Solution Architect for Global
Bioeconomy & Cleantech Opportunities

arvi
Material Value Chains

7.10.2016

Tommi Vuorinen
Harri Joki
Outi Härkki

VTT Technical Research
Centre of Finland

Report: Colour Removal from Recycled Plastics

ARVI Theme plastic and rubber

Subtask 4.1.1

Subtask 4.1.1 – Characterisation and modification

Odour and/or colour removal from recovered plastic wastes – VTT, Borealis, Ekokem

- A kick-off meeting on Feb. 4th at Borealis
  - It was decided to focus on polyolefin plastic flows (HDPE and PP),
  - An ultimate target is in **a colourless or clear recycled polyolefin raw material**, because of their highest value in the market.
  - In this work the focus is in the means **to remove pigment colour and printing ink** from a recycled plastic flow.
  - Due to the limited resources it was decided primarily not to study odour removal in this task.
  - A comprehensive literature review will be carried out by the end of April.
  - A selected and focused experimental work is planned to be carried out by the end of September.

Literature Review Conclusions

- Reactive removal techniques (e.g. peroxide oxidation) may have negative affect on polymer chains (PP is degraded and PE can be cross-linked). In addition, additives are not removed but they are just decomposed and residuals are left in polymer matrix as impurity.
- Supercritical extraction techniques have not been shown efficient methods for decolourisation. According to reports, the practice has not yet followed the assumptions.
- **The techniques used by, e.g., Ioniqa and CreaSolv, are suggesting that combinational solution based extraction and dissolution and precipitation techniques can open possibility to create an effective decolouring technique which does not modify polyolefin resin.**

Colour Removal Process – Hypothesis

Solution processing → cost and energy intensive.
REACH must be taken into account (solvents and the extracted additives)

1. Plastic type identification & sorting

2. Colourant type identification & sorting

The techniques, e.g., NIR-spectroscopic methods already in use/under development → more efficient sorting and/or marker/identification required? One way to distinguish between pigments and dyes is to monitor transparency/translucency of the articles (dyes transparent, while pigments translucent)

3. Extraction of small molecule dyes and other additives

Organic solvents required → utilization of existing industrial chemistry processes

4. Dissolution of polymer matrix

Polyolefins are very inert, thus harsh organic solvents and solvation conditions are required. There are existing solution processes for polyolefins. Removal of carbon black might by e.g. flotation be included in this step.

5. Precipitation and removal of pigments

Control of aggregation of pigment particles. Selective precipitation of plastic components with solvent systems? Use of "molecular sieves" as adsorbent?

6. Solvent removal and drying of polymer

Requires heat and energy. Closed loop solvent processes. Solvent residues may cause odour and other issues.

