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Recent advances in supercritical fluid dyeing

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Supercritical fluid dyeing is a promising technology first proposed in the 80s to overcome the high energy demand and water consumption of conventional textile coloration. This review covers its advances from 2014 to present, from the successful industrial implementation of supercritical fluid dyeing of polyethylene terephthalate to the most recent results obtained for the dyeing of other synthetic and natural textiles. Specific attention is also dedicated to the most innovative applications of supercritical fluid dyeing such as the functionalization of textile and non-textile substrates, which may give rise to the development of other sustainable processes or novel advanced materials in the next future.

1. Introduction

The traditional aqueous dyeing of textiles is a high-water consumption technology. It has been estimated that about 100-150 L of water are consumed to dye 1 kg of fiber [1] and that approximately 280000 tons of textile dyes are discharged in wastewater industrial effluents every year, which involves a direct threat to aquatic life and human health [2]. Another consequence of water consumption in dyeing is the high energy costs connected to heating large volumes of water [2], which may range from 8 to 18 MJ per kg of processed textile [3]. Stricter legislation to protect the environment [4] and the necessity to reduce the costs of water treatment and energy consumption have boosted the development of new sustainable processes in textile dyeing [2, 5]. Supercritical fluid

dyeing (SFD) is one of the possible candidates since it is a green process that completely replaces water with CO₂ as the solvating medium [2, 3, 5].

Supercritical CO₂ (scCO₂) is an economic, non-toxic, non-flammable and green solvent that possess unique physical properties. Its low gas-like viscosity allows its penetration in many solid substrates and its liquid-like solvent power allows many organic compounds to be solubilized. Many researches aimed at the industrial application of scCO₂ can be found in the literature, such as extraction, particle formation, drying, soil treatment, chemical reactions, etc. [6, 7]. Apart from the possibility of eliminating water as the dyeing medium, the interest of the textile industry in this fluid lies in many other advantages such as simpler dye formulation (without auxiliaries), shorter dyeing time and minor energy consumption. Simple depressurization allows the unused dye to be recovered, the CO₂ to be recycled and the dyed fabric to be obtained so avoiding the high-energy-consuming drying step.

SFD is not a novelty since its first experiments date back to the 80s and many previous comprehensive reviews can be found in the literature [8-10]. This work is mainly focused in the recent advances of this technology from 2014 to present. In the last few years, in fact, a great deal of research activities has been performed, which is probably connected to the ever-increasing environmental concerns. The first part of this review is dedicated to the last technological advances in the SFD of polyethylene terephthalate (PET), the first fiber to be successfully dyed and for which many industrial-scale dyeing machines are spreading all around the world. Specific sections are dedicated to the dyeing of other synthetic textiles as well as natural fibers, where the latter continue to remain the final challenge of this technology. The final sections are dedicated to other uses of SFD, such as imparting new functionalities to the fabrics, which can be included in the larger context of the supercritical finishing of textiles, or the coloration of non-textile materials, which can promise significant advances in other industrial fields.

2. Supercritical fluid dyeing of PET

The mechanism of SFD of PET has been widely investigated since this technology was first proposed in the 80s and can now be considered completely elucidated [8, 9]. Its success lies both in the fact that disperse dyes, which are those commercially employed in conventional aqueous dyeing of this textile, display higher solubility in scCO₂ than water, and in the significant swelling/plasticizing action of the supercritical solvent towards this particular synthetic fiber. The small CO₂ molecules, in fact, can easily penetrate and enlarge (swelling) the free volume among the polymer chains so increasing their mobility (plasticization), which results in the reduction of the glass transition temperature and in the diffusion enhancement of the dye [11, 12]. At the end of the dyeing process, the system is depressurized, the gaseous CO₂ is released by the textile while the dye is entrapped inside the polymeric matrix of the fiber [9].

The main research efforts in this field have always been directed towards the solution of the technological issues connected with the process optimization and scale-up. In 2014 Long and coworkers [13] reported a detailed overview of the main dyeing machines developed all over the world since the first lab-scale experiments were conducted in 1988 in Germany [8]. The first important and practical contribution to the pilot scale development of the process was given in 1995 by UHDE GmbH (Germany) that constructed a 30 L equipment suitable for both fabric beam and yarn bobbin dyeing [8]. Since then, many other prototypes have been realized in Europe [13, 14, 15], America [13, 16] and Asia [13, 17, 18] with dyeing vessels of different scale, ranging from 24 to 450 L [13].

In 2008 the Dutch company DyeCoo was founded to supply beam dyeing equipment at industrial scale [13]. By the end of 2018 DyeCoo had a total of 12 dyeing machines operating in Taiwan, Thailand and Vietnam and in the next future is expected to expand in India and Europe [19]. Each DyeCoo dyeing machine allows 800000 kg of PET to be processed per year, effectively saving 32 million L of water and avoiding the use of 160000 kg of chemicals; furthermore 95% of the CO₂ can

be recycled after each batch [20, 21]. In addition, by the end of 2014 Nike, one of the biggest supplier of sports apparel, launched a new collection of tennis polo shirts dyed without water in cooperation with DyeCoo [20, 22]; however, at present, it is not clear if this garment product is available in retail stores. A possible explanation of the still limited diffusion of this technology lies in the high price tag of the final product, which doesn't cope with the consumer expectations for inexpensive clothing. This has probably prevented a wider support of fashion brands to SFD and other waterless technologies [23].

In the above cited context, the academic research of the last years has often been conducted in cooperation with textile companies to improve the technology of the process aiming at increasing the production efficiency [1, 4, 13, 24-28]. However, lab-scale investigations [18, 29-32] or simulation studies [33] aimed at disclosing other aspects of the process mechanism have also been conducted as well as tests with natural or new synthetic dyestuffs [34-37].

2.1 Recent technological advances (2014-2019)

Table 1 reports an overview of some recent lab- to industrial-scale prototypes and innovative technological solutions for SFD of PET. All entries reported in the table refer to research conducted in China, which reflects the economic growth and industrial development of this country in the last decade [38]. The main difference among the solutions reported in Table 1 lies in the layout of the dyeing vessel while the overall scheme of the plant and operation procedures are quite similar.

Figure 1 reports a simplified scheme of a typical plant for SFD of textiles, which may approximately describe the main operation steps of many pilot- and industrial-scale plants [1, 4, 13, 24, 25]. Briefly, gaseous CO₂ is condensed and stored in a tank that feeds a pressurization pump; pressurization of the dyeing vessel (valve 1 and 2 open, valve 3 closed) occurs simultaneously with the dissolution of the dye in the stirred dyestuff vessel. When the temperature and pressure of the supercritical dyeing medium has reached the set levels, the dyeing process is conducted circulating the scCO₂ with the

pre-dissolved dye molecules by means of a circulation pump (valve 2 open, valve 1 and 3 closed). Eventually (valve 2 and 3 open, valve 1 closed), the scCO₂ is expanded in a separation subsystem, which may consist in one or more separators, to recover the dye and allow the gas to be recycled after a final purification step. In addition, a cleaning step (not shown in the figure) is generally conducted to remove the unfixed dye from the textile as well as that precipitated in the dyeing vessel and tubes: this can be conducted with pure liquid or scCO₂ as well as mixing it with some cosolvents [1, 13, 24]. It has been calculated that a 92-95% CO₂ recycling efficiency can be achieved [1, 24, 28] and about 40% of the dye can be recovered [4].

The temperature and pressure of the process are generally included in the 80-140 °C and in the 17-29 MPa ranges, respectively, while the duration of the dyeing step varies between 20 and 120 min [1, 13, 24-28]. The dyestuff dosage varies between 0.2-4% o.m.f. (on the mass of fiber) when loose fibers, yarn bobbins or fabrics are dyed [1, 13, 24-27], while lower amount (0.012-0.25 o.m.f.) is employed when zipper tape is processed [4, 28]. Tests with a single dye [1, 4, 13, 24-26, 28] as well as dye mixtures [27, 28] are reported.

The dye uptake of the colored textiles is usually quantified in terms of color strength (K/S) while color fastness is checked according to national textile standards. The different reports agree with the fact that satisfactory and commercially acceptable products with good level dyeing property, high reproducibility of coloration and good fastness are generally obtained [1, 4, 13, 24-26, 28]. Furthermore, a comparison with water dyeing has pointed out that higher values of K/S could be obtained with SFD of zipper tapes even though the employed amount of dyes was lower [4].

Much of the technological investigation of the last years has been devoted at improving the quality of the dyed products (i.e. uniformity of dyeing) and the efficiency of the process. This is the reason why different layouts of the dyeing vessel have been proposed (Table 1). First generation dyeing plants were designed and constructed to dye yarn bobbins or fabrics with the beam dyeing method where the textile was kept in a static mode inside the dyeing vessel during the whole process [13].

The fluid was circulated only by means of the circulation pump and the option to reverse the flow in the dyeing bath from inside-to-outside (I/O) to outside-to-inside (O/I) of the textile package was the only option to improve the evenness of dye distribution in the product [9].

In 2014 Soochow University built a pilot-scale plant that performed fabric rope dyeing in dynamic mode [13, 24]. A fabric rope was loaded into the dyeing vessel by a drive reel (a fabric guide cylinder) that was magnetically driven by a reversible motor that allowed clockwise and anticlockwise rotation of the textile. This allowed the mass transfer between the supercritical bath and the polymer to be improved as well as fast and uniform coloration to be obtained: the standard deviation of the K/S values ($\sigma_{K/S}$) measured from 20 different sites of an individual PET fabric was below 0.08 [13]. A similar device was adopted by the Fujian Institute of Research since the dyeing vessel was equipped with a rotating warp beam [25]: during the dyeing process the fabric was wrapped around the rotating warp shaft that allowed a cyclical circulation. Experimental evidence of higher dyeing uniformity is not reported; however, the authors investigated the dyeing of PET and cotton fabric with three newly synthesized azo dyes. The results pointed out that even though commercially acceptable products were obtained, higher color strength and deeper shades were obtained for PET. Furthermore, the paper reports, for the first time, preliminary dyeing tests on zipper tapes [25].

