POLYAMIDE AND POLYPROPYLENE TEXTILE DYEING USING SUPERCRITICAL CARBON DIOXIDE (sc-CO2)

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The main objective of the present work was the development of an alternative textile dyeing method using supercritical carbon dioxide (sc-CO2). GAIKER-IK4 has studied sc-CO2 dyeing for two polyamides (PA-6, PA-6.6) and polypropylene with an acid dye. Firstly, solubility of the dye in sc-CO2 and co-solvent requirement was studied. At analytical scale, different ways of introducing polymer samples and dye powder were evaluated, and supercritical dyeing process parameters were studied (pressure, temperature, co-solvent, CO2 and co-solvent flows, %dye (w/w) and time). After process optimization, sc-CO2 dyeing of PA-6.6 was carried out at pilot scale, for later evaluation by AITEX. AITEX evaluated different characteristics of the samples, as tensile strength, mass per unit area, and the fastness properties as colour fastness in sunlight, to rubbing and to washing. Tests proved that it is possible to dye PA-6.6 fibres with this supercritical dyeing method, and that the dyed product was of the same quality as in aqueous dyeing.

Keywords: Textile dyeing; Supercritical carbon dioxide; Polyamides; Polypropylene; Alternative dyeing method.

1. INTRODUCTION

The main disadvantages of typical dyeing processes are water consumption and the generation of polluted aqueous streams that need treatment for decontamination. The most important source of pollution in textile dyeing is the use of dyes, which contain heavy metals and generate water colouring, resulting in environmental impact. Moreover, dyed textiles usually need textile cleaning and drying, requiring great energy consumption that makes processes more expensive and less ecological. Due to legislation enforcing and the growing consideration of environmental consequences, textile enterprises are looking for solutions to design environmentally friendly dyeing processes.

AITEX has taken into account this environmental concern, and in collaboration with GAIKER-IK4, has researched on sc-CO2 dyeing. This technique has been strongly studied during the last decades, in order to water substitution in dyeing processes. It is considered a good alternative for conventional dyeing, because it removes or reduces water consumption in dyeing and cleaning steps, and generates less water waste avoiding its treatment for decontamination. Sc-CO2 dissolves the dye and following it impregnates textiles under fixed conditions, reaching fibre porous very easily, afterwards textile fibres do not need drying. Additionally, sc-CO2 dyeing employs less dye quantity, and the left dye can be recuperated and introduced again in the process.

In supercritical dyeing processes, carbon dioxide is the most widely used fluid. Among polymers, PET has been studied most due to its high production rate. However, due to the required innovation in textile sector, other polymers and synthetic fibres have been studied, such as polyamides [1-8], polypropylene [9-12] and aramides [13]. Good results have been obtained for polyamides and aramides in supercritical dyeing, but polypropylene is considered a difficult polymer to be dyed in sc-CO2, because of colour intensity problems. Research is based on looking for alternative processes that improve dye adhesion to the fibre and on fibre surface changing for dye affinity enhancement. According to the dyes employed in supercritical dyeing processes, the most commonly used are disperse dyes, due to their solubility in sc-CO2. However, other type of dyes can be employed, but the use of co-solvents will be necessary to improve dye solubility in sc-CO2.

In this work polyamides (PA-6, PA-6.6) and polypropylene (PP) have been dyed with an acid dye in sc-CO2, being the use of a co-solvent necessary for dye solubilisation. After supercritical dyeing, results have been compared with those obtained in conventional dyeing process to evaluate the designed supercritical process.

2. MATERIALS AND METHODS

2.1. SET-UP

The two most important processes for supercritical textile dyeing are classified in: a) *two-step dyeing*, in which sc-CO2 dissolves the dye that is fed in a cell, afterwards the dissolved dye is led to a second cell for polymer dyeing, Figure 1; b) *one-step dyeing*, in which the polymer and the dye are fed in a unique cell, where dye solubilisation and polymer dyeing take place, Figure 2. If the use of a co-solvent is necessary for the dyeing process, an auxiliary pump and storage tank will be required. Moreover, different ways for polymer support inside the cell will be designed if it is needed.

