et al. (2004) studied the hermosol polyester dyeing with twenty vat dyes and dissolving agents like urea, glycerine and poly (ethylene glycol) (PEG). This study confirmed that polyester fabrics could be dyed with vat dyes in their pigment form, in a similar way than the disperse dyes in the thermosol process. Colour depth increased due to presence of urea in the padding bath [10].

Today, the research on thermosol process is mainly focused in the selection of the auxiliary products and migration inhibitors.

Other researchers have studied the feasibility of using lecithin in the polyester exhaustion dyeing processes [11], and due to presence of lecithin higher absorption level of dyestuff inside polyester was achieved [12-14]. Hence, it would be interesting to study the possible use of lecithin and its effects in the thermosol continuous dyeing of PET with a low molecular disperse dye. The molecular weight of lecithin is 750 $g \cdot mol^{-1}$ which is more than twice of the molecular weight of a low molecular disperse dye (around 300 $g \cdot mol^{-1}$), so its action on the thermosol dyeing process would be to modify the dispersion of the dye in the padding bath and the distribution of solids on the fabric surface during the drying process. Lecithin is a bio-based amphoteric surfactant with no toxicity that can be used in textile industry as a wetting, dispersing, emulsifying, softening, and stabilizing agent. Due to its non-toxicity also has been used also in food industry [12].

This study aims to analyse the effect of lecithin on continuous dyeing behaviour of polyester fabric with Solidokoll N as migration inhibitor, Lyogen DFTN liq as dispersing agent, and a low molecular weight disperse dye (C.I. Disperse Blue 56) at two impregnation times (1 minute or 24 hours), and at 3 thermosol temperatures (160ºC, 180ºC and 200ºC) in a form of micro-dispersion system. Since the time available for the dye diffusion into the fabric is very short, the degree of disaggregation of the dye in solid form at the fibre surface is critical for starting the diffusion process of the disperse dye to the fibre. In this work we compare the effect of lecithin as an auxiliary in the padding bath on the dyeability of PET in PET/CO fabrics.

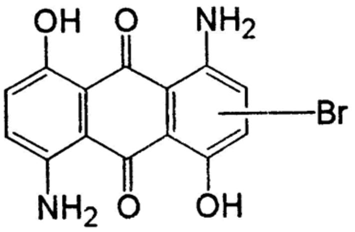
6.2. Experimental

Materials

Polyester/cotton (51/49) plain woven fabric (215 g/ m^2) industrially prepared for dyeing was used.

Dyestuff and amphoteric surfactant

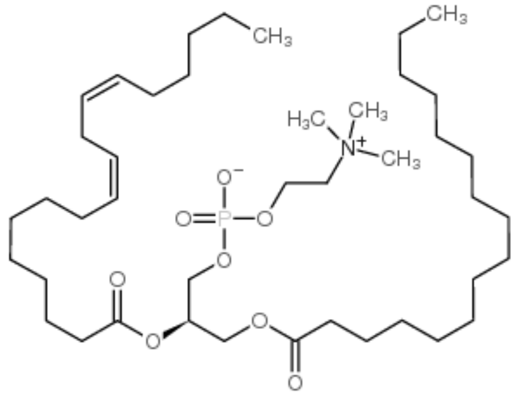
Antraquinone type of low molecular weight disperse dye Serilene Blue RL 100 (C.I. Disperse Blue 56) supplied by Yorkshire was used. According to the technical information supplied by Yorkshire, the light fastness of the dye is 6, and the sublimation fastness 5, being very suitable for a thermosol dyeing process. Pure soya lecithin was purchased from Carlo Erba (Spain). The chemical structure of these products is shown in figure 6.1.



CAS Number = 12217797

M_W = 365.18 g·mol^{-1}

C.I. Disperse Blue 56



CAS Number =8002-43-5

M_W =750 g·mol^{-1}

Lecithin

Figure 6.1. Chemical structure of the dye and lecithin

Chemicals and dyeing auxiliaries

N,N-Dimethylformamide (DMF), (MW = 73.10 g·mol^{-1}) with 99.8% purity supplied by Panreac (Barcelona, Spain) was used to determine the concentration of the dye into the polyester fibre. Sodium Hydrosulfite, supplied by BASF (MW = 174.11 g·mol^{-1}), and analytical-grade sodium hydroxide, supplied by Panreac were used for post reductive washing. As dispersing agent Lyogen DFTN liq a non-ionic surfactant supplied from Clariant with properties as wetting and dispersing agent. Solidikoll N (Clariant) was used, as anionic migration inhibitor.

Continuous dyeing procedure

Samples of the fabrics were cut 12 cm x 42 cm (warp x weft), weighting around 11 g. The fabric samples were impregnated, during 1 minute or 24 hours at room temperature, with orbital agitation. Fabrics were padded with the padding baths indicated in the Table 1, at a pressure of 3 kg/cm^2 and speed of 2 m/min. Then, the padded fabrics were dried for 2 minutes at 110 ºC, and the thermosol dyeing process was carried out at 160 ºC, 180 ºC or 200 ºC for 1 minute. Then a reductive washing was carried out by using 4g/L of Sodium Hydrosulfate, 4g/L of NaOH and 2g/L of Lyogen DFTN at 80 ºC for 10 minutes, at a liquor ratio of 20:1, followed by rinsing and neutralizing, and samples drying at room temperature for 24h.

The thermosol equipment was Werner Mathis AG (Switzerland).

Table 6.1. Formulation of the padding baths

Padding bath without Lecithin	Padding bath with Lecithin
Dye: 20 g/L	Dye: 20 g/L
Lyogen DFTN: 1.007 g/L	Lyogen DFTN: 1.007g/L
Solidokoll N: 7.6 g/L	**Lecithin: 1.45 g/L**
	Solidokoll N: 7.6 g/L
pH= 5.5 (adjusted with citric acid)	pH= 5.5 (adjusted with citric acid)
Mechanical stirring: 120 sec	Mechanical stirring: 120 sec
Ultra-sonic agitation: 180 sec at the frequency of 20 Hz and potential of 300 w	Ultra-sonic agitation: 180 sec at the frequency of 20 Hz and potential of 300 w

Cotton fibre elimination from the PET/CO dyed fabrics

The cotton elimination from the dyed fabrics was done with a sulphuric acid solution (2:1 sulphuric acid:water) with a bath ratio 50:1 for 60 minutes with continuous agitation at room temperature. The remaining PET fabric was treated with 3g /L of sodium carbonate for 5 minutes at room temperature, followed by rinsing with cold water, and drying at room temperature for 24 hours.