In 2016 Zheng and coworkers [1] from Dalian Polytechnic University described the operation of an industrial scale multiple plant for the SFD of PET yarn bobbins. This is probably the plant with the highest capacity (two vessels, each one with a capacity of 500 L) ever described in the scientific literature. In this case the dyeing vessels were equipped with a rotating bobbing dyeing frame composed of different perforated tubes mounted on a rotor device. According to the authors the same dyeing frame can also be used to dye fabrics, garments, skeins and balls. The dyeing procedure coupled the rotation of the dyeing frame inside the vessel with the I/O and O/I external circulation as well as the execution of “Dynamic/Static” cycles, which were achieved by on/off cycles of the pump. Furthermore, the plant was equipped with sensors and Hd cameras, which allowed the dyeing

conditions in the vessels to be monitored. The $\sigma_{K/S}$ measured from 10 different sites of an individual PET bobbin varied between 0.038 and 0.097, which depended on the employed dye and the working temperature. Commercially acceptable color uniformity was achieved, and it was found that the $\sigma_{K/S}$ values were decreased when the dyeing temperature was increased from 100 to 120 °C [1].

Dalian Polytechnic University proposed other innovative layouts of the dyeing vessel [26, 27]. The first one consists of a special tubular dyeing frame set inside the vessel, which allowed loose fibers to be dyed [26]. The coloration of loose fibers could allow richer and more uniform color levels to be obtained after spinning so resulting in a much more efficient and cost-effective process than yarn or fabric dyeing [26]. The second one is a new technique to achieve color graphic dyeing, where the PET fabric was folded into fan shape and wrapped with cotton fabrics to provide free and abstract patterns on the textile [27]. Coloration was conducted with dye mixtures at different mixing ratios and temperatures. Results were preliminary; however, color graphics dyeing could be achieved thanks to the blocking effect of the cotton fabric, which acted as an anti-dyeing barrier, and the different dependence from temperature of the diffusion coefficients of the dyes [27].

In 2017-2019 the Fujian Institute of Research in cooperation with the University of Chinese Academy of Science and Fujian SBS Zipper Ltd., which is a major zipper manufacturer in China, have proposed the continuous dyeing of zipper tape in scCO₂, both at lab-scale [28] and pilot-scale [4]. The main novelty of the plant layout is the use of two horizontal dyeing vessels arranged side by side. With respect to vertical dyeing autoclaves, the horizontal arrangement resulted in even fluid distribution so avoiding dye accumulation at the bottom of the vessel. This could ensure uniform dyeing; in fact, the K/S values of the upper, middle, and lower layers of the dyed zipper tape were almost the same [4] even though the textile was probably arranged in a static beam inside the vessel (no details about the possibility of moving or rotating the textiles during dyeing are provided in the papers). In addition, arranging the two dyeing vessels side by side allowed other advantages. First, the scCO₂ dyeing in the first autoclave and the CO₂ recycling in the second could be carried out simultaneously. Second,

when the dyeing step of the first vessel was finished half of the gas could be transferred to the second one that could, then, begin dyeing in the “half pressure zone”: this not only reduced the heating and pressurization energy requirement, but also saved the cost of CO₂ recovery [4, 28]. Furthermore, a new color-matching dyeing vessel was designed, which allowed the dyes to be injected into the dyeing circulation loop so enhancing their dissolution rate and reducing the dyeing time [4].

Many of the above cited papers [1, 4, 24, 26, 28] report a comparison of the total running costs of conventional and SFD of PET: these are summarized in Table 2. It is widely recognized that investing in scCO₂ dyeing is costly with respect to the conventional water process [28]; however, running cost is generally considered lower due to the simpler dye formulation, shorter dyeing times, elimination of the drying step, etc. [8, 9]. Data in Table 2 confirm that total running costs of the supercritical process are always lower than those of the aqueous one; however, the economic analyses conducted from 2014 to 2016 do not show such a significant advantage and, in practice, costs can be considered comparable, which gives reason of the still limited diffusion of this technology [23]. As far as the most recent analyses are concerned (2017-2019), the results point out that the two-side-by-side-vessels layout recently proposed for the continuous dyeing of zipper tape [4, 28] succeeds in a significant abatement of the running costs that decrease to about 20 to 45% of those of the aqueous process. This can be considered quite promising for the future of this technology.

2.2 Investigation of the process mechanism

The influence of the process operating conditions on color strength and fastness of the dyed product is widely investigated in pilot-scale plants [1, 4, 24, 26]. Furthermore, specific lab-scale investigation was performed by means of the “factorial design of experiment technique” to investigate the effect of temperature, pressure, dyeing time and dye-to-fiber mass ratio on the color strength and wash fastness of PET dyed with CI Disperse Orange 30 [29]. The model revealed a statistically significant and positive effect of all factors on color strength while only temperature had a positive and statistically important effect on wash fastness [29]. This suggests that while many “degrees of

freedom” (i.e. the variation of temperature, pressure, etc.) are available to tune the color intensity of textiles, to achieve an acceptable level of color fastness only requires a certain temperature threshold to be crossed.

The use of dye mixtures to produce a variety of shades is crucial for scCO₂ dyeing at industrial level. However, this subject continues to be rarely investigated in the literature [9]. The trichromatic combination of CI Disperse Orange 30, CI Disperse Red 167 and CI Disperse Blue 79 in SFD at 120 °C and 25 MPa was first investigated in 2013 [18]. It was found that the build-up and the dyeing rate of the three dyes were comparable, which proves their compatibility even though the uptake of the dyes in a mixture was slightly lower than that of the corresponding dyes when they were used alone. A comparison with the conventional aqueous process pointed out that the uptake and exhaustion of the dyes were similar even though some changes in the color of the fabric could be observed when two out of three dyestuffs were employed. Recently, the solubility of the same trichromatic combination in scCO₂ at a molar ratio of 1:1:1 has been investigated at different temperatures and pressures and compared with the solubility of each single dye at the same operating conditions [30]. The solubility of each dye in the quaternary system was from 8 to 15% lower than that of the corresponding binary one due to the competing dissolution effect between dyes in multicomponent systems [39]. However, the effect of solubility variation on dye uptake and partition coefficient is still under investigation [30]. This could be of great interest since different color shades could be obtained by simply tuning temperature and pressure instead of changing the mass or molar ratio of the dyes in the trichromatic mixture [9]. So far, the above cited trichromatic combination has been successfully employed to dye zipper tapes in scCO₂ [28]. Different color shades with excellent consistency were obtained by varying the dosage of the dyes without changing the temperature (90 °C) and pressure (23 MPa).

Other very recent investigations aim at elucidating, for the first time, the role of the solid dyestuff in the supercritical process [31, 32]. A first paper [31] investigates how the supercritical treatment may

affect the physicochemical properties and application characteristics of the reprecipitated solid dyes. This is particularly interesting since the recovered dye (Figure 1) is intended to be reused in a subsequent dyeing batch. Experiments were conducted by treating CI Disperse Red 167 at 30 MPa and 70 min at different temperatures (included in the 100-160 °C thermal range) and by analyzing the reprecipitated dye. The supercritical treatment of the dye resulted in a crystal form change from β -type to α -type, which involved a change in the melting point and a depression of the thermal decomposition temperature, while the color characteristics in N,N-dimethylformamide solutions did not change. The crystal form change occurred gradually when temperature was above 120 °C. However, despite the physicochemical changes of the dye, dyeing tests with the recycled CI Disperse Red 167 did not show any significant change in colorimetric or colorfastness properties of the final product [31]. On the other hand, a different research group investigated the effects of dye particle size on the dissolution rate and overall dye uptake on PET [32]. CI Disperse Red 60 and CI Disperse Blue 359 were first micronized by means of the Rapid Expansion of Supercritical Solution (RESS) technique, which consists in the rapid reprecipitation of a solute from a supercritical solution. After, their dissolution rate and overall dye uptake on PET at 120 °C and 25 MPa were monitored in a vessel without internal or external circulation and compared with those of the unprocessed dye. The dissolution rate of the micronized dye particles showed a significant enhancement especially as far as CI Disperse Orange 30 is concerned. For both dyes, the RESS processed particles exhibited a faster and higher uptake on PET within 60 min. The mechanism requires further elucidation since the faster dissolution rate and dye uptake enhancement may be related to the significant size reduction and narrower size distribution of the dyestuff as well as the physicochemical changes of the reprecipitated dyes, which exhibited lower degree of crystallinity and lower heat of fusion. It is clear, then, that deeper investigation of the changes in the morphology and physical properties of recycled dyes is necessary to understand at what extent these may affect the dyeing kinetics or the color intensity of textiles.

Computational fluid dynamics has recently been used to simulate the scCO₂ flow characteristics in fabric beam dyeing in absence of the dye [33]. Simulation results reveal that non-uniformity of the flow (i.e. the velocity profile of the fluid in the axial direction) increases with the increase in the scCO₂ mass flow rate while higher operating pressure, lower inlet temperature and flow reversal operation are beneficial to flow distribution levelness. The work is a fluid dynamic investigation and does not evaluate the dye evenness in the fabric. However the two phenomena should probably be related and the outcome that high CO₂ flow rates favor flow unevenness seems to be in contrast with the evidence that more uniform dye distribution in yarn bobbins can be obtained by operating at higher CO₂ flow rates [40, 41] and pumps with high circulating flow rates are generally selected in industrial-scale prototypes [1]. This point definitely deserves deeper investigation. Further simulation studies should be strongly encouraged since the use of mathematical modelling in SFD is a real novelty and could be a powerful tool to achieve information useful for process optimization.

