SOLVENT-BASED RECYCLING TOWARDS RECOVERY OF 
TiO$_2$ FROM WASTE PLASTICS 

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PLASTICS (WASTE) PRODUCTION

Source: Plastic Europe Market Research Group (PEMRG) and Conversio Market & Strategy GmbH
PLASTICS RECYCLING ROUTES

*Figure from https://cefic.org/a-solution-provider-for-sustainability/chemical-recycling-making-plastics-circular/

**Figure from Cruz Sanchez (2020) Plastic recycling in additive manufacturing: A systematic literature review and opportunities for the circular economy.
MANY ADDITIVES: WHY TiO$_2$?

Dyes (14%)

Pigments (86%)

Titanium Dioxide

TiO$_2$ (59%)

*Source: GRID Arendal.
**CIRCULARITY TiO₂ PLASTICS**

**SULFATE PROCESS**
- Concentrated sulfuric acid
- Solid and acid waste
- 117 MJ/kgTiO₂ **

**CHLORIDE PROCESS**
- Petroleum coke chlorine gas
- Direct CO₂ emissions
- 106 MJ/kgTiO₂ **

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*Source: Chemours
**From Liao (2012), Thermodynamic resource indicators in LCA: a case study on the titania produced in Panzhihua city, southwest China.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon footprint kgCO₂e/kgcompound</th>
<th>Price €/kg (2021)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>4.90</td>
<td>2.6-3.2</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LD)PE</td>
<td>1.98</td>
<td>1.2-1.3</td>
</tr>
<tr>
<td>PVC</td>
<td>2.51</td>
<td>~1.2</td>
</tr>
<tr>
<td>PS</td>
<td>3.68</td>
<td>~1.6</td>
</tr>
</tbody>
</table>
PROCESS

Set-up (dead-end filtration)

Solvent + Polymer containing TiO₂

Precipitation

Recovered polymer

Antisolvent

Permeate

Retentate
TiO$_2$ SEPARATION
Solvent influences the flow rate and cake resistance.

\[ \frac{t}{V} = \frac{\mu_0 \alpha C_m}{2 A^2 \Delta P} \cdot V + \frac{\mu_0 R_M}{A \Delta P} \]
WASTE SAMPLES

Waste samples significantly higher cake resistance.

PVC

Membrane

Waste PVC in THF

98.8% turbidity reduction

(HI)PS

Membrane

Waste (HI)PS in limonene

98% turbidity reduction

Wastes, 0.1μm membrane

V [m^3]

V [m^3]

0.0E+00 1.0E-05 2.0E-05 3.0E-05

0.0E+00 1.0E+00 2.0E+00 3.0E+00

0.0E+00 5.0E+00 1.0E+01 1.5E+01 2.0E+01

White PVC waste, 1w% in THF, 15 bar
Waste (HI)PS, 1w% in limonene, 1.35w% TiO2 in waste, 2.5 bar

PS+TiO2, 1w% in limonene, 0.28w% TiO2 in PS, 3 bar
Waste (HI)PS, 1w% in limonene, 1.35w% TiO2 in waste, 2.5 bar
RECOVERY
COMPOUNDS RECOVERY

Almost pure polymer sheet is obtained (4w% (anti)solvent trace)

TiO₂ can be separated from organic compounds
CONCLUSIONS & FUTURE PROSPECTIVE

• **Solvent-based** recycling **promising** route for plastic recycling
• **Concurrent recovery** of polymer and TiO$_2$ is possible
• Filtration efficiency depends on: solvent, concentration, polymer, additives
• Optimization of the process required to treat real waste streams
• Assess recovered polymer properties
• Explore alternative routes for TiO$_2$ purification
Thank you for your attention!

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PLASTICS RECYCLING RATES

*Source: Plastic Europe Market Research Group (PEMRG) and Conversio Market & Strategy GmbH.

**Source: Creacycle
DISSOLUTION-PRECIPITATION PROCESS

*Figure adapted from Mangold (2022), The Frontier of Plastics Recycling: Rethinking Waste as a Resource for High-Value Applications.
## FILTRATION CURVES

### Pure TiO$_2$ filtration (R-350)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Pressure (bar)</th>
<th>Turbidity reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ 0.5wt%</td>
<td>Xylene</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>Limonene</td>
<td></td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

No significant compressibility
PURE POLYMER FILTRATIONS

Pure PS, 0.1µm membrane

Pure LDPE, 0.1µm membrane

Pure polymers, 0.1µm membrane

Styrenic polymers, 0.1µm membrane
<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Pressure (bar)</th>
<th>Turbidity reduction (%)</th>
<th>Polymer retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS+TiO$_2$, 5w% solution (0.28w% TiO$_2$ in PS)</td>
<td>Xylene</td>
<td>1.5</td>
<td>98.6</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>99.5</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Limonene</td>
<td>1.5</td>
<td>97.5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>98.7</td>
<td>3.4</td>
</tr>
<tr>
<td>PS+TiO$_2$, 1w% solution (0.28w% TiO$_2$ in PS)</td>
<td>Xylene</td>
<td>1.5</td>
<td>96.7</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>96.8</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>Limonene</td>
<td>1.5</td>
<td>96.7</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>96.6</td>
<td>0.0</td>
</tr>
<tr>
<td>PS+TiO$_2$, 7w% solution (10w% TiO$_2$ in PS)</td>
<td>Xylene</td>
<td>9</td>
<td>98.9</td>
<td>5.4</td>
</tr>
</tbody>
</table>

TiO$_2$ can be easily separated from pure PS by filtration.
FILTRATION CURVES

Styrenic polymers

- **Waste sample behaves similar to high concentration of pure PS+TiO₂ solution**
- **Solvent influences cake resistance**
- **Increasing concentration, cake resistance increases significantly**

# FILTRATION EXPERIMENTS

## LDPE+TiO$_2$ (R-350)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Pressure (bar)</th>
<th>Turbidity reduction (%)</th>
<th>Polymer retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE+TiO$_2$, 1w% solution (0.24w% TiO$_2$ in LDPE)</td>
<td>Xylene</td>
<td>1.5</td>
<td>98.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>99.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Limonene</td>
<td>1.5</td>
<td>97.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>98.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

TiO$_2$ can be easily separated from pure LDPE by filtration.
# FILTRATION EXPERIMENTS

## PVC (Deceuninck)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Pressure (bar)</th>
<th>Turbidity reduction (%)</th>
<th>Polymer retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC, 1w% (0.5w% TiO₂ in PVC+additives)</td>
<td>THF</td>
<td>1.5</td>
<td>98.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Waste PVC, 1w%</td>
<td></td>
<td>15</td>
<td>99.9</td>
<td>76.3</td>
</tr>
</tbody>
</table>

* = optimization needed

TiO₂ can be separated from PVC by filtration *(also for waste sample)*