Determination of dye concentration on the fabrics with PET component

The dyestuff inside the thermosolated polyester samples was extracted with DMF to measure dye concentration into the fibre (mg dye/g of fibre). All determinations were done at the maximum absorbance of the dye ($\lambda_{max=}$ 640nm). A spectrophotometer model M 330 UV–Visible, Camspec (UK) was used.

In figure 6.2, the Beer-Lambert law [15] calibration curve is shown for the C.I. Disperse Blue 56 at different concentrations.

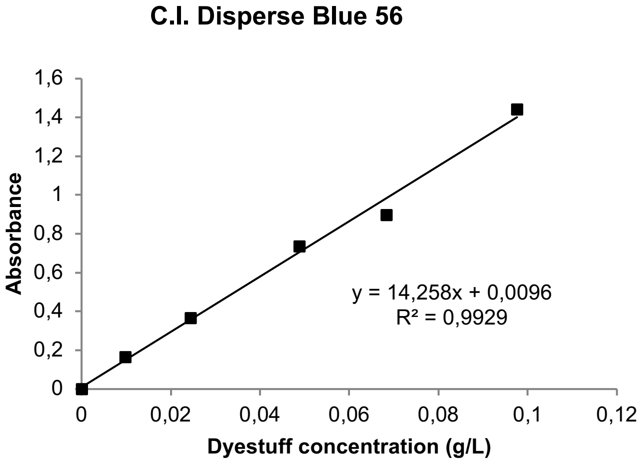


Figure 6.2. The Beer-Lambert law calibration curve for C.I. Disperse Blue 56

Particle Size Analysis

For evaluating the particle size of the padding dye bath, that will be deposited on the fibre surface after padding and drying, the particle size measurements were assessed. Zetasizer nano series device from Malvern (UK) was used at 90° with respect to the incident laser beam at 25 °C [16], to determine and compare the homogeneity and the reproducibility of the padding baths.

Wettability

Vertical wicking test was performed according to AATCC standard [17].

Drop test was performed by applying a constant volume drop of distilled water on each fabric surface, and measuring the time to reach the complete the absorption of the drop on each fabrics surface of PET/CO and PET.

Determination of Colour Strength

The colour strength $(K/S)_{\text{corrected}}$ of the thermosolated fabrics after cotton elimination was calculated with the Kubelka-Munk equation (equation 6.1) [18] using a spectrophotometer Datacolor SF600 plus-CT. The values from the average of four random measures of the fabrics were obtained. The illuminant D65 and observer 10 º were used.

$$(\mathrm{K/S})\ corrected = \frac{(1-R)^2}{2R} - \frac{(1-\mathrm{Rw})^2}{2\mathrm{Rw}} \qquad (5.1)$$

where R= % R/100 is the reflectance of the PET component after the dyeing process and Rw=% Rw/100 which is the reflectance of white PET fabric at $\lambda_{\text{min}= 630\text{nm}}$ and K and S are the absorption and scattering coefficients respectively.

Determination of dyeing efficiency

Dyeing efficiency was determined using equation 6.2.

$$\text{Efficiency } \% = 100 - \frac{\mathrm{C}\infty - \mathrm{Cf}}{\mathrm{Cf}} \times 100 \qquad (6.2)$$

Where C_f is the measured concentration of dye inside the fibre (mg dye/ g of fibre) and C_∞ is the maximum concentration of dye inside the fibre (mg dye/ g of fibre) in our experimental conditions.

Colour Fastness

Colour fastness to washing was tested according to the UNE-EN ISO 105-C06 method using the A2S test showed in aforementioned standard test. The samples were washed with 2g/L of IEC 60456 Base Detergent Type A at 40 °C for 30 min and ten steel balls, at liquor ratio 50:1 [19]. Atlas launder-o-meter was used. Figure 6.3. shows a summary scheme of the experimental procedure followed in this research.