2.3 Novel dyes for PET supercritical fluid dyeing

The search for new dyes suitable for SFD is an important challenge for this technology, especially as far as the coloration of natural textiles is concerned (see section 4). In this context, SFD of PET with novel dyes rather than the well-known auxiliary-free commercial disperse dyes has also been investigated. These may be newly synthesized anthraquinone [34] or azo dyes [35] as well as natural compounds [36, 37]. Many reasons have been abduced, such as the enlargement of the number of scCO₂-soluble dyes [35], their synthesis from commercially inexpensive starting materials [34] or the employment of hypoallergenic molecules [36, 37]. Other innovative purposes are the use of special dyes to impart antibacterial, fluorescent or photochromic properties to the textile, which is discussed in section 5.

Among the above-cited works, perhaps, the most promising and up-to-date researches are those connected with the use of hypoallergenic natural colorants [36, 37]. The application of these natural compounds on synthetic textiles via conventional aqueous methods requires appropriate surface pre-

treatment of the fiber and the use of mordant chemicals, which may limit cost effectiveness and the benefit of a low environmental impact [36]. For this reason, the use of scCO₂ represents a viable alternative. Promising results with good color strength and levelness as well as satisfactory washing and rubbing fastness were obtained by impregnating a PET fabric with curcumin at 120 °C, 25 MPa and 1 h of dyeing time in a lab-scale equipment [36]. According to the authors the fastness performance is expected to improve in industrial-scale plants since cleaning of the unfixed dye through scCO₂ purging could be performed, which was not possible in the lab-scale facility [36].

Coloration of PET fabric with natural curcuminoid dyes was also achieved with an innovative approach by another research group [37]. This was performed by the simultaneous extraction of curcuminoid dyes from turmeric and PET dyeing in the same supercritical bath. The turmeric powder at different dosages was directly poured into a dyeing autoclave, which also contained the PET fabric, and dyeing was performed at 150°C and 20 MPa for 1 h. The results were compared with those obtained with conventional water dyeing at high temperature (100-130 °C) with ethanol-extracted dyestuff. Samples dyed with scCO₂ exhibited highest dye exhaustion, highest color strength and better fastness properties with respect to those obtained with the conventional method. However, regardless of the employed dyeing technique, light fastness appeared to be fair to moderate especially at higher dye concentrations. The authors explained that, under the influence of light, the curcuminoid dyes were probably converted from a keto to an enol form, which could result in their sublimation from the fabric surface [37].

3. Supercritical fluid dyeing of other synthetic polymers

An overview of recent researches conducted to dye synthetic polymers other than PET with scCO₂ is reported in Table 3.

Polyamide fibers, such as nylon 6, are widely used in textile industry, which involves a great interest in their coloration with the supercritical technology. However, the research reported in the literature on this topic is quite limited. Previous studies pointed out that nylon is less dyeable than PET with lower color strength and fastness due to the higher degree of crystallinity and the presence of polar functional groups [9], which often required the presence of small amounts of water to improve coloration [42, 43]. Recent researches have investigated the use of new disperse dyes to achieve coloration of nylon 6 without the use of any cosolvent [35, 44]. The first series of dyes were synthesized from β -oxoalkanenitriles [44] and were prepared to provide antibacterial activity to the textiles (see section 5). A second series of dyes with similar molecular structure has recently been synthesized by the same research group but it is not mentioned if they possess antibacterial activity or not [35]. Good coloration strength was obtained with K/S values up to 17 [44], which is comparable to the best results obtainable for PET coloration, where K/S values up to 20-26 can be obtained [1, 26, 29]. Excellent fastness properties were also obtained, and especially light fastness was much higher in comparison with conventional aqueous dyeing with the same dyes [44]. The success of this series of dyes was explained by the formation of specific intermolecular hydrogen bonds between the dyes and the nylon functional groups [35].

Meta-aramid fibers are aromatic polyamides and are very difficult to dye due to the extremely high glass transition temperature (270 °C) and high degree of crystallinity [45]. Conventional water dyeing is generally conducted with disperse dyes in presence of carriers, which promote polymer chain flexibility but may pose toxicity issues [46]. Tests to achieve coloration of meta-aramid fibers have also been conducted in scCO₂ in the presence of nontoxic carriers [45, 46]. In a first study Zheng and coworkers [45] pretreated the meta-aramid fabric by dipping it for 5-10 min and at 60-100% liquid rate in CYNDYE DNK, an aromatic amide compound, whose chemical structure was not reported for commercial confidentiality. The textile was then dyed with different disperse dyes in scCO₂. Later, the same research group employed CYNDYE DNK or other non-harmful carriers as cosolvents. In this case the fiber was not pretreated but the carriers were stored in an appropriate tank and mixed

with the CO₂ at 1-5 w/w% during pressurization [46]. Good coloration results were obtained in both cases and CYNDYE DNK was found to improve the color strength much more than other compounds. Even though the authors do not report the chemical structure of CYNDYE DNK, they claim that, being it an aromatic amide compound, it displays better affinity with meta-aramid fibers with respect to other employed carriers, such as dimethyltereftalate or ethylalcohol. Furthermore, the SFD procedure did not affect the chemical structure of the textile, whose decomposition temperature and breaking strength were at least slightly increased thanks to the expansion effect of the carrier that promoted a beneficial rearrangement of the macromolecular structure [45].

Ultra-high-molecular-weight polyethylene (UHMWPE) is another hard-to-be-dyed material due to its high crystallinity and dense molecular structure, which make it difficult for the polymer to interact with the dyes [47]. The same antibacterial hydrazonopropanenitrile disperse dyes that were used to dye nylon 6 [44] were used to achieve supercritical fluid coloration of UHMWPE [47]. Satisfactory coloration could be achieved when decaline, which is a paraffin oil previously employed for gel-spinning of UHMWPE [48], was added as a cosolvent. However, the combined plasticizing/swelling action of scCO₂ and decaline promoted reorientation of the polymer chains, which resulted in a strong reduction of the degree of crystallinity (from an initial value of 90%, it was reduced down to 60-70%). This involved a reduction of the maximal breaking strength of UHMWPE, which decreased from 1.74 GPa to approximately 1.3 GPa after a three-hour supercritical treatment [47].

Some of the above cited antibacterial hydrazonopropanenitrile disperse dyes [44] were also employed to dye polypropylene (PP) [49]. PP is a highly crystalline polymer with non-polar aliphatic structure that does not contain any sites to which conventional water-soluble dye may bind [49]. For this reason, SFD of PP with different disperse dyes was investigated in past years [9]. Successful coloration was obtained even though the light fastness was generally low [50]. In their recent investigation Abou Elmaaty and coworkers achieved good coloration of PP with three antibacterial disperse dyes [49]. The results were compared with those obtained with high-temperature (100-130

°C) water dyeing with the same dyes. Significantly higher color strengths were obtained with the supercritical process (100-130°C, 15-25 MPa); fastness to light was also improved up to practical use even though its rating did not reach the 4-5 levels of wash and rubbing fastness. Moreover, mechanical properties of PP were preserved after the supercritical treatment while a 25-90% breakdown was observed after processing the fabric with the water medium [49]. Recently, Abou Elmaaty and coworkers [51] have continued to investigate the SFD of PP fabrics both at laboratory and semi-pilot scale with novel azo based disperse dyes. The new dyes are multifunctional azopropanenitriles and azo amino pyrazole compounds and have again been employed both with the conventional aqueous process and the supercritical one. In analogy to the previously reported research [49], the K/S values and fastness properties obtained with the supercritical method are much better than the aqueous one; furthermore, in this case the fastness to light is further improved and higher ratings have been reached (4-5 or 5). After investigating the role of different operating conditions on scCO₂ dyeing at lab-scale, a test with the most promising dye was performed in a semi-pilot-scale plant with a 2.6 L-capacity of the beam dyeing vessel, at 120 °C, 25 MPa for 2 h, and at “saturation conditions” for the dye. Better results on the semi-pilot plant have been obtained with respect to the laboratory apparatus with a K/S value of 22.5 that is higher than the 10-20 range obtained at lab-scale.

Another relatively recent example of SFD of PP was reported by Hori and Kongdee in 2014 [52]. These authors investigated the dyeing of PET/co-PP composite fibers with three disperse dyes in scCO₂. Fibers were also annealed at 150°C for 1h: SFD of annealed and unannealed fibers was performed at different temperatures and pressures (60-120 °C, 50-25 MPa). A maximum dye uptake of approximately 45 mg_{dye}/g_{polymer} was obtained, which is comparable with that obtained for SFD of PET [14, 53] while fastness of the dyed fibers was not reported. The role of the annealing treatment depended on the employed dye. While for two out of three dyes the annealing process resulted in lower coloration, the opposite happened for the third one. A clear explanation was not provided: the phenomenon was ascribed both to a change in the structure of the fiber, due to annealing, and the different size of the dyes [52].

Supercritical fluid coloration of acrylic loose fibers was also achieved by Dalian Polytechnic University [54] in the same tubular-frame-equipped unit developed to dye PET (Table 1) [26]. The “factorial design of experiment technique” was employed to obtain the optimal working conditions (100 °C, 26 MPa, 1h) that correspond to the maximum K/S value (6.14). Commercially acceptable fastness results and satisfactory color strength were obtained even though K/S did not reach those values typical of PET dyeing [1, 26, 29].

