Green Technologies for Textile Industry

Smart Manufacturing and Materials Division
Textile industry is one of the biggest consumers of water

- On average, an estimated 100–150 liters of water are needed to process 1 kg of textile material
- In garment manufacturing, about 50% of waste water comes from textile dyeing and finishing processes
Stringent control on pollutant discharge

- The contaminated water must be treated prior to disposal or recycling.
Rising costs of water and wastewater treatment
Dirty Laundry
Unravelling the corporate connections to toxic water pollution in China

WATER MATTERS
DECISIONS TODAY FOR WATER TOMORROW

TODAY’S FIGHT FOR THE FUTURE OF FASHION
Is there room for fast fashion in a Beautiful China?

GREENPEACE
CHINA WATER RISK
(I) Plasma Technology
What is plasma?

- Ionized gas
  - A collection of molecules, atoms, excited species, electrons, cations, anions and free radicals.
Existence of plasma

- Over 90% of the matter in the observable universe is in the plasma state
  - Comet tail
  - Aurora
  - Lightning
## Types of plasma

<table>
<thead>
<tr>
<th></th>
<th>Thermal Plasma (Hot Plasma)</th>
<th>Nonthermal Plasma (Cold Plasma)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Definition</strong></td>
<td>Complete ionization</td>
<td>Partial ionization</td>
</tr>
<tr>
<td><strong>Degree of ionization</strong></td>
<td>100 %</td>
<td>$10^{-4} \sim 10^{-1}$ %</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>$\geq 1$ atm</td>
<td>$\leq 1$ atm</td>
</tr>
<tr>
<td><strong>Temperature of gas molecules</strong> ($T_g$)</td>
<td>$&gt; 10,000$ K</td>
<td>$\sim 300$ K (room temperature)</td>
</tr>
<tr>
<td><strong>Temperature of electron</strong> ($T_e$)</td>
<td>$T_e \approx T_g$</td>
<td>$T_e/T_g = 10 \sim 1000$</td>
</tr>
<tr>
<td><strong>Condition</strong></td>
<td>thermodynamic equilibrium</td>
<td>non-thermodynamic equilibrium</td>
</tr>
<tr>
<td>Thermal Plasma</td>
<td>Nonthermal Plasma</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------------</td>
<td>---------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>High temperature heating</td>
<td>Chemical applications</td>
<td></td>
</tr>
<tr>
<td>• Metallurgy</td>
<td>• Catalyst</td>
<td></td>
</tr>
<tr>
<td>• Welding</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Cutting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials synthesis and processing</td>
<td>Material processing</td>
<td></td>
</tr>
<tr>
<td>• Sintering of ceramics</td>
<td>• Surface treatment</td>
<td></td>
</tr>
<tr>
<td>• Waste treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Neon light, fluorescent lamp</td>
<td>• Plasma display</td>
<td></td>
</tr>
<tr>
<td>• Plasma display</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Plasma technologies for textiles

✓ Waterless process
✓ Applicable to most of textile materials
✓ Plasma has high chemical activity
  ➢ Chemical reaction can occur at mild condition
✓ Optimization of surface properties of textile materials
  ➢ Retain the bulk properties of the textile materials
Nonthermal plasma technologies

- Low-Pressure Plasma
  - Plasma is evenly distributed
  - Suitable for 3-D objects

- Atmospheric Pressure Plasma
  - Suitable for in-line processing
Surface treatment techniques

1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
Etching

1. Generation of etchant species
2. Diffusion to surface
3. Adsorption
4. Reaction
5. Desorption
6. Diffusion into bulk gas
Antipilling treatment

- Modifies the surface structure with Argon
  1. Smoothing of the edge of cuticular scales
  2. Abrasion of the fiber surface
# Antipilling treatment of 100% Merino Wool

<table>
<thead>
<tr>
<th>Control</th>
<th>Ar Plasma 5 min</th>
<th>Ar Plasma 8 min</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Control Image" /></td>
<td><img src="image2" alt="Ar Plasma 5 min Image" /></td>
<td><img src="image3" alt="Ar Plasma 8 min Image" /></td>
</tr>
<tr>
<td><img src="image4" alt="Control Image" /></td>
<td><img src="image5" alt="Ar Plasma 5 min Image" /></td>
<td><img src="image6" alt="Ar Plasma 8 min Image" /></td>
</tr>
<tr>
<td>3/3</td>
<td>3.5/4</td>
<td>4/4</td>
</tr>
</tbody>
</table>

ISO-12945-1:2000 [4hr; 14400 rotations]
An industrial-scale plasma treatment system for garment

- Set up at a knitwear manufacturer located in Dongguan Guangdong, China
- Two chambers system
  - Increase the production efficiency
  - Two chambers operate alternatively
- 10 parallel sets of electrodes
  - 20 pieces of knitwears can be treated as once
- Touch-screen panel
  - Controls and monitors treatment process
  - Keep treatment records

* R&D project funded by the ITC (GHP/053/10TP)
Surface treatment techniques

1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
Activation

- Non-polymer forming gases
  - $O_2$, $N_2$, $NH_3$ and inert gases, etc.