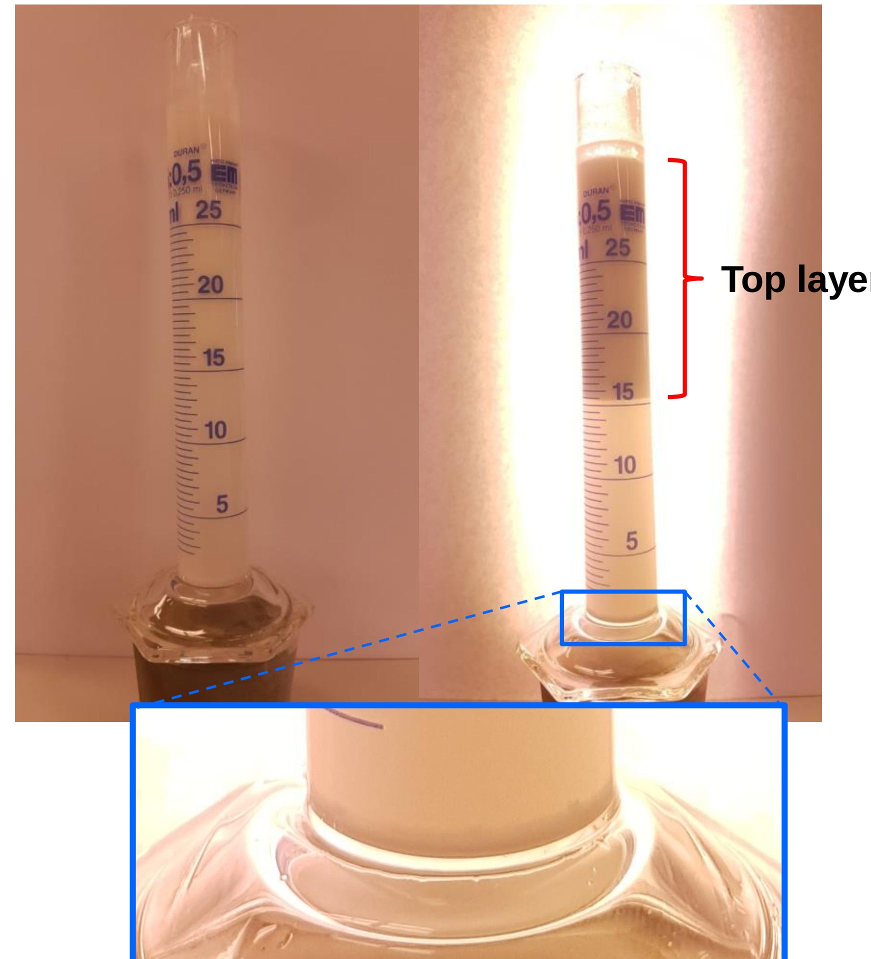
Experimental work, steps 4 & 5

TiO_2 pigment removal from polyethylene with o-dichlorobenzene: dissolving PE

- 2 g polyethylene granules
- 35 ml o-dichlorobenzene
- Heated at 140 °C for 5 hours
- Into cooled solution 35 ml o-dichlorobenzene added
- Additionally o-xylene was added into previous solution in ration 2:1 (DCB:xylene)

Experimental work

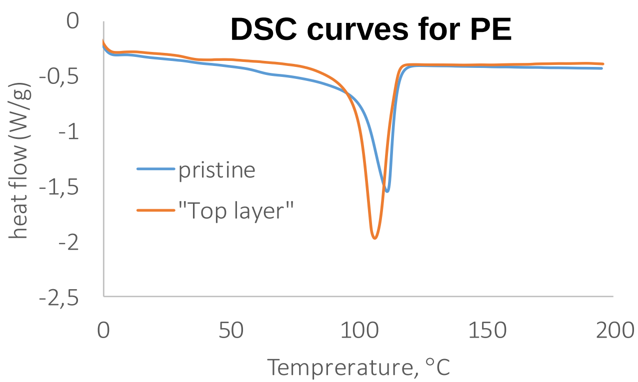
- PE + DCB solution was let to cool and stratify
- Three different layers visible (picture on right)
- Top layer contains PE with some TiO_2 particles in matrix (SEM-picture)
- Interlayer contains mainly o-dichlorobenzene with small TiO_2 particles
- At the bottom is TiO_2 particles