The coloration of polycarbonate (PC) pellets was attempted in scCO₂ by Varga and coworkers in 2016 [55]. PC is conventionally dyed by incorporating dyes and pigments in the polymer during its manufacture, which makes it difficult to achieve uniform coloration and to employ thermally labile compounds [55]. The SFD of PC with two disperse dyes resulted in uniform coloration even though the amount of dye uptake was quite limited (0.01-0.55 mg_{dye}/g_{polymer}). Furthermore, while after a three-hour treatment the PC samples remained transparent, after 6 h opaque pellets were obtained due to the crystallization induced by scCO₂ [56].

The above discussion has pointed out that, among the different synthetic polymers, the coloration of nylon and PP is reaching good K/S and fastness results, which may be considered quite close to those of PET. In particular, the above-mentioned positive results suggest that successful coloration of nylon and PP with scCO₂ is probably on the brink of being achieved at larger scale levels. While a first semi-pilot-scale experiment to dye PP has already been reported in the literature [51], pilot-scale coloration of nylon is also under investigation, as it has been reported in a recent interview with Femke Zijlstra, business development manager of DyeCoo [21].

4. Supercritical fluid dyeing of natural fibers

The SFD of natural hydrophilic fibers such as cotton, wool and silk is very difficult with respect to PET. This is connected with the non-polar character of scCO₂. In fact, this makes it difficult to

solubilize those commercial polar dyes that are used in conventional aqueous dyeing of natural textiles as well as to promote their diffusion into the interior of the fibers [9]. Furthermore, the supercritical environment hinders the occurrence of many chemical reactions between the dye moieties and the functional groups of the textile substrates, which are responsible for the successful fixation of the color [57].

In past years many techniques were proposed to attempt the coloration of natural fibers [8-10]. Among them, the solubilization of polar dyes in water/scCO₂ reverse micellar systems and the synthesis of novel reactive disperse dyes have been considered the most promising ones [9]. Water/scCO₂ reverse micellar systems are stable microemulsions of water dispersed in the continuous supercritical phase [58], which are generally obtained employing environmentally unacceptable fluorocarbon-tail surfactants [59]. This is probably the main reason why reverse micellar coloration of natural textiles has practically been abandoned after 2008 [60]. To the author's knowledge, the only recent application of this technique in the textile area is the removal of impurities from grey cotton fabrics [61, 62]. The synthesis of new reactive disperse dyes, then, remains the principal research topic of the last few years in this area.

4.1. Novel reactive disperse dyes for cotton, wool and silk

Reactive disperse dyes can be synthesized by functionalizing the scCO₂-soluble disperse dyes through the addition of appropriate reactive groups. This allows the chemical fixation on the hydrophilic fibers to be achieved after the supercritical impregnation. Many different reactive functionalities were proposed in the past years but it was recognized that the vinylsulphone and the triazine ones were the most successful, where the first was more adapt to dye proteinaceous textiles, such as wool and silk, and the second was more appropriate to achieve coloration of cellulosic fibers, such as cotton [9]. For these reasons, coloration tests with dyes belonging to these chemical families have also been conducted in the last few years as reported in Table 4, which, however, also includes research reports with other new reactive functionalities.

All the investigated reactive disperse dyes (Table 4) can be divided into two groups, which depends on their chromophore: those with an anthraquinone structure and those with an azo one, respectively. In fact, these two chemical structures are the most widely employed in SFD thanks to their high solubility in the solvent medium [10].

As it was pointed out in past researches [9] and is clearly confirmed by many of the most recent ones (Table 4), the coloration of natural fibers often requires the use of suitable solvents that act as swelling or cosolvent auxiliaries, which limits the “green” character of the supercritical process and increases its complexity.

Coloration efficiency is generally quantified by means of the color strength (K/S) and the fixation efficiency (F) [57, 63-70]. Two K/S values are generally evaluated: the first one on the “just-dyed” samples, the second after treating the textiles with appropriate high temperature solvent extraction to remove the unfixed dye. The data reported in Table 4 refer to the after-extraction K/S. Instead, F is the percentage of the initial K/S value that is maintained after solvent extraction and can be considered a measure of the percentage of dye molecules that have been fixed on the fabric during the supercritical fluid coloration.

According to Table 4, the chlorotriazine reactive group has been the most investigated in last years. It can easily react both with the amino and hydroxyl groups of proteinaceous and cellulosic fibers (Figure 2) even though the production of hydrochloric acid as a byproduct is considered a disadvantage due to corrosive concerns [70]. The data in Table 4 point out that different considerations can be done for the azo-structured and anthraquinone-structured chlorotriazine dyes. As far as the azo-structured chlorotriazine dyes are concerned, the best results were obtained on cotton by Gao and coworkers [63] who succeed in dyeing this fiber without the use of any carrier or cosolvent: K/S values up to 13 and fixation up to 92% with good fastness performance were obtained. On the other hand, the coloration of wool, which was conducted by another research group with different azo-structured chlorotriazine dyes, required the addition of small percentages of acetone to

achieve similar fastness and fixation efficiencies but lower color strength [64]. This is consistent with the previously reported information that triazine disperse reactive dyes are generally employed with cotton rather than wool [9]. However, a fair and more significant comparison would require that tests with the same dyes are conducted with the two kinds of fiber.

On the contrary very recent tests with anthraquinone-structured chlorotriazine dyes have revealed that better coloration and fixation efficiency could be obtained on wool and silk rather than cotton. Two series of dyes were prepared by the same research group in two different works [65, 66] to dye cotton, wool and silk in the presence of small amounts of acetone [65] or of a not-specified special dyeing auxiliary [66]. With respect to azo-structured chlorotriazine dyes, much lower K/S were obtained for all types of fibers. However, higher fixation efficiencies for wool (94-98%) and silk (90-96%) were achieved with respect to cotton (49-57%). This seems to suggest that the structure of the chromophore may play a role in the rate of diffusion and fixation efficiency of the reactive disperse dyes on different hydrophilic fibers, which could probably deserve further investigation. Previous works with triazine reactive disperse dyestuffs were mainly conducted with azo-structured dyes, which resulted in good coloration of cotton [9]. The use of anthraquinone-structured triazine dyes represents almost a novelty in the literature with the exception of a research conducted by Maeda and coworkers in 2002 [71]. These authors investigated the dyeing of cotton both with an azo-structured and an anthraquinone-structured fluorotriazine dye, which resulted in the first one achieving a color strength three times higher than the second, while the two fixation efficiencies were comparable (~80%). Further research could clarify any possible difference in the mechanism of dyeing of azo- and anthraquinone-structured triazine dyestuffs.

The vinylsulphone reactive group can also react both with the amino and hydroxyl groups of proteinaceous and cellulosic fabrics (Figure 3). However, the reaction with the hydroxylic groups usually requires their pre-activation by means of inorganic anions, such as OH^- , as reported in the simplified scheme of Figure 3.b [72]. With respect to the conventional water bath, the hydrophobic

properties of scCO_2 do not favor the solubilization of inorganic anions so such reactions cannot occur and, consequently, the fixation of vinylsulphone disperse reactive dyes on cellulosic substrates cannot be achieved [57]. For this reason, this reactive group is generally employed to dye wool and silk in scCO_2 rather than cotton [9].

In 2015, Long and coworkers [57] employed perfluoroalkylsulfonyl quaternary ammonium iodides (FC-134) as a phase transfer catalyst to achieve the fixation of a vinylsulphone disperse reactive dye on cotton. The process was carried out into two steps: the supercritical impregnation of the dye (80 °C, 20 MPa, 1 h, 0.2% o.m.f.) and its subsequent catalytic fixation by means of FC-134. The second step was also carried at supercritical conditions (140 °C, 12 MPa, 1 h) in a phase-transfer catalytic reactor with the scCO_2 passing through a 10%-FC-134 water solution with sodium carbonate before being contacted with the cotton substrate. The work is the prosecution of an older investigation where triethylene diamine was employed as the catalyst [73]. Cotton coloration could be achieved in both researches with comparable values of K/S. When triethylene diamine was used a maximum fixation efficiency of 92% could be obtained, which could be increased up to 98% when the cotton was pre-wet with water before the SFD step [73]. On the other hand, when FC-134 was employed, a fixation efficiency up to 96.4% could be reached without any water pretreatment [57]. A possible explanation of the phase reaction mechanism with FC-134 was provided. Being FC-134 an amphiphilic compound with a long perfluoro-fat chain and a quaternary ammonium group, it is soluble both in aqueous and supercritical solutions. This allows this compound to be used to transfer hydroxyl or carbonate anions from the liquid phase to the supercritical and substrate solid phases so achieving good fixation of the reactive dye [57]. Recently Luo and coworkers [67] employed the same vinylsulphone dyestuff investigated by Long's research group [57, 73] to dye wool and cotton in scCO_2 after a water pretreatment but without any kind of catalytic activation. The pretreatment consisted in soaking the textiles in water at room temperature: the amount of water ranged from 0 to 100 % o.m.f. Excellent fastness and fixation efficiency (F up to 99.4%) were obtained with wool. As far as cotton is concerned a maximum fixation efficiency of 66 % could only be obtained so confirming that catalytic

activation of cellulosic hydroxylic functionalities is necessary to achieve good coloration of this fiber with this class of dyes.