- Improvement of wettability, hydrophilicity, dyeability

⚠️ Loss of functionality after a period of time
Figure 3. Photographs of water droplets taken immediately after contacting (a) non-treated, (b,c) oxygen plasma-treated and (d,e) ammonia plasma-treated PLGA nanofibers. Treatment time was varied from (b,d) 30 to (c,e) 180 s [128].

Surface treatment techniques

1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
Grafting

- **Inert gases**
  - Ar, He

- **Reactive gases**
  - H₂, N₂, O₂, CF₄, CCl₄, etc.
Figure 1. General scheme of a covalent immobilization on a functionalized plasma deposited coating.
Surface treatment techniques

1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
Polymerization

- Formation of pinhole free and uniform thin film
- Highly cross-linked
- Applicable to almost all organic compounds
  - Straight-chain/branched alkenes, alkynes, arenes and heterocycles, etc.
Water repellency to cotton fabric

- Plasma polymerization of hexamethyldisiloxane (HMDSO)

After 4 laundering durability tests (equivalent to 20 machine washes)
# Applications of plasma polymerization

<table>
<thead>
<tr>
<th>Property</th>
<th>Material</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobicity</td>
<td>Cellulosic fibres, wool, silk, PET</td>
<td>Fluorocarbons, SF$_6$, siloxanes</td>
</tr>
<tr>
<td>Flame retardancy</td>
<td>Cellulosic fibres, synthetic fibres</td>
<td>Phosphorus compounds</td>
</tr>
<tr>
<td>Wrinkle resistance</td>
<td>Wool, silk, cellulosic fibres</td>
<td>Siloxanes</td>
</tr>
<tr>
<td>Antistaticity</td>
<td>Synthetic fibres</td>
<td>Chloromethylsilanes, acrylates</td>
</tr>
</tbody>
</table>
Surface treatment techniques

1. Etching
2. Activation
3. Grafting
4. Polymerization
5. Sputtering
Sputtering

DC plasma sputtering

Substrate/Anode
- to be coated in cathode material

Target/Cathode
- containing raw material that is sputtered off by the positive ions impacts

Background gas
Neutral target atom
Electron
Ionized atom

Negative Glow Plasma
Cathode dark space (CDS)
Metallic coating

• Add a metal coating onto fabric
• Combines with various gases for metal oxide, metal nitride, etc. coating
• To make conductive, heatable or cooling fabric
Heat reflective

- Aluminum coating
  - Temperature increased from \(~24\ \degree C\) to \(~25\ \degree C\)
  - Max. Temperature = 25.3 \degree C
Heatable clothing

- Aluminum alloy
  - Input: 3.7 V
    - Resistance: 1.8 Ω
    - Max. Temperature: ~40 °C
    - From room temp. to max temp: ~4 min

* R&D project funded by the ITC (ITP/003/14TI)
(II) Supercritical Fluid Dyeing Technology
What is a Supercritical Fluid?

A supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

- It exhibits both the properties of a gas and a liquid.
  - Dense like a liquid to dissolve materials
  - Low viscosity, high diffusivity, no surface tension like a gas

**Table 1. Order of magnitude comparison of physical properties substance**

<table>
<thead>
<tr>
<th>State</th>
<th>Density [g/cc]</th>
<th>Viscosity [g/cm-s]</th>
<th>Diffusivity [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>0.001</td>
<td>$10^{-1}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Supercritical fluid</td>
<td>0.1–1.0</td>
<td>$10^{-4}$–$10^{-3}$</td>
<td>$10^{-4}$–$10^{-3}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>1.0</td>
<td>$10^{-5}$</td>
<td>$10^{-2}$</td>
</tr>
</tbody>
</table>

*Source: (After Table 1 from “Supercritical Fluid Extraction,” TechCommentary, 6(1), Electric Power Research Institute, 1994).*
Carbon Dioxide (CO₂)

- Non-toxic
- Non-flammable
- Non-corrosive
- Does not contribute to smog
- No acute ecotoxicity
- Inexpensive
- Readily available
- Inexhaustible resource
Supercritical Carbon Dioxide

A ‘hybrid solvent’