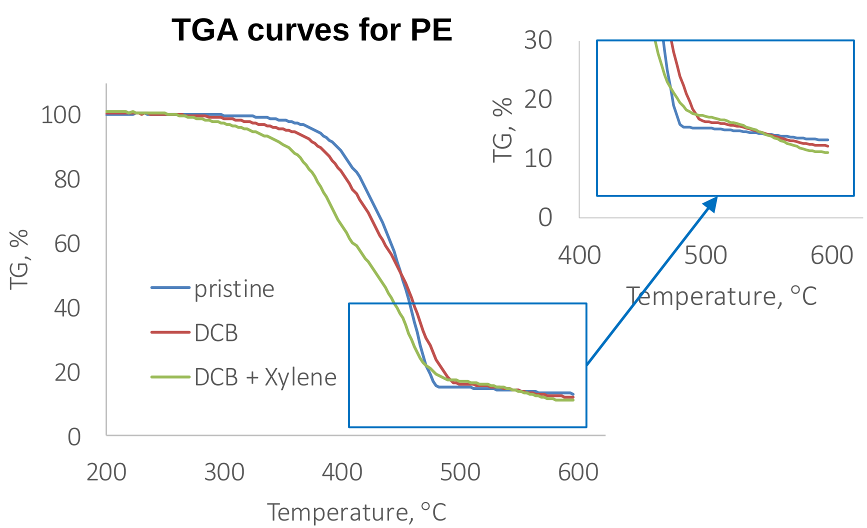


Thermal analysis for the top layer

- The DSC analysis indicated that PE did not degrade in the thermal dissolution process:
  - the on-set melting temperature remained the same (99 °C)
- The thermo gravimetric analysis indicated that titania content decreased 15 % (from 13.2 to 11.0 mass-%)

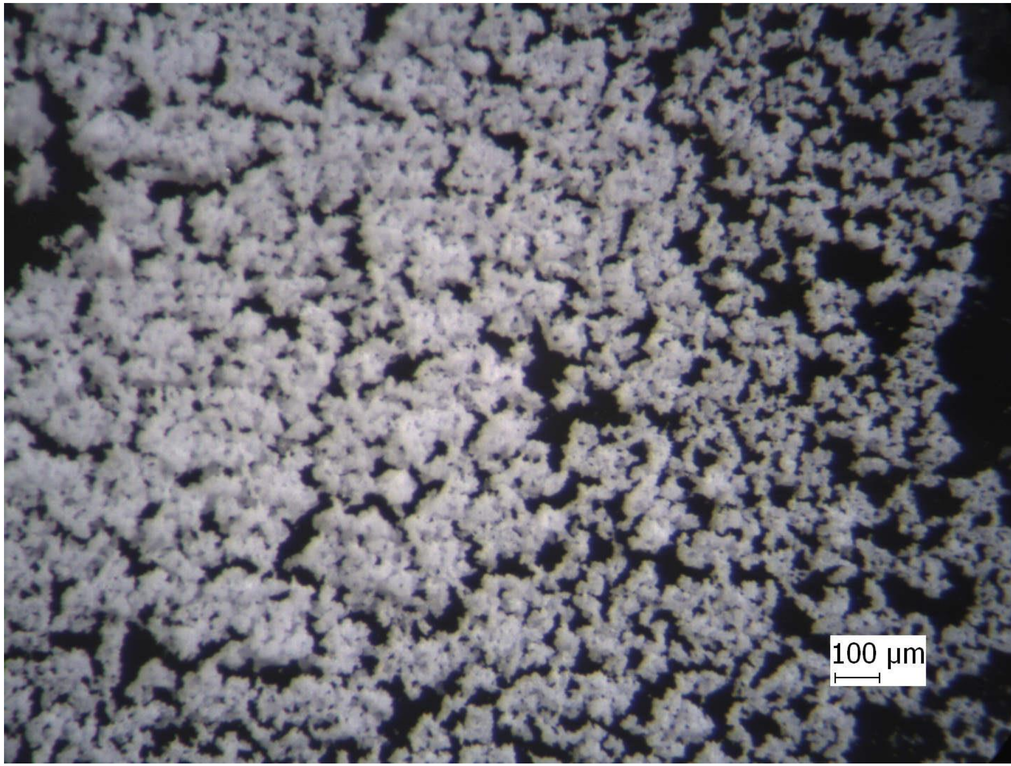
Sample	Recidual
Pristine CC7238	13.2 %
Dissolved with DCB	12.1 %
Dissolved with DCB & additional xylene	11.0 %