SFD of cotton was also performed with disperse dyes with other reactive groups, such as halogenated acetamide or acyl fluoride [68, 69] without the use of any cosolvent or preliminary water treatment (Table 4). Figure 4 reports the proposed fixation mechanisms, where, like triazine dyes, hydrohalic acids are the byproduct of the reactions. Good results were obtained with six different halogenated acetamide reactive disperse dyes in terms of color strength, fixation efficiency and fastness [68]. The results pointed out that, for the same parent body dyes, the bromoacetyl group exhibited stronger reactivity with cellulosic functionalities with respect to the chloroacetyl one and that, as far as the azo-structured dyes were concerned, the presence of a $-NO_2$ group in the chromophore resulted in higher K/S values. A comparison between azo-structured and anthraquinone-structured halogenated acetamide dyes indicated that while relatively higher maximum F values could be obtained with the first ones, slightly higher K/S could be achieved with the second ones [68]. Acyl fluoride reactive disperse dyes could also be successfully used even though the coloration performance of cotton appeared to be lower with respect to halogenated acetamide dyes (Table 4). In this case three dyes were investigated [69]. All dyes exhibited an azo structure of the chromophore; two out of three were provided with a single acyl fluoride reactive group while the latter had two. The dye with two acyl fluoride reactive groups led to lower fastness fixation efficiency (F~70%) with respect to those with a single reactive group (F~80%). This was explained by the authors with a possible thermal decomposition of one of the reactive groups of the bi-functional dye [69].

A recent investigation has also been conducted to prepare new reactive disperse dyes for the SFD of wool [70]. In a preliminary work SFD of wool with conventional disperse dyes was investigated, which pointed out that CI Disperse Red 153 and CI Disperse Blue 148 resulted in the highest K/S values (up to 2) and 80% fixation efficiency [74]. Subsequently, the new disperse dyes were synthesized [70]; they had structures similar to the above cited conventional disperse dyes but were

provided with specific functional groups: thiazole-OH, thiazole-N(CH₃)₂, thiazole-OCH₂, succinimidyl ester (NHS) and thiazole-NHS. Among all the investigated groups the NHS and the thiazole-NHS ones allowed a 100% fixation efficiency to be obtained [70], even though the K/S values were approximately halved with respect to those obtained with CI Disperse Red 153 and CI Disperse Blue 148 [74]. The authors also proposed a possible mechanism of reaction between the NHS reactive group and wool keratin, which is summarized in Figure 5.

Eventually Long's research group has recently reported some solubility data of a new reactive disperse orange dye in scCO₂ [75, 76]. Solubility in pure scCO₂ at different temperatures and pressures was comparable to that of conventional disperse dyes employed for PET dyeing [75]. When a mixture of cosolvents involving acetone and water was added, the solubility increased from 1.5 to 5 times [76]. The dye has an azo-structured chromophore and a β-sulfatoethylsulfonyl potential reactive group. At the moment, no experimental tests have been reported as far as the SFD of natural textiles is concerned and, for this reason, this dye has not been included in Table 4.

It is clear from the above reports that natural textiles can be dyed in scCO₂ with good fixation efficiencies, which depend on the appropriate match between the dye reactive group and the fiber functionality. Even though the K/S values (Table 4) were often considered commercially acceptable, they are much lower with respect to those obtained for PET dyeing [1, 26, 29]. The main research efforts of the last years were concentrated in testing the fixation mechanism of different reactive groups. However, the chemistry of reactive SFD still needs to be elucidated. A possible suggestion for future investigation is to better understand the role of the dye chromophore on the rate of diffusion inside the fiber, which could positively affect the color uptake. On the other hand, the use of polar auxiliaries probably cannot be completely avoided to achieve textile swelling and improve coloration.

4.2 Other dyes

Experiments with other types of dyestuff, different from the ad-hoc synthesized disperse reactive dyes mentioned in the previous paragraph, have also been conducted in the last few years. An overview is briefly reported in the following lines.

Commercial reactive dyes such as Lanazol Red G [77] and Reactive Golden Yellow K-2RA [78, 79] were tested to achieve SFD of natural textiles. Lanazol Red G was dissolved in different amounts of water before being mixed with scCO₂ and employed to dye wool at 90 °C and 20 MPa [77]. The wool fabrics were also wetted with different amounts of water before the dyeing process. High K/S values up to 9.6 were obtained by increasing the water amount employed to solubilize the dye up to 50 ml. However, fastness tests were not reported and the water/scCO₂ volume ratio was not indicated. Instead, Reactive Golden Yellow K-2RA was used to dye cotton both in pure scCO₂ [78] and in the presence of water as a cosolvent [79]. The water addition resulted in significant improvement of the color strength and fastness. Optimal conditions were obtained at 90°C, 20 MPa and 5 w/w% of water, which led to a K/S value after washing of approximately 5.5. A possible mechanism of the role of water in the dyeing process was also proposed. It was supposed that at low dyeing temperature (90 °C) water could form an aqueous film on the surface of cotton fabric, which would solubilize the dye molecules and help their diffusion inside the fibers during the circulation of the dyeing bath [79].

Three newly synthesized disperse non-reactive azo dyes were also used to dye cotton or PET fabrics in a pilot-scale plant (Table 1), where the dyeing vessels were equipped with a rotating warp beam [25]. Tests were performed at 80 °C, 18 MPa without the use of any polar cosolvent and this work represents a rare example of SFD of cotton at pilot scale. Better grades of fading and staining fastness were obviously obtained with PET as well as better color strength and fixation efficiency (K/S: 10.5-12.6; F: 90-95%); however, satisfactory results were also achieved with cotton (K/S: 6.5-10; F: 80-86%).

Curcumin-based dyes have recently been proposed to dye cotton, wool and silk [80]. They could represent an interesting alternative to some synthetic reactive disperse dyes thanks to the

biodegradation capacity of curcumin. Since curcumin exhibits low solubility in scCO₂ [81], it was proposed to modify the molecular structure of the dye by grafting different alkyl groups (ethyl, butyl, hexyl, octyl) in order to increase the hydrophobicity of the solute. Butyl curcumin resulted in the highest solubility enhancement and consequent better dyeing performance, which was conducted at 110 °C and 26 MPa. Furthermore, the authors investigated the effect of the addition of dimethylsulfoxide (DMSO) on natural fabric samples before dyeing (1:1 weight ratio). The results showed a significant increase in the color strength for all types of fabrics. In particular, silk dyed with butylcurcumin in the presence of DMSO resulted in a K/S value of 4.6, which was 22 times higher than that of silk dyed without DMSO. Satisfactory staining and crocking fastness results were obtained while fading fastness could not overcome level 3. A twofold role of DMSO on the supercritical process was proposed. First, DMSO could play a cosolvent role [82] in scCO₂ by further enhancing the solubility of alkyl curcumins. Second, scanning electron microscopy graphs evidenced the “formation of holes in the silk fabric” [80], which resulted in significant increase in the specific surface area so allowing easier penetration of the dye into the fiber.

4.3 Other natural fibers

The SFD process has also been occasionally extended to other natural fibers which are not as widespread as cotton, wool and silk. For example, ramie, which is a highly crystalline natural cellulosic material, was investigated in 2006-2008 [83, 84]. This textile was modified with benzoyl chloride so improving its dyeability but resulting in reduced tensile properties. In more recent years, experiments were conducted with kenaf fibers [85] and yak hairs [86].

Kenaf is a cellulose fiber widely used in China [85]. Degummed kenaf fibers were first modified with 1-butyl-3-methyl imidazole chloride salt and then dyed with capsanthin, a natural red colorant, in scCO₂ at 70-120 °C and 21-32 MPa. Very high K/S values up to almost 18 were obtained while the rubbing and washing fastness of the modified kenaf fibers reached level 4, which was higher than that of the unmodified kenaf [85]. However, the authors do not mention any experiments to check if

the tensile properties of the fiber were maintained after the chemical modification and the supercritical treatment, which would be of great interest for the practical application of the process.

Yak hair is a rare specialty animal fiber whose structure is similar to wool and whose productivity in China reaches 400000 tons/year [86]. Raw yak hairs have brown or black natural colors, which limits their applications unless a decolorizing process is performed. SFD of decolorized yak hairs with Reactive Disperse Blue R was performed at 80-120 °C and 21-25 MPa. The effect of the supercritical treatment on the mechanical properties of the textile was also investigated. In fact, the high temperature and pressure conditions could aggravate the mechanical damage of the fibers, which already suffer the stress caused by the decolorizing procedure. The authors concluded that the optimal dyeing parameters to obtain a satisfactory dyed and mechanically resistant product should be 100 °C, 23 MPa and 60 min of dyeing time. Furthermore, the depressurization rate should be as slowly as possible (below 10 g/min). The above cited conditions allowed a K/S value approximately equal to 4 to be obtained [86] while the color fastness properties were not reported.

5. Other uses of scCO₂ in textile processing-a focus on fabric functionalization through supercritical fluid dyeing

The supercritical fluid technology can also be used for many pretreatments and finishing operations of textiles to reduce costs, water and energy consumption as well as the employment of hazardous chemicals.

Many research works can be found on these subjects. As far as the textile pretreatment is concerned, recent examples of the use of scCO₂ are the sizing, desizing, scouring and bleaching of many natural and synthetic fibers [61, 62, 87, 88]. Sizing consists in the impregnation of the textiles with suitable agents to protect the yarn from damage during weaving [87] while desizing, bleaching and scouring are the removal of natural or human-induced (such as the previously added sizing agents) impurities

[61]. Supercritical fluid sizing can be obtained by impregnating the fibers with scCO_2 -soluble fluoropolymers [87] while impurities removal can be achieved through supercritical fluid extraction [87, 88] or enzymatic degradation in a supercritical environment [61, 62].