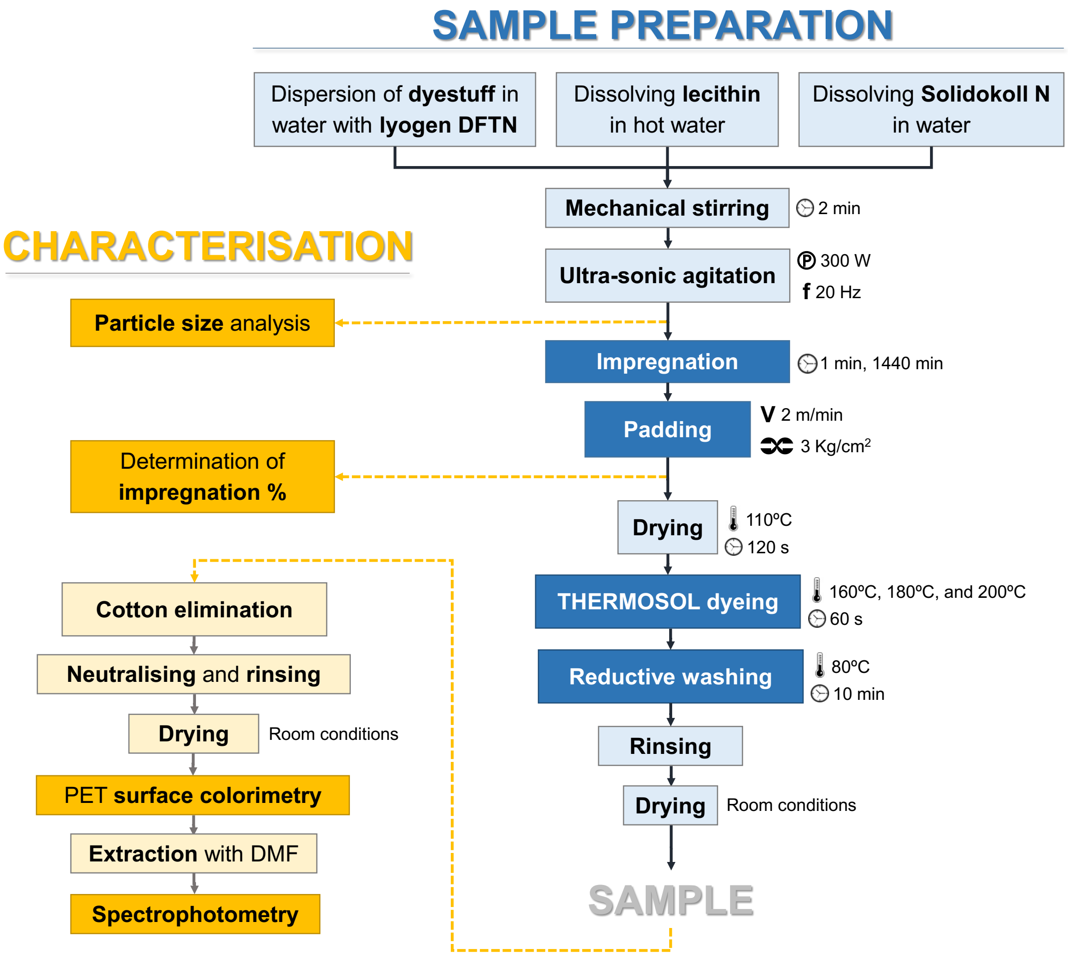


Figure 6.3. Scheme of the experimental procedure followed

6.3. Results and Discussion

Particle Size analysis

Before the continuous dyeing process, the particle size of the padding dye-baths was measured in the presence of C.I. Disperse Blue 56, Lyogen DFTN, Solidokoll N, with and without Lecithin. Moreover, the particle size of the padding baths with all components of the padding bath except the disperse dye was analysed with and without Lecithin. The average values are shown in Table 6.2.

Table 6.2. Particle size of padding dye-baths with and without Lecithin

Impregnation padding dye-bath	Particle size average diameter (nm)	Polydispersity
Dye: 20g/L Solidokoll N: 7.6 g/L Lyogen DFTN: 1.007 g/L	242.4 ± 4.51	0.307 ± 0.056
Dye: 20g/L Solidokoll N: 7.6 g/L Lyogen DFTN: 1.007 g/L **Lecithin: 1.45g/L**	170.3 ± 9.53	0.111 ± 0.0302
Solidokoll N: 7.6 g/L Lyogen DFTN: 1.007 g/L	186.2 ± 9.53	0.189 ± 0.0142
Solidokoll N: 7.6 g/L Lyogen DFTN: 1.007 g/L **Lecithin: 1.45g/L**	160 ± 5.61	0.106 ± 0.0232

As shown, on the baths with the dye the presence of Lecithin has reduced the particle size and polydispersity by 42% and 176% respectively. Apart from the reduction of the average particle size this means that the padding bath with Lecithin is more uniform compared to the padding bath without Lecithin. These results may justify the differences between the impregnation (in %) of the padding baths in the thermosol dyeing process.

In the same way than for the baths with dyes, the presence of Lecithin led to a reduction of the particle size and polydispersity by 14.07% and 43.9 respectively for the baths without dye, as expected. Moreover, the values of the particle size without the disperse dye are lower compared to those obtained with the disperse dye, as expected.

Wettability

To determine the changes in wettability of the samples, drop test and wicking test were performed on the the PET/CO fabrics and the fabric with 100% PET after cotton elimination.

Padding baths were prepared as indicated in Table 1 with Lecithin, but without the dyestuff, in two impregnation conditions:

1. 1minute of impregnation: drying at 110 ºC for 120 seconds or at ambient temperature.
2. 24 hours of impregnation: drying at 110 ºC for 120 seconds or at ambient temperature.

Drop test

A constant volume drop of distilled water was applied to each fabric surface, and the time to drop complete absorption on each fabric surface was recorded.

Wicking test

Vertical wicking test was performed according to AATCC standard.

Samples were cut 25mm in warp and 60 mm in weft, and water level line was set to 5mm. Values were calculated based on the formula 6.3:

$$W = d/t \qquad (6.3)$$

Where W is the wicking rate (mm/s), d is the wicking distance (mm), and t is the wicking time (s)

Figure 6.4. shows a photographic image of the vertical wicking test of PET/CO sample without impregnation.

Figure 6.4. Vertical wicking test of PET/Co without impregnation

Tables 6.3 and 6.4 show values obtained from wicking and drop tests for PET/CO and PET samples respectively.

Table 6.3. Values obtained from the wicking test and drop test for the PET/CO samples with and without the auxiliaries used

Samples	Initial wicking rate (mm/s)	Drop test (s)
PET/CO without impregnation (reference sample)	0.763	8.71
PET/CO impregnated during 1 minute and dried at ambient temperature	5.000	2.42
PET/CO impregnated during 1 minute and dried at 110 ºC for 120	4.347	2.35

PET/CO impregnated during 24 hours and dried at ambient temperature	5.000	2.43
PET/CO impregnated during 24 hours and dried at 110 ºC for 120 s	5.000	2.24

The initial wicking rate has not been affected either by the drying temperature, or by the impregnation time in the case of PET/CO fabrics. The drop test values confirmed the results of the wicking test.

Table 6.4. Values obtained from the wicking test and drop test for the PET samples (after cotton elimination) with and without auxiliaries used

Samples	Initial wicking rate (mm/s)	Drop test (s)
PET without impregnation (reference sample)	0.322	16.46
PET impregnated 1 minute and dried at room temperature	5.000	4.26
PET impregnated 1 minute and dried at 110ºC for 120 s	5.000	3.02
PET impregnated 24 hours and dried at room temperature	5.000	2.50
PET impregnated 24 hours and dried at 110ºC for 120 s	5.000	2.05

The initial wicking rate has not been affected either by the drying temperature or by the impregnation time in the case of PET fabric after cotton elimination. The values of drop test for impregnated samples of PET during 24 hour were slightly lower than the samples impregnated during 1 minute.

According to the results from the drop test, it can be seen that, impregnated samples require significantly less time to complete the absorption on the fabric surface. For both samples (PET/CO and PET), the shortest time of absorption on the surface was obtained for the samples impregnated during 24 hours and drying at 110 ºC for 120 second.

Based on the wicking test results, it was observed that, the initial wicking rate of impregnated fabrics increased dramatically compared to untreated fabrics (82.4% and 93.5% for PET/CO and PET after cotton elimination respectively), demonstrating the faster absorption rate on the fabric surface.