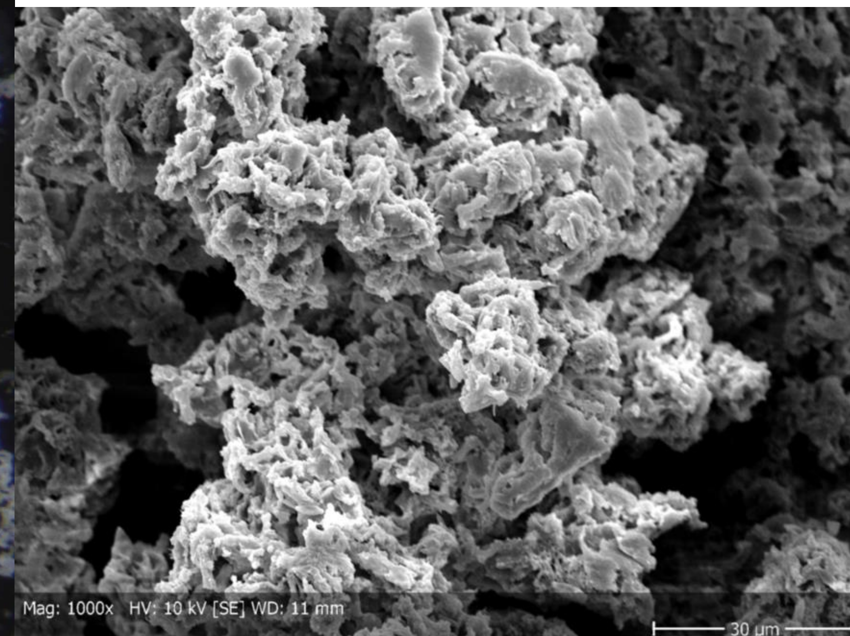


Microscopy for top layer

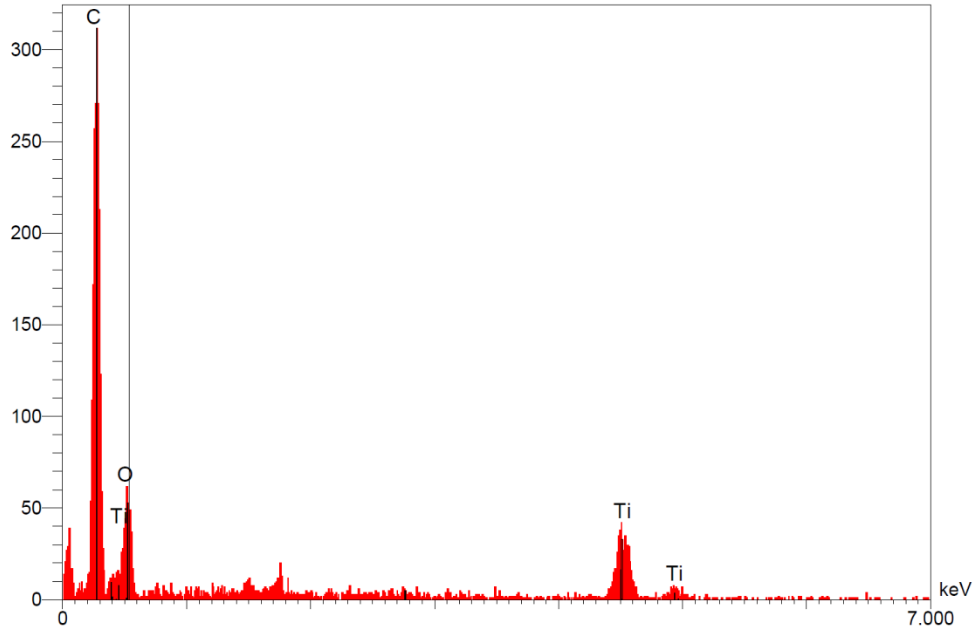
Stereo micrograph

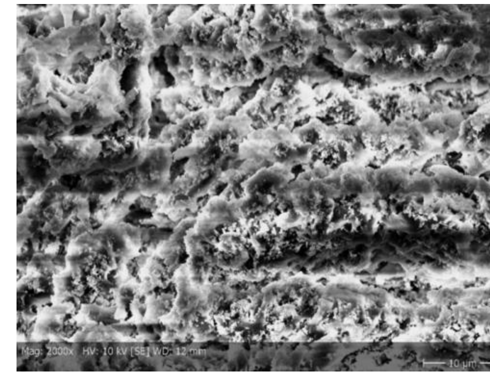


SEM micrograph

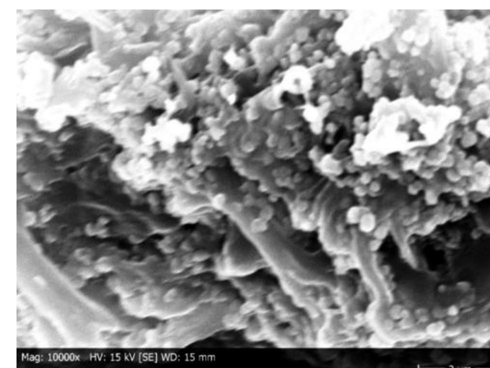


SEM/EDS for bottom layer





2000 x



10000 x

TiO_2 particles (size 350 nm) are aggregated and adhered together with some amount of polymer.

Summary: experimental work

3. Extraction of small molecule dyes and other additives	**4. Dissolution of polymer matrix**	**5. Precipitation and removal of pigments**	**6. Solvent removal and drying of polymer**

Testing in laboratory scale step 3 – 6

- Test material: well known plastic composition
  - PE or PP resin, colorants (inorganic pigments), typical additives
  - CC7238 PE colored with TiO_2.

3: extraction tests by organic solvents

4: dissolving polymer, e.g. hot o-dichlorobenzene, o-xylene

5: finding ways to separate inorganic fillers seems to be very challenging task

6: drying polymer resin

Tasks to enhance pigment separation

- Dissolution with mixture of o-dichlorobenzene and o-xylene
  - Density of solvent should be higher than that of plastic and lower than that of pigment
- Aid of ultra sound during dissolution under elevated temperature
  - Now PE probably forms a gel with hot DCB → polymer chains are not fully dissolved → pigments will not be totally separated from polymer → ultra sound or similar physical agitation may help pigment separation from the polymer chains.
- Separation of polymer and pigments at elevated temperature
  - "hot centrifuge" → possibility that inertia will drive pigments out from the polymer matrix
- Cascade processing will be more efficient than a batch process
  - Combination of steps including one or more solution techniques.