Finishing consists in imparting specific appearance or functionalities to the final textile product. Examples of textile finishing in scCO_2 are the yarn coating with fluoropolymers or copolymers to impart hydrophobic [89, 90] or omniphobic [91, 92] properties to the fabric as well as the scCO_2 -promoted electroless plating to obtain conductive yarns [93-96] for preparing electromagnetic wave shielding materials [93] or wearable photocatalytic devices [95].

SFD can also be used for textile finishing by coloring the yarns with special dyes able to provide specific functionalities to the fabric. In this context, recent examples are the bifunctional dyeing with antibacterial [44, 47, 97], fluorescent [98] or photochromic dyes [99].

Antibacterial textiles are attracting increasing interest in aseptic medical applications, such as wound healing [100], or in apparel industry due to the consumers' demand for more comfortable odor-free clothing [101]. Different supercritical-fluid-technology-based strategies can be adopted, such as the impregnation with natural phenolic compounds [100, 102] as well as the coating with synthetic polymers (i.e. polysiloxane) equipped with biocidal functionalities [103, 104] or the coating with biopolymers (i.e. chitosan) that possess intrinsic antimicrobial activity [105]. In 2014 Abou Elmaaty and coworkers first reported the synthesis of new monoazo disperse dyestuffs with antibacterial properties to dye PET in scCO_2 [97]. The scope was to propose a simple one-step procedure to obtain colored PET with additional antibacterial functional performance. The dyes were synthesized from β -oxoalkanenitriles, which are widely used as key intermediates for the preparation of many heterocyclic compounds in the dyestuff industry and display significant biological and pharmacological activities [101]. Experiments were performed at 80-120 °C and 5-15 MPa and results showed good color strength and fastness as well as excellent antibacterial activity. A comparison with tests conducted in water [101] pointed out that better light fastness and slightly better antibacterial

activity were obtained with the supercritical process. The antibacterial activity was ascribed to the presence of the antipyrine moiety in the chemical structure of the dyes and was interpreted in terms of nonspecific action. This means that the antibacterial activity can either be obtained by damaging the bacterial cells or by inhibiting specific bacterial targets [97, 101]. Very similar results were obtained by applying the same dyes on nylon 6 [44] with superior color strength and light fastness with respect to conventional water dyeing while no significant effect of the dyeing medium on the antimicrobial properties was evidenced. On the other hand, when these dyes were used to dye UHMWPE [47], an imperfect antimicrobial activity was found, which was attributed to the much lower dye uptake obtained on this fiber with respect to nylon and PET. UHMWPE, in fact, is a highly crystalline material very hard to be dyed and its coloration in scCO₂ (see section 3) could be possible only when decaline was added as a cosolvent [47].

The use of fluorescent dyes in the dyeing of textiles is another quite attractive research field since it causes a significant increase in color brightness and visibility so resulting in more fashionable and easily perceptible materials [98]. Among the different applications, the manufacturing of warning clothing for fire fighters and policemen is probably the most promising [98, 106]. Xiong and coworkers [98] employed CI Disperse Fluorescent Yellow 82 to dye PET with scCO₂ at 60-140 °C and 15-35 MPa. Good color strength and fastness were obtained, and the fluorescence intensity of the dyed fabric was found to be reasonably stable over time. The use of the confocal microscopy imaging technology allowed a uniform distribution of the fluorescence intensity from the surface to the centers of the fibers to be observed [98].

Eventually, a very recent investigation [99] employed scCO₂ (120 °C, 25 MPa) to impregnate a PET fabric with two different photochromic dyes (Reversacol Ruby Red and Reversacol Sea Green). Photochromic materials are subjected to reversible color change when irradiated with UV light and the development of photochromic textiles could be useful to develop smart and functional textile applications such as brand protection, responsive camouflage and UV sensors [99]. The properties of

the dyed photochromic fabrics were compared with those of the same dyes dissolved in hexane, which was selected as a solvent with similar polarity as scCO₂. The photochromic dyes dissolved in both media, i.e. PET and hexane, displayed a color change when exposed to UV light, which reverted to its original colorless state when UV radiation was removed [99].

6. Supercritical fluid dyeing of non-textile materials

Recent investigations have pointed out that SFD can also be applied to non-textile materials. This is a consequence of the peculiar characteristics of scCO₂ and the appeal of using an environmentally friendly process as an alternative to the conventional ones or to develop advanced materials.

A first example involves the SFD of cork, which was conducted by Aroso and coworkers in 2015 [107]. Cork is a natural-based product with remarkable properties such as high thermal and acoustic insulation, complete recovery of shape after compression, damping capacity, impermeability to liquids, etc. [107]. The purpose of the research was that of functionalizing this material with additional properties by exploiting the plasticizing and swelling power of scCO₂ to incorporate specific compounds (i.e. pigments, fungicidal or antibacteric agents). This was achieved by impregnating a disperse dye (CI Disperse Blue 14) as a model compound. Experiments were conducted at 40-60 °C and 10-20 MPa for 16 h on 5 mm cubic shaped samples. The morphological changes of cork were also observed during the impregnation process. It was found that both scCO₂ penetration and its subsequent gaseous release after depressurization occur progressively versus time. Furthermore, CO₂ sorption and desorption were accompanied by significant reversible morphological changes (collapse and expansion) that did not compromise the integrity of the samples as well as their compressibility properties. Also dye coloration occurred progressively with a nonhomogeneous depth of the penetration front, which was affected by the irregularities of the cork structure (i.e. growth

rings and lenticels). A comparison with a similar impregnation process conducted in acetone revealed that higher impregnation depth was obtained by using the supercritical solvent [107].

A recent research by Jaxel and coworkers [108] exploited the above cited results to investigate the feasibility of dyeing wood through $scCO_2$. The supercritical fluid coloration of wood could be of interest to furniture industry in order to achieve a more efficient and environmentally compatible dyeing approach [109]. Supercritical impregnation of three different types of wood (oak, beech and birch) with CI Disperse Blue 134 was conducted at 45°C, 20 MPa for 25 h and the results were compared with those obtained with a cork sample at the same working conditions. The experiments resulted in good coloration of cork while wood samples revealed poor dye uptake. This was explained by the different nature of the solid materials. The good coloration of cork was ascribed to the presence of suberin, an irregular macromolecular polyester present in the cork cell walls that could promote the diffusion of $scCO_2$ in the solid substrate. On the other hand, the principal constituents of woods are cellulose and hemicellulose, which are rich in hydroxyl groups that give rise to strong intra- and intermolecular hydrogen bonding that prevent the plasticizing action of $scCO_2$ [108]. According to this explanation, a second set of experiments was conducted by pre-treating the wood samples with alkyl ketene dimer (AKD). AKD is a paper sizing agent that is usually employed to impart hydrophobicity to paper; in this context it was selected to mimic the action of suberin in wood. The results pointed out the good plasticizing and swelling action of AKD on wood samples, which were successfully dyed, even though the homogeneity of coloration was not satisfactory [108]. In the most recent publication of this research group [109] the above-reported imperfect coloration of wood was ascribed to insufficient solubility of the employed dye in the supercritical solvent. For this reason, the authors proposed the synthesis of new anthraquinone dyes with long-chain alkyl substituents that should result in increased $scCO_2$ solubility [109]. Furthermore, the new dyes were designed to achieve a broader color variety towards red and blue shades, to get better visibility on the dyed materials since native European wood has generally an inherent yellow to brown coloration. Even

though the authors mention preliminary successful dyeing experiments with wood and plastic samples the solubility of these dyes in $scCO_2$ is still under investigation and has not been reported yet [109].

SFD has also been proposed to improve the preparation of dye-sensitized solar cells (DSSC) [110]. According to the authors, anthocyanin sensitized TiO_2 solar cells are promising DSSC thanks to their improved photoelectric conversion efficiency. The use of $scCO_2$ was proposed as an alternative solvent medium to achieve the incorporation of anthocyanin, a natural flavonoid dye, in nanocrystalline titanium dioxide photo-electrodes. Impregnation tests were performed at $40^\circ C$ and 15 MPa at different contact times (10-180 min) and compared with the traditional dipping method. After 10 min of dyeing time the supercritical process resulted in higher dye uptake with respect to the dipping method, which is quite promising in the prospect of using this technique to reduce the long incubation time (up to 24 h) of the photoelectrode in the conventional dye solution. Furthermore, the V-I testing of the photocells obtained using $scCO_2$ resulted in higher current and voltage production with respect to the conventional dye-dipped products [110].

Another recent application is the SFD of buttons made of different materials [111]. Even though buttons are non-textile materials, this application may have a potential obvious interest for the textile industry. The authors investigated the SFD of nylon, acrylic, polyester and casein buttons with CI Disperse Red 22. The experimental range of temperature, pressure and dyeing time was comparable to that adopted for the SFD of textiles; however, the specific values depended on the employed material and were selected according to preliminary experiments aimed at avoiding the formation of cracks, bubbles pores and darkened black spots on the plastic buttons [111]. Good coloration with satisfactory uniformity was obtained for all the materials and no variation of the buttons diameters was observed in the examined experimental range, which was also favored by a gentle depressurization of the dyeing system. By using the Taguchi design-of-experiments technique the optimal working conditions for the different materials were evaluated [111].

7. Conclusions

The technological research of the last few years has allowed the SFD of PET to definitely reach the industrial scale with many plants operating in different parts of the world, especially in Eastern countries. Among the different textiles, PET remains the most suitable substrate to be dyed with this technology but, despite the excellent coloration results, large scale clothing commercialization is hindered by the still prohibitive price of the final products with respect to conventional dyeing. However, promising results have been reached in the optimization of the process as demonstrated by the coloration of zipper tapes [4, 28], which could allow significant reduction of the total running costs and increase of the commercial competitiveness of the products. Furthermore, the technological achievements obtained for PET are now ready to be tested at pilot scale with other synthetic textiles, such as nylon and PP, for which very promising coloration results have also been obtained [21, 44, 51]. Recent investigations have also pointed out how SFD has started to overcome the frontiers of simple coloration of textiles. In fact, it can also be used to impart novel functionalities to textile or non-textile materials. This may give rise to the development of other sustainable processes or novel advanced materials in the next future.