Dye concentration in the fibre, colour strength & efficiency

Results for 1 minute impregnation time

We performed at laboratory scale, the thermosol process during 1 minute of impregnation time, before padding, to guarantee the best reproducibility of the experimental results.

Tables 6.5 and 6.6, show the values of dye concentration into the fibre (mg of dye per gram of polyester), colour strength and the dyestuff efficiency of the thermosolated samples with and without Lecithin, as a function of the thermosol temperatures respectively.

Table 6.5. Values of impregnation, dye content, colour strength and efficiency for the PET samples dyed using lecithin in the padding bath

PET dyed with **lecithin,** Lyogen DFTN, Solidokoll N and C.I. Blue 56	160 ºC/110 ºC Impregnation time: 1min	180 ºC/110 ºC Impregnation time: 1min	200 ºC/110 ºC Impregnation time: 1min
Impregnation (%)	68.01	68.03	68.04
mg dye/g fibre	12.39	17.55	20.18
(K/S) corrected	12.5	20.47	25.45
Efficiency (%)	46.91	66.45	76.36

In Table 6.5, it was observed that the values of impregnation % were constant for all studied temperatures, while increasing the thermosol temperature led to higher values of colour strength, dyestuff concentration on the fabrics and efficiency.

Table 6.6. Values of impregnation, dye content, colour strength and efficiency for the PET samples dyed without lecithin

PET dyed with Lyogen DFTN, Solidokoll N and C.I. Blue 56	160 ºC/110 ºC Impregnation time: 1min	180 ºC/110 ºC Impregnation time: 1min	200 ºC/110 ºC Impregnation time: 1min
Impregnation (%)	62.11	62.11	62.09
mg dye/g fibre	10.04	14.14	16.18
(K/S) corrected	9.52	18.02	20.74
Efficiency (%)	41.62	58.62	67.09

In similar way that for the baths without lecithin, the values of impregnation were almost constant in all studied temperatures and increasing the thermosol temperature from 160 to 200 ºC increased the values of colour strength, dyestuff concentration and efficiency.

According to tables 6.5 and 6.6, the presence of lecithin increased the impregnation of the padding bath on the fabric about 9.5 % independently of the thermosol conditions compared to samples dyed without Lecithin. This is related with a better wettability of the impregnated samples with Lecithin as was observed before on the results of drop and wicking tests. Increasing the thermosol temperature from 160 to 180 ºC with a constant concentration of lecithin led to an increase of the dyestuff concentration into the fibre of about 40.83 %. Increasing the thermosol temperature from 180 to 200 ºC with a constant concentration of lecithin led to an increase of the dyestuff concentration into the fibre of about 14.42%. Polyester fabrics dyed with Lecithin yielded higher colour strength than the polyester fabrics dyed without Lecithin. The efficiency increased 11.7% due to the presence of Lecithin independently of the thermosol conditions. Padding bath with Lecithin led to lower values of the particle size and polydispersity. This fact may facilitate the beginning of the dye diffusion into the fabric easier in the case of padding solution with Lecithin.

As expected, increasing the thermosol temperature had positive influence on dyestuff efficiency and colour strength of the fabrics, so highest values of dyestuff concentration, K/S and efficiency were obtained at 200 ºC in both thermosol dyeing methods (with and without Lecithin), during 1 minute of impregnation time.

Figure 6.5 indicates K/S values related to concentration of dyestuff (mg dye/g of fibre) for the samples dyed with and without lecithin for 1 minute of impregnation time.

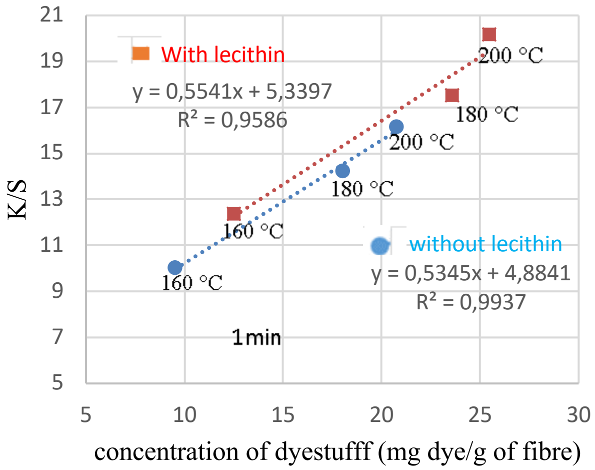


Figure 6.5. K/S values related to concentration of dyestuff (mg dye/ g of fibre) during 1 minute of impregnation

As shown in Figure 6.5, a linear correlation between K/S and dyestuff concentration was obtained in both cases (thermosol dyed PET with and without lecithin).

Table 6.7 shows the percentage of increase in impregnation related to the concentration of dyestuff into the fibre (mg dye/ g of fibre) due to presence of lecithin for 1 minute impregnation time.

Table 6.7. Percentage of increase of impregnation related to the dyestuff concentration into the fiber due to presence of lecithin (impregnation time: 1 min)

	% increase due to lecithin		
	160 ºC / 60 s Impregnation time: 1minute	180 ºC / 60 s Impregnation time: 1minute	200 ºC / 60 s Impregnation time: 1minute
mg dye/g of fibre	23.40	24.11	24.72
Impregnation (%)	9.49	9.53	9.58

With respect to Table 6.7, the presence of lecithin increases about 24% the dyestuff concentration into the polyester fibre independently of the thermosol conditions, remaining constant the increase of the impregnation due to presence of lecithin. The reduction of the particle size about 42% in the padding bath has contributed to facilitate the initial diffusion of the dye into the PET fibre during the thermosol stage, increasing the dyestuff concentration into the fibre by 24%.

Results for the 24 hour of impregnation time

The effect of 24 hours of impregnation time was evaluated to study the influence on polyester coloration in the case of the dyeing of PET/CO fabrics, by pad-batch (CO), and thermosol (PET). Moreover, the effect of the 24 hours of impregnation time was compared with 1 minute of impregnation time.

Tables 6.8 and 6.9 show values of concentration into the fibre (mg dye/g of fibre) colour strength and efficiency of polyester dyed with and without Lecithin as a function of the thermosol temperatures respectively.