- Can be tuned from liquid-like to gas-like without crossing a phase boundary

- Tunable solvating power
  - Tuning of solvent properties easily as a function of temperature and pressure.
  - Can dissolve compounds of different chemical structures

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Pressure (bar)</td>
<td>73.8</td>
</tr>
<tr>
<td>Critical Temperature (°C)</td>
<td>31.1</td>
</tr>
<tr>
<td>Critical Density (g/cm³)</td>
<td>0.468</td>
</tr>
</tbody>
</table>

Critical Pressure (bar) 73.8
Critical Temperature (°C) 31.1
Critical Density (g/cm³) 0.468
Carbon Dioxide

Increasing temperature and pressure:

- Gas
- Liquid
- Supercritical fluid
Applications

- Food industry
- Cosmetic industry
- Pharmaceutical industry
- Polymer and plastics industries
- Chemical industry
- Material industry
- Wood industry
- Textile industry
- ...

- Extraction
- Purification
- Sterilization
- Cleaning
- Micro- and nanoparticles synthesis
- Aerogel preparation
- ...

- Decaf
Supercritical Carbon Dioxide Dyeing

- **Supercritical carbon dioxide (scCO₂)**
  - Non-polar solvent – the dipoles of the two bonds cancel one another
  - Direct dissolve of disperse dyes

- **Disperse dyes**
  - Typically non-ionic and contain no strong hydrophilic (water loving) groups
  - Dye particles are held in dispersion by surface-active agent (surfactant)
  - Have substantivity for hydrophobic fibres, like polyester and acetate
Conventional Water-Based Dyeing Process

- **Scouring**: 
  - Base
  - Chelating agent
  - Wetting agent
  - Water ($H_2O$)

- **Dyeing**: 
  - Dyes
  - Dispersing agent
  - pH Buffering agent
  - Water ($H_2O$)

- **Reduction Clearing**: 
  - Base
  - Reducing agent
  - Water ($H_2O$)

- **Sewage**

- **Drying**

- **Product**
Supercritical Carbon Dioxide Dyeing Process

Scouring
- scCO$_2$
- Base
- Chelating agent
- Wetting agent

Dyeing
- scCO$_2$
- Dyes
- Dispersing agent
- pH Buffering agent

Clearing
- scCO$_2$
- Base
- Reducing agent

Product

Sustainable Process
- A recyclable process medium (CO$_2$)
- Minimum input of chemicals (only dyes, no auxiliaries)
- Minimum input of energy (short dyeing times, fusion of processes, no drying)
- Minimal emissions
- Minimal waste production

Gaseous CO$_2$

Recycling

Residual dyestuff
Supercritical Carbon Dioxide Dyeing Process
ScCO$_2$ Dyeing Systems

- *Lab* and *pilot* scale systems
- *Industrial* scale systems
- Two processing cauldrons (500 L capacity) allow parallel processing
- Process up to 2000 yards of fabric
- Equipped with a fully automated hydraulic-door with a double locking system
- External chemical addition tanks for easy addition of dyes/finishing agents
For textile finishing manufacturers, process conditions of up to **300 bar** are very unusual

- Withstand up to **350 bar** (25% more than the normal operating pressure of 280 bar)
- **Safety valves** are installed at processing cauldrons, CO₂ storage tank, chemical addition tanks, separation tank, pressurizing pump and CO₂ incoming pump
- **Separated control room** → Remotely monitors and controls the system
Integration of Functional Treatment Process

Scouring
- scCO₂
- Base
- Chelating agent
- Wetting agent

Dyeing
- scCO₂
- Dyes
- Dispersing agent
- pH Buffering agent

Clearing
- scCO₂
- Base
- Reducing agent

Functional Treatment
- scCO₂
- Functional material

Product

Gaseous CO₂

Recycling

Residual dyestuff and functional material
# Economic Evaluation of scCO$_2$ Dyeing

## I. Capital Costs

<table>
<thead>
<tr>
<th></th>
<th>scCO$_2$ Dyeing</th>
<th>Aqueous Dyeing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment cost (HK$)</td>
<td>8,500k</td>
<td>2,000k</td>
</tr>
<tr>
<td>Annual capital charge (HK$)$</td>
<td>1,150k</td>
<td>270K</td>
</tr>
<tr>
<td>Labour cost (HK$/month)$</td>
<td>8,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Batch time (min)</td>
<td>120</td>
<td>210</td>
</tr>
<tr>
<td>Production capacity (kg/batch)</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>Production capacity (kg/year)$</td>
<td>315k</td>
<td>360k</td>
</tr>
<tr>
<td>Capital charge (HK$/kg)</td>
<td>3.96</td>
<td>1.02</td>
</tr>
</tbody>
</table>