  - This far the pigment removal efficiency has been roughly 15 %. The target would be higher, ~30 % efficiency.

Future questions

- Aromatic solvents are toxic and carcinogenic, thus they need to be substituted in industrial process.
  - How sensitive the concept is to solvent
    - Dissolution of plastics
    - Physical separation (densities)
- Recovery of polymer
  - How to minimize solvent residues and make sure they do not cause problems for polymer utilization
- Utilization of separated pigments as pigments
  - Reuse of pigments can increase profitably of color removal process.

arvi
Material Value Chains

Brief Review on Color Removal

Next slides will give a brief overview on background for the experimental work presented on previous slides.

Summary of plastic colour removal

- Techniques for removing colour or colourants and other additives from plastic
  - Extraction by solvent combined with filtering or with precipitation and filtering
  - Supercritical extraction
  - Peroxide oxidation
  - Reactive extrusion (Milliken)
- Types for colourants
  - Inorganic pigments
  - Organic pigments
  - Organic reactive colourants
  - Colourant fillers

Picture: http://www.pittsplas.com/

Colorants mixed in plastics

- **Pigments**:
  - Inorganic compounds, usually insoluble/immiscible or only partially soluble in polymers
    - E.g. oxides, sulphides, carbonates, carbon black
    - Oxides of iron, titanium, nickel, antimony, chrome, zinc cobalt are stable at high temperatures and are easily dispersed into plastics
    - Sulphides have usually low resistance to acids
    - Size ~10 nm – 1 µm
  - Organic compounds
    - E.g. phthalocyanines
    - Phthalocyanines can cause nucleation and crystal growth in polyolefins resulting in e.g. warpage
- **Liquid colourants**
  - Mainly used in PET, usage decreasing