Table 6.8. Polyester dyed with auxiliaries, disperse with lecithin (impregnation time: 24h)

PET dyed with **lecithin**, Lyogen DFTN, Solidokoll N and C.I. Blue 56	160 ºC/110 ºC Impregnation time: 24h	180 ºC/110 ºC Impregnation time: 24h	200 ºC/110 ºC Impregnation time: 24h
Impregnation (%)	68.42	68.12	68.38
mg dye/g fibre	17.19	25.74	26.95
(K/S) corrected	15.55	23.59	26.46
Efficiency (%)	64.5	97.31	99.81

As it can be seen from the Table 6.8, impregnation values were remain almost constant at different studied thermosol temperature, however values of dyestuff concentration, colour strength and efficiency increased as the thermosol temperature increased.

Table 6.9. Polyester dyed with auxiliaries, disperse without lecithin (impregnation time: 24h)

PET dyed with Lyogen DFTN, Solidokoll N and C.I. Blue 56	160 ºC/110 ºC Impregnation time: 24 h	180 ºC/110 ºC Impregnation time: 24 h	200 ºC/110 ºC Impregnation time: 24 h
Impregnation (%)	63.10	62.98	63.02
mg dye/g fibre	15.43	23.08	24.12
(K/S) corrected	13.05	23.47	25.74
Efficiency (%)	62.95	94.02	98.55

As the thermosol temperature increased, values of dyestuff concentration, colour strength and efficiency increased, while values of impregnation % were constant in function of thermosol temperature.

With respect to Tables 6.8 and 6.9, it was observed that, presence of Lecithin increased the % impregnation on the fabric about 8.3% independently from the thermosol conditions. Increasing the thermosol temperature from 160 to 180 ºC and 180 to 200º C with Lecithin increased the dyestuff concentration into the fibre by 49.73 % and 4.70 % respectively. Due to presence of lecithin, the efficiency of the thermosolated samples increased with an average of 2.4%.

As expected, increasing the thermosol temperature produces higher colour into the fabric. Furthermore the micro-dispersion padding system of 24 hours (or 1 day) may be an efficient system in the case of fabrics with PET/CO blends by a PAD-BATCH (Cotton dyeing) – THERMOSOL (Polyester dyeing).

Figure 6.6. Indicates K/S values related to dyestuff concentration (mg dye/ g of fibre) dyed with and without Lecithin for 24 hour of impregnation time.

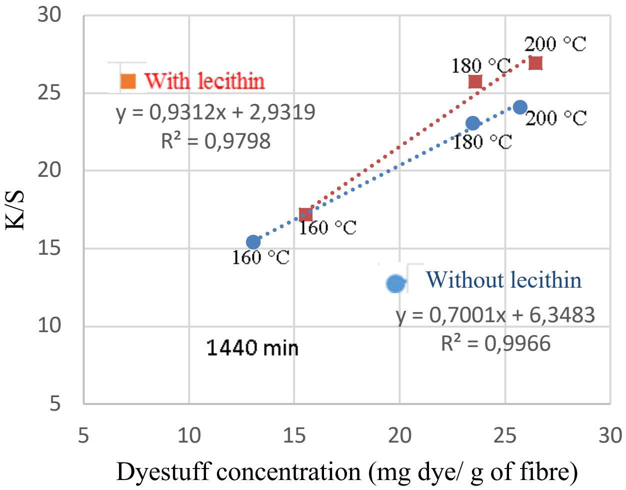


Figure 6.6. K/S values related to dyestuff concentration (mg dye/ g of fibre)

A linear correlation between K/S and dyestuff concentration was obtained in both cases (PET dyed with and without Lecithin), showing the effectiveness of the method. In addition, it was observed that colour strength and concentration into the fibre increased due to presence of lecithin in the padding solution.

Table 6.10 exhibits, the percentage of increase in impregnation related to the concentration of dyestuff into the fibre (mg dye/ g of fibre) due to presence of lecithin during 24-hour treatment.

Table 6.10. Percentage of increase in impregnation related to the concentration of dyestuff into the fibre due to presence of lecithin (impregnation time 24h)

	% increase due to lecithin		
	160 ºC / 60 s Impregnation time: 24h	180 ºC / 60 s Impregnation time: 24 h	200 ºC / 60 s Impregnation time: 24h
mg dye/g fibre	11.40	11.52	11.73
Impregnation	8.43	8.16	8.50

With respect to Table 10, the presence of lecithin increases about 11% the dyestuff concentration into the polyester fibre independently of the thermosol conditions, remaining constant the increase of the impregnation due to presence of Lecithin.

The results of 24 hours of impregnation time proved the importance of developing efficient impregnation systems for the industrial padding baths.

Colour difference measurement

To determine colour difference between PET dyed with and without lecithin during1 minute and 24 hours of impregnation time, a colorimetric analysis of surface colour difference ($DE_{CIE\text{-}Lab}$) was assesed.

Table 6.11 and Figure 6.7 indicate the colour difference ($DE_{CIE\text{-}Lab}$) between polyester samples thermosolated with and without Lecithin in presence of Disperse Blue 56, Solidokoll N and Lyogen DFTN at 160, 180 and 200 ºC of thermosol temperature as a function of impregnation time (1 minute and 24 hours).

Table 6.11. Colour difference between PET samples dyed with and without lecithin during different impregnation times (1 min or 24h) and thermosolated at 160, 180 or 200 ºC.

	160 ºC	180 ºC	200 ºC
$DE_{CIE\text{-}Lab}$(with lecithin with respect without lecithin) Impregnation time: 1min	4.39	2.36	3.77
$DE_{CIE\text{-}Lab}$ (with lecithin with respect without lecithin) Impregnation time: 24 h	3.51	1.85	2.76

Table 6.11 confirms that lecithin yields higher values of colour strength (K/S) in the dyed fabrics at the two impregnation times. The average colour difference of polyester dyed with and without lecithin at the three studied temperatures during 1 minute and 24 hours of impregnation time were 3.50 and 2.70 colour difference units respectively.