$^a$The annual capital charge is 13.5%; $^b$1 operator for each machine; $^c$14 hr/day and 25 days/month
# Economic Evaluation of scCO₂ Dyeing

## II. Operational Costs

<table>
<thead>
<tr>
<th>Compound/utility</th>
<th>scCO₂</th>
<th>Aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount/batch</td>
<td>Price (HK$)</td>
</tr>
<tr>
<td>Electricity</td>
<td>60 kWh</td>
<td>78</td>
</tr>
<tr>
<td>Water</td>
<td>0 m³</td>
<td>0</td>
</tr>
<tr>
<td>Wastewater treatment</td>
<td>0 m³</td>
<td>0</td>
</tr>
<tr>
<td>Steam</td>
<td>90 kg</td>
<td>18</td>
</tr>
<tr>
<td>CO₂</td>
<td>15 kg</td>
<td>0.9</td>
</tr>
<tr>
<td>Dyes</td>
<td>3 kg</td>
<td>300</td>
</tr>
<tr>
<td>Dispersing agent</td>
<td>0 kg</td>
<td>0</td>
</tr>
<tr>
<td>Other chemicals</td>
<td>0 kg</td>
<td>0</td>
</tr>
<tr>
<td>Maintenance</td>
<td>0 kg</td>
<td>12</td>
</tr>
<tr>
<td><strong>Operating cost (HK$/kg)</strong></td>
<td>2.73</td>
<td></td>
</tr>
</tbody>
</table>

a For dyeing, washing and rinsing; b For dyeing, washing, rinsing and drying; c Maintenance is 3% of equipment cost
As energy and water/wastewater costs differ very much from country to country, a concrete comparison of the water and scCO₂ dyeing process is not possible in great detail.

- The water cost in Netherlands is much higher (2.27 €/m³) and the processing for scCO₂ dyeing is 50% lower comparing water dyeing.
### Environmental Considerations

<table>
<thead>
<tr>
<th>Compound/ utility</th>
<th>scCO₂</th>
<th>Aqueous</th>
<th>scCO₂</th>
<th>Aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount /batch</td>
<td>Amount /kg</td>
<td>Amount /batch</td>
<td>Amount /kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>60 kWh</td>
<td>0.4 kWh</td>
<td>100 kWh</td>
<td>0.33 kWh</td>
</tr>
<tr>
<td>Water</td>
<td>0 m³</td>
<td>0 m³</td>
<td>5 m³</td>
<td>0.017 m³</td>
</tr>
<tr>
<td>Steam</td>
<td>90 kg</td>
<td>0.6 kg</td>
<td>1380 kg</td>
<td>4.6 kg</td>
</tr>
<tr>
<td>CO₂</td>
<td>15 kg</td>
<td>0.1 kg</td>
<td>0 kg</td>
<td>0 kg</td>
</tr>
<tr>
<td>Dyes</td>
<td>3 kg</td>
<td>0.02 kg</td>
<td>6 kg</td>
<td>0.02 kg</td>
</tr>
<tr>
<td>Dispersing agent</td>
<td>0 kg</td>
<td>0 kg</td>
<td>6 kg</td>
<td>0.02 kg</td>
</tr>
<tr>
<td>Other chemicals</td>
<td>0 kg</td>
<td>0 kg</td>
<td>3 kg</td>
<td>0.01 kg</td>
</tr>
</tbody>
</table>

✓ ScCO₂ dyeing requires less energy with 95% of the CO₂ is recycled and therefore is associated with **about 45% lower CO₂-emission**, reduces about 100,000 kg of CO₂-emission for yearly production of 300,000 kg polyester fabric.

✓ ScCO₂ dyeing requires only dyes and therefore can **save 60% of chemicals**.
Outlook

Does scCO₂ dyeing have a future in the textile industry?

✓ Environmental advantages
  • Waterless process → no wastewater discharge
  • Reuse of CO₂
  • Requires less chemicals and energy
  • Lower CO₂-emission

✓ Fully met all of the quality standards for polyester as in water dyeing
  • High colour yields are obtained
  • High levelness of dyeing, i.e. no colour differences at the inside, middle, and outside of the fabric pack
  • Very good washing, rubbing and sublimation fastness properties
The production and demand of polyester have continued to grow at a significantly faster rate than all other fiber types.

Polyester makes up 95%+ of future global synthetic fibre production growth.

From 1980–2014, total fiber demand growth has been 40.7 million tons – 73.4% of which is down to polyester.
Services

• New function development
• Feasibility test and trials
• Technology transfer
• Production system design, fabrication and installation
• Facilities layout design
• In-house training
Dr. Jimmy Lee

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