- Masterbatches
  - Typical composition: 40 – 60 % of pigments.
    - While the pigment content in ready product can vary from ~1 to 15 % depending on the pigment type and color.
  - Pigment dispersion can be stabilized by e.g. polyacrylate or ester waxes

arvi
Material Value Chains

Picture: http://acceleratingscience.com/

Properties of a good pigment

- Strong covering (color) power
- Thermal stability (240 – 280 °C) and light fastness
- weather and chemical resistance
- Resistance to bleeding and migration
- Pigmental properties depend on
  - Chemical structure of the pigment (class)
  - Size and shape of the particles and size distribution
  - Particle crystallinity and crystal form
  - Polymer/plastic and their processing conditions
- For example PP has high processing temperature, thus only inorganic pigments usually can be used
- Perylene pigments are widely used especially for melt coloration of PP and PE

arvi
Material Value Chains

Picture: http://acceleratingscience.com/

Pigments & colors

Examples of inorganic pigments

- White: TiO_2, ZnS, ZnO, lead oxide, $BaSO_4$, $CaCO_3$, and aluminum, calcium, or magnesium silicates
- Yellow: various chromates, hydroxides alone or treated with colloidal silica
- Red: Fe_2O_3, $PbCrO_4$, $PbMoO_4$, $PbSO_4$, etc.
- Green: Cr_2O_3, CoO + ZnO
- Blue & violet: Prussian blue, manganese violet
- Brown and black: iron oxide brown, carbon black, black As_2S_3, black antimony sulfide

Examples of organic pigments:

- Red: monoazo and diazo pigments, perylene, flavanthrone, quinacridones
- Blue & green: indigo, anthraquinone, phthalocyanine
- Yellow: polycyclic and diazine pigments, diarylene

Examples of special pigments

- Pearlescent: thin platelets of mica coated with TiO_2 or iron oxide
- Metallic flakes: copper, copper alloys, aluminum, and aluminum alloys