On the other hand, the SFD of natural fibers is still far from commercialization. Significant results have been obtained as far as the fixation efficiency of the dyes on cotton, silk and wool is concerned. The choice of modifying disperse dyes with appropriate reactive groups able to bind with the textiles functionalities seems to be the winning strategy, which has allowed fixation efficiencies up to 98-100% to be obtained [65, 67, 70]. However, the intensity of coloration is still much lower with respect to PET and other synthetic polymers. Future investigations could probably be directed at deepening the chemistry of coloration in the supercritical environment. This could elucidate if the size and chemical structure of the chromophore may affect the rate of diffusion inside the fibers so resulting in improved dye uptake.

It is evident, anyway, that the coloration of hydrophilic materials in the non-polar supercritical environment suffers from a lack of solvent swelling of the fibers, which is confirmed by the fact that many researchers are trying to make the technology work by using pretreatments or other wet processes [57, 64-67, 77, 79, 80]. This is the downside of SFD. As conventional aqueous dyeing of PET requires the use of auxiliaries to promote dye diffusion into the hydrophobic polymer, the dyeing of hydrophilic fibers in scCO₂ cannot probably do without polar carriers or cosolvents. The author's personal opinion is that feasibility studies should be performed to investigate the most efficient way to include polar cosolvents or carriers in the pilot plant layout. The use of liquid solvents in pilot- or industrial-scale plants for SFD of PET is not a novelty since many cleaning post-dyeing steps have been implemented [1, 13]. From a theoretical point of view, the tunable solvent power of scCO₂ could allow the dye and the solvent to be selectively recollected and recycled at the end of the coloration process. Of course, in the practice, this would definitely increase the risk of making the whole process combination more complex, expensive and less environmentally responsible than the conventional one.

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Table 1

An overview of some recent lab- to industrial-scale prototypes and innovative technological solutions for supercritical fluid dyeing of PET

Year	University or research centre	Capacity of the dyeing vessel	Details	References
2014	Soochow University (China)	180 L / 1.187 kg _{PET}	Fabric rope dyeing: a fabric rope cyclically circulated on a magnetically driven reel set inside the dyeing vessel	[13, 24]
2015	Fujian Institute of Research on the Structure of Matter (China)	2×7 L / 2×300 g _{PET}	Fabric mounted on a rotating warp shaft set inside the dyeing vessel	[25]
2015	Dalian Polytechnic University (China)	Not provided	A tubular frame of loose fibers set inside the dyeing vessel	[26]
2015	Dalian Polytechnic University (China)	Not provided	Graphics dyeing: PET fabric folded into fan shape and wrapped with cotton fabrics to provide free and abstract patterns on the textile	[27]
2016	Dalian Polytechnic University (China)	2×500 L	Industrial-scale plant equipped with a rotating dyeing flame suitable to dye bobbins, fabrics, loose fibers, garments, skeins and balls	[1]
2017	Fujian Institute of Research on the Structure of Matter / University of Chinese Academy of Science / (China)	1.5 kg _{PET} (lab-scale)	Zipper tape dyeing conducted into two alternative horizontal vessels allowed continuous operation and cost reduction	[28]
2019	Fujian Institute of Research on the Structure of Matter / University of Chinese Academy of Science / Fujian SBS Zipper Ltd. (China)	2×100 L / 2×25 kg _{PET} (pilot -scale)	Zipper tape dyeing conducted into two alternative horizontal vessels allowed continuous operation and cost reduction	[4]

Table 2

Comparison of total running costs of conventional and supercritical fluid dyeing of PET*

Year	Technological device	Aqueous dyeing	Supercritical fluid dyeing	References
2014	Fabric rope dyeing in dynamic mode (pilot-scale)	1.20 CNY/m	1.10 CNY/m	[24]
2015	Tubular frame of loose fibers	3.23 CNY/kg	3.07 CNY/kg	[26]
2016	Industrial-scale plant with rotating dyeing flame	3.22 CNY/kg	3.07 CNY/kg	[1]
2017	Zipper tape dyeing with two side-by-side horizontal vessels (lab-scale)	5.92 CNY/kg	1.36 CNY/kg	[28]
2019	Zipper tape dyeing with two side-by-side horizontal vessels (pilot-scale)	6.15 CNY/kg	2.74 CNY/kg	[4]

*Costs are expressed in Chinese currency (CNY) referred to the mass of PET, except for fabric rope dyeing where the cost is referred to the length of the fabric.

Table 3

Recent reports of supercritical fluid dyeing of various synthetic polymers other than PET

Polymer	Working conditions	Carrier or cosolvent	Dyes	Color strength (K/S) or dye uptake	Fastness	Year	References
Nylon 6 fabric	80-120°C 5-25 MPa 1-3 h 2-6% o.m.f.	-	New antibacterial hydrazonopropanenitrile disperse dyes	K/S~7-17	Excellent	2015	[44]
	100-130°C 15-25 MPa 1-3 h 2-4% o.m.f.	-	New hydrazonopropanenitrile disperse dyes	K/S~3-6	Excellent	2018	[35]
Meta-aramid fabric	80-160 °C 18-34 MPa 10-90 min 1.5-5.5% o.m.f.	Fiber pre-treated with CYNDYE DNK (aromatic amide)	CI Disperse Red 60 CI Disperse Yellow 114 CI Disperse Blue 79	K/S~2-5.5	Excellent	2014	[45]
		Different cosolvents (1-5 w/w%): dimethyltereftalate, ethylalcohol, CYNDYE DNK	Disperse Blue Black 79 Disperse Rubine H-2GL Disperse Yellow EC-3G	K/S~1-4.5	Excellent	2017	[46]
UHMWPE fabric	120°C 20 MPa 1-3 h 2-6% o.m.f.	Cosolvent decaline (7 mol%)	New antibacterial hydrazonopropanenitrile disperse dyes	K/S~0.5-4	Good	2019	[47]
PP fabric	100-130°C 15-25 MPa 1-3 h 2-6% o.m.f.	-	New antibacterial hydrazonopropanenitrile disperse dyes	K/S~7-16	Good	2018	[49]
	110-130 °C		New azo based disperse	K/S~10-20	Excellent	2019	[51]

	15-25 MPa 2-4% o.m.f. 1-2 h		dyes	(lab-scale) K/S 22.5 (semi-pilot-scale)				
PET/co-PP composite fibers	60-120 °C 5-25 MPa 10% o.m.f.	-	Kayalon Orange R-SF200 Kayaset Red 802 Kayaset Blue N	0.5-45 mg/g	-	2014	[52]	
Acrylic fibers	80-100 °C 22-26 MPa 30-60 min 1-3% o.m.f.	-	CI Disperse Red 60	K/S~3-6	Good	2017	[54]	
PC pellets	40-60°C 10-30 MPa 3-24 h	-	CI Disperse Red 1 CI Disperse Red 13	0.01-0.55 mg/g	-	2016	[55]	

Table 4

Recent reports of supercritical fluid dyeing of various natural fibers with novel reactive disperse dyes

Reactive functional group	Working conditions	Carrier or cosolvent	Fibers	Color strength (K/S) and fixation (F)	Fastness	Year	References
Chlorotriazine (azo-structured dyes)	100 °C 20 MPa 1 h 0.5% o.m.f.	-	Cotton	K/S~9-13 F~80-92%	Good	2014	[63]
	120 °C 20 MPa 90 min 0.5% o.m.f.	Acetone (0.5 v/v%)	Wool	K/S~0.9-3.8 F~80-92%	Commercially satisfactory	2016	[64]
Chlorotriazine (anthraquinone-structured dyes)	120 °C 20 MPa 90 min 1% o.m.f.	Acetone (0.5 v/v%)	Cotton Wool Silk	K/S cotton~0.3 F cotton~49% K/S wool~1.4 F wool~98% K/S silk~1.1 F silk~90%	Commercially satisfactory (wool and silk better than cotton)	2019	[65]
	130 °C 20 MPa 1 h 0.5% o.m.f.	Special dyeing auxiliary (0.5 v/v%)	Cotton Wool Silk	K/S cotton~0.48 F cotton~57% K/S wool~0.41 F wool~94% K/S silk~0.9 F silk~96%	Very good	In press	[66]
Vinylsulphone (azo-structured dye)	80 °C 20 MPa 1 h 0.2% o.m.f.	Phase transfer catalytic reaction (10% FC134 in water, 140 °C, 12 MPa, 1 h)	Cotton	K/S~0.-0.3 F~45-96.4%	-	2015	[57]

	50-100 °C 14 MPa 10-100 min 5% o.m.f.	Water pretreatment (0-100 % o.m.f.)	Cotton Wool	F cotton~20-66% F wool~70-99.4%	Good (cotton) Excellent (wool)	2018	[67]
Halogenated acetamide (azo-structured dyes)	80-120°C 20MPa 1-3 h 0.5% o.m.f	-	Cotton	K/S~7-10 F~60-91%	Good	2014	[68]
Halogenated acetamide (anthraquinone - structured dyes)	60-120°C 20MPa 1-3 h 0.5% o.m.f	-	Cotton	K/S~11-13 F~85-90%	Good	2017	[69]
Acyl fluoride (azo-structured dyes)	110°C 25 MPa 2 h	-	Wool	K/S~0.3-1.3 F 100%	Good	2018	[70]