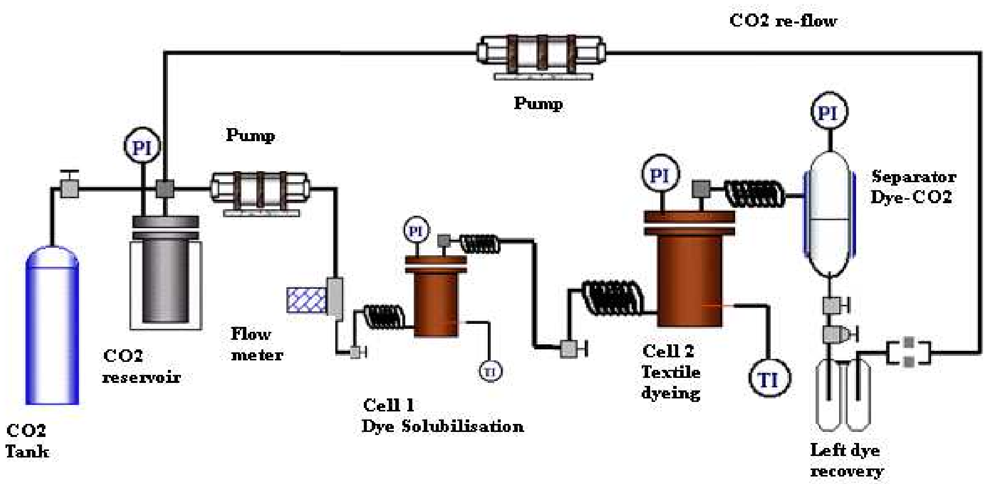

Figure 1: Two-step supercritical dyeing process scheme [14].

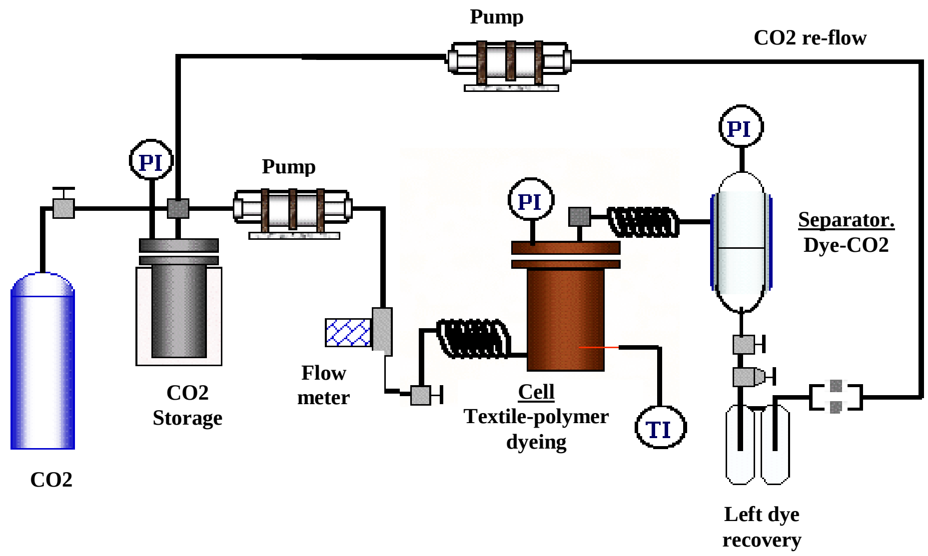

Figure 2: One-step supercritical dyeing process scheme [15].

In this work, textile sc-CO2 dyeing process was designed according to the one-step dyeing process. Dye solubility, polymer-dye support design and process parameters were optimized at analytical scale using the supercritical fluid equipment Thar R100 System, with an auxiliary SFE-10ml cell as the dyeing vessel, Figure 3.