arvi
Material Value Chains

Picture: http://acceleratingscience.com/

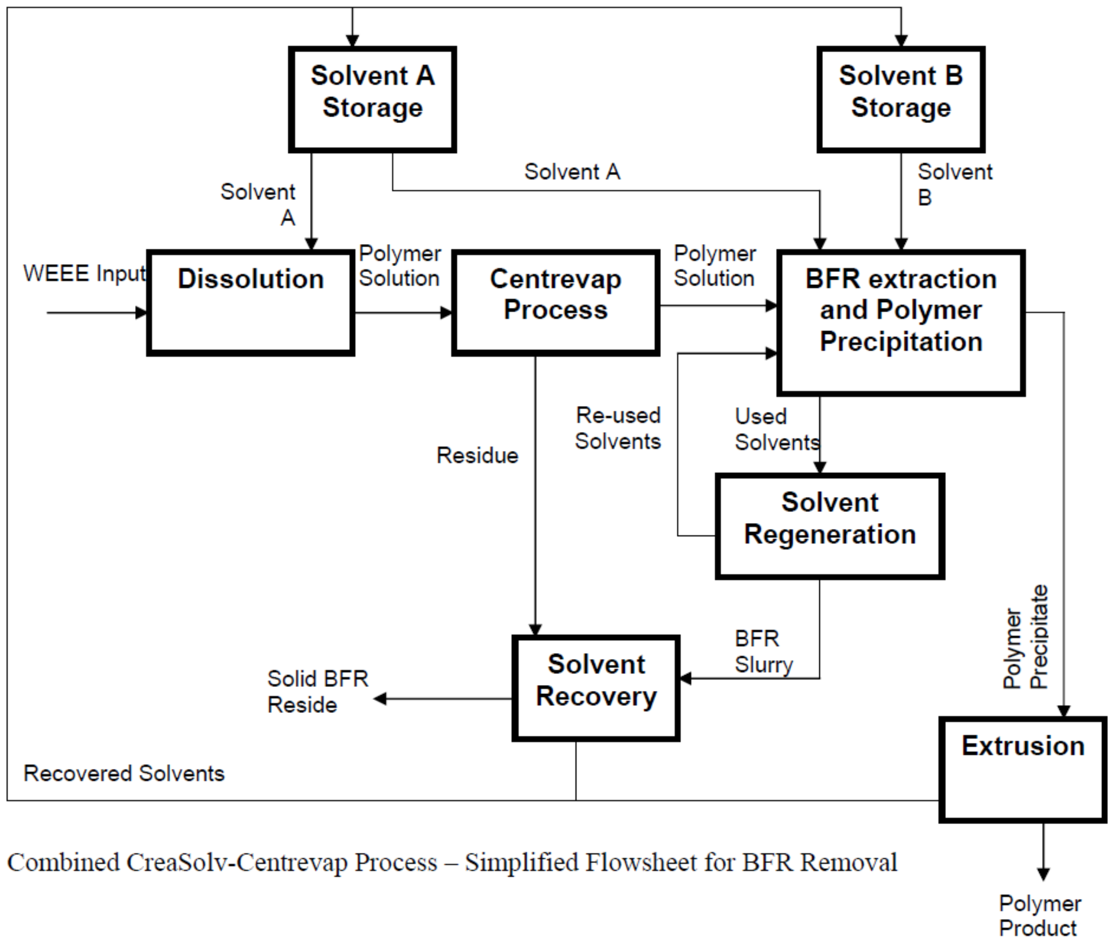
Removing colour from PET

- Developed by a Dutch company Ioniqa Technologies.
- The technique is based on magnetic particles with suitable functional linkers.
- The process has following steps
  - Dissolving of mixed coloured PET with ethylene glycol including magnetic particles, at ~180 °C for ~1 hour
  - Magnetic separation of particles which have linked with colourants and pigments
  - Recrystallisation of PET from EG solution
  - Movie available: https://goo.gl/mzzOd4
- The company has built a 100 litre pilot scale reactor with capacity of 20 ton/year. The company targets for 1000 litre pilot reactor with capacity of 2000 ton/year
- www.ioniqa.com

arvi
Material Value Chains

Picture: http://www.ioniqa.com/

CreaSolv/Centrevap (Fraunhofer)



Combined CreaSolv-Centrevap Process – Simplified Flowsheet for BFR Removal

CreaSolv/Centrevap: Mass Balance

A full scale mass balance has been prepared for the Creasolv-Centrevap process at a throughput of 10,000te/yr WEEE polymer. This mass balance is based on the experimental results measured in the technical scale trials. The detailed results of this mass balance are confidential but the mass balance may be summarised as follows:

	INPUT (te/yr)			**OUTPUT (te/yr)**	
Stream No.	**WEEE Input**	**Make-Up Solvents**	**Drying Agent**	**Polymer**	**Residue to Landfill**
Polymer	7,920	0	0	7,534	386
BFR	1,000	0	0	3	997
Antimony	80	0	0	0	80
Inerts	1,000	0	0	0	1,000
Solvents	0	155	0	38	117
Drying Agent	0	0	582	0	582
Total	**10,000**	**155**	**582**	**7,575**	**3,162**

Total Input: **10,737 te/yr**

Total Output: **10,737 te/yr**

Relatively high yield of the CreaSolv process is promising from viewpoint of our approach.

Part of the solvent that is consumed will be lost in the residue that is disposed to landfill and part will be present at less than 1% in the final polymer product. At this level it is not expected that the solvent will have any detrimental effect on product quality or moulding performance. The residual solvent in the product is non-toxic.

arvi
Material Value Chains

References & Links

- Handbook of Polyolefins, 2nd Edition, Ed. Cornelia Vasile, CRC Press 2000
- http://dyes-pigments.standardcon.com/
- http://www.dyes-pigments.com/colorants-for-plastic-industry.html
- http://www.cabotcorp.com/solutions/products-plus/masterbatches-and-conductive-compounds/masterbatches
- www.ioniqa.com
- Method of incorporating carbon black in a polymer of ethylene or propylene; US 2952656 A
- Plastics recycling: challenges and opportunities (*Phil. Trans. R. Soc. B* **2009**, *364*, 2115–2126)
- Polymers and Dyes: Developments and Applications (*Polymers* **2015**, *7*, 717–746)
- ”Develop a process to separate brominated flame retardants from WEEE polymers” Final Report; The Waste & Resources Action Programme; November 2006; ISBN: 1-84405-315-6