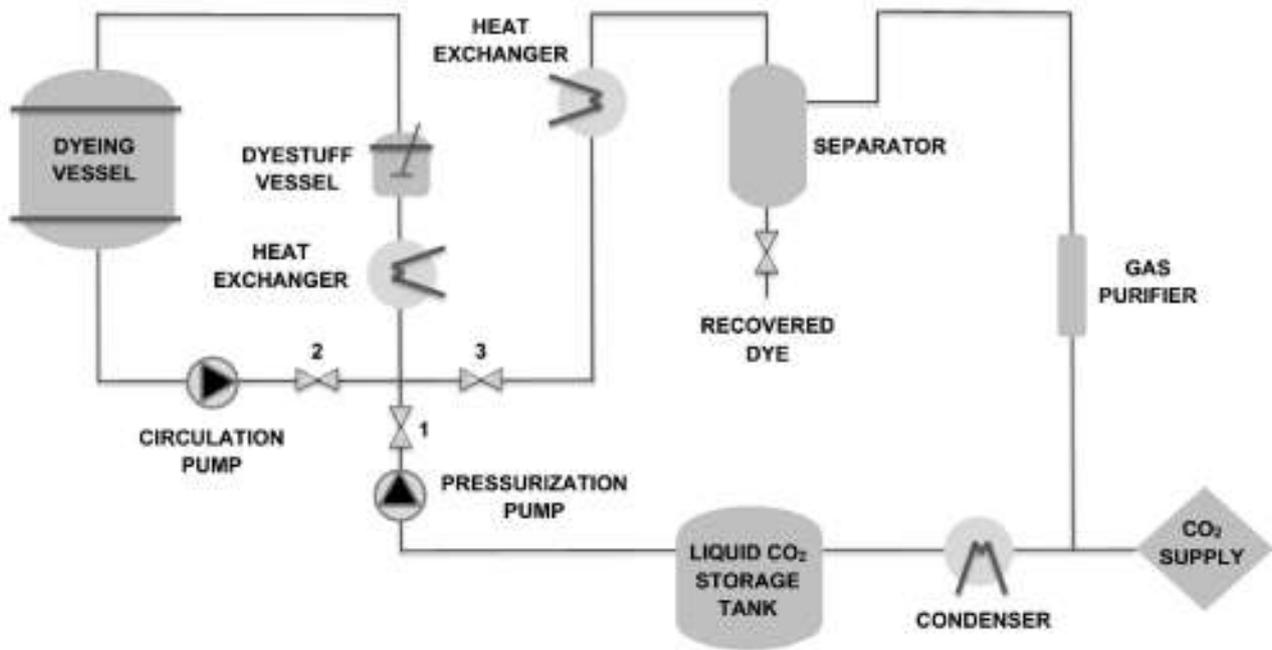
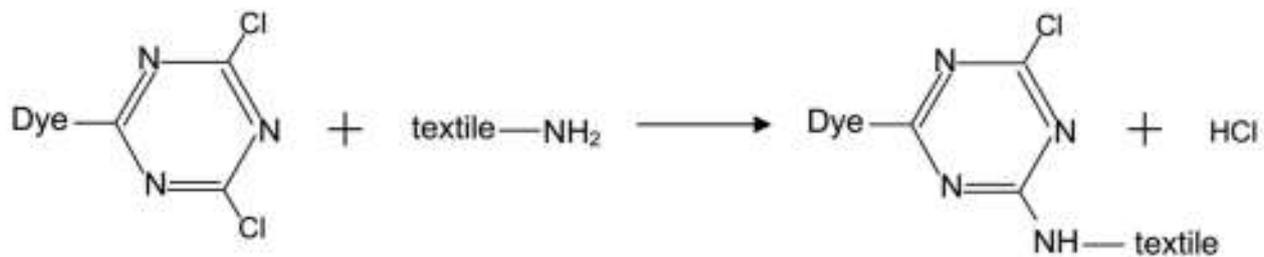
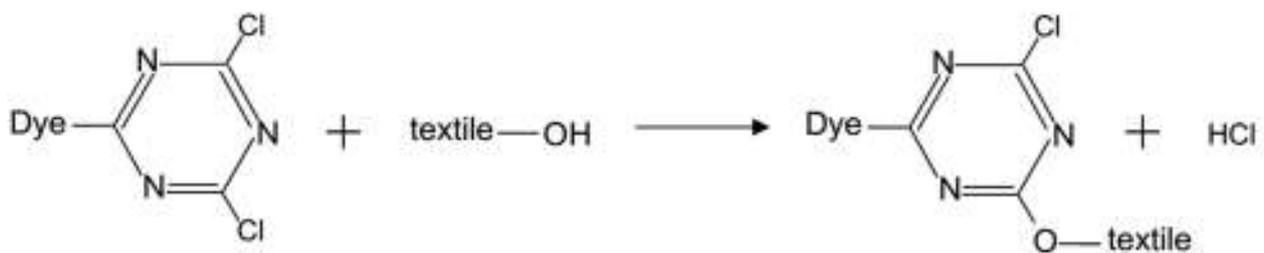


Figure 1 A simplified scheme of a typical plant for supercritical fluid dyeing of textiles (modified from [24]).

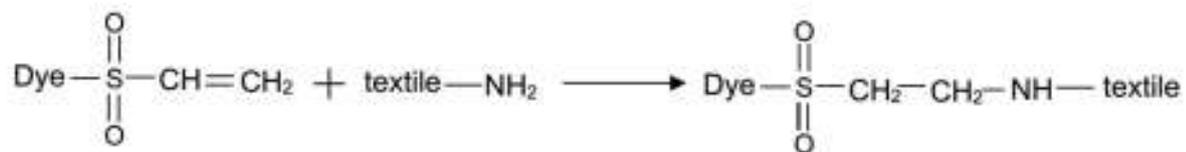


(a) reaction with an amino group

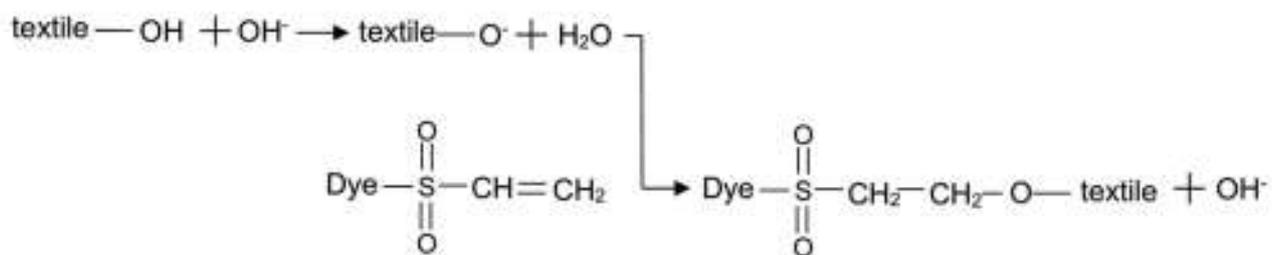


(b) reaction with a hydroxyl group

Figure 2 Reaction of dichlorotriazine dyes with amino (a) or hydroxyl (b) groups of proteinaceous and cellulosic textiles [65].

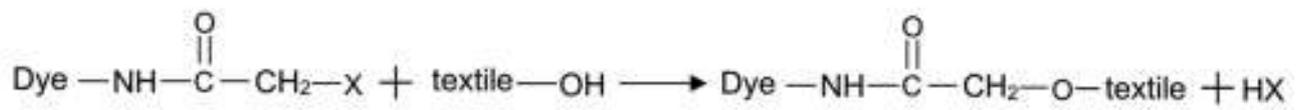


(a) reaction with an amino group



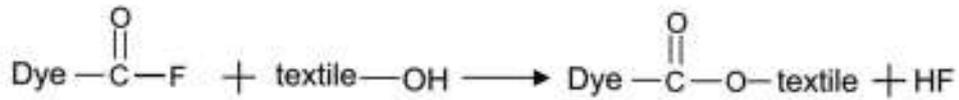
(b) reaction with a hydroxyl group

Figure 3 Reaction of vinylsulphone dyes with amino (a) or hydroxyl (b) groups of proteinaceous and cellulosic textiles [43, 72].



X = Cl, Br

(a) halogenated acetamide reaction



(b) acyl fluoride reaction

Figure 4 Reaction of halogenated acetamide (a) and acyl fluoride (b) dyes with hydroxyl groups of cellulosic textiles [68, 69].

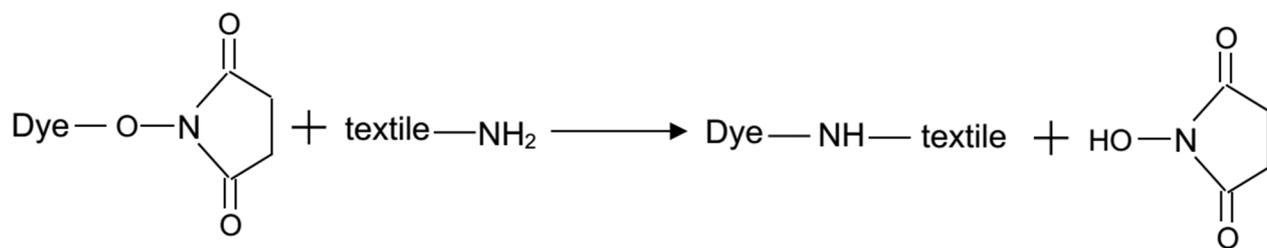


Figure 5 Reaction of succinimidyl ester dyes with amino groups of proteinaceous textiles [70].