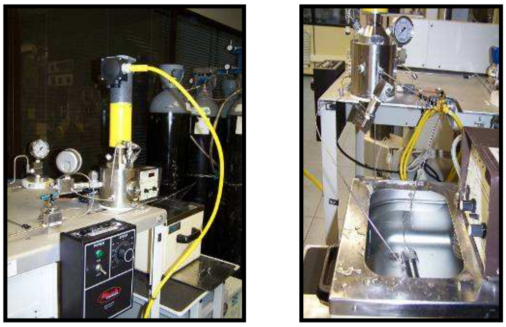

Figure 3: Supercritical fluid Thar R100 system with an auxiliary SFE cell as the dyeing vessel employed in analytical scale tests.

After optimization, textile dyeing was carried out in the supercritical pilot plant of GAIKER-IK4, which is equipped with a 375ml SFE cell, Figure 4. Liquid carbon dioxide is drawn from a dip tube cylinder (CO2) and pumped through a membrane pump system directly to a 375ml cell as the dyeing vessel (V1), after being heated up to the operating temperature in a pre-heater that works with a thermal fluid. Co-solvent is added with a pump and mixed with the CO2 flow in a pre-mixer. Once the supercritical flow gets the dyeing cell, the acid dye is dissolved and the polymer is dyed. The outlet is led to a three-step decompression module (S1, S2 and S3) where the left dye and the co-solvent are collected. The dyed polymer is taken from the autoclave and kept back for evaluation.

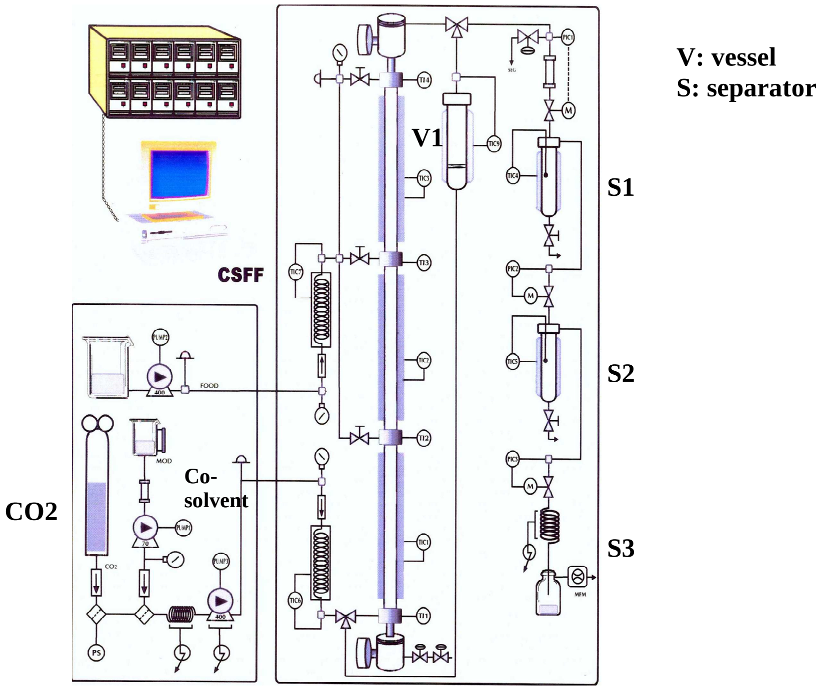

Figure 4: Supercritical fluid SFE pilot plant. (Iberfluid Instruments S.A)

2.2. MATERIALS

Different polymers, PA-6, PA-6.6 (Nylon) and PP, were chosen for supercritical dyeing evaluation and were supplied by AITEX. Isolan Red 2S-RB ® DyStar acid dye, which contains chromium metallic complexes, Cr (III) 3.6%, was selected by AITEX for the dyeing process. Co-solvents used in this study were Milli-Q water, methanol HPLC grade (Merck), ethanol 96% (V/V) (Panreac) and acetone 95% HPLC grade (LAB-SCAN). The supercritical fluid was carbon dioxide supercritical grade supplied by Air Liquide. All materials were used as received by suppliers.