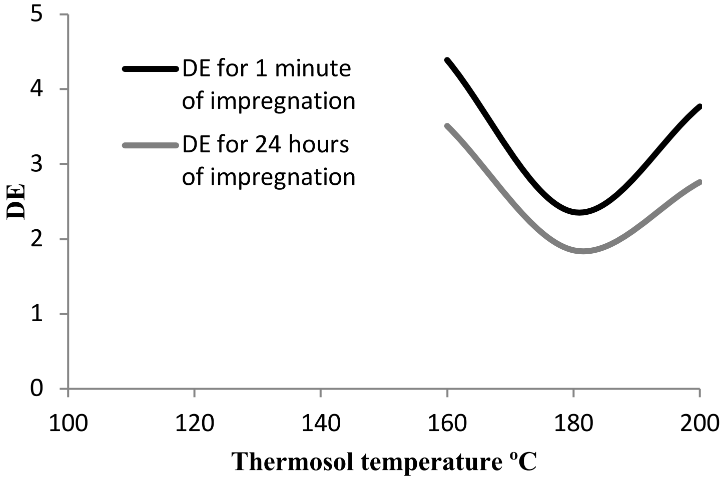


Figure 6.7. Colour difference between PET samples thermosolated with and without lecithin during different impregnation times, at 160, 180 and 200 ºC

The average values of colour differences during 1 minute of impregnation time are slightly higher than the 24 hours of impregnation time for thermosolated polyester samples at three studied temperatures. The highest colour difference was obtained at 160 ºC, and the lowest colour difference was reached at 180 ºC for both impregnation times.

Washing fastness

To study if Lecithin and impregnation times influence on the washing fastness properties, colour fastness to washing have been tested according to the UNE-EN ISO 105-C06.

Tables 6.12, and 6.13 show values of colour fastness to domestic washing of the fabrics dyed as described in the Table 1 with and without lecithin as a function of impregnation time treatment (1 minute and 24 hours) respectively.

Table 6.12. Colour fastness to washing of thermosolated PET samples with 1 minute of impregnation

Samples / Impregnation time: 1min	Grey scale (change in colour)	Polyester (staining)	Cotton (staining)
Polyester dyed without lecithin at 160 ºC	4-5	4	4-5
Polyester dyed without lecithin at 180 ºC	4-5	4	4
Polyester dyed without lecithin at 200 ºC	4-5	3-4	4
Polyester dyed with lecithin at 160 ºC	5	4-5	4-5
Polyester dyed with lecithin at 180 ºC	4-5	4	4-5
Polyester dyed with lecithin at 200 ºC	4-5	4	4

The values of domestic washing fastness are ranging between 4 and 5 in all cases.

Table 6.13. Colour fastness by washing of thermosolated PET samples with 24 hours of impregnation

Samples / Impregnation time: 24 hours	Grey scale (change in colour)	Polyester (staining)	Cotton (staining)
Polyester dyed without lecithin at 160 ºC	5	4-5	4-5
Polyester dyed without lecithin at 180 ºC	5	4-5	4-5
Polyester dyed without lecithin at 200 ºC	4-5	4	4-5
Polyester dyed with lecithin at 160 ºC	5	5	4-5
Polyester dyed with lecithin at 180 ºC	5	4-5	4
Polyester dyed with lecithin at 200 ºC	4-5	4-5	4

As shown, there is no negative influence of lecithin on the washing fastness properties of thermosolated fabrics. Moreover, it was observed that the impregnation time did not have influence in the final domestic washing fastness properties of thermosolated fabrics either.

6.4. Conclusions

Based on particle size analysis it was observed that, presence of lecithin reduces the particle size and polydispersity about 42 % and 176% respectively, due to its wetting properties.

Based on the wicking test results, it was observed that the initial wicking rate of impregnated fabrics significantly increased compared to untreated fabrics (82.4% and 93.5% for PET/CO and PET after cotton elimination respectively). This fact proved the wettability of the treated samples increased significantly.

The use of 1.45 g/L of lecithin in the padding solution increased the percentage of impregnation in padded fabrics about 9.5% during 1 minute, and 8.3% during 24 hours of impregnation independently from the thermosol conditions. It means that to obtain the same shade in the fabric, less dyestuff will be needed.

Lecithin increases the degree of disaggregation of the dye in solid form on the fibre surface, which facilitates the start of the diffusion process of the dye into the fibre.

For 1 minute impregnation it was found that increasing the thermosol temperature from 160 to 180 ºC and from 180 to 200ºC in presence of lecithin led to an increase of the values of dyestuff concentration into the fibre by 40.83% and 14.42% respectively. Moreover, the efficiency of dyestuff in the fibre increased 11.7% due to the presence of lecithin independently of the thermosol conditions.

In the case of 24 hours of impregnation time, the polyester dyed via thermosol process with lecithin increased the efficiency with an average of 2.4% and this value is lower compared to 1 minute of impregnation.

After the thermosol dyeing, higher values of K/S, dyestuff concentration into the fibre and efficiency in all thermosolated samples were found in presence of lecithin at the two impregnation times studied with respect to the thermosolated samples without lecithin.

The thermosolated samples after 24 hours of impregnation time had higher values of dye concentration into the fibre, efficiency and colour strength than the thermosolated sample with the 1 minute of impregnation in all studied cases (with and without lecithin). Hence this study opens the possibility of further research with pad-batch thermosol dyeing sequences, for dyeing PET/CO blended fibres.

The average values of colour differences for the thermosolated samples at different temperatures, treated during 1 minute of impregnation time were slightly higher than with the 24 hours of impregnation time.

Either, the use of lecithin in the padding baths and the impregnation times (1 minute or 24 hour) did not change the final domestic wash fastness characteristics of the thermosolated fabrics.

