Viability of Dyeing of Natural and Synthetic Fibers with Nanopigments in Supercritical CO$_2$

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INTRODUCTION

- **Supercritical CO\(_2\):** Solvent

- Properties
  - Low cost
  - Non-Toxic
  - Density: liquid
  - Viscosity: Gas
  - Recycling up to 90%
  - Inert
  - Non-explosive
  - Low critical point
    - Pressure: 73.858 ± 0.005 bar
    - Temperature: 31.05 ± 0.05 °C
DYEING IN SUPERCRITICAL CARBON DIOXIDE

- ADVANTAGES
  - No waste water (problem in textile industry)
  - No require additives
  - No final drying
  - Recycling
    - Solvent
    - Colorants
  - Environmental friendly

- DRAWBACKS
  - Investment
  - Solve colorants
  - Time of process
NANOPIGMENTS

- NANONATERIALS: since 90’s
  - Hybrid materials consisting of organic dyes and layered silicate nanoparticles
  - Nanoclay: particle size < 20nm
  - Ionic-exchange reaction: Colorant + Nanoclay (H⁺)
  - Nanoclays: Smectite group
    - Montmollonite: laminar
    - Sepiolite: acicular
Scheme of nanopigments’ synthesis at laboratory

Stage 1
- Nanoclay
- Sieving
- Dispersion
- H$_2$O deionized

Stage 2
- Colorant solution
- Ionic Exchange
- Washing and Filtering
- Drying

APPLICATIONS:
- Coloration of Plastics
- Printing Inks
- Functional materials
Schematic representation of clay sheet, dye molecule (methylene blue) and blue Nanopigment.
OBJECTIVES: PROJECT AITEX-AINIA-UA

1. STATE OF THE ART

2. SELECTION / MATERIAL DEVELOPMENT
   - 2.1. POLYMERS
   - 2.2. COLORANTS
   - 2.3. ANTIBACTERIAL AGENTS

3. DISSOLUTION OF MATERIALS IN SC CO₂

4. POLYMER IMPREGNATION IN SC-CO₂

5. CHARACTERIZE TREATED MATERIAL WITH SC-CO₂

6. REENGINEERING

7. VIABILITY / ECONOMIC

8. RESULTS AND DEFUSION
STATE OF THE ART

- Colorants that can be solved in scCO₂
- Textile dyes classification:
  - Directs
  - Reactive
  - Acids/Basics
  - Sulphur
  - Vat
  - Mordant
  - Disperse
  - Pigments

DISSOLVED IN SC-CO₂

NOT DISSOLVED IN SC-CO₂
COLORANT SELECTION

DISPERSE DYES

- Azoic $[-\text{N}=\text{N}]-$
  - The most important disperse dyes
  - Cheaper and easy manufacture
  - From non polar fibers

- Anthraquinone
  - It’s more soluble [1]
  - More expensive

MORE SOLUBILITY
COLORANT: SELECTION

REACTIVE DISPERSE DYES [2]

- (mono-di-)chlorotriazine
  - Dyeing of natural fibers
  - Protein or synthetic fibers
- (mono-di-)fluorotriazine
  - Dyeing cotton
  - Using different co-solvents
  - Methanol improves the solubility

REACTIVE GROUPS CHANGE THE COLORANT’S SOLUBILITY
COLORANT SELECTION

REACTIVE DYES

- Vinylsulphone: Improve fixations [3]
- Are suitable for dyeing textiles containing polyester, nylon, silk or wool.
- Fixations between 70 – 90%

Solubility: [4]
- Decrease: OH, NH₂, COOR’
- Increase: HX NO₂
[X=F, Cl, Br, ..]
Dyeing steps

- Transport of dye to the fibres: **SOLUBILITY**
  - Works: different cosolvents
    - Acetonitrile
    - Methanol
    - Water
    - Acetone
- Reaction of the dye with the textile: **AFFINITY**
- **DIFFUSION** of dye into the fibres: \( D \) coefficient.

**PROCESS VARIABLES**

- IMPROVE THE RESULTS
- REACTIVE GROUPS
- \( D \) coefficient
- PARTICLE SIZE
EQUIPMENTS

- Gas cylinder
- Carbon dioxide pump
- Pump head cooler
- Stop valves
- Pressure gauge
- Back pressure regulator
- Cosolvent reservoir
- Cosolvent pump
- Dyeing vessel
- Stirrer
- Heating jacket
- Dyeing beam
EQUIPMENT: AINIA PILOT PLANT

Planta FSC500

Planta SFF-58_60

Planta PFS20
FIBRES

- PET the most studied
- Changes in the structure of polymers:
  - Plastics: $>\text{Tg}$
  - Size stability
- Natural fibres [5]
  - Pre-treatments: Hydrophobic and nonpolar
    - Polyurethane
    - DMDHEU
    - Solvents: Alcohol and water
We only can use non polar colorants in scCO$_2$:

These kind of colorant haven’t affinity of natural fibres.

There are a lot of variables in the process: Solubility can change with:

- Colorants (Reactive group, Particle size…)
- Pressure
- Temperature
- Substrates: Natural or synthetic fibers

The time of process is too long: 4h
SOLUTIONS / FUTURE PERSPECTIVES

- Pre-treated fibres:
  - PET: with UV, N,N-dimethylacrylamide
  - CO: DMDHEU, PUR, acetone...

- Changes in structure of colorants
  - [6] Novel reactive disperse dyes has been synthesized.

- Control the solubility and dye process
  - Equations to predict the solubility

- NANOPIGMENTS
ADVANTAGES OF NANOPIGMENTS

- Nanopigments are a viable and environmentally-friendly alternative to traditional pigments because of their easy synthesis and conventional processing.
- Increase the color gamut:
  - We can use a lot of conventional organic dyes.
- Increase the resistance of colors: UV, O₂, Temperature
- Improve substrate properties: stability, strength, permeability…
REFERENCES

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