2.3. METHODS

2.3.1. DYE SOLUBILITY IN SC-CO2

Due to the acid nature of the Isolan Red 2S-RB ® DyStar dye and the sc-CO2 non-polarity, the selected dye showed very low solubility in the supercritical medium. That is why the use of co-solvent was necessary for designing the sc-CO2 dyeing process. Different solvents were evaluated: water, methanol, ethanol and acetone. All these tests were carried out in relation to the one-step dyeing process under the same operation conditions: P=200bar; T=95ºC; % dye/textile (w/w) =10; Qco-solvent=5% QCO2, and t=60min, using a Thar 10ml SFE cell. The most suitable co-solvent was chosen according to the dyeing results in the tested polymers.

2.3.2. POLYMER-DYE SUPPORT DESIGN

In order to study the most suitable way of introducing the textile and the dye to obtain best dyeing results, different designs based on the one-step and two-step dyeing processes were tested (2.1). For the one-step dyeing test a 100ml cell of the supercritical fluid Thar R100 System and a 10ml SFE Thar cell were evaluated. To study the two-step dyeing process two different cells (5ml and 10ml SFE Thar cells) were connected in series connected to the Thar R100 System. All the tests were carried out under the same operation conditions: P=200bar; T=95ºC; % dye/textile (w/w)=10; Qco-solvent=5% QCO2, and t=60min. The most suitable polymer-dye support was chosen according to the dyeing results in the tested polymers.

2.3.3. SC-CO2 DYEING PROCESS

The supercritical dyeing process was designed optimizing the parameters that had more influence in textile dyeing at analytical scale using the supercritical Thar R100 System with an auxiliary Thar 10ml SFE cell. Pressure, CO2 and co-solvent flows, dye% (w/w) and temperature were evaluated for PA-6, PA-6.6 and PP sc-CO2 dyeing. Pressure has influence in textile colouring intensity; in general, the higher pressure the higher sc-CO2 density, which enhances dye solubility in the supercritical medium and dye adhesion onto the textile. Sc-CO2 density changes with temperature, so that parameter had to be also evaluated. The CO2 flow has influence in dyeing homogeneity, and usually higher CO2 flows achieve homogenized dyeing. Co-solvent flow was studied in order to establish the minimum flow necessary for good dyeing results and minimum co-solvent consumption. The dye percentage has influence in the tonality and intensity of textile dyeing.

Pressure, co-solvent and CO2 flows were studied using an experimental design based on a BOX-BEHNKEN 3^2 experimental matrix, changing three dependent parameters, Table 1. The independent parameters were fixed for carrying out the matrix experiments: t=60min; Vcell=10ml; T=95ºC, dye%=1% (w/w) and co-solvent: H_2O.

Table 1: Dependent parameters of the experimental matrix

Parameter	Low level (-1)	High level (-1)
X: Pressure (bar)	150	200
Y: Co-solvent (%)	1	5
Z: QCO2 (g/min)	2	4

After optimizing those parameters, dye% and temperature were evaluated using the best operation conditions for supercritical dyeing. Isolan Red 2S-RB ® DyStar dye percentage was varied from 1% to 10% (w/w), to establish which is the minimum dye quantity for obtaining a good colouration and dyeing homogeneity in the tested polymers.

Usually, in supercritical dyeing processes temperature is fixed at 100º-150ºC to enhance dye solubility in sc-CO2 in absence of co-solvents. However, in this study the use of co-solvent was necessary for solubilizing the acid dye in the supercritical medium, so that, temperature was evaluated below 100ºC, and it was varied from 40ºC to 95ºC.