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CHAPTER 7. GENERAL DISCUSSION & CONCLUSIONS

7.1. Conclusions and discussion of low temperature exhaustion dyeing

According to the analysis and results of the first and second paper, higher values of K/S and exhaustion (%) were obtained for polyester samples dyed with o-vanillin/n-butylacetate micro-emulsion system than the coumarin/n-butylacetate micro-emulsion system. Microparticles of the micro-emulsion collide with the fibre surface and depending on their instability into bath system they facilitate more or less their kinetics. Consequently due to higher hydrophilicity of o-vanillin bath system, their micro-emulsion particles are deposited easily than the coumarin/butyl acetate bath system (more hydrophobic). The facility of the deposition of the free dye molecule at the surface of the fibre (hydrophobic solid) after break the micro-particle promotes their kinetic absorption and later diffusion. Also, the highest values of the constant rate of the isotherms absorption and the activation energies of the disperse dyes were obtained for o-vanillin/n-butylacetate micro-emulsion system. From the apparent activation energy at the range of temperatures studied it was revealed that the action of the o-vanillin/n-butyl acetate micro-emulsion during the kinetic absorption process was more influenced by variation of temperature than was the coumarin/n-butyl acetate micro-emulsion. The activated enthalpy and activated entropy and was calculated by the theory of absolute rates of dyeing and diffusion in the activated state. Higher value for the enthalpy of activation indicates a greater energy releases in the dyeing process for absorbing the dyestuff and higher entropy of activation obtained in presence o-vanillin/butyl acetate produces higher changes in segmental mobility within the microstructure of the fiber. Table 4 shows the values of entropy and enthalpy of activation calculated from the theory of absolute rates of dyeing and diffusion of the activated state of the dye molecule.

Table 7.1. Entropy and enthalpy and of activation for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate at 95ºC

Activated state	polyester dyed with auxiliary products in microemulsion systems	ΔS* (Kcal·mol^{-1}K^{-1})	ΔH* (Kcal·mol^{-1})
		T=95 ºC	T=95 ºC
C.I. Disperse Blue 56 (0.333 g/L)	polyester dyed in microemulsion: coumarin/n-butylacetate/water (0.666/16.666g/L)	0.01305	3.19
	polyester dyed in microemulsion: o-vanillin/n-butylacetate/water (0.666/16.666g/L)	0.01422	6.30

The table above justifies the more efficiency of kinetic and diffusion inside the fiber than for coumarin/n-butylacetate system.

According to the transversal cross section analysis, it was observed that dyestuff was uniformly distributed into the fibres in presence of the proposed auxiliaries, demonstrating the efficiency of the exhaustion dyeing process presented in this thesis.

Figure shows 7.1 the microscopic images of the cross-section of the polyester samples dyed in presence of coumarin/co-solvent or o-vanillin/co-solvent compared with the one dyed without auxiliaries.

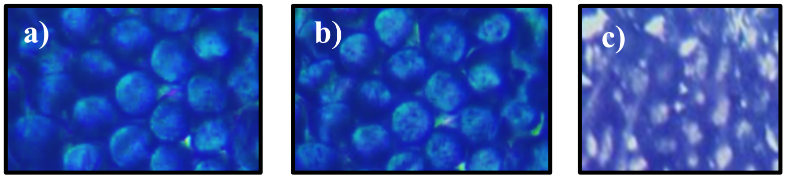

Figure 7.1. Microscopic images of the cross-section of the polyester fabrics: a) dyed with coumarin/co-solvent at 95 ºC during 120 minutes; b) dyed with o-vanillin/co-solvent auxiliaries at 95 ºC during 120 minutes and c) dyed without auxiliaries at 95 ºC during 120 minutes

As it was shown, the use of aformentioned auxiliaries led to a significantly better diffusion to the dye in the exhaustion dyeing process.

Comparing different molecular weight of disperse dyes, this study demonstrated that, polyester dyed via exhaustion process with low molecular weight disperse dye led to better absorption level and colour strength than high molecular weight dyes as expected. The same polyester sample dyed at 95 ºC with high molecular weight disperse dye (C.I. Disperse Blue 79) and low molecular weight disperse dye (C.I. Disperse Blue 56) lead to exhaustion values of 71.3% and 97.5% respectively. This means that, low molecular weight disperse dyes penetrate faster than high molecular weight disperse dyes, as already mentioned in the literature review. However, polyester samples dyed with high molecular weight disperse dyes led to better values of colour fastness to washing and ironing than the ones dyed with low molecular weight disperse dye.

Comparing this new exhaustion formulation process with a conventional one at 135 ºC, it was found that similar results in terms of colour strength were obtained with the process presented in this thesis, with a 40 ºC reduction of the dyeing temperature, Table 5 indicates that, there is no significant difference on the K/S values at the maximum wavelength and exhaustion% values for the microemulsion system at 95ºC and the conventional (HT) system at 135ºC.

Table 7.2. K/S values at λ=630 nm, exhaustion percentage and photographic images of the polyester fabrics dyed with o-vanillin and co-solvent at 95 ºC after 120 minutes and the ones obtained with the same fabric subjected to a conventional dyeing process at 135 ºC in presence of 2 g/L of dispersing agent Eganal.

Dyeing time=120 minutes	K/S (λ=640 nm)	Exhaustion (%)	Photographic image of the dyed fabrics
PET dyed with Disperse Blue 56 and in presence of o-vanillin in n-buthylacetate at 95 ºC (microemulsion system)	16.20	97.5	
PET dyed with Disperse Blue 56 and in presence of Eganal at 135 ºC (conventional system)	16.81	99.1	

This new process allows saving thermal energy and makes it possible to perform the dyeing process in open equipment and, in the case of dyeing blended fibres, significantly reduces the risk of damaging the weakest fibres. These facts demonstrate that the process presented can be appropriate for industrial applications and a real green alternative method for the industry because it requires less energy, lower cost and uses more environmentally friendly dyeing auxiliaries.

7.2. Conclusions and discussion of thermosol dyeing

Based on the third article results, it was observed that presence of lecithin in the padding solution, increased values of K/S, efficiency and dyestuff concentration into the polyester fabrics independently from the thermosol conditions. Moreover, thermosolated samples during the 24 hours of impregnation time had higher values of dye concentration into the fibre, efficiency and colour strength than thermosolated sample with the 1 minute of impregnation time in all studied cases (with and without lecithin). This means the preatment with lecithin for 24h at room temperature may have an effect opening the macracmolecular structure of the PET, facilitating the diffusion process during the thermosol process.

Table 7.3. and Figure 7.2 indicate the colour difference (DE $_{\text{CIE-Lab}}$) between polyester samples thermosolated with and without Lecithin in presence of Disperse Blue 56, Solidokoll N and Lyogen DFTN at 160, 180 and 200 ºC of thermosol temperature as a function of impregnation time (1 minute and 24 hours).

Table 7.3. Colour difference between PET samples dyed with and without lecithin during different impregnation times (1 min or 24h) and thermosolated at 160, 180 or 200 ºC.