2.3.4. SCALE-UP AND DYED TEXTILE EVALUATION

The sc-CO2 dyeing process was scaled-up in the SFE pilot plant of GAIKER (Iberfluid Instruments S.A) which is equipped with a 375ml vessel, using the most suitable supercritical conditions according to the results obtained at analytical scale. For that propose, only one polymer was chosen, PA-6.6 (Nylon). After sc-CO2 dyeing, AITEX evaluated different characteristics of the PA-6.6 sc-CO2 dyed samples, as tensile strength, mass per unit area, and the fastness properties as colour fastness in sunlight, to rubbing and to washing, in order to compare supercritical dyeing with conventional dyeing process.

3. RESULTS

3.1. CO-SOLVENT SELECTION

Due to the acid nature of the Isolan red 2S-RB ® DyStar dye, the use of co-solvent was necessary to obtain dyed textiles. Among co-solvents tested, water and ethanol showed the best dyeing results, Figure 5. Water was chosen as the most suitable co-solvent for sc-CO2 dyeing because of environmental reasons. Different results were obtained for the alcohols: good results were observed for ethanol, however, the use of methanol dealt in worse dyeing results. The worst dyeing results were obtained when acetone was used, because of the high solubility of the dye in this solvent and the poor dye fixation onto the polymer.

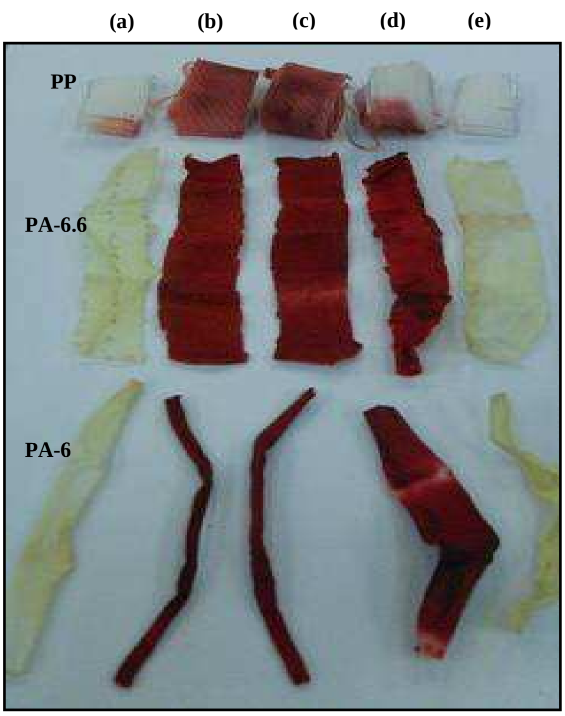

Figure 5: Sc-CO2 dyeing results with different co-solvents: (a) without co-solvent; (b) 5% Milli-Q H_20; (c) 5% EtOH; (d) 5% MeOH; (e) 5% Acetone.

3.2. POLYMER-DYE SUPPORT DESIGN

At analytical scale, the best dyeing results were obtained with an auxiliary Thar 10ml SFE cell connected to the supercritical fluid Thar R100 System, where the acid dye and the polymers were introduced together, Figure 3. That support design was useful for the one-step sc-CO2 dyeing process.

3.3. SC-CO2 DYEING PROCESS PARAMETERS OPTIMIZATION

According to the results obtained in the trials related to the experimental matrix, the most suitable operation conditions for sc-CO2 dyeing of polyamides (PA-6, PA-6.6) and polypropylene (PP) were: P=200bar; T=70ºC; t=60min; QCO2=3g/min; co-solvent: 5%H2O; dye%= 10% (w/w), Figure 6. Under pressures above 175bar better dyeing was obtained. Moreover, it was concluded that the dye percentage has a considerable influence in dyeing results. Temperature has influence in colour intensity, mainly in PA-6.6, but no influence in colour homogeneity was observed. For process scale-up, T=70ºC was selected according to the desired colour intensity.

In general, better dyeing results and dye homogenization were obtained for polyamides PA-6 and PA-6.6 rather than for polypropylene. In fact, polypropylene had less colour intensity than polyamides.

PA-6

PA-6.6

PP

Figure 6: Sc-CO2 dyeing results obtained with optimized parameters: P=200bar; QCO2=3g/min; 5% Milli-Q H20; 10% dye (w/w).

3.4. SCALE-UP RESULTS AND TEXTILE EVALUATION

The sc-CO2 designed dyeing process was scaled-up for PA-6.6. Pieces of PA-6.6 with 70cm x 30cm size were introduced in the 375ml cell of the SFE pilot plant of GAIKER-IK4, under optimized supercritical dyeing conditions (P=200bar; T=70ºC; t=60min; QH_2O= 5%QCO2; 10%dye (w/w)). Similar results than those obtained at analytical scale where observed in the scale-up, Figure 7, but in the scale-up a drying step was necessary in order to remove the left co-solvent in the sample. Moreover, it was concluded that textile (g)/Vcell was a considerable parameter to be taken into account.

Figure 7: SC-CO2 dyeing results obtained for PA-6.6 samples with 70cmx30cm size in the scaled-up process.

After textile sc-CO2 dyeing, AITEX evaluated different characteristics of the PA-6.6 dyed samples, as tensile strength, mass per unit area, and the fastness properties as colour fastness in sunlight, to rubbing and to washing. Tests proved that it is possible to dye PA-6.6 fibres with this supercritical dyeing method, and that the dyed product was of the same quality as in aqueous dyeing.

Table 2 shows the fastness values for the PA-6.6 used in the experimental test, under optimized supercritical dyeing conditions. The fastness data shown in Table 2 demonstrate the good results obtained for supercritical dyeing, especially when compared with those obtained with traditional aqueous dyeing for the same textiles, shown in Table 3.

Table 2: Fastness values for supercritical dyeing tests in pilot plant

WASHING (UNE-EN ISO 105-C06+AC2009)	**RUBBING** (UNE EN ISO 105-X12:2003)	**SUNLIGHT** (UNE EN ISO 105-B02:2001. Method 2)
4-5	4-5	5-6

Table 3: Fastness values for aqueous dyeing.

WASHING (UNE-EN ISO 105-C06+AC2009)	**RUBBING** (UNE EN ISO 105-X12:2003)	**SUNLIGHT** (UNE EN ISO 105-B02:2001. Method 2)
4-5	4-5	6-7

To investigate the influence of the process on the mechanical properties of the polyamide fibres, the tensile strength and the mass per unit area were measured, before and after the dyeing process.

Table 4: Mechanical properties of polyamide before and after supercritical fluids dyeing.

POLYAMIDE	SPECIFIC MASS (g/m2)	TENSILE STRENGTH	
		warp	**weft**
Untreated	86.21	188.29	238.03
Supercritical dyeing	110.68	190	200
Aqueous dyeing	107.84	210	270

As is shown in Table 4, there is a slight increase in specific mass, corresponding with a small degree of shrinking. This degree, however, is the same in current aqueous dyeing processes and therefore acceptable. Table 4 also shows that the strength of the textile is not affected significantly by the treatment.

4. CONCLUSIONS

The result of the present work is the development of a sc-CO2 one-step dyeing process for dyeing polyamides (PA-6 and PA-6.6) and polypropylene with the Isolan 2S-RB ® DyStar commercial acid dye. The use of co-solvent is necessary because of the dye insolubility in sc-CO2, and water was chosen because of environmental reasons. Good sc-CO2 dyeing results were obtained for pressures above 175bar, and temperature had influence in colour intensity. Sc-CO2 dyeing process was scaled-up under the best experimental conditions (P=200bar; T=70ºC; t=60min; QH_2O= 5%QCO2; 10%dye (w/w)) for PA-6.6, and it was concluded that dye percentage and textile (g)/Vcell ratio are considerable parameters to be taken into account for dyeing process design. Dyed textile evaluation by AITEX proved that it is possible to dye PA-6.6 fibres with this supercritical dyeing method, and that the dyed product was of the same quality as in aqueous dyeing.

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