	160 ºC	180 ºC	200 ºC
DE$_{\text{CIE-Lab}}$(with lecithin with respect without lecithin) Impregnation time: 1min	4.39	2.36	3.77
DE$_{\text{CIE-Lab}}$ (with lecithin with respect without lecithin) Impregnation time: 24 h	3.51	1.85	2.76

Table 7.2 confirms that lecithin yields higher values of colour strength (K/S) in the dyed fabrics at the two impregnation times. The average colour difference of polyester dyed with and without lecithin at the three studied temperatures during 1 minute and 24 hours of impregnation time were 3.50 and 2.70 colour difference units respectively.

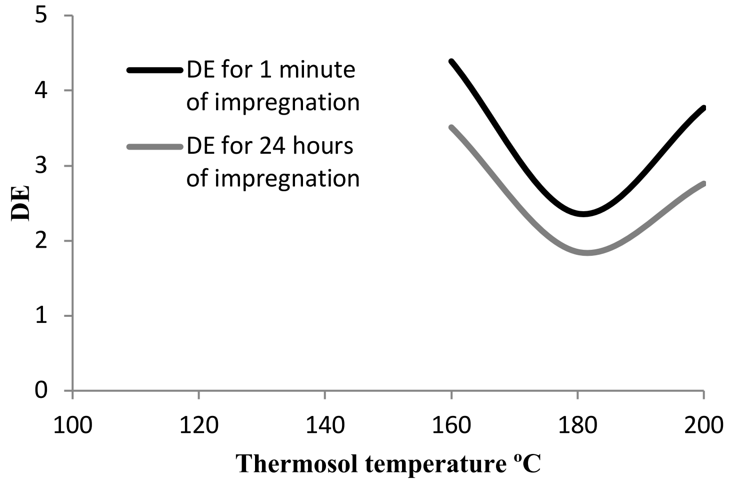

Figure 7.2 Colour difference between PET samples thermosolated with and without lecithin during different impregnation times, at 160, 180 and 200 ºC

The average values of colour differences during 1 minute of impregnation time are slightly higher than the 24 hours of impregnation time for thermosolated polyester samples at three studied temperatures. The highest colour difference was obtained at 160 ºC, and the lowest colour difference was reached at 180 ºC for both impregnation times.

Therefore, the proposed formulation will open the possibility of further research with pad-batch (cotton) and thermosol (PET) dyeing sequences, for dyeing two blended fibers of cotton/polyester.

7.3. General conclusions of the thesis

In both dyeing methods (exhaustion and thermosol), the presence of the auxiliaries in the padding or in the exhaustion baths lead to a decrease of particle size and polydispersity with respect to the conventional methods. It was observed that, the padding or dye baths using auxiliaries lead to dyed samples with more uniform color compared with similar systems without auxiliaries. These facts justified the effectiveness of auxiliaries used in this thesis.

Comparing the exhaustion and the thermosol process, this thesis proved that, to obtain same shade and colour strength as exhaustion process in the thermosol process, much higher amount of the dyestuff and auxiliaries will be required. However, thermosol process has advantages such as lower personnel costs, water and also the fabric is thermofixed during the dyeing process. As already mentioned in the literature review, for special shades and smaller quantity of fabric, the exhaustion process is more suitable, whereas for 5,000 m or higher color batch, the dye thermosol dyeing process is more attractive.

In terms of color fastness to washing and ironing the auxiliaries which have been used in the thesis did not modify the properties of the dyed fabrics. This justifies the potential future introduction of the proposed processes (low temperature exhaustion and thermosol) at industrial level. Moreover, all of the auxiliaries used such as o-vanillin, coumarin, n-butylacetate and lecithin in this thesis are non-toxic natural based products.

In both thermosol and exhaustion process we have improved the dyeability of the polyester at low temperatures with maintaining the same quality of the fabric in terms of dye absorption and color strength as industrial processes. For instance, in the exhaustion low temperature dyeing process proposed, we have obtained the same results than high temperature industrial processes with a reduction of 40ºC the dyeing temperature.

To be concluded, in both dyeing methods we have attempted to dye polyester in a manner as ecologically friendly and low cost as possible. The amount of auxiliaries and dyes were at a minimum level. These methods had several advantages, such as low-cost materials, low energy costs, no toxic chemicals, no deformation of the fabric due to low temperature and the possibility of reusing the waste water as a fertiliser. Dyeing processes presented in this thesis can be recommended as an ecological alternative method of dyeing polyester.

CHAPTER 8. FUTURE RESEARCH

The main future research lines derived of this thesis could be:

A) Study of dyeing polyester via both thermosol and exhaustion methods using 100% pure disperse dyes (with no additives) in order to understand and analyze better the efficiency and effectiveness of the mentioned auxiliaries used in this thesis.

B) Study pad-batch (cotton) and thermosol (PET) dyeing sequences for dyeing two blended fibres of cotton/polyester with 24 hours of impregnation treatment in presence of lecithin as an auxiliary.

C) Possibility of using the combination of the natural auxiliaries used in this thesis with natural dyes in order to minimize the risk of toxicity during the dyeing process, and possibility of substituting the synthetic dyes with the natural ones.

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Annex I. LIST OF PUBLICATIONS

List of publications

1. S Radei, FJ Carrión-Fité, M Ardanuy, JM Canal (2020): Thermodynamic and kinetic parameters of polyester dyeing with Disperse Blue 56 using bio-based auxiliaries and co-solvent microemulsion. Textile Research Journal, 9 (5-6), 523–536. **JCR Impact factor 1.54 (Q1 3/24)**.

2. S Radei, FJ Carrión-Fité, M Ardanuy, JM Canal (2018): Kinetics of Low Temperature Polyester Dyeing with High Molecular Weight Disperse Dyes by Solvent Microemulsion and AgroSourced Auxiliaries. Polymers 10 (2), 200. **JCR Impact factor 3.164 (Q1 17/87)**.

3. S. Radei, M. Ardanuy, J. M. Canal. Effect of a bio-based amphoteric surfactant on polyester thermosol dyeing process. Journal of the Textile Institute Under review. **JCR Impact factor 1.063 (Q2 9/24)**.

4. F J Carrion-Fite, S Radei (2017). Development auxiliaries for dyeing polyester with disperse dyes at low temperatures. Materials Science and Engineering 254